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MIXING MECHANISMS IN 2D REACTORS

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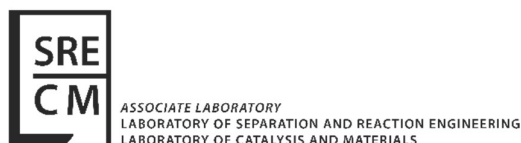
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Mixing Mechanisms in 2D Reactors

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To my parents and siblings

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Abstract

This thesis aims at the identification and the characterisation of the mixing mechanisms in 2D reactors. The 2D nature of flow and mixing in these reactors stems from the fact that the mixing dynamics is well-represented by 2D time-dependent maps, and the energy transfer mechanisms between flow scales are described from bidimensional turbulence theory.

Flow dynamics and mixing of two fluids in 2D mixers are studied numerically from Computational Fluid Dynamic (CFD) simulations and experimentally from Planar Laser Induced Fluorescence (PLIF) techniques, using reactive and non-reactive tracers. The 2D mixers/reactors in this thesis are rotational devices, Split-and-Recombine (SR) mixers, and two opposed jets mixers: Confined Impinging Jets (CIJ) and T-Jets.

Rotational devices are suggested as small-scale batch laboratory mixers. These devices can replicate industrial mixing conditions in 2D reactors, which have a great application on rapid formulation processes. This methodology is applied for the pre-screening of formulations for reactive polyurethanes to generate formulation and process data for Reaction Injection Moulding processes.

Fully resolved CFD simulations in opposed jet mixers are out of reach for engineering practice. The order of magnitude for the required number of computational cells for micromixing simulation of a reactor with ~ 1 cm is around 10^{11} . A lamellar model is demonstrated in this thesis to describe micromixing in CIJ mixers. This model considers the striation thinning and diffusion at the interface of the mixing fluids enabling the resolution of all mixing scales. This work contributes to extending previous work on mixing of dissimilar fluids with viscosity ratios ranging from 2 to 10 and different densities. The experimental study on mixing of two dissimilar fluids required a methodology to match the refractive indices of two liquids. Experimental and numerical studies show that CIJ and T-Jets mixers can mix efficiently dissimilar fluids.

For this, the inlet jets must be well-balanced and impinged at the mixing chambers axis.

A Kinetic Energy Model, based on the kinetic energies of the inlet jets, is described as the best model for the impingement point position in CIJ mixers for a wide range of working conditions. For T-Jets mixers, an elastic analogue of the two inlet jets is used to predict the impingement point position. These results were validated using PLIF images and 3D CFD simulations. This study validates the models that can be used as design tools for opposed jets mixers. The industrial case study selected to validate the jets impingement point position models is the production of mayonnaise in CIJ mixers.

3D CFD simulations are also performed to study the flow dynamics in SR mixers. These mixers typically operate in the Stokes flow regimes, and the distribution of striation thickness is determined from the fully-developed velocity profile. An explicit design expression is presented to calculate the maximum and minimum striation thickness in each phase, which is the limiting step for mixing in SR mixers.

This thesis extends the existing knowledge on mixing in 2D reactors, giving rise to solutions for industry. The main contributions of this thesis are a new formulation process for high throughput material development, the modelling of micromixing in chemical reactors, and the introduction of design equations for 2D mixers, enabling the efficient operation at symmetrical and unsymmetrical flow conditions.

Resumo

Esta tese visa a identificação e caracterização dos mecanismos de mistura em reatores 2D. A natureza 2D do escoamento e da mistura nesses reatores deve-se à dinâmica do escoamento que é definida por um mapa 2D dependente do tempo e à transferência de energia entre as escalas de escoamento, que é bem descrita no âmbito da teoria bidimensional da turbulência.

A dinâmica de escoamento e mistura de dois fluidos em misturadores 2D é estudada numericamente através de simulações de Computação em Fluidos Dinâmicos (CFD) e experimentalmente a partir de técnicas de Fluorescência Induzida por Laser (PLIF), usando traçadores reativos e não reativos. Os misturadores/reatores 2D descritos nesta tese são dispositivos rotacionais, misturadores *Split-and-Recombine* (SR) e dois misturadores de jatos opostos: *Confined Impinging Jets* (CIJ) e *T-Jets*.

Dispositivos rotacionais são sugeridos como misturadores laboratoriais de pequena escala. Estes dispositivos permitem reproduzir as condições de mistura industrial em reatores 2D, que têm uma grande aplicação em processos de formulação rápida. Esta metodologia é aplicada para a pré-triagem de formulações de poliuretanos reativos para gerar dados de formulação e processo para uma máquina de moldagem por injeção com reação química.

Simulações CFD totalmente resolvidas em misturadores de jatos opostos estão fora do alcance da prática de engenharia. De fato, a ordem de magnitude para o número de células computacionais necessário para simulação da micromistura num reator com ~ 1 cm é aproximadamente 10^{11} . Um modelo lamelar é demonstrado nesta tese para descrever a micromistura em misturadores CIJ. Este modelo considera o estriação e difusão na interface dos fluidos de mistura, permitindo a determinação de todas as escalas de mistura. Este trabalho alarga o conhecimento do trabalhos anteriores sobre a mistura de fluidos diferentes com razões de viscosidade variando de 2 a 10 e diferentes

densidades. O estudo experimental da mistura de dois fluidos diferentes exigiu uma metodologia para equalizar os índices de refração de dois líquidos. Estudos experimentais e numéricos mostram que os misturadores CIJ e T-Jets podem misturar fluidos diferentes com eficácia. Para isso, os jatos de entrada devem estar bem balanceados e injectados no eixo das câmaras de mistura.

Um modelo de energia cinética, baseado nas energias cinéticas dos jatos de entrada, é apresentado como o modelo que melhor descreve a posição do ponto de impacto em misturadores CIJ para uma ampla gama de condições de trabalho. Para os misturadores T-Jets, um análogo elástico de dois jatos de entrada é usado para prever a posição do ponto de impacto. Esses resultados foram validados usando imagens PLIF e simulações 3D CFD. Este estudo valida os modelos, que podem ser usados como ferramentas de projeto para misturadores de jatos opostos. O caso de estudo selecionado para validar os modelos de posição do ponto de impacto dos jatos é a produção de maionese em misturadores CIJ.

Simulações 3D CFD também são realizadas para estudar a dinâmica de escoamento em misturadores SR. Esses misturadores normalmente operam em regimes de escoamento de *Stokes*, e a distribuição da espessura das estrias é determinada a partir do perfil de velocidade totalmente resolvido. Uma expressão de design explícita é apresentada para calcular a espessura máxima e mínima de estriação em cada fase, que é a etapa limitante para a mistura em misturadores SR.

Esta tese alarga o conhecimento existente sobre mistura em reatores 2D, apresentando soluções para a indústria. As principais contribuições desta tese são um novo processo de formulação para o desenvolvimento de materiais de alto rendimento, a modelagem da micromistura em reatores químicos e a introdução de equações de projeto para misturadores 2D, permitindo a operação eficiente em condições de escoamento simétrico e assimétrico.

Résumé

Cette thèse vise à identifier et à caractériser les mécanismes de mélange dans les réacteurs 2D. La nature 2D de l'écoulement et du mélange dans ces réacteurs provient du fait que la dynamique de mélange est bien représentée par des cartes 2D dépendant du temps, et les mécanismes de transfert d'énergie entre les échelles d'écoulement sont décrits à partir de la théorie de la turbulence bidimensionnelle.

La dynamique d'écoulement et le mélange de deux fluides dans des mélangeurs 2D sont étudiés numériquement à partir de simulations de *Computational Fluid Dynamics* (CFD) et expérimentalement à partir de techniques de fluorescence planaire induite par laser (PLIF), en utilisant des traceurs réactifs et non réactifs. Les mélangeurs / réacteurs 2D décrits dans cette thèse sont des dispositifs rotatifs, des mélangeurs *Split-and-Recombine* (SR) et deux mélangeurs à jets opposés: les *Confined Impinging Jets* (CIJ) et les T-Jets.

Les dispositifs rotatifs sont décrits comme des mélangeurs de laboratoire par lots à petite échelle. Ces dispositifs peuvent reproduire les conditions de mélange industriel dans des réacteurs 2D, qui fonctionnent bien sur les processus de formulation rapide. Cette méthodologie est utilisée pour le pré-criblage des formulations pour les réactifs polyuréthanes afin de générer des données de formulation et de traitement pour les processus de moulage par injection-réaction.

Les simulations CFD entièrement réalisées dans des mélangeurs à jets opposés sont hors de portée pour la pratique de l'ingénierie. En effet, l'ordre de grandeur du nombre requis de cellules de calcul pour la simulation de micromélange d'un réacteur avec ~ 1 cm est d'environ 10^{11} . Dans ce travail de thèse, un modèle lamellaire est utilisé pour décrire le micromélange dans les mélangeurs CIJ. Ce modèle prend en considération l'amincissement des stries et la diffusion à l'interface des fluides de mélange permettant la réalisation de toutes les échelles de mélange. Ce travail contribue ainsi à étendre les

études antérieures sur le mélange de fluides différents avec des rapports de viscosité allant de 2 à 10 et des densités différentes. L'étude expérimentale sur le mélange de deux fluides différents a nécessité une méthodologie pour faire correspondre les indices de réfraction des deux liquides. Des études expérimentales et numériques montrent que les mélangeurs CIJ et T-Jets peuvent mélanger efficacement des fluides différents. Pour cela, les jets d'entrée doivent être bien équilibrés et avoir un impact sur l'axe des chambres de mélange.

Un modèle d'énergie cinétique, basé sur les énergies cinétiques des jets d'entrée, est décrit comme le meilleur modèle pour la position du point d'impact dans les mélangeurs CIJ, dans une large gamme de conditions de travail. Pour les mélangeurs T-Jets, un modèle analogue élastique des deux jets d'entrée est utilisé pour prédire la position du point d'impact. Ces résultats ont été validés à l'aide d'images PLIF et de simulations CFD 3D. Cette étude valide les modèles pouvant être utilisés comme des outils de conception pour les mélangeurs à jets opposés. L'étude de cas industriels sélectionnée pour valider les modèles de position des points d'impact des jets est la production de mayonnaise dans les mélangeurs CIJ.

Des simulations CFD 3D sont également effectuées pour étudier la dynamique des flux dans les mélangeurs SR. Ces mélangeurs fonctionnent généralement dans les régimes d'écoulement de Stokes, et la distribution de l'épaisseur de la striation est déterminée à partir du profil de vitesse lui-même. Une formule de conception explicite est présentée pour calculer l'épaisseur de striation maximale et minimale dans chaque phase, ce qui constitue l'étape limite pour le mélange dans les mélangeurs SR.

Cette thèse enrichit les connaissances existantes sur le mélange dans les réacteurs 2D, donnant lieu à des solutions pour l'industrie. Les principales contributions de cette thèse sont un nouveau processus de formulation pour le développement de matériaux à haut débit, la modélisation du micromélange dans les réacteurs chimiques et l'introduction d'équations de conception pour les mélangeurs 2D, permettant un fonctionnement efficace dans des conditions d'écoulement symétriques et asymétriques.

Resumen

Esta tesis tiene como objetivo la identificación y caracterización de los mecanismos de mezcla en reactores 2D. La naturaleza 2D del flujo y la mezcla en estos reactores se debe al hecho de que la dinámica de la mezcla está bien representada por mapas 2D dependientes del tiempo y los mecanismos de transferencia de energía entre escalas de flujo se describen a partir de la teoría de turbulencia bidimensional.

La dinámica de flujo y la mezcla de dos fluidos en mezcladores 2D se estudia numéricamente a partir de simulaciones de dinámica de fluidos computacional (CFD) y experimentalmente a partir de técnicas de fluorescencia inducida por láser planar (PLIF), utilizando trazadores reactivos y no reactivos. Los mezcladores / reactores 2D de esta tesis son dispositivos rotacionales, mezcladores *Split-and-Recombine* (SR) y dos mezcladores de chorros opuestos: chorros de impacto confinados (CIJ) y chorros en T.

Los dispositivos rotacionales se utilizan como mezcladores por lotes a escala de laboratorio que pueden replicar las condiciones de mezcla industrial en reactores 2D, que tienen un gran potencial de aplicación en procesos de formulación rápida. Esta metodología se aplica para la preselección de formulaciones de poliuretanos reactivos para generar datos de formulación en procesos de Moldeo por Inyección de Reacción.

Las simulaciones CFD realizadas íntegramente en mezcladores de chorro opuesto están fuera del alcance de la práctica de la ingeniería. El orden de magnitud para el número requerido de celdas computacionales para la simulación de micromezcla de un reactor con ~ 1 cm es alrededor de 10^{11} . En esta tesis se demuestra un modelo laminar para describir la micromezcla en mezcladores CIJ. Este modelo considera el adelgazamiento de las estrías y la difusión en la interfaz de los fluidos de mezcla, lo que permite la resolución de todas las escalas de mezcla. Este trabajo contribuye a extender el trabajo previo sobre la mezcla de diferentes fluidos con relaciones de viscosidad que van de 2 a

10 y diferentes densidades. El estudio experimental sobre la mezcla de dos fluidos diferentes requirió una metodología para igualar los índices de refracción de dos líquidos. Los estudios experimentales y numéricos muestran que los mezcladores CIJ y T-Jets pueden mezclar fluidos de manera eficiente. Para ello, los chorros de entrada deben estar bien equilibrados e incididos en el eje de las cámaras de mezcla.

Un modelo basado en las energías cinéticas de los chorros de entrada se describe como el mejor modelo para la posición del punto de impacto en los mezcladores CIJ para una amplia gama de condiciones de trabajo. Para los mezcladores T-Jets, se utiliza un análogo elástico de los dos chorros de entrada para predecir la posición del punto de impacto. Estos resultados fueron validados mediante imágenes PLIF y simulaciones 3D CFD. Este estudio valida los modelos que se pueden utilizar como herramientas de diseño para mezcladores de jets opuestos. El caso de estudio industrial seleccionado para validar los modelos de posición del punto de impacto de los chorros es la producción de mayonesa en mezcladores CIJ.

También se realizan simulaciones 3D CFD para estudiar la dinámica de flujo en mezcladores SR. Estos mezcladores generalmente operan en los regímenes de flujo de Stokes y la distribución del espesor de las estrías se determina a partir del perfil de velocidad completamente desarrollado. Se presenta una expresión de diseño explícita para calcular el espesor de máximo y mínimo de las estrías en cada fase, que es el paso límite para mezclar en mezcladores SR.

Esta tesis amplía el conocimiento existente sobre mezcla en reactores 2D, dando lugar a soluciones para la industria. Las principales contribuciones de esta tesis son un nuevo proceso de formulación para el desarrollo de materiales de alto rendimiento, el modelado de micromezclas en reactores químicos y la introducción de ecuaciones de diseño para mezcladores 2D, que permiten la operación eficiente en condiciones de flujo simétricas y asimétricas.

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Notation

a - truncated gap between cone and plate

a_0 - parameter that corresponds to even or odd mixing element

A - Area [m^2]

A_1 - 1-naphthol

A_1 - molar fraction of A_1

A_2 - 2-naphthol

A_2 - molar fraction of A_2

A_0 - initial interfacial area [m]

A_{inj} - injector area [m^2]

A_{int} - interfacial area [m^2]

A_{water} - parameter for the calculation of water's viscosity

A_{glycerol} - parameter for the calculation of glycerol's viscosity [$\text{mPa}\cdot\text{s}$]

b - parameter for the calculation of the viscosity of aqueous solutions of glycerol

B - diazotized acid

B - molar fraction of diazotized acid

B_{water} - parameter for the calculation of water's viscosity [K]

B_{glycerol} – parameter for the calculation of glycerol’s viscosity

c – parameter for weighting factor calculation

c_L – speed of light in vacuum [m/s]

$\mathbf{C}$ - right Cauchy-Green deformation tensor

C – Concentration [kg m⁻³]

$\bar{C}$ - average concentration [kg m⁻³]

Ca - Capillary number

$C_{\text{fluorescein}}$ - Concentration of fluorescein [mg L⁻¹]

C_{int} - Integration constant

C_N – Courant Number

C_{water} – parameter for the calculation of water’s viscosity [K⁻¹]

C_i^{feed} – feed concentration of species i [mol m⁻³]

$C_{i,0}$ – initial concentration of species i [mol m⁻³]

d – CIJs injector diameter [m]

d_{Hjet} – hydraulic diameter of the injectors [m]

$\bar{d}$ - mean diameter [m]

d_{oil} - diameter of oil droplet [m]

$dl(t)$ – interfacial area of an element of fluid [m]

dx – edge of an element of fluid [m]

dX - initial edge of an element of fluid [m]

dy - edge of an element of fluid in the normal direction of x [m]

$\mathbf{D}$ - stretching tensor

D - mixing chamber diameter [m]

Da - Damköhler number

D_i - diffusivity coefficient of species i [$\text{m}^2 \text{s}^{-1}$]

D_m - diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]

D_H - hydraulic mixing chamber diameter [m]

D_{water} - parameter for the calculation of water's viscosity [K^{-2}]

e - depth of the mixing chamber [m]

E - proportional factor

Eu - Euler number

E_p - potential energy [J]

$\dot{E}_{K,\text{inj}}$ - kinetic energy rate at the injectors [W]

f - factor that depends on μ_0 [$\text{m}^3 \text{kg}^{-1}$]

$\mathbf{F}$ - deformation gradient tensor

F - force [N]

G_{glycerol} - parameter for the calculation of glycerol's viscosity [K]

G_{ij} - interaction parameter which is a function of the components i and j

G_{water} – parameter for the calculation of water's viscosity [K]

h - headspace of the opposed jets mixing chamber [m]

h_p - gap between the two parallel plates or between the cone and plate [m]

$h_{\text{r/s}}$ - distance between rotor and stator [m]

H - mixing chamber height [m]

$\mathbf{I}$ - identity tensor

I_s - intensity of segregation

J - fed jet's momentum rate [kg m s⁻²]

k - spring's constant [N m⁻¹]

k_0 - factor that accounts for the repulsive colloidal forces acting among dispersed particles

k_1 – rate constant of the reaction $A_1 + B \xrightarrow{k_1} R$ [m³ mol⁻¹ s⁻¹]

k_2 – rate constant of the reaction $R + B \xrightarrow{k_2} S$ [m³ mol⁻¹ s⁻¹]

k_3 – rate constant of the reaction $A_2 + B \xrightarrow{k_3} Q$ [m³ mol⁻¹ s⁻¹]

K - identification number for flow regime transition

l – distance between interfaces or spring length variation [m]

l_v – ratio of control volume over the cross-sectional area of the mixing chamber

L - width of an element represented by a square [m]

m_1 – slope of the coordinates of two successive particles

m_2 – the inverse of m_1

$m_{\text{CaCl}_2\cdot\text{H}_2\text{O}}$ – mass of calcium chloride [g]

m_{IR} - factor that depends on $x_{0,\text{glycerol}}$ [L g⁻¹]

m_{solution} – mass of glycerol in solution [g]

m_{glycerol} – total mass in solution [g]

$\mathbf{M}$ - parameter which defines the symmetry of the problem

$\mathbf{n}$ - normal direction of the interface

n - number of mixing chamber diameters over which turbulent mixing occurs

n_{me} - number of mixing elements

n_i – molar fraction of i component

n_j – molar fraction of j component

n_{samples} - total number of samples

$n_{\text{samples}} \big|_{d_i \leq d_{\text{oil}} \leq d_i + \Delta d}$ - number of particles belonging to the interval $d_i \leq d_{\text{oil}} \leq d_i + \Delta d$

n_t - time discretization

n_x - spatial discretization

np - number of particles

N – number of turns

N_e - number of cubic elements

Pe - Peclet number

p - pressure [Pa]

P_{water} - parameter for the calculation of water's viscosity [mPa·s]

P_{glycerol} - parameter for the calculation of glycerol's viscosity [mPa·s]

P_{int} - perimeter of the interface [m]

Pr - probability density function

q - mass flow rate of each fluid [kg s⁻¹]

Q - 2,4-bis[(4'-sulfophenyl)azo]-2-naphtol

Q - molar fraction of Q

Q - volume flow rate of each fluid [m³ s⁻¹]

r - radial coordinate [m]

r_s - flow rate ratio

R - generic reaction product product or $R = \text{o-R} + \text{p-R}$ where o-R is 2-[(4'-sulfophenyl)azo]-1-naphtol and p-R is 4-[(4'-sulfophenyl)azo]-1-naphtol

R - molar fraction of R

Re - Reynolds number

RhB - Rhodamine B

RhB_{oxi} - oxidized Rhodamine B

Re_{Hjet} - hydraulic Reynolds number at injectors

Re_{HJet1} – hydraulic Reynolds number at injector 1

Re_{HJet2} – hydraulic Reynolds number at injector 2

$Re_{HJet,LV}$ – hydraulic Reynolds number at less viscous liquid stream

$Re_{HJet,MV}$ – hydraulic Reynolds number at more viscous liquid stream

Re_{LV} – Reynolds number at less viscous liquid stream

Re_{MV} – Reynolds number at more viscous liquid stream

Re_{oil} – Reynolds number at the injector where sunflower is injected

R_i - reaction expression [$\text{mol m}^{-3} \text{s}^{-1}$]

RI – refractive index of a system water-glycerol

RI_{water} – refractive index of water

RI_{glycerol} – refractive index of glycerol

RI^* - refractive index of the mixture of an aqueous solution of glycerol and calcium chloride dehydrated

RI_0 - refractive index of a glycerol-water system where the concentration of calcium chloride is 0

R_p - radius of the plate [m]

s - striation thickness [m]

s_0 – initial striation thickness [m]

s_1 - striation thickness at the impingement point position [m]

s_2 – final striation thickness at the formation of pancake[m]

s_3 – final striation thickness formed from vortices [m]

S – 2,4-bis[(4'-sulfophenyl)azo]-1-naphtol

S - molar fraction of S

S_{BT} - elementary of Baker's Transformation

S_s - scale of segregation [m]

St – Strouhal number

t – time [s]

t_D - characteristic diffusion time [s]

$t_{\text{micromixing}}$ - micromixing time [s]

t_R - reaction time [s]

T - period [s]

$\mathbf{u}$ – velocity vector field [m s⁻¹]

U – dimensionless velocity [m s⁻¹]

V – volume [m³]

w - width of injectors [m]

w_V - weighting factor

We – Weber number

W - width of the mixing chamber [m]

x – space coordinate [m]

$\mathbf{x}^*$ – momentum source [m]

x_{IP} - jets impingement point displacement [m]

x_{glycerol} – mass fraction of glycerol

$x_{0,\text{glycerol}}$ – initial mass fraction of a glycerol-water system where the concentration of calcium chloride is 0

$x_{\text{CaCl}_2\cdot\text{H}_2\text{O}}$ – mass fraction of calcium chloride in a glycerol-water system

$\mathbf{x}$ – position vector [m]

$\mathbf{X}$ – initial position vector [m]

X_i – selectivity of species i

y – space coordinate [m]

Y – initial edge of an element of fluid [m]

z – cylindrical coordinate [m]

Greek Letters

α' – dimensionless interfacial area

$\alpha(\mathbf{X},t)$ - rate of expansion and contraction around a particle $\mathbf{X}$ [s⁻¹]

β – angle between cone and plate [rad]

β_c – aspect ratio of the channel

β_1 – ratio between the initial concentrations of A_1 and B

β_2 – ratio between the initial concentrations of A_2 and B

$\dot{\gamma}$ – shear rate [s^{-1}]

γ_i – thickness of each component in a lamellar structure [m]

γ_{A_1} – stoichiometric ratio between the initial concentration of A_1 and B

γ_{A_2} – stoichiometric ratio between the initial concentration of A_2 and A_1

Γ - reduced time

Γ^* - warped time

Γ_{MZ} – dimensionless time, $\Gamma_{\text{MZ}} = t / \tau_{\text{MZ}}$

δ - thickness of a stria [m]

δ_A - thickness of phase A [m]

δ_B - thickness of phase B [m]

Δd - bin of diameter of oil droplet [m]

Δp – pressure drop [Pa]

Δt – time step [s]

ΔV – electric potential [V]

Δx – edge of one element of the mesh [m]

ε - energy dissipation rate per unit of mass [$\text{m}^2 \text{s}^{-3}$]

ε_1 – ratio between k_2 and k_1

ε_2 – ratio between k_3 and k_1

η - ratio between the initial striation thickness and the striation thickness

θ – temperature [K]

θ_{ow} – wall contact angle for an oil and water interface [°]

ι - parameter for weighting factor calculation

κ - parameter for weighting factor calculation

λ - stretch ratio

λ_e - excitation wavelength [m]

λ_f - fluorescence wavelength [m]

λ_k - Kolmogorov scale [m]

Λ - Lyapunov exponent

μ – viscosity [Pa·s]

μ^* - viscosity of the mixture of an aqueous solution of glycerol and calcium chloride dehydrated [Pa·s]

μ_0 – initial viscosity of a glycerol-water system where the concentration of calcium chloride is 0 [Pa·s]

μ_{glycerol} - viscosity of glycerol [Pa·s]

μ_m – viscosity of the dispersed medium [Pa·s]

$\mu_{\text{normalized}}$ - normalized viscosity

μ_{water} - viscosity of water [Pa·s]

ν - kinematic viscosity [$\text{m}^2 \text{s}^{-1}$]

ξ - dimensionless impingement point position

ξ^* - dimensionless spatial coordinate

ρ - density [kg m^{-3}]

ρ_{glycerol} - density of glycerol [kg m^{-3}]

ρ_{water} - density of water [kg m^{-3}]

ρ^* - density of the mixture of an aqueous solution of glycerol and calcium chloride dehydrated [kg m^{-3}]

$\rho_{\text{CaCl}_2 \cdot \text{H}_2\text{O}}$ - density of calcium chloride [kg m^{-3}]

σ - interfacial tension [N m^{-1}]

σ_C^2 - spatial variance of the volume fraction

ζ - dimensionless space time for square ducts

τ - shear stress [Pa]

τ_{CIJ} - residence time in the CIJ mixer [s]

τ_{MZ} - average residence time in the mixing zone [s]

v - velocity magnitude [m s^{-1}]

v_c - critical velocity [m s^{-1}]

ν_{chamber} – velocity at the mixing chamber [m s^{-1}]

ν_{inj} – injector velocity [m s^{-1}]

ν_{medium} – speed in a specific medium [m s^{-1}]

ν_p – velocity of the top plate [m velocity in the radial coordinate [m s^{-1}]

ν_r – velocity in the radial coordinate [m s^{-1}]

ν_z – velocity in the z coordinate [m s^{-1}]

ν_φ – velocity in the φ coordinate [m s^{-1}]

ψ^* – dimensionless spatial coordinate

φ – cylindrical coordinate [rad]

ϕ – volume fraction

ϕ_K – jet's energy feeding rate ratio

ϕ_M – jets' momentum rate ratio

ϕ_m – volume fraction of the dispersed particles at which the viscosity reaches an infinite value

ϕ_v – vortex shedding frequency

χ – position of the striations interface

Ψ^* – dimensionless spatial coordinate

ω – angular velocity [rad s^{-1}]

Mathematical Operations

$\langle \rangle$ - spatial average

$| |$ - absolute value

$\nabla(\cdot)$ - gradient operator

Subscripts

1 – jet 1

2 – jet 2

Acid – acid stream

Base – base stream

e – elements

H₂O₂ – stream that contains hydroxide peroxide

i – particle or iterations

inj - injector

Iron – stream that contains iron

j – index of the time step number

LV – Less viscous

me – mixing element

MV – More viscous

RhB – Rhodamine B

Abbreviations

2D – Two dimensional

3D – Three dimensional

AB-RPLIF - acid/base reaction with a pH tracer, uranine

CIJ – Confined Impinging Jets

CFD – Computational Fluid Dynamics

CNC - Computer Numerical Control

EAM – Elastic Analogue Model

HBL – Hydrophilic-lipophilic

HTMD – High Throughput Material Development

LDA – Laser Doppler Anemometry

LM – Lamellar mixing

LMS – Lagrangian Mixing Simulations

LV – Less viscous

LIF – Laser-Induced Fluorescence

KEM – Kinetic energy model

MIF – Material Innovation Factory

MM – Momentum model

MV – More Viscous

o/w – Oil/water

oxi-RPLIF – Fenton’s reaction with a tracer, Rhodamine B, that is oxidized in the reaction region

PD – Product Development

PLIF – Planar Laser Induced Fluorescence

PIV – Particle Image Velocimetry

PTV – Particle Tracking Velocimetry

PMT – Photomultiplier Tube

PU-RIM – Polyurethanes made in RIM machines

R&D – Research and Development

RTD – Residence Time Distribution

RhB – Rhodamine B

RIM – Reaction Injection Moulding

RPLIF – Reactive Planar Laser Induced Fluorescence

SF – Stopped-Flow

SPIRE - Sustainable Process Industry through Resource and Energy Efficiency

SR – Split and recombine

VOF – Volume-Of-Fluid

w/o – water/oil

1 Introduction

Mixing is commonly defined as the increase of homogeneity in terms of composition, properties and temperature, in order to achieve a desired final product. Mixing has a significant impact on chemical processes, particularly for fast reactions, where the mixing time of the liquid reactant streams plays a role on the selectivity of a reaction or the morphology of a solid material. Furthermore, the scales and times of mixing have several effects, including the rates of heat and mass transfer, process operating time, cost and safety, as well as in product quality. The link of mixing to the final product makes it necessary to have accurate control of the mixing scales during industrial processes. The nexus of mixing to product properties is often the reason that scaling-up of processes from lab to industrial scales is a complex trial and error procedure.

Mixing units are parts of plants in several industries, such as fine chemicals, pharmaceuticals, petrochemicals, biotechnology, polymer processing, paints and automotive products, cosmetics, food, drinking water, wastewater treatment, pulp and

paper industry. The chemical reactions where mixing units have a key role comprehend combustions, biological growth, neutralisation, precipitation and polymerisation.

The broad practice of mixing in industrial processes comprises the usage of tanks equipped with impellers and baffles. The advantages of these reactors are the low construction cost, easy maintenance and operation. However, low efficiencies are associated to these processes. The energy for mixing is not injected directly into the contacting interface of the reactants liquid streams, which may cause poor mixing, longer mixing times, less energy efficiency for mixing, and the production of undesired secondary products. The selectivity of a process is actually a major limitation regarding the environmental impact of an industrial process. SPIRE (Sustainable Process Industry through Resource and Energy Efficiency) technological platform points the improvement of mixing as a major goal with a huge impact on separation operations that accounts for 40% of energy consumption in chemical processes (Tello and Weerdmeester, 2019). This goal is one of the cornerstones to enable the industry to keep on decreasing its carbon footprint.

As an alternative to mechanical mixers, static mixers without moving parts and with great energy efficiencies have been increasingly used in industrial processes. The potential advantages of static mixers compared to mechanically agitated vessels are the small space requirements, low equipment cost, no moving parts, the short span of residence times, good mixing at low shear rates, flexible production of different products and possibility to introduce self-cleaning technologies (Thakur et al., 2003). Static mixers have several applications, such as, in the pharmaceutical, petrochemical, food, cosmetics, biotechnology, wastewater and plastics industries.

The academic research on mixing has contributed to significantly increase the know-how on design, optimisation and scale-up of chemical reactors. Over the last decade, mixing principles, concepts and tools have been developed, enhancing the industrial design and operation of mixing equipment. With the advent of the mixing science and

more recently the dissemination of Computational Fluid Dynamics, static mixers have also emerged in the literature, and its industrial implementation became widespread. In the last 20 years, the Associated Laboratory LSRE-LCM has been researching on a number of static mixers, namely Confined Impinging Jets (CIJ), T-jets mixers and NETmix technology (Santos et al., 2002; Erkoç et al., 2007; Laranjeira et al., 2009; Lopes et al., 2013). These devices enable large flow throughputs with very fast and well-controlled mixing times.

Experimental and numerical studies on the fundamentals of mixing made at LSRE-LCM provided evidence of an interesting particularity of CIJ, T-Jets mixers and NETmix: the 2D nature of the flow dynamics and mixing. The small and micro-sized dimensions of these reactors (meso and microreactors) ensure that mixing occurs at laminar flow regimes, and it is mainly enhanced by chaotic fluid motion. The flow dynamics at chaotic flow regimes causes the fast elongation of fluid elements and the corresponding reduction of the length scales, which is made at the same rate as the stretching. Thus, the flow dynamics is defined by a 2D time-periodic map (Mohr et al., 1957; Chien et al., 2006). Furthermore, the energy transfer between flow scales in 2D reactors is well-described within the framework of the 2D turbulence theory. In this theory, the energy is injected from smaller scales, approximately with the dimensions of feed flow streams, and then it is fed to larger eddies, with roughly the dimension of the reactor diameter or width (Gonçalves et al., 2017). Therefore, in the classical turbulence theory, the large flow scales are dissipated by 3D turbulence from the mechanism of vortex stretching, that ends up dissipating energy to heat at the smallest scale of a vortex cascade. This is quite brilliantly summarised in Lewis Richardson poem on turbulence (Richardson, 1922),

Big whorls have little whorls

That feed on their velocity,

And little whorls have lesser whorls

And so on to viscosity.

Mixing in 3D turbulence theory is based on turbulent dispersion, where the small scale eddies homogenise the concentration of chemical species giving rise to plumes. In 2D flows, the energy dissipation is mainly caused by the viscous stresses around the large vortices evolving through the reactor, which are fed from the inlet jet streams. In 2D flows, the main mixing mechanism is the generation of the interfacial area between the flow streams. In this way, the energy injection from flow into mixing is more efficient, and the mixing mechanisms are better controlled. This opens a very interesting prospect in terms of energy efficiency and product quality in industrial processes. Based on 2D time-dependent maps and 2D turbulence theory arguments, the mixers in this thesis are considered 2D.

The vast know-how on 2D reactors has contributed to the generation of useful data and solutions for robust experimental designs based on the fundamental understanding of mixing mechanisms. This thesis brings more advances in this field. The long-term objective of this work is the collection of design tools to implement 2D reactors in plants and on product development methodologies targeted at these mixers. The key audience is the one that deals with mixing issues, such as engineers, operators and scientists.

1.1 Mixing Problems and Costs

The successful manufacturing of products in the industry strongly depends on the process issues related to the mixing efficiency. The failure of the mixing scale-up implies that the required product yield and quality of the final product is not achieved.

Furthermore, production costs may significantly increase. Table 1.1 describes the impact of poor mixing in the manufacturing costs in chemical, pharmaceutical, pulp and paper industries (Paul et al., 2004).

Table 1.1 Mixing issues and respective costs in chemical, pharmaceutical, pulp and paper industries (Paul et al., 2004).

Chemical industry	Pharmaceutical Industry	Pulp and Paper Industry
Paul et al. (2004) makes an estimative of the costs of poor mixing in the US chemical industry. In 1989, these costs were between \$1 billion and \$10 billion. In a leading multinational chemical company, the losses related to poor mixing were estimated at \$100 million in 1993.	The costs related to lower yields are approximately \$100 million. The lost value due to the problems in scale-up and process development is on the order of \$500 million. There are also mixing issues that prevent developed products from reaching the market. The loss of value from this is exorbitant.	A CPPA survey in 1980 reported chemical savings averaging 10 to 15% (Berry, 1990). Factories that invested in mixing equipment had returned the investment in approximately three months.

Although this cost analysis (Table 1.1) has more than 30 years, the impact of mixing in industry is timeless. The continuous advances in mixing technologies lead to a competitive economy in terms of product development. Thus, an exhaustive attempt at the exact control of the mixing scales is required to improve the quality of the final product from the chemical industry. In this sense, advances in mixing theory could underlie the introduction of practical tools to design reactors, enabling the direct scale-up of the mixing devices. This strategy guarantees that the enhancement of the mixing operations will contribute to savings in scale-up and process development.

The numbers in Table 1.1 and the requirements for the exact control of the mixing scales in industrial reactors have motivated further study on mixing dynamics in industrial processes.

1.2 Mixing Challenges in the Industry

There are industrial challenges on the application of 2D reactors, particularly regarding the most efficient operation modes. One important aspect that has not been approached in a systematic way for these mixers is the application to mixing of fluids with dissimilar properties at different flow rates. In fact, the German company KraussMaffei has already engaged in a successful industrial demonstration with LSRE-LCM team regarding a mixing process in a CIJ mixing chamber for two fluids with a viscosity ratio of 10. However, mixing science that enabled the efficient and fast mixing of dissimilar fluids was based on works with similar fluids at different flow rate ratios (Fonte et al., 2016).

The present thesis studies the mixing mechanism of dissimilar fluids in a very controlled flow with the completely defined shear field. Data from these studies will be used to make a systematic analysis of mixing in 2D reactors.

Another industrial challenge is the process scaled-down to closely replicate the industrial plant conditions in the lab, simplifying the formulation process. Formulations usually occur under intensive mixing conditions at the lab-scale, which do not correspond to the actual industrial operational conditions or even in pilot-scaled devices. This makes that, in most cases, the formulation recipe may fail in the production stage.

In this thesis, a rotational device is introduced as a product development methodology to generate data for mixing studies in 2D reactors. In rheometric devices, there is complete control of mixing that can be set from the geometry of the devices and rotation speed. Data from mixing and chemical reaction generated in rotational devices

will be used for the design of 2D reactors. The main goal is providing useful data and robust solutions for experimental development of products and process design based on the understanding of mixing mechanisms, that will contribute to direct scale-up methodologies and the reduction of production costs.

1.3 Previous Work

This work is the follow up of the PhD theses of Fonte (2012), Sultan (2013) and Torres (2014). Although these theses address different topics, it was the starting point for this work.

Sultan (2013) studied the mixing in T-Jets mixers from Planar Induced Laser Fluorescence (PLIF), Computational Fluid Dynamics (CFD) simulations and test chemical reactions. The influence of geometrical and operational parameters on the flow regimes in T-Jet mixers was demonstrated for the mixing of similar fluids. The parameters considered in Sultan (2013) were mixing chamber width, injector width, mixing chamber depth and headspace.

Fonte (2012) described the mixing mechanisms and the flow regimes in CIJ mixers from experimental and numerical results. The position of the impingement point position under balanced and unbalanced conditions was also addressed in Fonte (2012) for similar fluids. From the flow visualisations and numerical results, a new model was described to predict the impingement point position in the mixing chamber and the best operational conditions for fluids.

In Torres (2014), a method for efficient mixing in rheometers was developed using a polymerisation reactor. This method consists of a modified cone and plate rheometer, including the rounded holding cell with a separator that splits the cell into two equal volumes. The height of the sample can be modified by changing the measuring position of the cone. This method, called Holding Cell, may be applied to measure the rheological properties of a polymeric mixture during the polymerisation reaction.

The aforementioned works were follow-ups of PhD theses of Santos (2003) and Teixeira (2000). Teixeira (2000) set up the initial CFD modelling for CIJ reactors based on a 2D simplification of the process. This was actually the first time that the flow in CIJ mixers was conceptualised in a 2D framework. This approach was subject to criticism at the time, but it revealed more and more with time to provide the best mind set for the study of mixing in CIJ mixers. Teixeira (2000) also introduced the first proofs of heterogeneous flow dynamics in CIJ mixers and a concentration of spectral energy in typical frequencies rather than a cascade of energy transfer towards viscous dissipation. This provided strong evidence that although the flow was quite dynamic, with very strong oscillations in the direction of inlet jets, it was not well-described from classical turbulence. These concepts were then explored in detail by Santos (2003), who showed the relation between typical frequencies and the two vortices scales that exist in CIJ dynamic flows. Santos (2003) provided extensive validation on the ability to simulate the flow dynamics in CIJ mixers with a 2D representation of a dynamic laminar flow at the axial plan of the mixing chamber.

1.4 Thesis Objectives and Layout

The main objectives of this thesis are the identification of the mixing mechanisms in 2D mixing technologies, such as rotational devices, CIJ, T-Jets and Slip-and-Recombine mixers. Mixing of similar and dissimilar fluids under balance and unbalance conditions are studied in 2D static mixers. Experimental studies use sets of model fluids tuned with glycerol for visualisation of mixing. Numerical simulations focus on the description and validation of CFD models for mixing of dissimilar fluids.

The state-of-the-art is presented in the beginning of each chapter according to its relevance. In Chapter 2, a rotational device is proposed with the particularity that it can mimic the mixing conditions of 2D reactors at the production stage. The geometries addressed are well-known in rheometry as plate-plate and cone-plate. The main advantages of this method are the requirement of small amounts of reactants, short

operating times and the simultaneous measurement of rheological properties during the formulation process. The mixing of similar and dissimilar fluids was obtained using CFD simulations. Characteristic mixing length scales in the flow, such as striation thickness and interfacial area, were determined using a Lagrangian approach as the metrics to assess the quality of mixing. The topology, i.e. the initial relative position of each fluid, was also changed and its influence on the degree of mixing was reported. This chapter adds further understanding about the fundamentals of the rheometric flow and the generation of mixing scales to the PhD thesis of Torres (2014).

Chapter 3 focuses on the methods of flow visualisation and assessment of micromixing. This chapter is divided into two parts. In Part I, a set of steps is described as a method for matching the refractive index of glycerol solutions for flow phenomena studies. This methodology was applied in experiments conducted in CIJ and T-Jets mixers (Chapters 4 and 5) using optical techniques for mixing of two different fluids. In Part II, two methods were selected for micromixing assessment based on chemical reaction selectivity. The test-reactions used were an acid-base reaction with fluorescein as the reaction sensitive tracer and the Fenton's reaction, with rhodamine-B as the reaction tracer. Both test-reactions were studied in a stopped-flow equipment to define suitable operational conditions, namely chemical composition of the inflow streams, concentration of reagents and fluorophore, and suitable excitation light wavelength.

In Chapter 4, the mixing mechanisms are studied in CIJ mixers. This chapter is divided into four parts, as follows:

- Part I - A theoretical methodology to describe micromixing in CIJ mixers using a lamellar model is presented. It considers the dynamics of striation thinning and diffusion at the interface of the mixing fluids. A lamellar micromixing (LM) model based on mixing evolution functions was applied to simulate chemical reactions;

- Part II – Flow dynamics and mixing efficiency in CIJ mixers were characterised experimentally for fluids with a viscosity ratio range from 2 to 9 for balanced and unbalanced flow conditions. The experimental characterisation was made with PLIF images. This work adds a further understanding of mixing mechanisms in CIJ mixers to Fonte (2012);
- Part III – The interaction of jets was studied theoretically, experimentally and numerically for the mixing of two dissimilar fluids. Three models are introduced as candidates to describe the impingement point interactions in the mixing chamber. The first model was introduced by Fonte (2012), and it is based on an elastic analogy of the two jets. The second one considers the balance of the kinetic energy of two lagrangian particles inside of each jet. And the last one was described assuming the balance of the linear momentum of two lagrangian particles in each fluid stream. These models were validated experimentally and numerically from PLIF images and 3D CFD simulations, respectively. This work extends the prediction of the impingement point position for similar fluids in Fonte (2012) to dissimilar fluids;
- Part IV – Two case studies in CIJ mixers are addressed as applications of the previous results. The formulation methodology in rotational devices, as presented in Chapter 2, is applied to the production of polyurethanes in Reaction Injection Moulding (RIM) machines using CIJ mixing chambers. The mixing length evolution in rheometers and in RIM machines are matched from the angular speed in rotational devices. The second case is the design of an emulsification process in CIJ mixers. The production of mayonnaise was selected as the case study. The operation conditions were estimated from the models demonstrated in Part III.

In Chapter 5, the mixing mechanisms in T-Jets mixers are studied numerically and experimentally from CFD simulations and PLIF images. This chapter is divided into three parts:

- Part I - Flow regimes and mixing of similar and dissimilar fluids are identified from 2D concentrations fields obtained from PLIF images. These fields are used to qualitatively describe the effect of Reynolds number, the geometrical parameters and the physical properties of fluids on mixing. This work extends the characterisation of mixing of similar fluids in Sultan (2013) to dissimilar fluids;
- Part II - The impingement point position in T-Jets mixing chamber is studied from 3D CFD simulations. A model based on the elastic analogy of the two jets is also presented to predict the impingement point position. The respective validity range of this model is defined from CFD simulations;
- Part III - The operation conditions of reactive PLIF methods determined as suitable for mixing studies in Chapter 3 were tested in T-jets mixers. The mixer was illuminated in the axial plane with a laser light sheet. Results enable to select the best method to be applied for the micromixing assessment.

In Chapter 6, the flow in a Split-and-Recombine (SR) mixer is characterised from 3D CFD simulations. The mixing performance is quantified by the distribution of the mixing length scales, which were tested for symmetrical and unsymmetrical flow conditions using two Newtonian fluids at Stokes flow regime. The impossibility of ensuring a plug flow of viscous fluids in SR mixers led to a non-homogeneous distribution of the mixing length scales in these devices. Thus, the efficiency of mixing controlled by the diffusion at molecular scale is questioned due to the non-idealised striation thickness decay. In this chapter, a more conservative way to estimate the mixing length scales than the ideal transformation maps is demonstrated.

Finally, Chapter 7 condenses the main conclusions of the previous chapters. The results of this thesis are presented in six sections: mixing mechanisms in inertial and non-inertial flow regimes in 2D reactors, topology of mixing in chemical reactors, fully resolved modelling and simulation to assess micromixing in opposed jets mixers, mixing of dissimilar fluids in opposed jets mixers, design of processes for static mixers and

methods of flow visualisation in transparent reactors. Suggestions for future work are also presented in Chapter 7.

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2 High-Throughput Material Development for 2D Reactors

2.1 Introduction and State of the Art

The development of new materials and its launch on the market takes a long time because multiple stages are required. The demand of product development is related to a wide range of combinations between compositions and processing conditions, such as temperature, flow rates and mixing conditions. A set of tools has been implemented to accelerate the process of material development, contributing to the high-throughput material development (HTMD). HTMD was formally described by Hanak (1970), who published for the first time the concept of testing multiple samples at the same time. Experiments involve accurate planning, selection and then the performance of a wide range of compositions and operating conditions in a short period of time.

The first HTMD experiments come from the early 1920s, when 4000 catalysts combinations had to be screened for the industrial ammonia synthesis using the Haber process, enabling the industrial implementation of one of the reactions that most changed the world. The development of computational resources has empowered the

analysis of a wide range of samples and the testing of multiple materials. Thus, different applications of the multiple sample concept to HTMD were published in the 1990s, including the formulation of new polymers, metals and inorganic phosphors (Fodor et al., 1991; Xiang et al., 1995; Dagani, 1999; Jandeleit et al., 1999; McFarland and Weinberg, 1999).

The automation of HTMD has made the formulation process even faster. The great advantage is the reduction of time to market by months and the costs of inherent formulation processes. In R&D centres, such as Material Innovation Factory (MIF) at the University of Liverpool, high-performing formulation robots associated to the automated design of experiments have accelerated the materials discovery and product development. The automated formulation robot (GEOFF), Formax, and high throughput rheometers are some of the automated technologies installed at MIF that enable the fast design of formulations (Unilever, 2018; Liverpool, 2019).

One of the most challenging product development (PD) cases, as far as scale-up is regarded, is the formulation of reactive polymers for Reaction Injection Moulding (RIM). RIM is a common process for the production of polyurethanes and polyureas (Malguarnera and Suh, 1977; Ritcher and Macosko, 1978; Lee et al., 1980; Tucker and Suh, 1980). In RIM process, two extremely viscous monomers, isocyanate and polyol, are impinged at a velocity range of 10 to 150 m s⁻¹ through two opposed injectors with 1-3 mm of diameter. The two impinged fluid streams are mixed for 10-100 ms in a cylindrical mixing chamber with 3 -15 mm diameter and a length around 5 times the diameter. At the outlet of the mixing chamber, the mixture is discharged at throughputs ranging from 10 to 100 kg min⁻¹ into a mould, where most of the polymerisation occurs, and the plastic part is formed (Oertel, 1985).

The formulations for industrial RIM machines are usually designed at lab-scale and then tested in a pilot plant. Formulation development at lab-scale usually occurs under intensive mixing conditions, which do not correspond to the industrial operating

conditions and even to the ones in pilot-scaled devices. In most cases, this results in the failure of the formulation recipe in the production stage.

Inconsistencies of the lab tests in pilot machines associated to experimental requirements make this process very expensive and time-consuming (Ranz, 1986; Macosko, 1989; Berins, 1991). The longer process time step in the pre-commercial production plant is associated to the filling of the storage tanks, which have a volume that is larger than 20 L, and to the operation time of the experimental set-up associated with thermostabilising fluids. In addition, the efficient cleaning of the RIM machines is a long and important step in the development of new products because it avoids contaminations of the final product. When the operational parameters in RIM machines are not optimised, one of the most common problems during product development stages is the clogging of the mixing head caused by the polymerisation of the reactive mixture in the RIM mixing chamber nozzles. All these reasons show that the full control of mixing conditions at lab-scale will make the product formulation process less time-consuming and more cost-effective.

A procedure to design formulations at lab scale is presented in this work to reduce the complexity of product development. The objective is the development of a fast formulation process at lab-scale with the advantage of requiring a small volume of reagents and reducing the waste. This lab-scale method for product development must ensure the complex interactions between chemical reaction and reagents mixing that occur at industrial scale. For that, characterisation of the mixing length scales and times in a lab-scale unit is needed to ensure that the mixing scales mimic the industrial process scales. A particular implementation of this method is in RIM machines for PU processing.

Two geometries are addressed in this work: plate-plate and cone-plate rotational rheometers. Both geometries are widely used in rheological measurements. Rheometer is a laboratorial equipment that measures the rheological properties of the samples, i.e.

the dynamic viscosity, under controlled temperature and for a given measurement time. The formulation development in rheometric devices is particularly interesting in the development of new products because it provides relevant data for the manufacturing industry, such as the gel time and the viscosity rise in the reactive system. This method can be easily adapted at polyurethane production sites to perform kinetic studies to be used in RIM machines.

In this work, a new PD method is introduced using rotational devices. In the next section (Section 2.2), mathematical foundations related to the mixing mechanics are detailed. These concepts describe the liquid-liquid mixing, and they will be applied to quantify the mixing scales in rheometric devices. After the description of mixing concepts, the chapter is divided into two main parts: the mixing of similar fluids (Section 2.3) and the mixing of dissimilar fluids (Section 2.4).

2.2 Mechanistic Mixing Models – Mathematical Foundations

In liquid-liquid reactive mixing processes, advection, reaction and diffusion are the three main phenomena involved. These mechanisms control the mechanical properties of the final product that can be evaluated from the conversion, selectivity and yield of the reaction system.

In non-reactive mixing systems, such as mixing of two viscous fluids, the main mixing mechanism is the deformation of the interface between fluids that ensures the increase in the concentration gradient for molecular diffusion.

Spencer and Wiley (1951) started to describe mixing from the deformation of the interfacial area between two representative fluids caused by shear. One year later, Danckwerts (1952) defined two measurements of mixing: the scale of segregation and the intensity of segregation. The scale of segregation measures the lack of distribution of each component from the volume fraction. The intensity of segregation measures the deviation from the mean of the species concentration in fluid clumps. Mixing

mechanisms influence these two mixing quantities in different ways. The scale of segregation is affected by the supplied shear to fluid elements, and the intensity of segregation depends on the molecular diffusion (Mohr et al., 1957a).

Mixing of fluids is frequently analysed from a kinematic point of view. This investigation addresses the mixing phenomena conceptually. The first descriptions of mixing were analysed in shear flows, which occurs in purely laminar systems. In these flows, the goodness of mixing depends on the flow shear conditions. Two parameters can be used as metrics for the mixing degree: the generation of interfacial area (Spencer and Wiley, 1951) and the striation thickness (Mohr et al., 1957a).

Mohr et al. (1957a) introduced the concept of striation thickness from the visualisation of a dye dispersed into a fluid and enclosed between two parallel plates. The top plate is moving, and both fluids have the same viscosity and density, and the diffusion between them was neglected. The result is the stretching of dye and the increase of the interfacial area between the representative fluids. The visualisation of motion shows the creation of thin lamellae of dye, whose width is the striation thickness. This experiment showed that the deformation field and the orientation of fluid elements greatly impact the laminar mixing.

The mixing analysis in shear flows has been applied in industrial processes. An example is the single-screw extruders, which are widely used as a mixing device in the plastic industry (Mohr et al., 1957b).

In shear flows, stretching creates a linear growth of the interfacial area for a long time (Ottino and Wiggins, 2004). The interface growth can be empowered in a chaotic flow regime. Ottino (1989) describes the mechanical mixing in chaotic flows as the stretching and folding, in space and time, of an element of fluid tracked in the system.

Ottino et al. (1979) defined a model, the lamellar model, which describes the mechanical mixing. This model considers that mixing occurs by stretching and folding, giving rise

to lamellae or strips. Figure 2.1 shows the concept of striation thickness, s , for an ideal binary mixture, which is given by

$$s = \frac{\delta_A + \delta_B}{2} \quad (2.1)$$

where δ_A and δ_B are the thicknesses of each component (Ottino et al., 1979). The description of striation thickness in mixing processes is quite useful for the measurement of the mixing degree. For example, when $s \leq 50 \mu\text{m}$, the good level of mixing is achieved at least for PU processing (Ranz, 1986).



Figure 2.1 Striation thickness in an ideal lamellar structure.

Striation thickness is also a quantity of the scale of segregation defined by Danckwerts (1952). For a binary mixture with uniform lamellae, the scale of segregation, S_s , is related to the striation thickness by (Tadmor and Gogos, 2006)

$$s = 4S_s \quad (2.2)$$

Ottino et al. (1979) also described the stretching properties of flow from a Lagrangian approach, from the tracking of an element of fluid. An infinitesimal spherical element with an initial radius $|dX|$ is advected with time. The stretching caused by the shear flow promotes the elongation of this element. The radius deformation is described by

$|dx|$. The deformation of this element can be defined from the stretch ratio, which represents the fraction between the variation of the element radius and its initial radius,

$$\lambda = \frac{|dx|}{|dX|} \quad (2.3)$$

If $0 < \lambda < 1$, the element is compressed and for $\lambda > 1$, the element is stretched (Ottino and Wiggins, 2004). In a continuous laminar flow system, the deformation of fluid elements occurs in the principal direction of shearing, $\lambda > 1$, and the respective compression takes place in the normal direction of shearing. This means that the key aspects of mixing are entirely described by 2D flows, providing the base case for understanding the more complex systems.

Approaches that consider shearing as the only mixing mechanism assume that fluids are immiscible, and so the interfacial area is passive (Aref and Tryggvason, 1984). However, the analysis of miscible flows is rather more difficult (Aref and Tryggvason, 1984). In this case, the interface is active, and some flow modifications related to the flow convection can occur. The description of mixing of miscible fluids is normally approached to the tracking of a non-diffusive tracer. The mechanical mixing promotes the generation of interfacial area for mass transfer and the decrease of striation thickness. These mechanisms promote the squeezing of concentration gradients accelerating the inter-diffusion of components (Ottino, 1980) by steeping the concentration gradients around the interface. Ottino (1980) described the concentration field in a system with multicomponent diffusion from the lamellar model.

2.3 Part I: Mixing of Similar Fluids in a Rotative Device

3D Computation Dynamics Flow (CFD) simulations were performed as a preliminary study to describe the flow dynamics in a plate-plate rotational device and the effect of topology on mixing, i.e the initial placements of fluids in rheometer (Section 2.3.1). The validation of CFD results is made from the comparison with analytical expressions.

The conditions tested in 3D CFD simulations are at low Reynolds number, $Re \ll 1$, resulting in creeping flow regime without secondary flow or flow separation. The evolution of mixing dynamics and structures is described in a plate-plate rheometer for mixing of two fluids with the same physical properties, i.e. similar fluids. The mixing length scales, such as the generation of interfacial area and striation thickness, are computed from CFD simulations and calculated from a Lagrangian approach.

Then, a 2D CFD simulation is validated by the analytical expression of the 2D velocity profile and from the comparison of 2D and 3D contour maps (Section 2.3.2). 2D CFD simulations were run at typical angular speeds in rheometers. The evolution of mixing scales will be compared for both cases: 3D CFD (creeping flows) and 2D CFD simulations.

2.3.1 Plate-Plate Geometry - 3D CFD Simulation

2.3.1.1 Physical Domain

The plate-plate rotational rheometer was introduced by Mooney (1934) and consists in a disk rotating over a cylindrical cavity with slippery walls. Figure 2.2 shows a sketch of two parallel plates used as the flow domain for CFD simulations. This device has a radius-to-height ratio $R_p / h_p = 5$, where $h_p = 1$ mm.

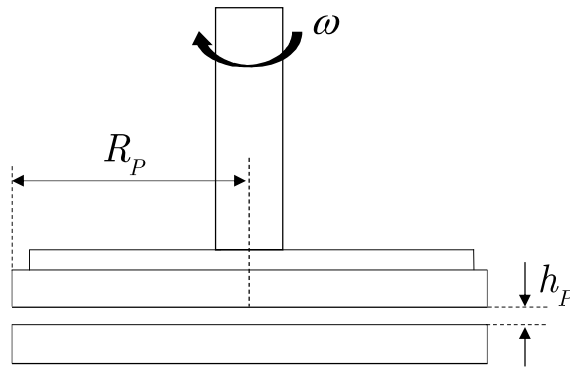


Figure 2.2 Sketch of a 3D parallel plates rheometer where R_p is the radius of the plate, h_p is the gap between the two parallel plates and ω is the angular speed of the top plate.

2.3.1.2 Boundary and Working Conditions

The top plate rotates at angular velocity ω , and the bottom plate is stationary. In the 3D CFD simulation, the boundary conditions were set to the following particular values of velocity: at the top plate, $\omega = 0.01 \text{ rad s}^{-1}$, and at the bottom plate, $\omega = 0 \text{ rad s}^{-1}$. At the top and bottom walls, no-slip boundary conditions are assumed, i.e. the velocity components are set to zero. The fluid enclosed between the two parallel plates has a density $\rho = 1260 \text{ kg m}^{-3}$ and a viscosity $\mu = 0.79 \text{ Pa} \cdot \text{s}$.

At this condition, the Reynolds number, which is determined from $\text{Re} = \rho \omega R_p h_p / \mu$, is $\text{Re} = 8 \times 10^{-5}$, resulting in a creeping flow without secondary flow or flow separation.

2.3.1.3 Domain Discretisation and Governing Equations

The 3D domain was discretised with 6.6×10^6 elements uniformly sized hexahedral finite volumes with an edge length of 0.05 mm. The flow equations were simulated using Finite Volume software package ANSYS/Fluent to solve the continuity equation,

$$\nabla \cdot \mathbf{u} = 0 \quad (2.4)$$

and the momentum equation,

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u} \quad (2.5)$$

where $\mathbf{u}$ is the velocity vector, ρ and μ are density and viscosity, respectively, p is the pressure vector and t is the flow time.

2.3.1.4 Steady-State Simulation

CFD simulations were first performed at steady-state, setting the dynamic term of Equation (2.5) equal to zero. SIMPLE scheme was used for the pressure-velocity coupling, and Second Order Upwind schemes were used for the spatial discretisation of

pressure and advective terms of the momentum conservation equation. All flow variables were initialised with a value equal to zero, and the convergence criteria for the maximum residuals of continuity and momentum were 10^{-6} .

Figure 2.3 shows the velocity map obtained from the steady-state simulation. The velocity profile at the top plate is given by $v = \omega r$, and thus the velocity is $v = 0 \text{ m s}^{-1}$ at the top plate rotation axis ($r = 0$) and maximum at the plate radius $r = R_p$, where $v = \omega R_p$ (see Figure 2.3). Therefore, the flow is described by a set of concentric circular streamlines, as shown Figure 2.3.

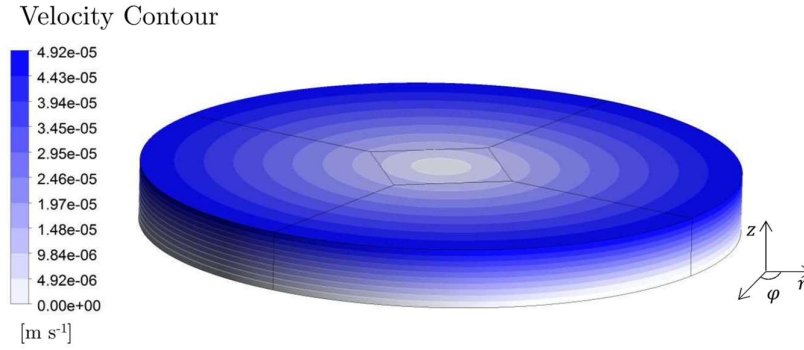


Figure 2.3 Velocity magnitude map in parallel plate-plate rheometer.

Figure 2.4 shows the velocity vectors in the z -direction at $r = R_p$ (using a cylindrical coordinate system) obtained from the steady-state simulation. A linear velocity profile is generated between the two parallel plates. The rotation of the top plate induces the flow between the two plates causing the adjacent layers of fluid to slide over each other with different speeds due to the gradient of velocity in the z -direction.

Mooney (1934) showed that, for a steady, laminar and isothermal flow and if $v_r = v_z = 0$ and considering no slip at the top and bottom plates, the velocity profile between the two parallel plates is given by

$$v_{\varphi}(r, z) = \frac{r\omega z}{h_p} \quad (2.6)$$

where h_p is the space between plates and ω is the angular velocity of the top plate. Equation (2.6) shows that the velocity profile in the z -direction depends on the radial position at the plate, r , and the height between plates, h_p (Macosko, 1989).

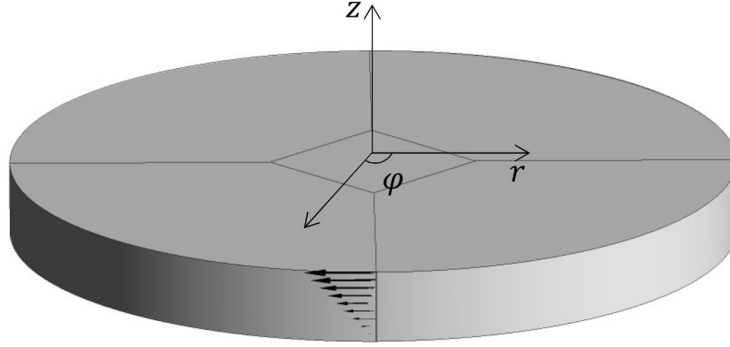


Figure 2.4 Velocity profile in the z -direction and cylindrical coordinates system.

Figure 2.5 shows the velocity profiles in z -direction at different distances from the rotation axis calculated from CFD simulations: $r = 0.1R_p$, $r = 0.5R_p$, $r = 0.9R_p$ and $r = R_p$ described by CFD simulation and the respective analytical expression (Equation (2.6)). This figure shows that Equation (2.6) is a good fit of the velocity profile obtained from 3D CFD simulations, validating the 3D CFD model. The CFD simulation was made to check the correct 3D description of this flow without imposing symmetric conditions and to generate the velocity field for the analysis of mixing in this device.

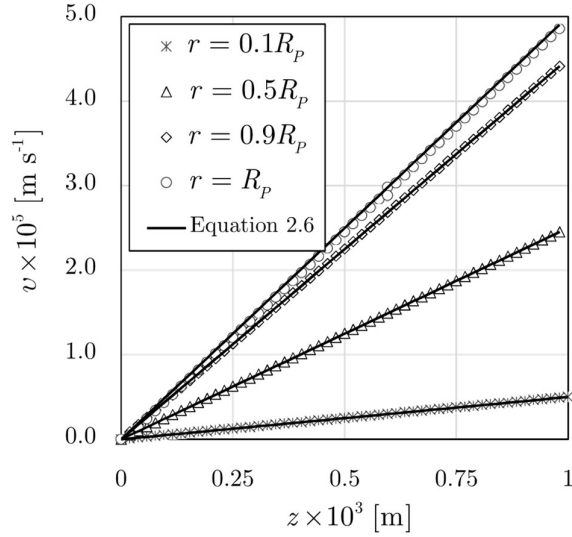


Figure 2.5 Velocity profiles in the z -direction at different positions from the centre of plate-plate rheometer: symbols correspond to CFD simulation and lines correspond to Equation (2.6).

2.3.1.5 Dynamic Simulation

The flow field at steady-state conditions was used as the initial solution for the transient simulations of mixing. The flow of two similar fluids between the two rotational parallel plates will enable the characterisation of the advective mixing mechanisms and the visualisation of the lamellar structure formed in well-defined shear conditions. Two different initial placements of fluids, that is, two different topologies, will be set to test the influence of topology on mixing.

The first initial condition consists of loading two similar fluids, black and white, side-by-side. This initial placement of fluids is called Topology 1. Figure 2.6a shows the contour map of volume fraction of each fluid, black and white, at the initial instant, for Topology 1.

An Eulerian-Eulerian approach is used with the Volume-of-Fluid (VOF) model to simulate the dynamics of mixing of two fluids in the flow. This model tracks the interface between two immiscible phases with equal physical properties. The surface tension and the diffusional mass transfer are neglected. For VOF simulation, a value

of zero for the diffusion coefficient between the two phases is a good assumption for modelling of the mixing length scales.

In VOF model, the mass transfer is given by

$$\frac{\partial \phi_i}{\partial t} + \mathbf{u} \cdot \nabla \phi_i = 0 \quad (2.7)$$

where ϕ_i is the volume fraction of i component. When $\phi_i = 0$, there is no i component and when $\phi_i = 1$, it means that there is only i component.

In transient simulations, SIMPLE scheme was used for pressure-velocity coupling, PRESTO! and First Order Upwind were used for pressure and momentum. First Order Implicit scheme was used for the discretisation of the transient terms of momentum and continuity equations. Geometric Reconstruct scheme was set for the reconstruction of the interface position. The time step between iterations, Δt , was chosen according to the Courant number, $C_N = \omega R_p \Delta t / \Delta x$, where Δx is the edge length of an element of the computational grid.

Figure 2.6 shows the volume fraction contour maps for the mixing of two similar fluids in a parallel plate rotational device, initially placed according to Topology 1. Figure 2.6a corresponds to the initial time ($N = 0$), Figure 2.6b, Figure 2.6c and Figure 2.6d show the position of each phase after half-turn of the top plate ($N = 0.5$), one turn ($N = 1$) and two turns ($N = 2$), respectively. Figure 2.6 shows that the interfacial area between fluids is stretched out by the shear rate generated between the two parallel plates.

After one rotation of the top plate ($N = 1$), the gap between plates is divided in two lamellae, one black strip and one white strip (Figure 2.6c) and after two turns (Figure 2.6d), the formation of a structure with four lamellae in the z -direction is observed. The formation of this lamellar structure is a result of the stretching of the interface between the representative fluids and respective deformation of each phase.

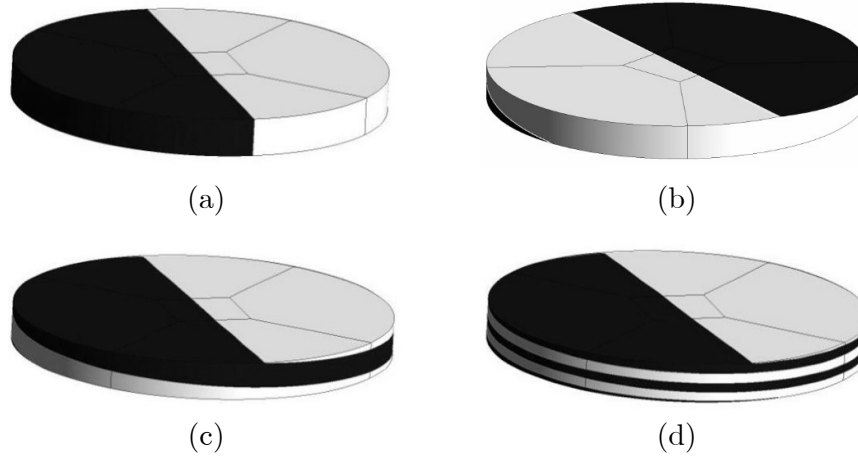


Figure 2.6 Different stages of rotation of the top plate for Topology 1 (a) initial time; (b) half turn; (c) one turn; (d) two turns.

Another initial placement of the fluids is addressed in this work, Topology 2, that consists of the placement of two phases over each other, parallel to the rotating top plate. Figure 2.7 shows the contour map of the volume fraction of two fluids initially placed according to Topology 2 obtained from the dynamic CFD simulation. Figure 2.7a corresponds to the initial time, $N = 0$, and Figure 2.7b to $N = 1$. These results show that, for Topology 2, the interface between the two phases is not stretched and the lamellar structure does not change. At this working condition, the interfacial area between fluids is parallel to the velocity field, and so, the shear rate promotes the rotation of interface, remaining it invariant.

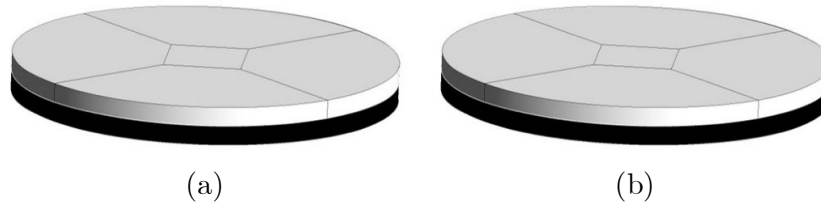


Figure 2.7 Two different stages of rotation for Topology 2: (a) initial time; (b) one turn.

These results are the definitive proof that topology has an impact on mixing in laminar flows. The most efficient mixing of fluids achieved in the plate-plate rheometer

corresponds to Topology 1. This means that when the interfacial area is initially placed perpendicularly to the velocity field, the interfacial area is increased by shearing. On the other hand, when the interfacial area has the same direction as the velocity field, the mixing length scales remain invariant.

The full characterisation of mixing in a plate-plate rheometer comprises the calculation of the mixing length scales, such as the growth of the interfacial area and the striation thickness decay. Matos et al. (2018) proposed the Lagrangian Mixing Simulations (LMS) to quantify the mixing scales in laminar flows. This model uses particles to track the interface between two fluids to determine the interfacial area between fluids and the computation of segregation scales. LMS uses an Eulerian velocity field from a 2D CFD simulation of the flow. Thus, the application of LMS over a plate-plate rheometer requires the modelling of 2D CFD simulations and the respective physical validation of the 2D results.

2.3.2 2D CFD Simulation

2.3.2.1 Physical Domain and Discretisation

A 2D physical representation of the flow in a plate-plate rheometer was set corresponding to the projection of the outer cylinder wall between the two parallel rotating plates. This domain consists of a rectangular geometry, where the top wall is moving, and the bottom wall is stationary. A relevant feature in plate-plate geometry is that the strain rate is not homogeneous along the radius. Mooney (1934) demonstrated that the strain rate is $\dot{\gamma} = dv / dz = \omega r / h_p$ according to Equation (2.6). This dependence of the strain rate on the radius shows that the conditions of the projection of the outer circle are only valid for $r = R_p$. Thus, the evolution of mixing scale from this simulation is not valid for other circles, i.e. for any value of r .

Figure 2.8 shows the sketch of the domain simulated in 2D CFD simulation and the respective coordinate system. The geometrical parameters in Figure 2.8 do not

correspond to 3D CFD simulations, i.e. the length of top wall does not correspond to the perimeter of the outer circle, $2\pi R_p$. The 2D geometry consists of two parallel walls with 10 mm length and spaced by 2 mm. Nevertheless, these dimensions are in the range of the typical geometrical conditions in rheometers.

The simulated domain was discretised with 1×10^5 rectangular elements with an edge of 5.05×10^{-6} m. Grid was compressed in the y -direction, and so smallest grid elements with respect to height were generated around the walls. This refinement avoids numerical problems during the tracking of the interface. When the interface between fluids is inclined towards the horizontal direction by the flow action, the layer of fluid next to the walls becomes very thin. If the mesh is not refined enough, the thinnest parts of the layer are erased and the contact points between the fluids at the walls, which are fixed, seem to slip. Care was taken to verify if the grid was enough for the description of mixing next to the walls.

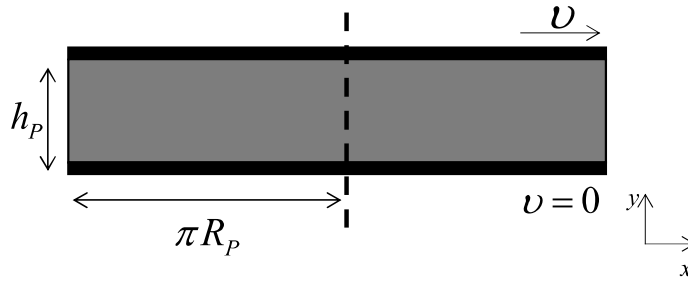


Figure 2.8 Sketch of a 2D parallel plates rheometer.

2.3.2.2 Boundary and Working Conditions

The boundary conditions imposed in the simulation are the velocities of the walls. For the bottom wall, $v = 0 \text{ m s}^{-1}$ and, for the top wall, $v_p = 1.4 \times 10^{-3} \text{ m s}^{-1}$, which corresponds to an angular speed of $\omega = 0.87 \text{ rad s}^{-1}$ in a plate-plate rheometer presented in Section 2.3.2. Periodic flow conditions were set on the right and left walls to simulate continuous flow in the entire domain, corresponding to the circular

pathlines of the 3D geometry. This condition guarantees to simulate a closed circle as the outer wall in the 3D geometry. The fluid enclosed between the two parallel walls has the same physical properties set in 3D model: a density $\rho = 1260 \text{ kg m}^{-3}$ and a viscosity $\mu = 0.79 \text{ Pa} \cdot \text{s}$.

2.3.2.3 Steady State Simulations

CFD simulations were initially performed at steady-state, setting the time dependent term of Equation (2.5) equal to zero. In steady-state simulations, SIMPLE scheme was used for the pressure-velocity coupling. Second Order and Second Order Upwind schemes were used for numerical spatial discretisation of pressure and advective terms of momentum equation.

The physical validation of 2D CFD steady-state solution was made from the 2D velocity profile, $v = R_p \omega y / h_p = v_p y / h_p$ (using the cartesian coordinates of Figure 2.8). Results show that the analytical solution fits the CFD results. This validates the 2D model as a simplification of 3D flow with direct application to the simulation of mixing.

2.3.2.4 Dynamic Simulation

The steady-state flow field was used as the initial solution for the dynamic CFD simulations. The flow of two similar fluids in 2D plate-plate rheometer was computed using the VOF model in ANSYS Fluent. SIMPLE scheme was set for the pressure-velocity coupling. PRESTO! and Second Order Upwind were used for pressure and momentum. First Order Implicit scheme was set for the discretisation of the transient terms of momentum equation and continuity equation. The reconstruction of the interface position between the two phases was made from Geometric Reconstruct scheme.

Mixing dynamics were simulated from the 2D model and with the initial condition according to Topology 1, that is, the 2D domain was initially divided into two similar fluids, black and white, side-by-side.

Figure 2.9 shows the contour maps of the volume fraction of each fluid obtained from 2D CFD simulation at $N = 0$, $N = 1$ and $N = 2$. The number of turns, N , corresponds to the period of time that a particle takes to resume to the initial position. From $N = 0$ to $N = 2$, the interface is stretched by the shear rate, decreasing the striation thickness of each phase. Figure 2.9 shows that two lamellae are formed in the y -direction (using the cartesian coordinates of Figure 2.8) for $N = 1$, and four lamellae are generated for $N = 2$.

Figure 2.6c and Figure 2.9b show two lamellae, black and white strips, are formed at $N = 1$, both for 3D and 2D CFD simulations. Figure 2.6d and Figure 2.9c correspond to $N = 2$, where a structure with four lamellae are formed. Again, this comparison shows the 2D CFD simulation makes an accurate description of mixing in the actual 3D device.

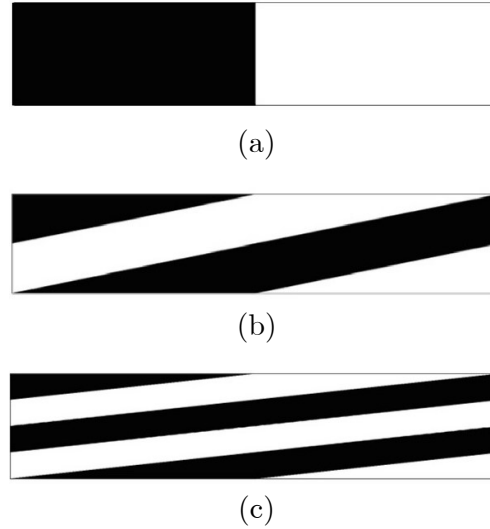


Figure 2.9 2D contour maps of phases in different stages of rotation for two similar fluids at (a) $N = 0$; (b) $N = 1$; (c) $N = 2$.

2.3.2.5 Lagrangian Mixing Simulation Model

The validated 2D flow field in a plate-plate rotational rheometer can be used for the Lagrangian Mixing Simulations, LMS, using the Eulerian velocity field. LMS follows the process of interfacial area generation between two fluids by tracking a set of passive particles positioned at the interface. The LMS algorithm was implemented in Matlab using the velocity field from 2D CFD simulation. In LMS, the position vector of each particle is determined by,

$$\mathbf{X}_{i,j+1} = \mathbf{X}_{i,j} + \mathbf{u}_{i,j}\Delta t \quad (2.8)$$

where Δt is the time step, $\mathbf{u}_{i,j}$ is the velocity vector of a particle, i represents the index of the particle and j is the index of the time step. The LMS algorithm was adapted from Matos et al. (2018) as follows:

1. Load the first velocity field data file;
2. Set the initial position of particles at the interface between the two fluids;
3. Calculate the distance between successive particles;
4. Insert a new particle at the midpoint if the distance between successive particles is larger than $r = 1 \times 10^{-5} \text{ m}$;
5. Calculate the velocity of each particle by interpolation from the Eulerian velocity field;
6. Calculate the position of each particle from Equation (2.8);
7. Load the velocity field for the next iteration;
8. Repeat the steps 3-8 until the final time.

The initial condition for the LMS corresponds to the placement of 35 particles into the left phase (red particles) and 35 particles into the right phase (black particles). Figure 2.10 shows the position of each cluster of particles in the 2D domain. Figure 2.10a corresponds to $N = 0$, Figure 2.10b and Figure 2.10c show the position of each particle for $N = 1$ and $N = 2$, respectively. Figure 2.10 clearly shows that the line

formed by the cluster of particles, which is initially positioned through the gap between the two parallel plates, is stretched over the motion of the top wall. The overlapping of the phases causes the reduction of the striation thinning rate of each phase.

LMS enables the determination of the interfacial area between the two fluids, which corresponds to the length of the line that is formed by the tracking particles,

$$A_{\text{int}}(t) = \sum_{i=1}^{np} |\mathbf{X}_{i,j} - \mathbf{X}_{i,j+1}| \quad (2.9)$$

where np is the total number of particles. In Figure 2.11, the dashed line describes the dimensionless interfacial area, $\alpha' = A_{\text{int}}(t) / A_0$, as a function of the number of turns, N , calculated from LMS. The initial interfacial area corresponds to the gap between parallel plates, $A_0 = h_p$. The interface increases with the number of turns, as expected from 3D and 2D CFD simulations. The growth of the interfacial area is, on average, linear with time for $N > 0.5$.

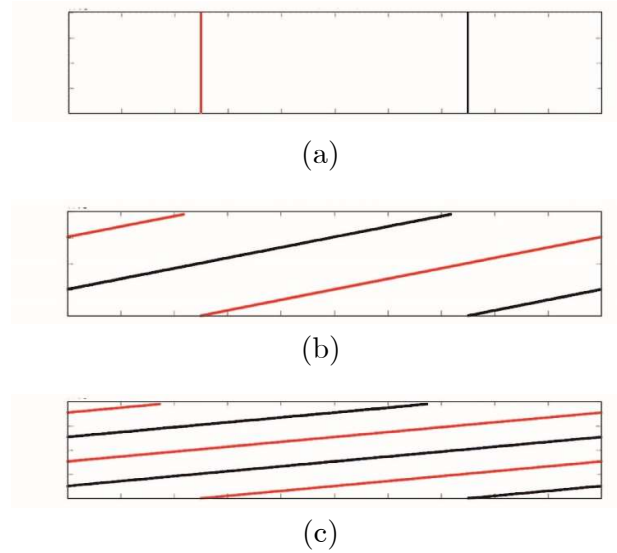


Figure 2.10 Position of particles calculated from LMS model at (a) $N = 0$; (b) $N = 1$; (c) $N = 2$.

Figure 2.10 shows that the interfacial area growth creates thin layers delimited by the tracking line. The concept of distance between two segregated fluids was defined by Mohr et al. (1957a) as the striation thickness. The striation thickness generated

between the two parallel plates can also be calculated from LMS. For that, a medium point between two successive particles into the same fluid (x_1, y_1) is considered. Then a tangent to the current particle and the respective slope, m_1 , was calculated. The perpendicular line to the tangent curve is obtained from $m_2 = 1 / m_1$. The perpendicular line will cross the other interface, and the interception point is determined (x_2, y_2) . Then the distance between interfaces can be determined by,

$$l_i = \sqrt{(x_{i+1} - x_i)^2 + (y_{i+1} - y_i)^2} \quad (2.10)$$

If the perpendicular curve does not cross the other interface, l_i is not calculated by LMS. This procedure is repeated for all particles in the flow front that is being tracked. The striation thickness corresponds to the minimum length from the set of line segments crossing both interfaces perpendicularly: $s = \min(l_i)$. The same procedure is used for the complete time of the dynamic simulation.

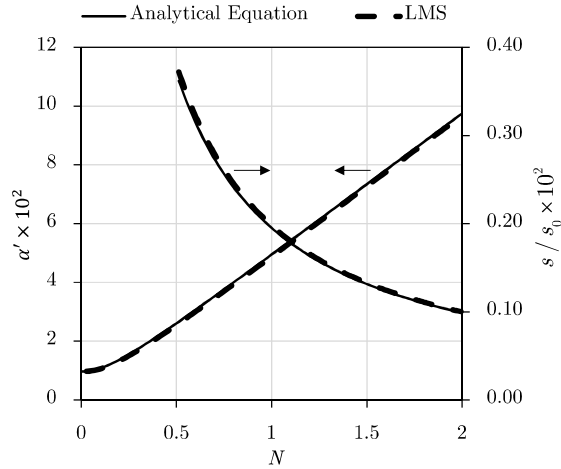


Figure 2.11 Interfacial area generation rate and striation thickness evolution calculated from LMS and analytical equations for mixing of two similar fluids.

The dashed line for s / s_0 axis in Figure 2.11 shows the mean normalised evolution of striation thickness as a function of the number of turns, N , calculated from LMS. The initial striation thickness, s_0 , corresponds to half of the perimeter of the top plate,

according to Figure 2.8 and the striation thickness decreases along of the number of turns. The validation of $\alpha'(t)$ and $s(t)/s_0$ determined by LMS comprises the description of both mixing metrics from an analytical expression.

2.3.2.6 Kinematics of Deformation

In pure shear flows, as those generated in a plate-plate rotational rheometer, mixing is characterised by the deformation of fluids. The stretching properties of flow are studied in this chapter from a Lagrangian point of view, tracking a passive material element. Figure 2.12 shows the deformation of a material element placed in a pure shear flow. This element of fluid is initially a square wherein the edges are dy and s_0 . For $t > 0$, the particle is deformed continuously by the flow and the edge dy is stretched out, causing the deformation of this length, dl , as shown in Figure 2.12.

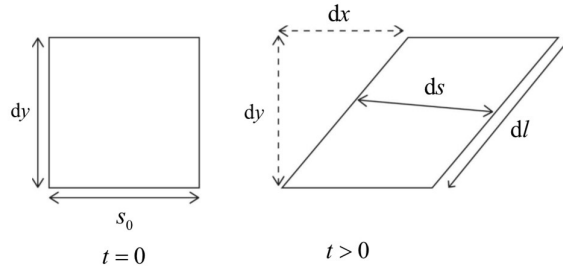


Figure 2.12 Stretching of a material element with time in a pure shear flow.

The interfacial area and the striation thickness are easily quantified by the stretching of a material element illustrated in Figure 2.12. The evolution of interfacial area is described by $dl(t)$, and the striation thickness is given by the normal length between sides, which is represented by ds in Figure 2.12. The interfacial area and the striation thickness are quantified for the two topologies addressed in this chapter: Topology 1 (Figure 2.6) and Topology 2 (Figure 2.7).

In Topology 1, the two fluids are initially side-by-side. It was considered that an element of fluid corresponds to a single-phase and thus $dy \sim \Delta y = h_p$. The differential

can be extended throughout the entire height because the interface is always a straight line. For $N = 0$, the initial interfacial area corresponds to the gap between the two parallel plates, $A_0 = h_p$. The evolution of the interfacial area, $A_{\text{int}}(t)$, is calculated from $dl(t)$, which is obtained from the motion of the top wall, dx , and the height of the domain, dy , as shown in Figure 2.12. It results in

$$dl(t) = \sqrt{dx^2 + dy^2} \quad (2.11)$$

where, for $dy \sim \Delta y = h_p$, $dx \sim \Delta x(y = h_p) = \nu_p t$. Thus, the dimensionless interfacial area, $\alpha' = A_{\text{int}}(t) / A_0$, may be calculated from Equation (2.11), resulting

$$\alpha'(t) = \sqrt{\left(\frac{\omega r t}{h_p}\right)^2 + 1} \quad (2.12)$$

where $\omega r = \nu_p$. This equation can be rewritten as a function of the number of turns since $t = NT$, where T is the time required for one complete turn, $T = 2\pi / \omega$. So, Equation (2.12) becomes $\alpha'(t) = \sqrt{1 + (2\pi Nr / h_p)^2}$.

Mooney (1934) demonstrated that the shear rate for a plate-plate geometry is given by $\dot{\gamma} = \omega r / h_p$, thus Equation (2.12) can be written according to the general expression $\alpha'(t) = \sqrt{1 + (\dot{\gamma} t)^2}$.

The evolution of striation thickness (ds in Figure 2.12) can also be calculated from the tracking of a material element. For an incompressible fluid, the relationship between the initial striation thickness, s_0 , and the evolution of striation thickness is given by

$$dy s_0 = dl s \quad (2.13)$$

where dy , s_0 , dl and s are illustrated in Figure 2.12. As it was also considered that each fluid element corresponds to a single-phase ($dx \sim \Delta x(y = h_p) = \nu_p \Delta t$ and $dy \sim \Delta y = h_p$), the combination of Equations (2.11) and (2.13) results in

$$s(t) = \frac{s_0}{\sqrt{1 + \left(\frac{\omega r t}{h_p}\right)^2}} \quad (2.14)$$

Equation (2.14) describes the reduction of striation thickness in a plate-plate rotational rheometer. At $t=0$, striation thickness is $s = s_0$ and for $t>0$, the lamellae striation thickness decreases due to the shear rate generated between the two plates. The general expression of $s(t)$ as a function of $\dot{\gamma}$ is given by $s(t) = s_0 / \sqrt{1 + (\dot{\gamma}t)^2}$.

The validation of Equations (2.12) and (2.14) comprises the comparison with LMS. Figure 2.11 shows the dimensionless interfacial area as a function of the number of turns calculated from LMS (dashed line) and Equation (2.12) (solid line). This plot clearly shows that Equation (2.12) fits the LMS data making it a good prediction for the description of the dimensionless interfacial area in a plate-plate geometry.

Figure 2.11 also shows the evolution of striation thickness as a function of the number of turns calculated from LMS (dashed line) and Equation (2.14) (solid line). Equation (2.14) gives a good prediction of the decrease of the striation thickness along with the number of turns. Figure 2.11 also shows that the fluid element undergoes a linear stretching and the respective evolution of the striation thickness is given by $s(t) \sim s_0 / t$, which is a feature of non-chaotic flows (Ottino and Wiggins, 2004). These results support the argument that the flow is non-chaotic in this range of Reynolds number.

Figure 2.13 shows a sketch of the 2D phase position at $N = 0$, $N = 1$ and $N = 2$ for Topology 2. The interfacial area at $N = 0$ corresponds to the perimeter of the plate, $A_0 = 2\pi R_p$, which is illustrated by a red line in Figure 2.13a. At $N = 1$ and $N = 2$, the interfacial area is $A_{\text{int}}(N = 1) = 2\pi R_p$ and $A_{\text{int}}(N = 2) = 2\pi R_p$, as shown in Figure 2.13 by the green line. From this analysis, the evolution of the dimensionless interfacial area

is given by $\alpha'(t) = 1$. The striation thickness is also independent of the number of turns and corresponds to half of the gap between the two plates, $s(t) = h_p / 2$.

The demonstration of mixing metrics expressions shows that a greater interfacial area is obtained for Topology 1 and so, thinner striation thicknesses are generated. For Topology 2, the mixing length scales are kept constant with the number of turns. Therefore, topology plays an important role in the evolution of mixing scales in mixing devices.

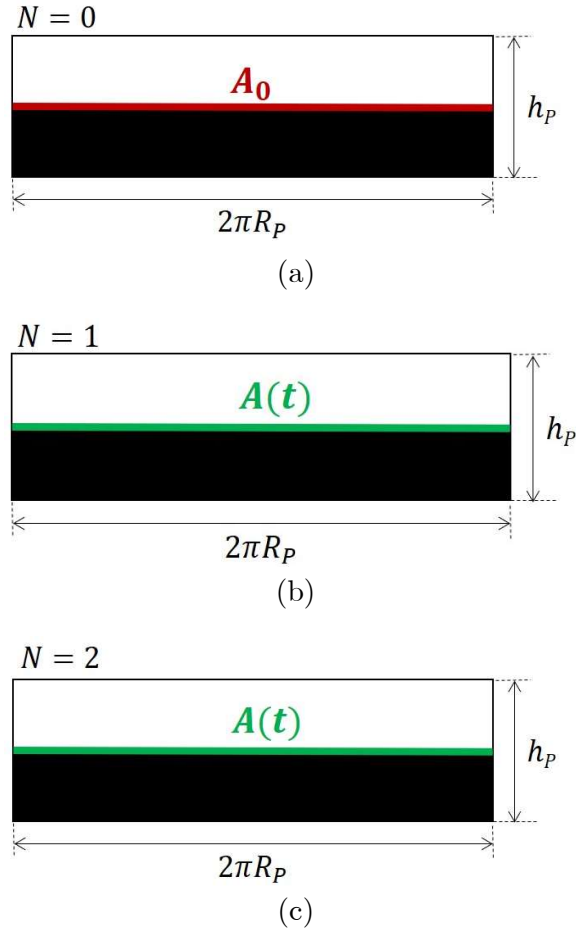


Figure 2.13 Sketch of the position of each phase in the outer circle of a 3D plate-plate rotational rheometer for Topology 2 at $N = 0$, $N = 1$ and $N = 2$ where the interface between fluids is tracked for (a) $N = 0$, (b) $N = 1$ and (c) $N = 2$.

2.3.3 Cone-Plate Geometry

The fluid dynamics and the evolution of the mixing length scales were also described for cone-plate rheometers. Figure 2.14 shows the sketch of a cone-plate geometry of rotational rheometers and a schematic representation of the gap between cone and plate. In this case, the velocity profile is given by,

$$v_{\theta}(r, z) = \frac{r\omega}{\beta} \arctan \frac{z}{r} \quad (2.15)$$

where β is the cone angle (Macosko, 1989). For this geometry, the shear rate is constant at every radial location in the cone-plate geometry, $\dot{\gamma} = \omega / \beta$ (Macosko, 1989). Since the flow between cone and plate has uniform shear conditions in the entire domain, it is possible to simulate the flow field in a 2D domain which corresponds to the projection of the outer circle of the geometry for $r = R_p$ and $z \in [0, h_p]$. Therefore, the 2D CFD simulation presented previously for the plate-plate configuration can also represent the flow field from a representative part of the cone-plate 3D flow, and the mixing length scale can be obtained from that simulation. For a cone-plate geometry and for the initial conditions according to Topology 1, analytical equations of the dimensionless interfacial area and striation thickness can be described from the general expressions where $\dot{\gamma} = \omega / \beta$: $\alpha'(t) = \sqrt{1 + (\omega t / \beta)^2}$ and $s(t) = s_0 / \sqrt{1 + (\omega t / \beta)^2}$.

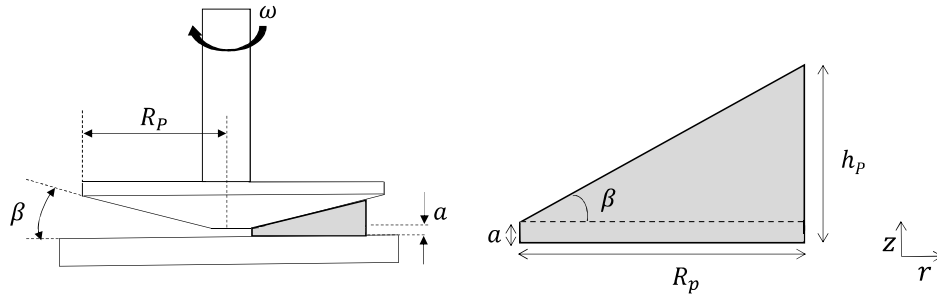
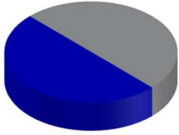
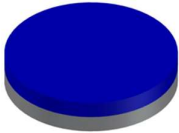
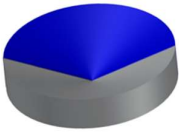


Figure 2.14 Schematic representation of the gap between cone and plate and respective dimensions: β is the angle between cone and plate; a is the height of the truncated region; h_p is the gap between plate and cone; R_p is the radius of plate.

Table 2.1 summarises the relationships of the dimensionless interfacial area and striation thickness evolution for plate-plate geometry with Topologies 1 and 2, and for cone-plate geometry with Topology 1. Topology 2 is not analysed for cone-plate rheometer because the two boundaries are not parallel and so the two liquids would have to be overlaid with an interface located at the bisection of angle β . This initial placement of the two fluids is not practical and would require the development of particular technology for liquids injection into the geometry.

Table 2.1 Mixing scales length obtained in Topology 1 and 2.

	Contour maps	Dimensionless Interfacial Area	Striation Thickness
Topology 1, plate-plate		$\alpha'(t) = \sqrt{1 + \left(\frac{\omega r t}{h_p}\right)^2}$	$s(t) = \frac{s_0}{\sqrt{1 + \left(\frac{\omega r t}{h_p}\right)^2}}$
Topology 2, plate-plate		$\alpha'(t) = 1$	$s(t) = \frac{h_p}{2}$
Topology 1, cone-plate		$\alpha'(t) = \sqrt{1 + \left(\frac{\omega t}{\beta}\right)^2}$	$s(t) = \frac{s_0}{\sqrt{1 + \left(\frac{\omega t}{\beta}\right)^2}}$

2.4 Part II: Mixing of Dissimilar Fluids in Rotational Devices

Mixing is a core unit in several industrial processes, which has a significant effect on the properties of the final product. In most industries, mixing occurs between two fluids with different properties, i.e. fluids with different viscosities, densities and interfacial tension. The following industrial processes are illustrative examples that involve the mixing of dissimilar fluids:

- Plastic industry – RIM is an industrial process for the production of plastic parts. In this process, isocyanate and polyol, are injected by two opposed jets in a cylindrical mixing chamber, where the mixing is promoted. These monomers have quite different viscosities: isocyanate has a viscosity in the $0.1 \text{ Pa} \cdot \text{s}$ range and polyols around $1 \text{ Pa} \cdot \text{s}$ (Oertel, 1985);
- Food industry – the emulsification process of one of the most known sauces in the world, mayonnaise, requires an effective mixing between oil and water in high shear devices. Mayonnaise is an oil/water emulsion with a typical commercial formula with, approximately, 80% of oil, 12% of water and 3% of egg yolk (Kerkhofs et al., 2011). The remaining ingredients are added to modify the flavour. Oil is the dispersed phase, water is the continuous phase, and egg yolk is the emulsifier. Water and oil have quite similar densities; however, they have a viscosity ratio of 66 and an interfacial tension of 0.0248 N m^{-1} (Bhatluri et al., 2015).

These two industrial processes are examples that represent thousands of processes that handle dissimilar fluids. The feasible implementation of the lab-scale formulation methodology, described in Section 2.3, in processes with quite dissimilar properties requires a further description to conclude the influence of properties on flow dynamics. The simple assumption that fluid properties do not affect the mixing in rheometric devices may cause a lack of accuracy in the analysis of PD methodology.

A cone-plate rotational rheometer is the geometry addressed in this section. The selection of this configuration was made according to the constant shear rate in the plate radial position, $\dot{\gamma} = \omega / \beta$. This feature in cone-plate rheometers avoids the effect of dissimilar fluids dragging along the radial direction, as expected for the plate-plate configuration, where the shear rate depends on the radial position, $\dot{\gamma} = \omega r / h_p$.

The 2D CFD domain described in Section 2.3.2 is the model used to simulate the mixing of dissimilar fluids in a cone-plate rheometer. Metrics for mixing (the interfacial

area and the evolution of striation thickness) are quantified from the 2D CFD simulations. Three parameters are addressed in this section: viscosity ratio, density ratio and interfacial tension.

2.4.1 CFD Simulation

The detailed description of 2D CFD domain and the discretisation are well-established in Section 2.3.2.1. The geometry corresponds to the outer circle of the 3D domain, which consists of two parallel walls with a specific distance between them.

2.4.1.1 Boundary and Working Conditions

The boundary conditions are the same set in Section 2.3.2.2: $v = 0 \text{ m s}^{-1}$ for the bottom wall and $v_p = 1.4 \times 10^{-3} \text{ m s}^{-1}$ for the top wall, except for studies on interfacial tension where different top plate velocities were tested. The periodic conditions were also defined at the domain sidewalls.

The working conditions analysed in this section are listed in Table 2.2. The liquids enclosed between walls have different physical properties depending on each parameter. The name of each test was defined according to each condition: V is followed by the viscosity ratio, D by the density ratio and IT by the value of the interfacial tension.

The viscosity and density ratios are designated in this section by $(\mu_1 / \mu_{LV}) : (\mu_2 / \mu_{LV})$ and $(\rho_1 / \rho_{LV}) : (\rho_2 / \rho_{LV})$, where μ_{LV} and ρ_{LV} are the viscosity and density of the less viscous (LV) fluid.

In viscosity studies, liquids have the same density, different viscosities – 2:1, 4:1 and 10:1 – and the interfacial tension is neglected. For density studies, only one condition was simulated: liquids have viscosity and density ratios of 2:1. For interfacial tension studies, oil and water were the working fluids, and thus their characteristic physical properties were set in CFD simulations.

Table 2.2 Test Conditions of mixing of dissimilar fluids.

	Test Name	Viscosity Ratio	Density Ratio	Description of Conditions
Studies on viscosities of liquids	V2D1IT0	2:1	1:1	$\mu_1 = 1.44 \text{ Pa} \cdot \text{s}; \mu_2 = 0.71 \text{ Pa} \cdot \text{s}$ $\rho_1 = \rho_2 = 1000 \text{ kg m}^{-3}$
	V4D1IT0	4:1	1:1	$\mu_1 = 1.44 \text{ Pa} \cdot \text{s}; \mu_2 = 0.39 \text{ Pa} \cdot \text{s}$ $\rho_1 = \rho_2 = 1000 \text{ kg m}^{-3}$
	V10D1IT0	10:1	1:1	$\mu_1 = 1.44 \text{ Pa} \cdot \text{s}; \mu_2 = 0.14 \text{ Pa} \cdot \text{s}$ $\rho_1 = \rho_2 = 1000 \text{ kg m}^{-3}$
Studies on densities of liquids	V2D2IT0	2:1	2:1	$\mu_1 = 1.44 \text{ Pa} \cdot \text{s}; \mu_2 = 0.71 \text{ Pa} \cdot \text{s}$ $\rho_1 = 2000 \text{ kg m}^{-3}; \rho_2 = 1000 \text{ kg m}^{-3}$
Studies on interfacial tension	V66D1IT25	66:1	1:1.1	$\mu_1 = 0.066 \text{ Pa} \cdot \text{s}; \mu_2 = 0.001 \text{ Pa} \cdot \text{s}$ $\rho_1 = 916 \text{ kg m}^{-3}; \rho_2 = 998 \text{ kg m}^{-3}$ $\sigma = 24.8 \text{ mN m}^{-1}$

2.4.1.2 Numerical solution of steady-state simulation

The flow was simulated using Finite Volume software package ANSYS Fluent to solve continuity (Equation (2.4)) and Navier Stokes (Equation (2.5)) equations. The set of equations chosen for the flow description considers incompressible fluids.

The steady-state simulations were run, setting the fluid properties of the most viscous fluid for each case. SIMPLE scheme was used for the pressure-velocity coupling. In addition, Second Order and Second Order Upwind schemes were set for the numerical

spatial discretisation of pressure and advective terms of Navier-Stokes equation, respectively.

2.4.1.3 Numerical Solution of the Dynamic Simulation

On mixing of dissimilar fluids, VOF model is the model set to track the interface between liquids. A brief explanation of this model is in Section 2.3.1.5. The time step was set according to each boundary condition in order to define a Courant number equal or smaller than the unity. The initial position of each liquid corresponds to Topology 1, when the two phases are initially side-by-side, as shown in Figure 2.9a.

For transient simulations, SIMPLE scheme was used for the pressure-velocity coupling, PRESTO! and Second Order Upwind were set for pressure and momentum. First Order Implicit scheme for the discretisation of the transient terms of Navier-Stokes and continuity equations. On the other hand, Geometric Reconstruct scheme was used in the reconstruction of the interface position.

2.4.1.4 Influence of Viscosity Ratio on Mixing

The working conditions analysed in this section are described in Table 2.2 as V2D1IT0, V4D1IT0 and V10D1IT0.

The results of V2D1IT0 are in Figure 2.15, that shows the contour maps of the volume fraction of each fluid at $N = 0.5$, $N = 1$, $N = 1.5$ and $N = 2$. The black phase corresponds to the more viscous (MV) fluid, $\mu_1 = 1.44 \text{ Pa} \cdot \text{s}$, and the white phase is the less viscous (LV) fluid, $\mu_2 = 0.71 \text{ Pa} \cdot \text{s}$. The interface of both liquids is stretched by the velocity profile generated in the gap between the two walls. After one turn ($N = 1$), the gap is divided into two strips (Figure 2.15b), and after two turns, two strias composed by white and black lamellae were formed (Figure 2.15d).

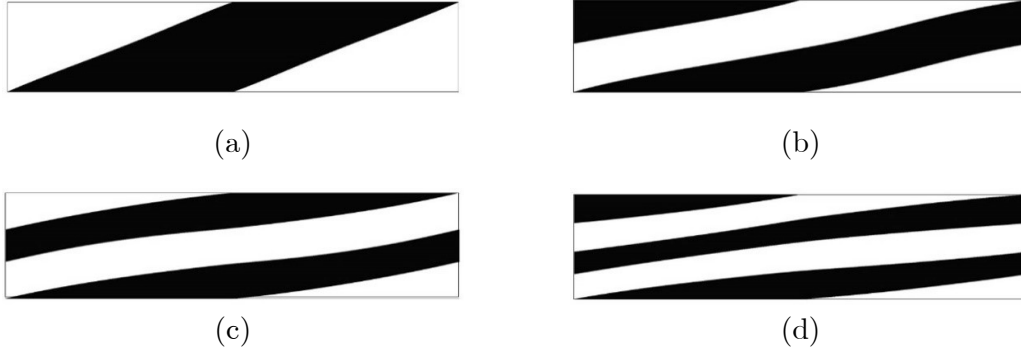


Figure 2.15 2D contour maps of phases at different stages of rotation for V2D1IT0 at (a) $N = 0.5$; (b) $N = 1$; (c) $N = 1.5$; (d) $N = 2$.

The contour maps in Figure 2.15 indicate that the interface between fluids is not as well-established as the one created for similar fluids because instabilities are created at the interface. These instabilities are caused by the differences in deformation undergone by fluids. This disparity on shear rates is associated with the velocity profile generated within fluids. Figure 2.16 shows the velocity profile along the gap between the two walls ($2y/h_p$) and the volume fraction distribution of the MV fluid (ϕ_{MV}) at $N = 2$. This figure makes a clear comparison between the velocity profile for similar fluids (red lines) and V2D1IT0 (black lines).

The velocity profile for similar conditions (red dashed line) is a linear curve for the entire gap. Thus, fluids are subjected to the same deformation in the y -direction. In V2D1IT0, the velocity profile (black dashed line) has different slopes over the entire gap caused by viscosity differences. This is the direct effect of Newtonian viscosity law, $\tau = \mu\dot{\gamma}$, where the deformation within LV fluids is greater than in MV fluids. Therefore, regions where $\phi_{MV} = 1$ corresponds to lower shear rate conditions. This is clearly shown from the black dashed line in Figure 2.16, where a smaller slope in the velocity profile, calculated from $dv/dy = \dot{\gamma}$, is observed for $-1 < 2y/h_p < -0.5$ and $0 < 2y/h_p < 0.5$. These positions correspond to the regions where $\phi_{MV} = 1$.

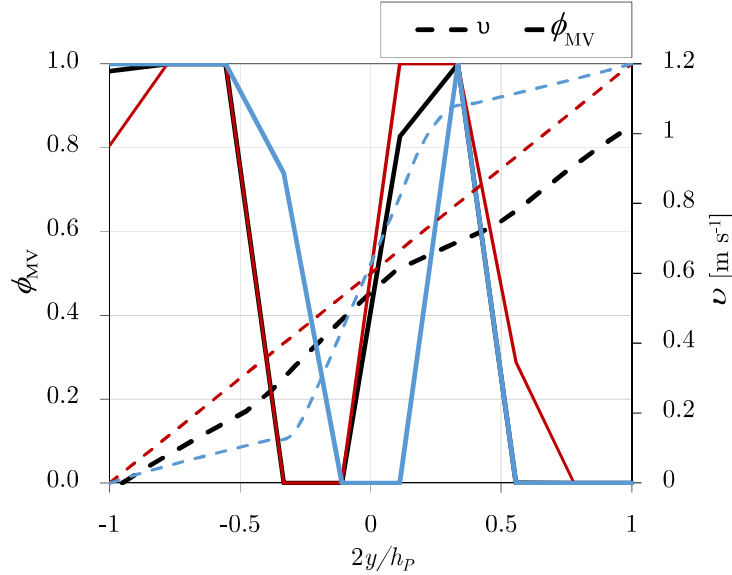


Figure 2.16 Velocity profiles and the volume fraction of MV fluid at the vertical axis of the domain and for $N = 2$ where the black lines correspond to V2D1IT0, the blue lines to V10D1IT0 and the red lines to the conditions of the similar fluid. The dashed lines are the velocity profiles, and the solid lines are the mass fraction curves.

A viscosity ratio 4:1 is the following condition studied. The contour maps are in Figure 2.17, where four instants are displayed: $N = 0.5$, $N = 1$, $N = 1.5$ and $N = 2$. The black phase is the MV liquid, $\mu_1 = 1.44 \text{ Pa} \cdot \text{s}$ and the white phase is the LV fluid, $\mu_2 = 0.39 \text{ Pa} \cdot \text{s}$. Figure 2.17 shows that the interface between two dissimilar fluids is stretched by the action of the top plate. For this case, instabilities are still more marked than for a viscosity ratio 2:1 (Figure 2.15), mainly for $N \geq 1$ (Figure 2.15b to Figure 2.15d and Figure 2.17b to Figure 2.17d). This is caused by the accentuated differences in the velocity profile slopes, associated with the quite distinct deformation regions.

The volume fraction contour maps for V10D1IT0 are displayed in Figure 2.18 for four instants, $N = 0.5$, $N = 1$, $N = 1.5$ and $N = 2$. The black fluid corresponds to the MV fluid, $\mu_1 = 1.44 \text{ Pa} \cdot \text{s}$, and the white liquid is the LV fluid, $\mu_2 = 0.14 \text{ Pa} \cdot \text{s}$. For these conditions, the instabilities are more marked than for V2D1IT0 and V4D1IT0.

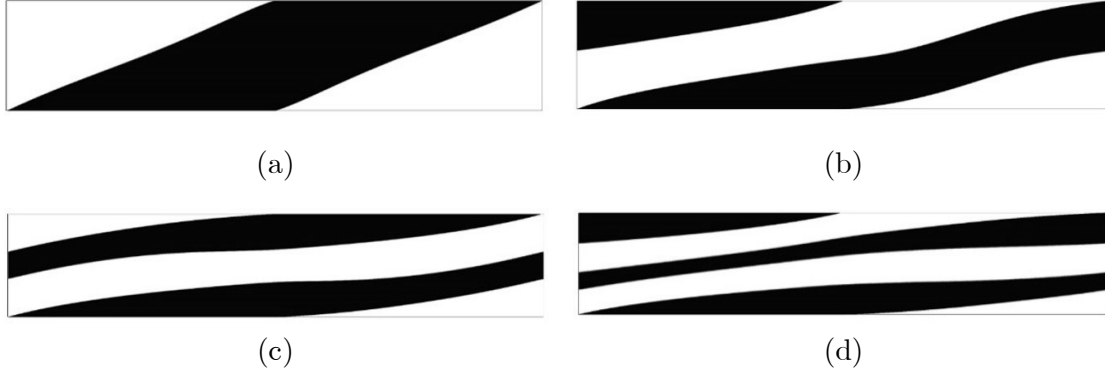


Figure 2.17 2D contour maps of phases at different stages of rotation for V4D1IT0 at (a) $N = 0.5$; (b) $N = 1$; (c) $N = 1.5$; (d) $N = 2$.

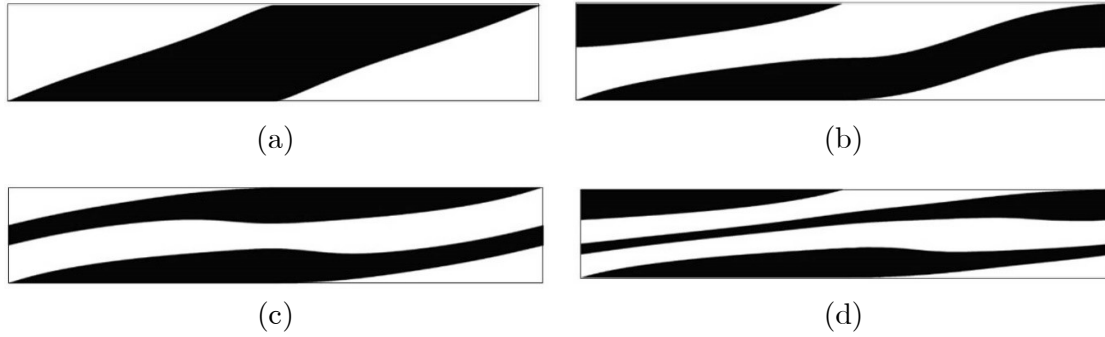


Figure 2.18 2D contour maps of phases at different stages of rotation for V10D1IT0 at (a) $N = 0.5$; (b) $N = 1$; (c) $N = 1.5$; (d) $N = 2$.

Figure 2.16 compares the mass fraction of MV liquid (solid lines) and the velocity profile (dashed lines) for a viscosity ratio 2:1 (black lines) and 10:1 (blue lines). For V10D1IT0, the differences in the velocity profile slopes are much more pronounced than in V2D1IT0. Lower slopes occur for $\phi_{\text{MV}} = 1$, which is clear at $-1 < 2y / h_p < -0.75$ and $0.25 < 2y / h_p < 0.5$. Higher slopes are associated with LV fluid regions, which is clear at $-0.75 < 2y / h_p < 0.25$ and $0.5 < 2y / h_p < 1$. These marked variations result in quite discrete deformation regions promoting instabilities at the interface.

Mixing length scales may be quantified from LMS, as described in Section 2.3.2.5. First of all, it is important to distinguish two types of interface: when the LV liquid squeezes

the MV liquid (LV-MV) and when the MV liquid squeezes the LV liquid (MV-LV). The generation of LV-MV interface was measured from LMS injecting a cluster of 35 particles into the LV fluid, and the evolution of MV-LV interface was quantified from the tracking of 35 particles belonging to MV fluid.

Figure 2.19 shows the dimensionless interfacial area calculated from LMS for V2D1IT0, V4D1IT0 and V10D1IT0. These results were compared with Equation (2.12) for similar conditions (red curve in Figure 2.19). A larger dimensionless interfacial area is formed for LV-MV interface. This is in agreement with the results of Figure 2.16, where LV fluids undergo higher deformation gradients than MV liquids.

For $0 < N < 0.8$, LV-MV and MV-LV interfacial areas raise similarly as for similar fluid conditions, i.e. it is independent of the viscosity ratio. In this time interval, the stretching of the interface is identical for any working condition because the overlapping between two dissimilar fluids just occurs at $N > 0.5$.

The striation thickness was also calculated from LMS, computing the distance between the particles belonging to MV and LV liquids. The method to determine the average striation thickness is described in Section 2.3.2.5. Figure 2.20 compares the evolution of striation thickness for the conditions studied. The reduction of striation thickness for $N < 0.8$ is analogous to the mixing of similar fluids. For $0.8 < N < 2$, the striation thickness achieves smaller values than for the mixing of similar fluids. Again, these results are evidence that the striation overlapping affects the deformation of the interface.

Figure 2.20 indicates that the striation thickness is not always thinning over the number of turns. For $N > 1.5$, the thickness increases significantly for higher viscosity ratios. This results of the non-homogenous distribution of shear rate in the gap between plates, that promotes a non-uniform distribution of phases in the system. This is clearly observed from the mass fraction contour maps (e.g. Figure 2.18), where the MV fluid tends to agglomerate in the low shear regions, i.e. next to the walls.

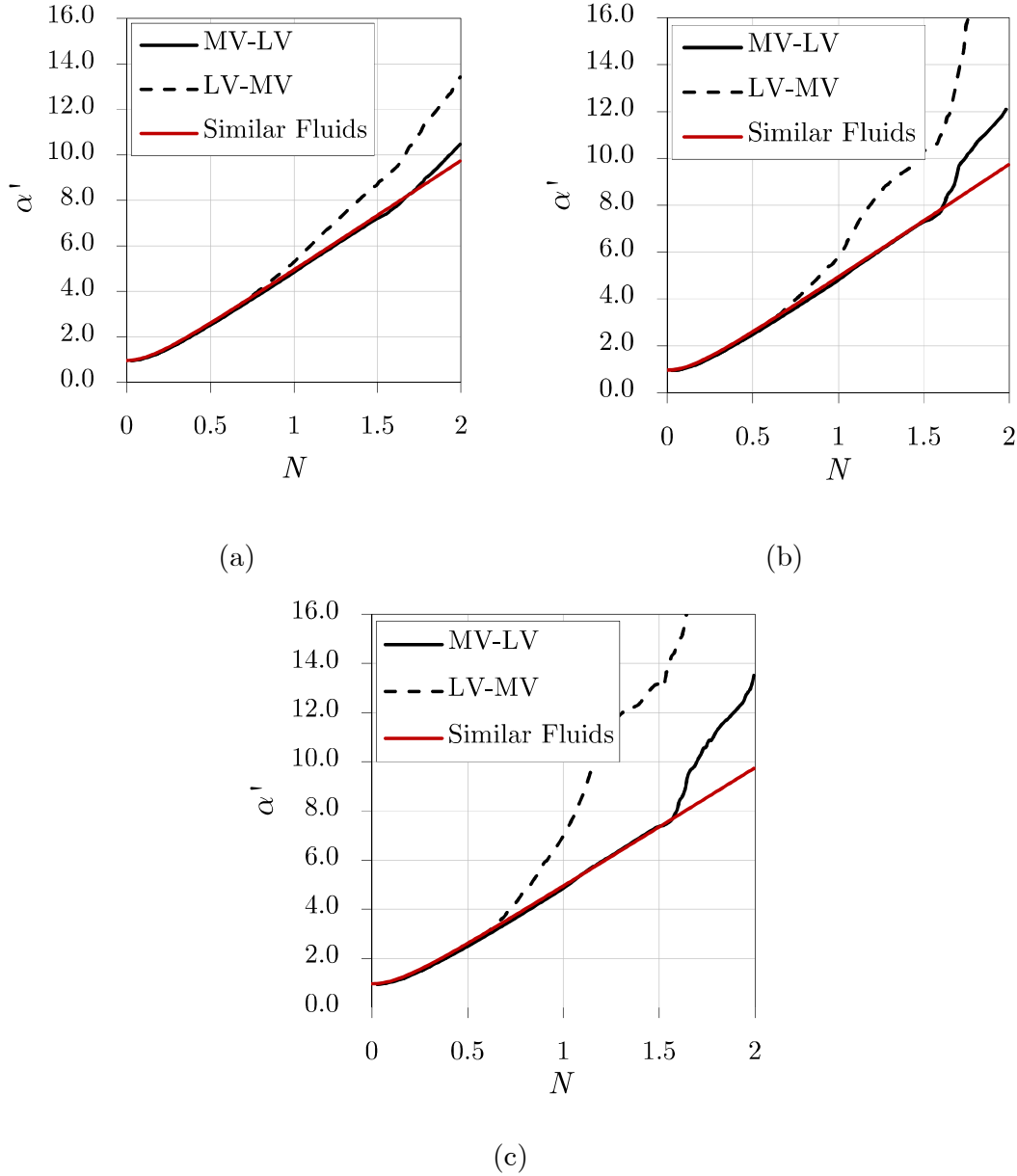


Figure 2.19 Evolution of the dimensionless interfacial area calculated from LMS for LV-MV and MV-LV interfaces, for (a) V2D1IT0, (b) V4D1IT0 and (c) V10D1IT0.

CFD results were validated from rheological tests using a rheometer Anton Paar MCR 92 SN82478971. The measuring system was a plate-plate geometry with a diameter of 50 mm. The temperature in these tests was controlled using a Peltier module integrated into the stationary bottom plate. The operational temperature was set at 20 °C.

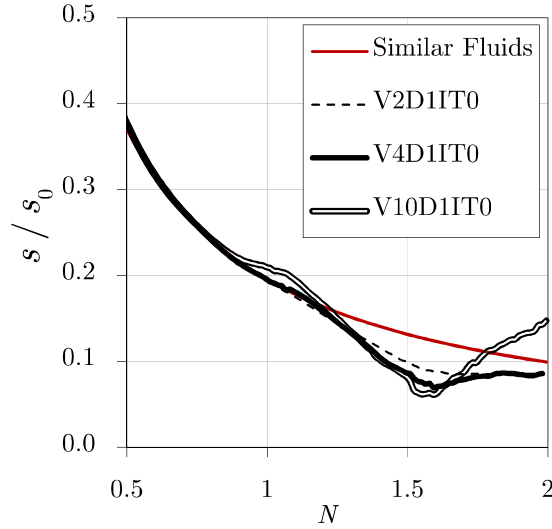


Figure 2.20 Evolution of striation thickness computed from LMS for V2D1IT0, V4D1IT0, V10D1IT0 and similar conditions.

Rheological tests were performed for a viscosity ratio 2:1 (V2D1IT0). The apparent viscosity of the mixture was registered and compared with CFD results for the same conditions. A preliminary rheological test was carried out to check the viscosity of two oils: $\mu_1 = 1.02 \text{ Pa} \cdot \text{s}$ and $\mu_2 = 0.51 \text{ Pa} \cdot \text{s}$ (viscosity ratio 2:1). The two oils were loaded in the rheometer bottom plate, according to Topology 1. A holding cell similar to the one presented in Torres (2014) was used to ensure the initial conditions. This holding cell divides the gap between the two plates in two equal spaces.

The shear rate, the number of points and the duration of each point were specified in the rheometer software, RheoCompass 1.20, as 10 s^{-1} , 200 points and 5 s each. Figure 2.21 shows the normalised viscosity changes of a mixture of two oils (viscosity ratio 2:1) during two turns.

The apparent viscosity evolution was also determined from 2D CFD results. The average shear stress at the top wall was exported for each time step simulated. Then, viscosity was calculated from $\mu = \tau / \dot{\gamma}$, where $\dot{\gamma}$ is the shear rate imposed in this system, $\dot{\gamma} = v_p / h_p$.

Two aspects must be considered in the direct comparison between experimental and numerical data:

- Assumption that the 2D flow simulation describes the flow in a plate-plate configuration. For this geometry, 2D model only describes the flow of a 3D specific region because the shear rate depends on the radial position;
- Lack of precision in loading the gap between two plates with 50/50% of each fluid.

These two aspects should not be overlooked during the critical comparison between both results. Figure 2.21 shows the experimental and numerical results for two turns. The apparent viscosity oscillates along the number of turns trending to a constant value for higher mixing time, $N > 1.5$. The only apparent reason for this is the overlapping of liquids and so the position changes of each phase. This fact reduces the striation thickness of each liquid, and from a certain stage of rotations, the apparent viscosity keeps constant.

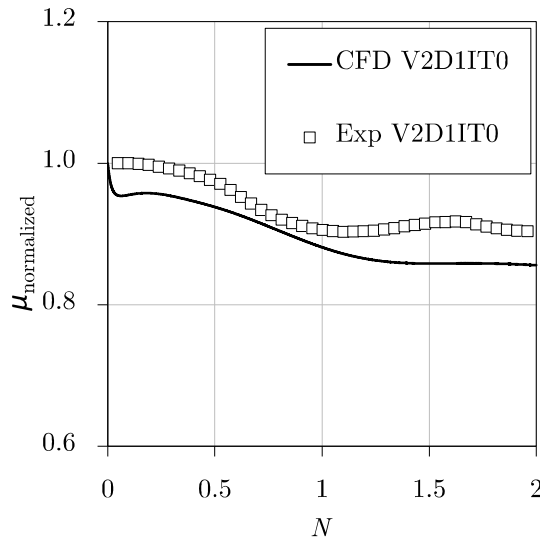


Figure 2.21 Normalised viscosity versus the number of turns for Topology 1 and for V2D1IT0 conditions.

At the first turns, Figure 2.21 shows an abruptly decrease in numerical results, which is not observed in experimental tests. In fact, this behaviour would only be detected from the rheometric data if the measuring time of each experimental point was shortened. The evolution of the apparent viscosity during the period to acquire each experimental point does not enable the steady-state measurement for each point, and at these conditions, the rheological tests would not be feasible. Nevertheless, both results show that the viscosity sharply decreases until approximately $N = 1$ and then it oscillates around an average value.

The fact that the same trends for the apparent viscosity evolution are observed for numerical and experimental results validates the 2D model.

2.4.1.5 Influence of Density Ratio on Mixing

Dissimilar fluids involved in mixing processes usually have different densities. The role of density on mixing is studied in this section from two different conditions: in the first one, the gravitational forces were neglected, while in the second one, the gravitational forces were set in CFD simulations. The working fluids have different viscosities, $\mu_1 = 1.44 \text{ Pa} \cdot \text{s}$ and $\mu_2 = 0.71 \text{ Pa} \cdot \text{s}$, and the densities of each liquid are $\rho_1 = 2000 \text{ kg m}^{-3}$ and $\rho_2 = 1000 \text{ kg m}^{-3}$ (as listed in Table 2.2 as V2D2IT0). The interfacial tension is not considered.

The boundary conditions were described in Section 2.4.1.1. In this case, the black fluid is the MV liquid and simultaneously the densest, and the white fluid is the LV and the least dense fluid. The two liquids are initially side-by-side, according to Topology 1.

The time step in the transient simulation was also defined as variable, setting an ending time of two turns ($t = 14.44 \text{ s}$), a minimum step size of 0.001 s and a maximum step size of 0.01 s . The time step was defined from the determination of Courant number, that has to be equal or less than 1.

Figure 2.22 shows the contour maps of the volume fraction of each phase at $N = 0.5$, $N = 1$, $N = 1.5$ and $N = 2$, considering no gravitational forces. These results are similar to those run for V2D1IT0, where a lamellar structure is formed along with the number of turns, and no motion of the phases are observed in y -direction (as defined in Figure 2.8). For this condition, the density ratio does not have an impact on the mixing process.

Figure 2.23 shows the contour maps at $N = 0.5$, $N = 1$, $N = 1.5$ and $N = 2$ when the gravitational forces are considered. Equations considered the gravitational forces and so,

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u} + \rho \mathbf{g} \quad (2.16)$$

where $\mathbf{g}$ is the gravitational acceleration vector. The densest fluid, i.e. the black one, tends to agglomerate next to the bottom plate due to the density ratio. Therefore, the flow dynamics are affected by the density ratio because the body forces promote a faster stratification. In this case, the Navier-Stokes

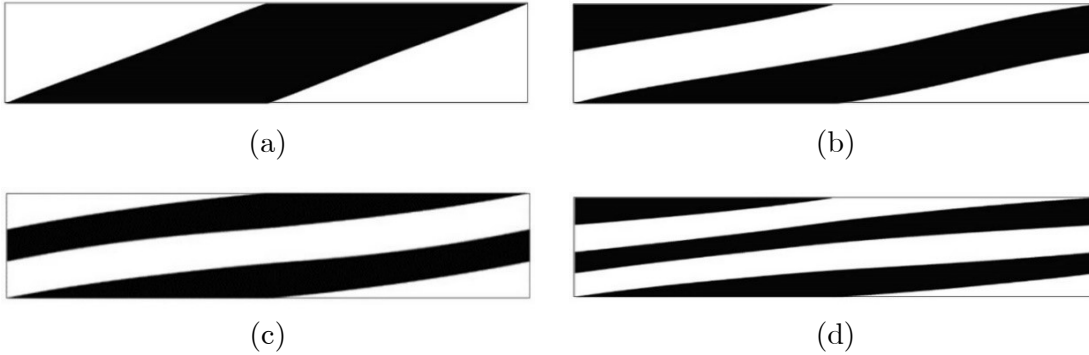


Figure 2.22 2D contour maps of phases at different stages of rotation for V2D2IT0, at (a) $N = 0.5$; (b) $N = 1$; (c) $N = 1.5$; (d) $N = 2$ and the gravitational forces are neglected.

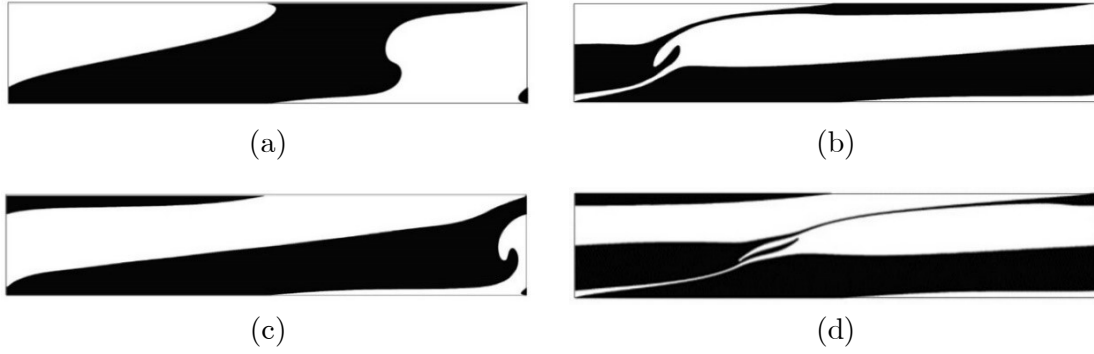


Figure 2.23 2D contour maps of phases at different stages of rotation for V2D2IT0, at (a) $N = 0.5$; (b) $N = 1$; (c) $N = 1.5$; (d) $N = 2$ and the gravitational forces are considered.

2.4.1.6 Influence of interfacial tension on mixing

The role of interfacial tension in rotational devices was studied from the mixing of oil and water. Oil and water have quite similar densities, $\rho_{\text{oil}} = 916 \text{ kg m}^{-3}$ and $\rho_{\text{water}} = 998.2 \text{ kg m}^{-3}$ at 20°C , but the viscosity ratio is 66, $\mu_{\text{oil}} = 0.066 \text{ Pa} \cdot \text{s}$ and $\mu_{\text{water}} = 0.001 \text{ Pa} \cdot \text{s}$. The viscosity of oil and water were measured in Anton Paar MCR 92 SN82478971 rheometer and then set as working conditions in CFD simulations.

In a system of dissimilar fluids, the interfacial tension and the contact angle guarantee the stabilisation of the liquid-liquid interface creation. Bhatluri et al. (2015) reported that the typical interfacial tension of a water-sunflower oil system is $\sigma = 24.8 \text{ mN m}^{-1}$. The wall contact angle was measured from post-processing imaging of a sunflower oil drop contacting an acrylic plate in water, as shown in Figure 2.24. The measured contact angle is $\theta_{ow} = 47^\circ$. Note that the setting of a contact angle in CFD simulations supposes that the device walls are made of acrylic.

VOF model was set to simulate the flow dynamics of oil and water in the rheometric flow. The interfacial tension was defined as a phase interaction, and the contact angle between interface and walls, $\theta_{ow} = 47^\circ$, was defined as wall adhesion.

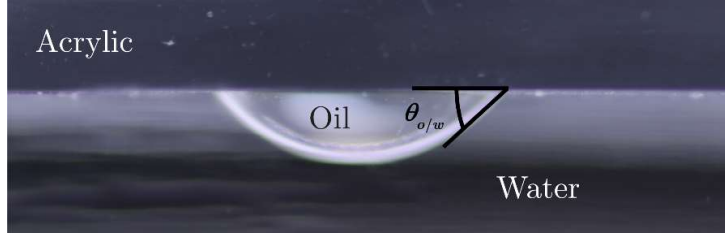


Figure 2.24 Contact angle of sunflower oil-water system.

Boundary conditions are listed in Table 2.3. For each case, Weber number ($We = \rho D_H v^2 / \sigma$) and capillary number ($Ca = \mu v / \sigma$) were changed in order to study its influence in flow dynamics. Weber number characterises the relative importance of inertial forces and interfacial tension. And capillary number describes the relative effect of viscous drag forces versus the surface tension at the interface of two immiscible fluids. At low Weber numbers ($We < 1$), the inertial forces may be neglected while for moderate Weber numbers, the interface is deformed and there is the creation of drops. At low capillary number ($Ca < 10^{-5}$), the flow is dominated by the capillary forces in comparison to the viscous forces. We and Ca in Table 2.3 were determined using the oil properties, and the hydraulic diameter corresponds to the gap between plates.

The time step in transient simulation was set to obey a Courant number equal or less than the unity. The time steps defined for each case are listed in Table 2.3. In these simulations, gravitational forces were neglected; however, these conditions are not far from reality because the density ratio is approximately 1:1 and so gravitational forces will not influence the position of each phase during the rotation of the top plate.

Figure 2.25 to Figure 2.30 show the volume fraction contour maps at different rotation stages for conditions of Table 2.3. Black fluid represents oil, and white fluid corresponds to water. For V66D1IT25_We1e-4 and V66D1IT25_We0.03, the interface is not stretched by the action of the shear rate generated between walls. A drop of oil is clearly formed after the contact to water, and the motion of the top wall promotes its flow along the gap. Although the velocity at the bottom wall is $v = 0 \text{ m s}^{-1}$, this

boundary condition seems to be violated because the interface is moving next to the bottom wall. The apparent reason for this stems from the definition of wall adhesion conditions, $\theta_{ow} = 47^\circ$, which requires the formation of a drop, promoting the slippage of interface next to the bottom wall.

In V66D1IT25_We0.3 and V66D1IT25_We0.5, Weber number is still lower than the unity. In Figure 2.27 and Figure 2.28, different behaviours are observed: for V66D1IT25_We0.3, the stretching of the interface is not enough to promote the overlapping of phases and the formation of a lamellar structure. In V66D1IT25_We0.5, a lamellar structure composed of white and black strips is formed at $N = 2$. Nevertheless, the lamellar structure is not stratified as for similar fluids.

Table 2.3 Boundary conditions imposed in 2D CFD simulations for V66D1IT25 conditions.

Case	ν_p [m s^{-1}]	We	Ca	Time step [s]
V66D1IT25_We1e-4	1.4×10^{-3}	1.4×10^{-4}	3.68×10^{-3}	1×10^{-4}
V66D1IT25_We0.03	0.02	0.03	0.05	1×10^{-4}
V66D1IT25_We0.3	0.06	0.27	0.16	1×10^{-5}
V66D1IT25_We0.5	0.08	0.47	0.21	1×10^{-5}
V66D1IT25_We1	0.12	1	0.32	4.2×10^{-5}
V66D1IT25_We47	0.8	47.3	2.13	6.3×10^{-5}



Figure 2.25 2D volume fraction contour maps at different stages (a) $N = 1$; (b) $N = 2$ for conditions V66D1IT25_We1e-4.

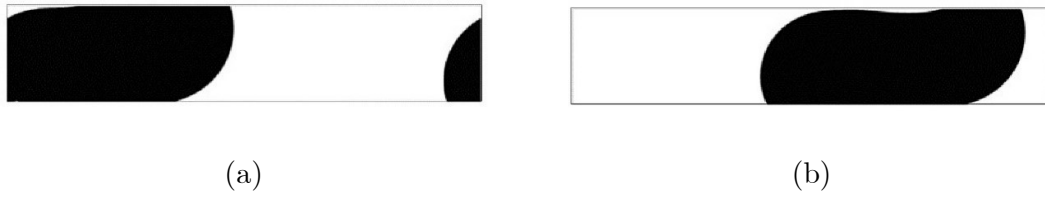


Figure 2.26 2D volume fraction contour maps at different stages (a) $N = 1$; (b) $N = 2$ for conditions V66D1IT25_We0.03.

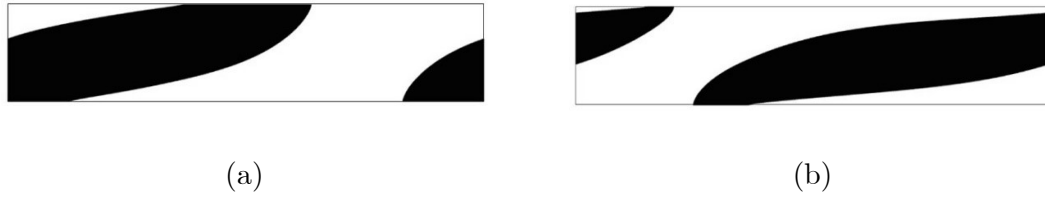


Figure 2.27 2D volume fraction contour maps at different stages (a) $N = 1$; (b) $N = 2$ for conditions V66D1IT25_We0.3.

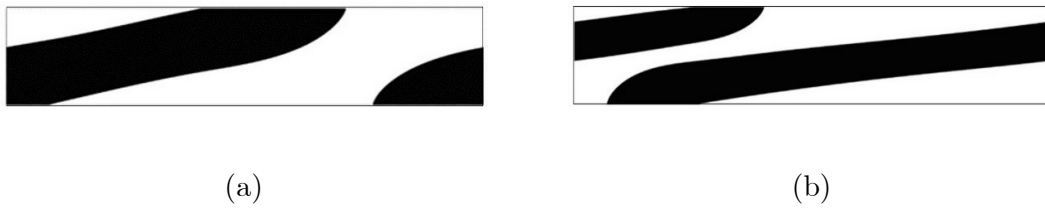


Figure 2.28 2D volume fraction contour maps at different stages (a) $N = 1$; (b) $N = 2$ for conditions V66D1IT25_We0.5.

Figure 2.29 and Figure 2.30 show the formation of a lamellar structure for $We = 1$ (V66D1IT25_We1) and $We = 47.3$ (V66D1IT25_We47). In V66D1IT25_We1, the capillary number is $Ca < 1$, and the contour maps show that there is the formation of

a lamellar structure with a different distribution of each phase compared to similar fluids. For $We > 1$ and $Ca > 1$ (Figure 2.30a), two lamellae, one white and one black, are formed at $N = 1$, four lamellae are generated at $N = 2$ (Figure 2.30b) and nine strips at $N = 4.5$ (Figure 2.30c). These results are quite similar to those that do not consider the interfacial tension between phases. Furthermore, Figure 2.30 also shows the slippage of the interface next to the bottom plate, which is not as pronounced as the previous cases.

In V66D1IT25_We47 and at $N = 6$, there is a breakup of the lamellar structure, and some droplets tend to form. This occurs when the viscous forces become larger than the interfacial tension ($We \gg 1$), even at laminar flow regime ($Re = 22.21$).

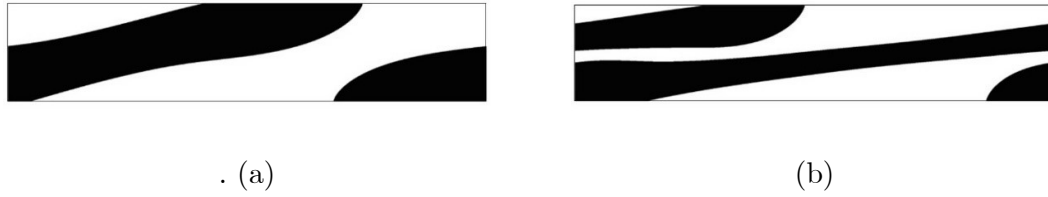


Figure 2.29 2D volume fraction contour maps at different stages (a) $N = 1$; (b) $N = 2$ for conditions V66D1IT25_We1.

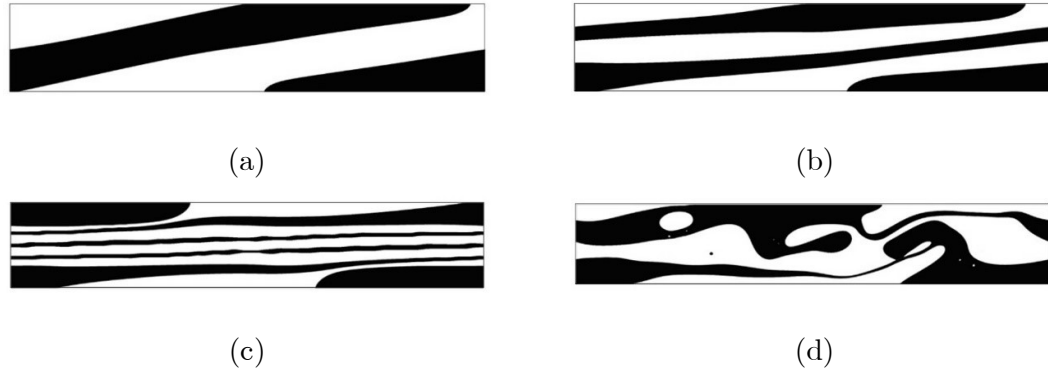


Figure 2.30 2D volume fraction contour maps at different stages (a) $N = 1$; (b) $N = 2$; (c) $N = 4.5$; $N = 6$ for conditions V66D1IT25_We47.

This section shows that the growth of the interfacial area and the striation thickness thinning occur when the inertial forces and the drag forces overcome the surface

tension, i.e $We > 1$ and $Ca > 1$. Moreover, the onset for droplet formation is determined by the number of turns and the Weber number, that must be $We \gg 1$.

2.5 Conclusions

Rotational mixers based on rheometric devices were applied for high throughput material development for reactive processes. Two rheometric configurations were addressed in this work: plate-plate and cone-plate rotational rheometers. Mixing in these devices was quantified, and design equations were introduced in terms of striation thinning and interfacial area generation.

In the first part of this chapter, mixing of two fluids with the same properties was modelled and computed. CFD simulations and LMS showed that a larger interfacial area is obtained for Topology 1, that is when the two fluids are initially placed side-by-side, resulting in thinner striation thicknesses. For Topology 2, where the fluids are initially placed one on top of the other, the mixing length scales remain unchanged with the number of turns of the top plate. These results prove that topology plays an important role in the evolution of mixing scales in mixing devices.

In the second part of this chapter, CFD simulations consider that both fluids have different physical properties, initially placed according to Topology 1. Three viscosity ratios were studied: 2:1, 4:1 and 10:1. Results showed that the instabilities are generated at the interface, due to the velocity profiles created in the gap between the two parallel plates. LMS also showed that the interface, where the less viscous fluid squeezes the more viscous fluid, has a larger growth and the respective striation thickness is thinner than for a viscosity ratio 1:1.

The effects of density and viscosity were also studied. Mixing is affected by the density ratio because the gravitational forces accelerate the stratification of fluids. The influence was reported for a density ratio of 2:1, which overcame the phenomena associated to the viscosity ratio of 2:1. Regarding studies on interfacial tension, the

generation for a lamellar structure occurs when the inertial forces and the drag forces overcome the surface tension, i.e. $We > 1$ and $Ca > 1$. The onset of the formation of droplets is determined by the conditions where the inertial forces must be much larger than the interfacial forces, i.e. the characteristic Weber number must be much larger than the unity.

A rotational device is so proposed in this chapter as a fast lab-scale formulation process. This device gives a 2D analysis of the laminar mixing that can be particularly interesting to mimic the mixing conditions in 2D reactors. The main advantages are the requirement of small amounts of reactants, short operation times and the simultaneous measurement of rheological properties during the formulation process. This methodology will be applied in Chapter 4 to an industrial case study, RIM machine, as a method to design RIM-formulations.

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3 Design of Model Fluids for Flow Phenomena Studies

3.1 Introduction and State of the Art

Flow phenomena studies are typically conducted using fluids with generic physical properties, model fluids. These experiments are generally performed in transparent reactors, and fluids must accomplish some requirements:

- Constant viscosity and density, at least in a narrow temperature range;
- Non-reactive with experimental setup materials, such as plastics and transparent materials (acrylics).

Model fluids can be classified as non-reactive and reactive according to their ability to cause reaction in the system. This classification enables to apply them in two different methods for the quantification of mixing. Physical methods use non-reactive fluids, which measure the homogeneity of mixing degree, while the reactive fluids are used for chemical methods, which use the spectrum of products from a chemical reaction (Santos et al., 2012).

Physical methods comprise the incorporation of a non-reactive tracer in the fluid stream. From that injection, the tracer concentration is measured at the reactor outlet through the measurement of physical properties, such as electrical conductivity, pH, light absorption, refractive index, among others (e.g. Danckwerts (1952); Nadeau et al. (1996)). The measurement of the tracer concentration history at the reactor outlet is a classic method known as residence time distribution (RTD).

Optical techniques are also classified as physical methods, which have enabled the visualisation of the flow trajectories (e.g. Buchmann and Mewes (1998,2000)). Flow paths are observed from the tracking of a fluid using a marker. Dyes and small particles with the same density of the fluid are commonly used as markers. Particle Tracking Velocimetry (PTV), Particle Image Velocimetry (PIV) and Laser-Induced Fluorescence (LIF) are examples of visualisation techniques from the entire reactor.

Both PIV and PTV are quantitative techniques used to measure the flow velocity. PIV is an Eulerian approach that comprises the injection of seed particles in the flow stream. A laser sheet illuminates the seed particles, and then a digital camera records consecutive image frames. From these images, the flow velocity is determined from the displacement of each particle for a short time interval (Tropea et al., 2007). PTV is a Lagrangean method that determines the fluid velocity from the tracking of an individual point. The velocity is calculated from the displacement of particles in a short time interval. Consecutive images are captured and correlated to determine the particle displacement. Laser Doppler Anemometry (LDA) is another widespread non-intrusive method that enables high frequency measurement of velocity data in a small measuring volume inside the flow. In LDA, the flow velocity is determined from the Doppler effect, which relates the frequency shift between moving bands of light in the measuring volume and scattered light emitted by the seed particles injected in the flow.

In LIF technique, a tracer is injected into the reactor and excited using a laser. A camera records the intensity of light emitted by the tracer. The concentration field can

be obtained from the relationship between the fluorescent tracer concentration and the excited fluorescence intensity (Liu et al., 2009). Wadley and Dawson (2005) attributed the success of this technique to the fact that it is non-intrusive, enabling the entire cross-section to be measured simultaneously and having a high temporal and spatial resolution.

Techniques, as LIF, PIV, LDA and PTV, are optically limited to clean systems with a constant refractive index. Thus, fundamental studies on mixing of dissimilar fluids using optical techniques are compromised by the differences in the refractive indices of two different liquids. For a successful implementation of this technique, the refractive index of both fluids must be matched by adding substances, a process known as refractive index-matching.

Physical methods identify the macroscopic convective and dispersion transport of materials following the main flow paths in the reactor (macromixing). The transport of materials is visualised from the concentration distribution of a tracer (RTD), a dye (LIF) or the velocity field obtained from seed particles (PTV and PIV). These studies are sufficient to identify the flow regimes. However, the whole mixing process is not described, such as, the set of phenomena that promote the contact of fluids down to molecular scales (micromixing). These set of phenomena can be determined from chemical methods.

Chemical methods are based on test-reactions, where product yield or reagent consumption are used to monitor reaction course and infer micromixing degree. This method consists in the injection of reagents into the reactor. The product distribution is determined by collecting samples of fluid at the outlet of a continuous reactor. For an efficient implementation of this method, the following characteristics should be fulfilled (Bourne et al., 1977; David and Villermaux, 1987; Bourne et al., 1992):

- An efficient contact of two or more reagents must occur, which is determined by micromixing. The effect of mixing on the chemical reaction was reported by

Zwietering (1959), who concluded RTD and mixing have an essential impact on the chemical reaction course;

- Comprehensive knowledge of the mechanisms and kinetics of the test reactions should be available. For example the dependence of reaction rate on all concentrations, ionic strength, pH, solvent, temperature and homogenous catalysts including acids and bases;
- Test reactions with non-linear kinetics are required to measure the conversion at the reactor outlet (Bourne, 1984), and the mixing sensitive reactions must have kinetics orders higher than the unity (Weinstein and Adler, 1967). The selectivity of the homogeneous first-order or pseudo-first-order reactions are not affected by the mixing degree. However, the reaction of molecules depends on the micromixing for non-linear kinetics;
- At least one reaction in the system of test-reactions should be faster than the micromixing process. The other(s) should have a rate comparable in magnitude to the mixing rate or smaller. Reactions should be irreversible, and thus the product distribution describes the mixing history over the reaction zone;
- All reagents and products should be soluble in water, and low concentrations should be used to avoid any phase change that can affect the overall reaction rate;
- Accurate quantitative analysis is essential to determine the product distribution. And so, routine, inexpensive, and reliable instrumental analytical methods should be available.

A new family of methods for the assessment of micromixing has gained importance in the literature. A combination of chemical and physical methods was proposed by Buchmann and Mewes (1998,2000) to assess micromixing. This technique consists in the injection of a reactive dye into the reactor. The marker concentration field was measured from the light absorption using an RGB-CCD camera (Buchmann and Mewes, 1998,2000). The vanishing of dye during the reaction course enables to track

the concentration distribution along the reactor, being a quantitative measurement of micromixing extent. There are also two main types of optical methods suitable for this purpose: fluorescence-based techniques, particularly LIF and chemiluminescence-based techniques.

In this chapter, aqueous solutions of glycerol are addressed as non-reactive model fluids for optical techniques applications. The modelling of glycerol solutions involves an accurate description of physical properties. Viscosity, density and refractive index of aqueous solutions of glycerol were measured for a mass fraction of glycerol from 0 to 1. The issue related to the matching of refractive indices of two different aqueous solutions of glycerol is also addressed in this chapter. Calcium chloride is added to aqueous solutions of glycerol, and the variations of viscosity, density and refractive index were reported. Expressions based on the experimental data are then proposed for the calculation of the physical properties of aqueous solutions of glycerol and calcium chloride.

The design of two test reactions with reactive tracers is also addressed in this chapter as a method to visualise the reactive fronts in reactors. These reactants will be marked with a dye, which has a particular characteristic that makes them optically sensitive to the reaction course. The flow will be tracked from the differences in the fluorescence intensity emitted by a tracer during the reaction course. The two selected test-reactions are: (i) an acid-base reaction with fluorescein as the reaction sensitive tracer and (ii) the Fenton's reaction, with rhodamine B as the reaction tracer. These two test-reactions were selected according to the characteristics already described for its efficient performance. Nonetheless, there are no conditions for the order of kinetics in the reaction systems, because the goal is only to observe the reactive fronts across the flow. In this work, product distribution is not used to assess mixing, and reaction should be non-irreversible first order. Nevertheless, it is crucial to ensure that the reaction time is faster than the residence time.

Both test-reactions were studied in stopped-flow equipment to define suitable operational conditions for the implementation of this method in an industrial reactor or even in pilot-scale devices. From these results, the chemical composition of the inflow streams, the concentration of reagents and fluorophore and excitation light wavelength are shown.

This chapter is organised into two main sections. In section 3.2, physical properties of aqueous solutions of glycerol and calcium chloride are reported. In section 3.3, the performance of reactive tracers is addressed for two test-reactions.

3.2 Non-Reactive Model Fluids for Optical Techniques: Aqueous solutions of Glycerol and Calcium Chloride

Glycerol-water systems provide a wide range of Newtonian liquids with viscosities by over three orders of magnitude. Accordingly, glycerol solutions are widely used to tune the physical properties of fluids, such as viscosity, in order to be applied in flow phenomena studies. The use of glycerol solutions in flow phenomena enables to perform experiments at a wide range of Reynolds numbers. The accurate model of physical properties (density and viscosity) of glycerol solutions facilitates the design of experiments.

Glycerol solutions have also been used to fundamentally study the flow of two miscible fluids (Brito et al., 2018). Most of the fluids in mixers have different physical properties, such as viscosity and density (Renardy, 1988; Zhang and Zumbrunnen, 1996; Fradette et al., 2007; Azimi et al., 2015; Galletti et al., 2015; Barthès-Biesel, 2016; Chen et al., 2016; Häfeli et al., 2016; Håkansson et al., 2016; Liu et al., 2016; Mori, 2016; Ramsay et al., 2016; Sarbanha et al., 2016; Yang et al., 2016; Galletti et al., 2017; Piroozian et al., 2017; Tsaoulidis and Angeli, 2017; Brito et al., 2018; Forte et al., 2019; Grecco Zanotti and Gonçalves dos Santos, 2019; Marcos et al., 2019). In the flow phenomena studies, different visualisation techniques have been used to track the flow of two liquid streams. The differences in refractive indices compromise the performance of the optical

techniques for mixing studies with dissimilar liquids. In order to overcome this problem, calcium chloride is the index-matching substance added to the aqueous solutions of glycerol to manipulate the refractive indices of solutions. The goal is the matching of the same refractive indices for both liquid streams.

Different approaches are proposed in the literature to calculate viscosity, density and refractive indices of aqueous solutions of glycerol. In contrast, few works about the influence of salts on the physical properties of glycerol solutions have been reported. In this chapter, empirical correlations for the calculation of viscosity, density and refractive index are compared with experimental results. Experiments were performed using industrial and analytical glycerol at temperatures in a range from $\theta = 288.16$ K to $\theta = 303.16$ K. The differences between the two glycerol grades are related to purity, which is approximately 15%. The analytical glycerol has higher purity than the industrial glycerol. The particular objective of this study is to report the influence of purity of glycerol on the physical properties of model fluids.

Aqueous solutions of glycerol with different concentrations of calcium chloride were prepared. Calcium chloride is the salt used to match the refractive indices of solutions. The refractive index was measured in a refractometer for a temperature range between $\theta = 293.15$ K and $\theta = 303.15$ K. The density and viscosity of solutions of glycerol and calcium chloride were reported at $\theta = 292.15$ K and $\theta = 295.15$ K, respectively. Expressions based on the experimental results were demonstrated in order to describe viscosity, density and refractive indices.

3.2.1 Experimental Section

3.2.1.1 Materials

The aqueous solutions of glycerol were prepared using industrial glycerol or analytical glycerol and tap water. The analytical glycerol was purchased in a pharmacy while the industrial glycerol was supplied by a local company which trades raw materials and

chemicals for the manufacturing industry, Sociedade Portuense de Drogas. The analytical glycerol usually has a purity of $\geq 99.7\%$ while the industrial glycerol has a purity of $\sim 85\%$.

In aqueous solutions of glycerol and calcium chloride, the salt is added to the aqueous solutions of glycerol. Calcium chloride dehydrated, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, was purchased in VWR (VWRC22322.466). This compound has a limit of solubility in water of 1345 kg m^{-3} at $\theta = 333.15 \text{ K}$.

3.2.1.2 Methods

The aqueous solutions of glycerol were prepared in glass vials measuring the mass of glycerol and then the total mass of solution. The densities of aqueous glycerol solutions were measured using a pycnometer of 25 mL. An analytical balance with an accuracy of $\pm 0.001 \text{ g}$ was used in the preparation of solutions, and also for the density calculations. The experiments were performed at $\theta = 288.16 \pm 0.5 \text{ K}$, $\theta = 298.16 \pm 0.5 \text{ K}$ and $\theta = 303.16 \pm 0.5 \text{ K}$.

The viscosity of solutions was measured using a rheometer Anton Paar MCR 92 SN82478971. The geometry used for these measurements was a plate-plate system, whose diameter is 50 mm. The gap between the two parallel plates is 0.5 mm. Rheological tests were performed at $\theta = 293.15 \text{ K}$, $\theta = 295.15 \text{ K}$ and $\theta = 298.15 \text{ K}$.

The refractive indices of solutions were measured using a digital ABBE Refractometer (AB-R-100D) with an accuracy of ± 0.0001 . The refractometer is connected to a water bath in order to control the operating temperature. The measurements of the refractive index were performed at $\theta = 293.15 \text{ K}$, $\theta = 298.15 \text{ K}$ and $\theta = 303.15 \text{ K}$.

3.2.2 Results and Discussion

3.2.2.1 Density of Glycerol Solutions

The first study addresses the variation of density with the mass fraction of glycerol using analytical and industrial glycerol. The mass fraction of glycerol is defined as $x_{\text{glycerol}} = m_{\text{glycerol}} / m_{\text{solution}}$ where m_{glycerol} is the glycerol mass in solution and m_{solution} is the total mass of solution.

Figure 3.1 shows the variation of density with the mass fraction of glycerol at $\theta = 288.16$ K for an aqueous solution of analytical glycerol and an aqueous solution of industrial glycerol. As Figure 3.1 shows, the density increases linearly with x_{glycerol} and no significant differences in the densities are reported for solutions of analytical and industrial glycerol. These results show that the purity of glycerol does not influence the density.

Density also depends on the operating temperature and thus the density of aqueous solutions of analytical glycerol was reported for three distinct temperatures. Figure 3.2 shows the variation of density for $0.7 < x_{\text{glycerol}} < 1$ at $\theta = 288.16$ K, $\theta = 298.16$ K and $\theta = 303.16$ K, and the respective trendlines. Figure 3.2 shows that the density of aqueous solutions of glycerol can be obtained from

$$\rho = x_{\text{glycerol}} \rho_{\text{glycerol}} + (1 - x_{\text{glycerol}}) \rho_{\text{water}} \quad (3.1)$$

where ρ_{glycerol} is the density of glycerol in kg m^{-3} and ρ_{water} is the density of water in kg m^{-3} (Takamura et al., 2012), which depend on the operating temperatures according to,

$$\begin{aligned} \rho_{\text{water}} &= -0.23\theta + 1064.6 \\ \rho_{\text{glycerol}} &= -0.61\theta + 1440.5 \end{aligned} \quad (3.2)$$

where θ is the temperature in Kelvin degrees.

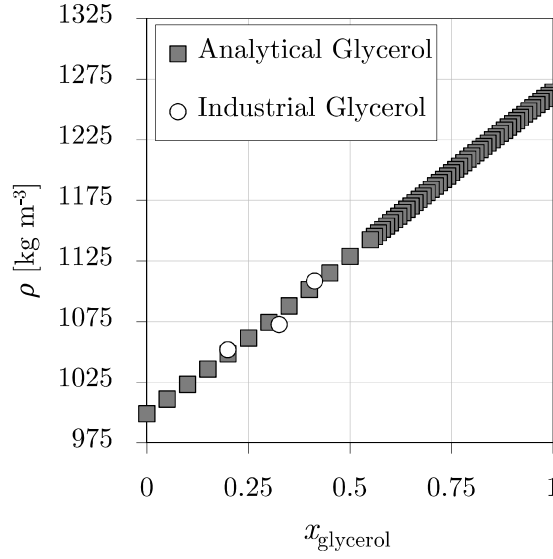


Figure 3.1 Density of glycerol solutions versus the mass fraction of analytical/industrial glycerol,

x_{glycerol} , at $\theta = 288.15$ K.

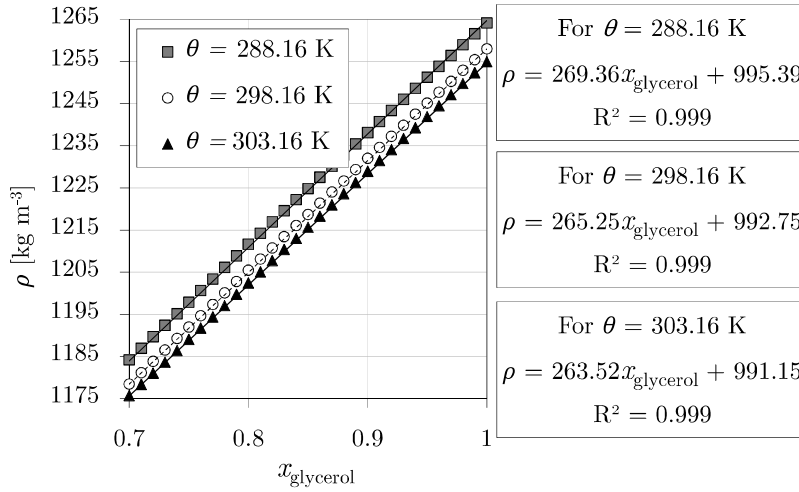


Figure 3.2 Density of glycerol solutions versus the mass fraction of analytical glycerol between 0.7 and 1 and the respective trendlines.

The experimental results and respective expressions were compared to data in the literature (Perry and Chilton, 1973; Takamura et al., 2012). In the temperature range

between $\theta = 293.15$ K and $\theta = 303.15$ K, the maximum deviation of experimental and literature data is 0.55% for Perry and Chilton (1973) and 0.22% for Takamura et al. (2012).

3.2.2.2 Viscosity of Glycerol Solution

The variation of viscosity with x_{glycerol} was studied using industrial and analytical glycerol. Figure 3.3 and Figure 3.4 show viscosity versus the mass fraction of glycerol at temperatures 293.15 K and 298.15 K. Figure 3.4 compares the viscosity of industrial and analytical glycerol at $\theta = 298.15$ K. The shear rate conditions in rheological tests were from 10 to 100 s⁻¹. The viscosity increases exponentially with x_{glycerol} and small variations of viscosities are caused by an increase of 5 K in temperature, as shown in Figure 3.3 and Figure 3.4.

Figure 3.4 shows that no significant differences between industrial and analytical glycerol are reported at $\theta = 298.15$ K. This means that the purity of glycerol does not have a considerable effect on the viscosity of aqueous solutions of glycerol.

The experimental results were compared with the expressions presented in the literature. Reid et al. (1987) suggest the method Grunberg and Nissan (Grunberg and Nissan, 1949) to determine the viscosity of binary systems. In this method, the viscosity for binary mixture is given by

$$\ln(\mu) = n_i \ln(\mu_i) + n_j \ln(\mu_j) + n_i n_j G_{ij} \quad (3.3)$$

where i and j are the viscosities of the two pure components in the binary system, n_i and n_j are the molar fractions of i and j , μ_i and μ_j are the viscosities of each component and G_{ij} is an interaction parameter which is a function of the components i and j .

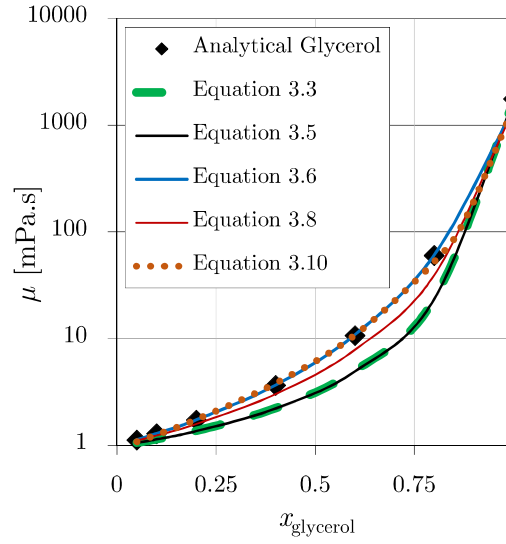


Figure 3.3 Influence of the mass fraction of glycerol on the viscosity at $\theta = 293.15$ K .

For water and glycerol systems, μ_{water} and μ_{glycerol} can be determined by

$$\ln(\mu_{\text{water}}) = A_{\text{water}} + \frac{B_{\text{water}}}{\theta} + C_{\text{water}}\theta + D_{\text{water}}\theta^2 \quad (3.4)$$

$$\mu_{\text{glycerol}} = A_{\text{glycerol}}\theta^{B_{\text{glycerol}}}$$

where μ_{water} and μ_{glycerol} are the viscosity of water and glycerol in $\text{mPa}\cdot\text{s}$, θ is the temperature in Kelvin degrees, and the constants are $A_{\text{water}} = -24.71$, $B_{\text{water}} = 4.209 \times 10^3$, $C_{\text{water}} = 4.527 \times 10^{-2}$, $D_{\text{water}} = -3.376 \times 10^{-5}$; $A_{\text{glycerol}} = 3.426 \times 10^{73}$ and $B_{\text{glycerol}} = -2.85 \times 10^{-1}$ (Reid et al., 1987).

The variable G_{ij} in Equation (3.3) can be determined from different methods as proposed by Reid et al. (1987). According to Isdale et al. (1981), for a water and glycerol system, $G_{ij} = -0.3387$ at $\theta = 298.15$ K and $G_{ij} = -0.3623$ at $\theta = 293.15$ K .

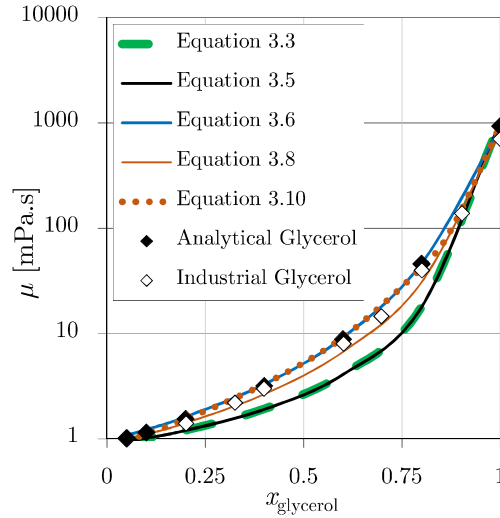


Figure 3.4 Influence of the mass fraction of glycerol on viscosity at $\theta = 298.15$ K.

Isdale et al. (1981) reported that G_{ij} is independent of the composition of the mixture in some cases. However, for other mixtures, G_{ij} is a function of n_i according to $G_{ij}(n_i) = 1.433 - 0.685n_i$. For this case, the term G_{ij} is substituted in Equation (3.3),

$$\ln(\mu) = n_i \ln(\mu_i) + n_j \ln(\mu_j) + n_i n_j (1.433 - 0.685n_i) \quad (3.5)$$

The viscosity of an aqueous solution of glycerol can be described from Equation (3.3) using the term G_{ij} independent of the mixture composition. On the other hand, G_{ij} can be calculated from the dependence on the molar fraction of both components according to Equation (3.5). Figure 3.3 and Figure 3.4 compare Equation (3.3), Equation (3.5) and experimental data at $\theta = 293.15$ K and $\theta = 298.15$ K.

Figure 3.3 and Figure 3.4 show that curves described by Equation (3.3) and Equation (3.5) mostly have the same trend, and so the methods used to calculate G_{ij} do not affect the viscosity curve. Furthermore, both curves describe the tendency of viscosity but do not fit the experimental data.

In the last decades, authors suggested other expressions for the viscosity of aqueous solutions of glycerol. Cheng (2008) proposed an empirical formula to describe the viscosity of a glycerol-water mixture for a mass fraction of glycerol in the range between 0 and 1,

$$\mu = \mu_{\text{water}}^{w_V} + \mu_{\text{glycerol}}^{1-w_V} \quad (3.6)$$

where μ_{glycerol} and μ_{water} are the viscosities of glycerol and water, respectively, and w_V is the weighting factor varying from 0 and 1, which is defined by

$$w_V = 1 - x_{\text{glycerol}} + \frac{\kappa \iota x_{\text{glycerol}} (1 - x_{\text{glycerol}})}{\kappa x_{\text{glycerol}} + \iota (1 - x_{\text{glycerol}})} \quad (3.7)$$

where coefficients κ and ι are $\kappa = 0.705 - 0.017(\theta - 273.15)$ and $\iota = [4.9 + 0.036(\theta - 273.15)]\kappa^{2.5}$ where θ is the temperature in Kelvin degrees. In this sense, Cheng (2008) determined the expressions to calculate the viscosity of water and

$$\text{glycerol: } \mu_{\text{water}} = 1.790e^{\left[\frac{[-1230-(\theta-273.15)](\theta-273.15)}{36100+360(\theta-273.15)}\right]} \quad \text{and} \quad \mu_{\text{glycerol}} = 12100e^{\left[\frac{[-1230-(\theta-273.15)](\theta-273.15)}{9900+70(\theta-273.15)}\right]}$$

where θ is the temperature in Kelvin degree and the viscosity units are $\text{mPa} \cdot \text{s}$.

Van de Ven (1989) and Takamura and Van De Ven (2010) proposed an expression that describes the viscosity of colloidal dispersions as

$$\mu = \mu_m \left[\frac{1 - \phi / \phi_m}{1 - (k_0 \phi_m - 1) \phi / \phi_m} \right]^{(-2.5\phi_m)/(2-k_0\phi_m)} \quad (3.8)$$

where μ_m is the viscosity of the dispersed medium, ϕ and ϕ_m are the volume fraction of the dispersed particles at which the viscosity reaches an infinite value and k_0 is a factor that accounts the repulsive forces between the dispersed particles relative to the hydrodynamic forces.

Equation (3.8) may be used to calculate the viscosity of a glycerol-water system by an analogy with a dispersion, considering that water is the continuous phase and oil is equivalent to the solid particles dispersed in water. For aqueous solutions of glycerol, $\mu_m = \mu_{\text{water}}$, $\phi_m = 1.20$ and k_0 is given by

$$k_0 = -0.012\theta + 4.74 \quad (3.9)$$

where θ is the absolute temperature.

Santos et al. (2008) also proposed an expression that describes the viscosity of a glycerol-water system, which was obtained from experimental data in the ranges of $293.15 < \theta < 298.15$ K and $0 < x_{\text{glycerol}} < 0.88$. The expression is given by

$$\mu = \left[(1 - x_{\text{glycerol}}) \left(P_{\text{water}} e^{\frac{G_{\text{water}}}{\theta}} \right)^a + (x_{\text{glycerol}}) \left(P_{\text{glycerol}} e^{\frac{G_{\text{glycerol}}}{\theta}} \right)^a \right]^{1/a} \quad (3.10)$$

where μ is viscosity in $\text{mPa} \cdot \text{s}$, θ is the temperature in Kelvin degrees, and the constants are: $P_{\text{water}} = 5.17 \times 10^{-4} \text{ mPa} \cdot \text{s}$, $G_{\text{water}} = 2.22 \times 10^3 \text{ K}$, $P_{\text{glycerol}} = 7.06 \times 10^{-9} \text{ mPa} \cdot \text{s}$, $G_{\text{glycerol}} = 7.64 \times 10^3 \text{ K}$ and $a = -0.32$.

Equations (3.6), (3.8) and (3.10) were plotted in Figure 3.3 and Figure 3.4 at two operating conditions, $\theta = 293.15$ K and $\theta = 298.15$ K. Equations (3.6) and (3.10) are the ones that best fit the experimental results.

The experimental results were also compared to data in the literature (Weast and Astte, 1974). In the temperature range between $\theta = 293.15$ K and $\theta = 303.15$ K, the maximum deviation of the experimental and literature data is 3.6% for Weast and Astte (1974).

3.2.2.3 Refractive Index of Glycerol Solution

Refractive index changes were reported for a range of x_{glycerol} between 0.6 and 1. Samples of industrial and analytical glycerol solutions are used to study the refractive index, which is defined as

$$RI = \frac{c_L}{v_{\text{medium}}} \quad (3.11)$$

where c_L and v_{medium} are the speed of light in the vacuum ($c_L = 3 \times 10^8 \text{ ms}^{-1}$) and in a specific medium, respectively (Takamura et al., 2012).

Figure 3.5 shows the variation of the refractive index versus the mass fraction of analytical and industrial glycerol at $\theta = 298.15 \text{ K}$. Slight differences in refractive indices are reported between solutions of analytical glycerol and industrial glycerol.

Figure 3.5 also shows that the refractive index increases linearly with the mass fraction of glycerol. This behaviour can be expressed by

$$RI = RI_{\text{water}}(1 - x_{\text{glycerol}}) + RI_{\text{glycerol}}x_{\text{glycerol}} \quad (3.12)$$

where RI_{water} and RI_{glycerol} are the refractive indices of water and glycerol (Takamura et al., 2012). Literature reports that $RI_{\text{water}} = 1.3247$ (Larin et al., 2004) and $RI_{\text{water}} = 1.416$ at $\theta = 298.15 \text{ K}$ (Polyanskiy, 2008). The refractive indices of aqueous solutions of glycerol at $\theta = 298.15 \text{ K}$ were determined from Equation (3.12) and then plotted in Figure 3.5. There is a good agreement between the equation and experimental results.

The refractive index also depends on temperature. The increase in temperature causes a decrease of density, promoting the rising of the light speed in that liquid. According to Equation (3.11), the rise of light speed in a medium causes the decrease of the refractive index. Therefore, the refractive index is reduced by temperature. Table 3.1

reports refractive indices of two aqueous solutions of industrial glycerol, $x_{\text{glycerol}} = 0.20$ and $x_{\text{glycerol}} = 0.41$, at $\theta = 293.15$ K and $\theta = 303.15$ K. For an increase of 10 K, refraction index decreases 0.0009 for $x_{\text{glycerol}} = 0.20$ and 0.0002 for an aqueous solution of $x_{\text{glycerol}} = 0.41$. The rise in temperature promotes a decrease in the refractive index, as expected.

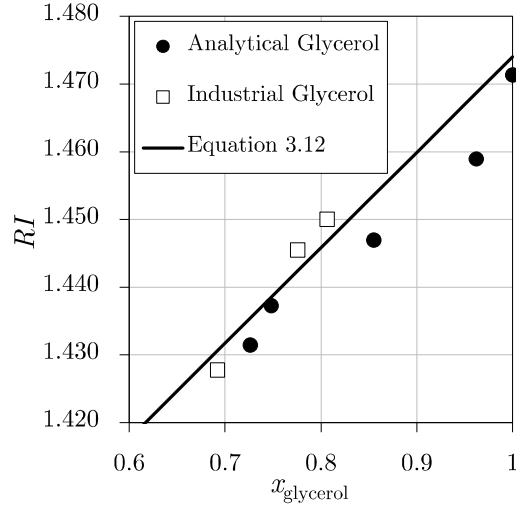


Figure 3.5 Refractive index of analytical and industrial glycerol solutions versus the mass fraction of glycerol at $\theta = 298.15$ K .

Table 3.1 Refractive index of two aqueous solutions of industrial glycerol, $x_{\text{glycerol}} = 0.20$ and $x_{\text{glycerol}} = 0.41$, at $\theta = 293.15$ K and $\theta = 303.15$ K .

x_{glycerol}	θ [K]	RI	$\Delta RI(\Delta\theta = 10 \text{ K})$
0.20	293.15	1.3585	-0.0009
	303.15	1.3576	
0.41	293.15	1.3878	-0.0002
	303.15	1.3876	

Figure 3.1, Figure 3.4 and Figure 3.5 show that the differences of density, viscosity and refractive indices for aqueous solutions of industrial and analytical glycerol are not

significant. Thus, the physical properties analysed in this work are not affected by the purity of glycerol. The same viscosity, density and refractive index results were achieved for analytical and industrial glycerol. The main advantage of this issue concerns the purchase cost of both liquids. The analytical glycerol is sold in a pharmacy for approximately 24 €/L while the industrial glycerol was purchased in a local company for 1.8 €/L. Since fundamental flow studies require large quantities of aqueous solutions of glycerol, the use of industrial glycerol will be more reasonable.

3.2.2.4 Refractive Index of Aqueous Solutions of Glycerol and Calcium Chloride Dehydrated

Refractive index can be manipulated using salts, such as calcium chloride or sodium chloride. In this work, calcium chloride dehydrated ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) was used to test its effect on the physical properties of aqueous solutions of glycerol. From the arguments presented in this work, viscosity, density and refractive index are not affected by the use of industrial or analytical glycerol. Therefore, aqueous solutions of glycerol and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ were prepared with industrial glycerol.

Refractive indices were reported for two aqueous solutions of industrial glycerol with $x_{0,\text{glycerol}} = 0.20$ and $x_{0,\text{glycerol}} = 0.41$, where $x_{0,\text{glycerol}}$ is the mass fraction of glycerol before adding calcium chloride dehydrated. The concentration of calcium chloride dehydrated was changed in a range from 0 kg m^{-3} to 600 kg m^{-3} , which is within the limit of solubility of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in water. The concentration of calcium chloride dehydrated is defined as $C = m_{\text{CaCl}_2 \cdot 2\text{H}_2\text{O}} / V$ where $m_{\text{CaCl}_2 \cdot 2\text{H}_2\text{O}}$ is the mass of calcium chloride dehydrated and V is the volume of an aqueous solution of glycerol and calcium chloride.

Figure 3.6 shows the variation of refractive index, RI^* , with the concentration of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ for an aqueous solution with $x_{0,\text{glycerol}} = 0.20$ at three distinct temperatures: 293.15 K, 298.15 K and 303.15 K. The refractive index increases linearly with the

concentration of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and an increase of temperature in 10 K does not have a significant impact on the refractive indices.

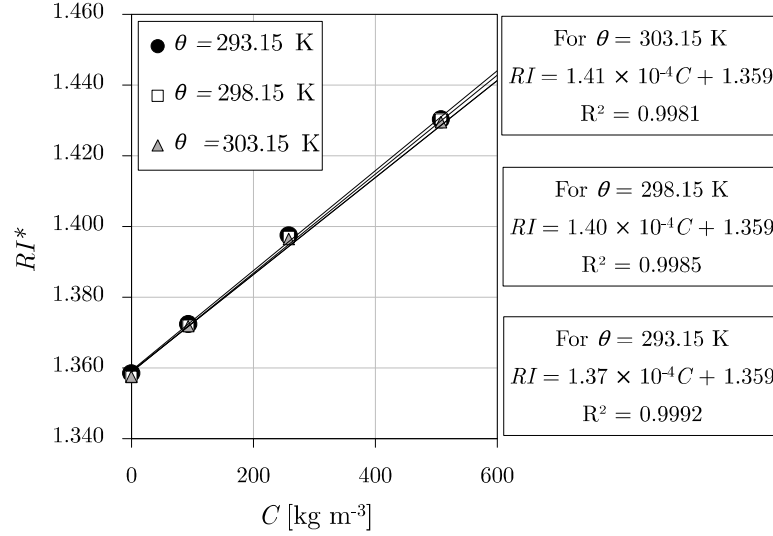


Figure 3.6 Refractive index of aqueous solutions $x_{0,\text{glycerol}} = 0.20$ versus the concentration of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

Figure 3.7 shows the variation of the refractive index with the concentration of calcium chloride dehydrated for a solution of glycerol with $x_{0,\text{glycerol}} = 0.41$ at temperatures: 293.15 K, 298.15 K and 303.15 K.

The expression that describes the variation of the refraction index as a function of the concentration of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ can be obtained from the trendlines drawn in Figure 3.6 and Figure 3.7,

$$RI^* = m_{\text{IR}} C + RI_0 \quad (3.13)$$

where RI^* is the refractive index of an aqueous solution of glycerol and calcium chloride dehydrated, C is the concentration of calcium chloride dehydrated in kg m^{-3} , m_{IR} is a factor that depends on $x_{0,\text{glycerol}}$ and RI_0 is the refractive index of a glycerol-water system for $C = 0 \text{ kg m}^{-3}$. Figure 3.6 and Figure 3.7 show that Equation (3.13) is valid for any operating temperature.

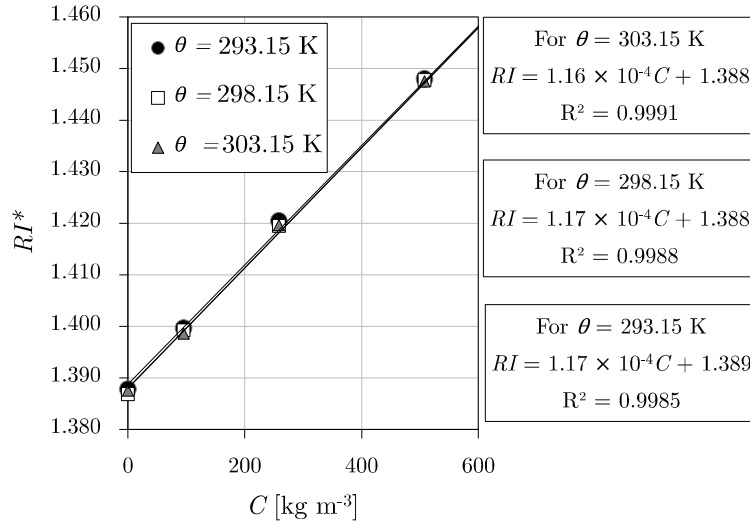


Figure 3.7 Refractive index of aqueous solutions $x_{0,\text{glycerol}} = 0.41$ versus the concentration of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

The variation of m_{IR} with $x_{0,\text{glycerol}}$ can be determined by the trend line of the slopes in Figure 3.6 and Figure 3.7 for $x_{0,\text{glycerol}} = 0.20$ and $x_{0,\text{glycerol}} = 0.41$. The function of m_{IR} with $x_{0,\text{glycerol}}$ is linear, $m_{\text{IR}} = -1.05 \times 10^{-4} x_{0,\text{glycerol}} + 1.62 \times 10^{-4}$. Considering this expression in Equation (3.13), it results in

$$RI^* = (-1.05 \times 10^{-4} x_{0,\text{glycerol}} + 1.62 \times 10^{-4})C + RI_0 \quad (3.14)$$

The experimental results were compared with Equation (3.14), where RI_0 is determined by the equation that describes the refractive index of a glycerol-water system, Equation (3.12). These results are summarised in Table 3.2. At $\theta = 298.15$ K, the maximum deviation between analytical and experimental data for $x_{0,\text{glycerol}} = 0.20$ is 1.32% and for $x_{0,\text{glycerol}} = 0.41$ is 1.98%.

Table 3.2 Comparison of refractive index measured in the refractometer and determined from the analytical equation, Equation (3.14).

$x_{0,\text{glycerol}}$	$C [\text{kg m}^{-3}]$	RI^*	RI^*
		Experimental measurement	Analytical Expression
0.20	0	1.3585	1.3430
	93.1	1.3724	1.3561
	258.1	1.3975	1.3794
	507.9	1.4303	1.4146
	606.0	1.4449	1.4284
0.41	0	1.3878	1.3621
	95.4	1.3997	1.3735
	258.5	1.4204	1.3929
	507.7	1.4408	1.4225
	605.6	1.4578	1.4342

Equation (3.14) describes the refractive index of an aqueous solution of glycerol and calcium chloride. This expression provides a tool for the design of model fluids to study flow phenomena from the matching of the refractive index of two liquids.

3.2.2.5 Density of Aqueous Solutions of Glycerol and Calcium Chloride Dehydrated

Calcium chloride dehydrated in aqueous solutions of glycerol could also affect other physical properties, such as the density of solutions.

The density of aqueous solution of glycerol and calcium chloride dehydrated was checked using a ROTA-Yokogawa Coriolis flowmeter (model RCCS33 M01A1SH). This flowmeter measures the mass of fluid in a unit of time flowing through a pipe. Moreover,

these devices measure the density of liquids. For that, these devices have incorporated a U-shaped tube wherein the fluid flows. Coriolis forces are generated at the outlet and inlet of the tube. The vibration frequency in the U-shaped tube depends on the mass of the tube and the mass of fluid. The mass of fluid can be calculated from the vibration frequency and the known mass of the tube. From that, the density is determined by dividing the mass of fluid and the known volume of fluid.

The density of two aqueous solutions of industrial glycerol and calcium chloride dehydrated was checked using a Coriolis flowmeter. Table 3.3 shows the densities of aqueous solutions of glycerol and calcium chloride dehydrated measured in Coriolis flowmeter at $\theta = 292.15$ K.

Table 3.3 Densities of aqueous solutions of glycerol and calcium chloride dehydrated at $\theta = 292.15$ K .

x_{glycerol}	$x_{\text{CaCl}_2 \cdot 2\text{H}_2\text{O}}$	$\rho^* [\text{kg m}^{-3}]$ Experimental measurement	$\rho^* [\text{kg m}^{-3}]$ Analytical Expression
0.05	0.49	1.37	1.42
0.12	0.43	1.34	1.37

The experimental results in Table 3.3 were compared with the analytical expression,

$$\rho^* = x_{\text{glycerol}} \rho_{\text{glycerol}} + \left(1 - x_{\text{glycerol}} - x_{\text{CaCl}_2 \cdot 2\text{H}_2\text{O}}\right) \rho_{\text{water}} + x_{\text{CaCl}_2 \cdot 2\text{H}_2\text{O}} \rho_{\text{CaCl}_2 \cdot 2\text{H}_2\text{O}} \quad (3.15)$$

where $x_{\text{CaCl}_2 \cdot 2\text{H}_2\text{O}}$ is the mass fraction of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\rho_{\text{CaCl}_2 \cdot 2\text{H}_2\text{O}}$ is the density of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Densities of solutions for $x_{\text{glycerol}} = 0.05$ and $x_{\text{glycerol}} = 0.12$ were determined from Equation (3.15) and are summarised in Table 3.3. For solution $x_{\text{glycerol}} = 0.05 \wedge x_{\text{CaCl}_2 \cdot 2\text{H}_2\text{O}} = 0.49$ the deviation is 3.16% and for $x_{\text{glycerol}} = 0.12 \wedge x_{\text{CaCl}_2 \cdot 2\text{H}_2\text{O}} = 0.43$, the deviation is 1.91%.

3.2.2.6 Viscosity of Glycerol Solution and Calcium Chloride

Calcium chloride dehydrated in aqueous solutions of glycerol also affects the viscosity of the final solution. Three different aqueous solutions of glycerol were prepared with an initial mass fraction of glycerol $x_{0,\text{glycerol}} = 0.21$, $x_{0,\text{glycerol}} = 0.45$ and $x_{0,\text{glycerol}} = 0.51$. The initial viscosity of each solution is calculated from Equation (3.10), $\mu_0(x_{0,\text{glycerol}} = 0.21) = 1.84 \text{ mPa} \cdot \text{s}$, $\mu_0(x_{0,\text{glycerol}} = 0.45) = 4.83 \text{ mPa} \cdot \text{s}$ and $\mu_0(x_{0,\text{glycerol}} = 0.57) = 9.01 \text{ mPa} \cdot \text{s}$. For each aqueous solution of glycerol, different concentrations of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ were prepared, and the respective viscosities were measured at $\theta = 295.15 \text{ K}$.

The variation of viscosity with the concentration of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is in Figure 3.8. The shear rate conditions in rheological tests were from 10 to 100 s^{-1} . The viscosity increases exponentially with the concentration of calcium chloride dehydrated. The range of concentrations studied is from 0 kg m^{-3} to 600 kg m^{-3} , which is lower than the solubility limit of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in water.

Figure 3.8 shows that the general expression that describes the viscosity curve for an aqueous solution of glycerol and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is given by

$$\mu^* = \mu_0 e^{fC} \quad (3.16)$$

where μ_0 is the viscosity of an aqueous solution of glycerol for $C = 0 \text{ kg m}^{-3}$ in $\text{mPa} \cdot \text{s}$, C is the concentration of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in kg m^{-3} and f is a factor that depends on the initial viscosity, μ_0 . Figure 3.9 displays the variation of f and μ_0 for three aqueous solutions, $\mu(x_{\text{glycerol}} = 0.21) = 1.7 \text{ mPa} \cdot \text{s}$, $\mu(x_{\text{glycerol}} = 0.45) = 4.3 \text{ mPa} \cdot \text{s}$ and $\mu(x_{\text{glycerol}} = 0.57) = 8.3 \text{ mPa} \cdot \text{s}$, where $x_{0,\text{glycerol}} = x_{\text{glycerol}}$, according to the experimental data. The term f increases linearly with the initial viscosity, and the respective trendline of the curve is a good approximation of f . From Figure 3.9, the factor f is given by,

$$f = 3.0 \times 10^{-5} \mu_0 + 3.5 \times 10^{-3} \quad (3.17)$$

Therefore, the expression that describes the viscosity curve for an aqueous solution of glycerol and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is given by the combination of Equations (3.16) and (3.17),

$$\mu^* = \mu_0 e^{(3.0 \times 10^{-5} \mu_0 + 3.5 \times 10^{-3})C} \quad (3.18)$$

As final note, Equation (3.18) is temperature-dependent because the term μ_0 is a function of temperature.

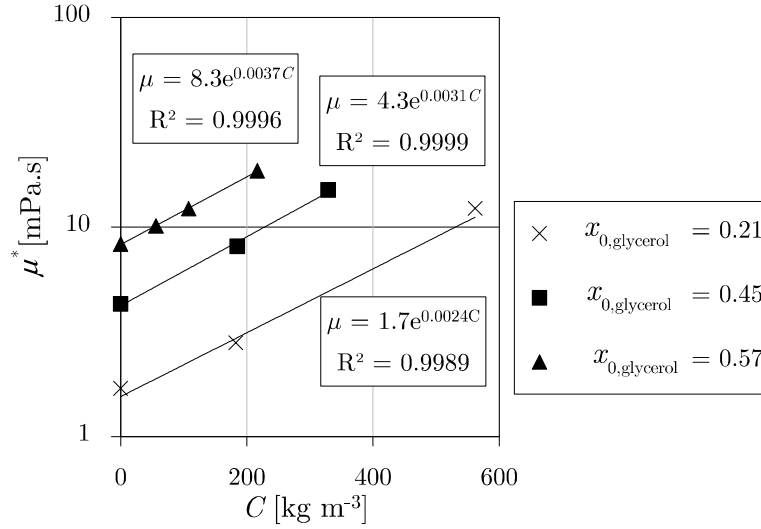


Figure 3.8 Influence of the concentration of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ on the viscosity of aqueous solutions of glycerol at $\theta = 295.15 \text{ K}$.

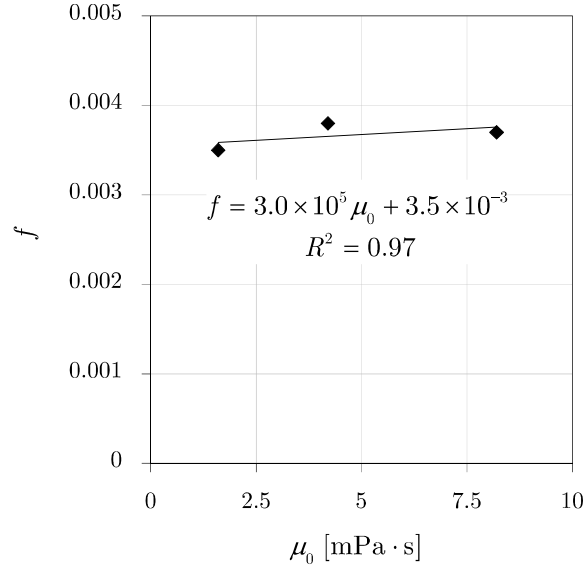


Figure 3.9 Constant f versus the initial viscosity of aqueous solutions of glycerol at $\theta = 295.15$ K .

3.2.3 Results Analysis

Empirical correlations that describe the physical properties of a glycerol-water system or aqueous solutions of glycerol and calcium chloride are proposed in this thesis. These expressions will be useful for the design of model fluids in flow phenomena studies. Glycerol is typically used to tune the viscosity of fluids. In mixing studies of two dissimilar liquids, a different mass fraction of glycerol and water can be added to achieve distinct physical properties. In most cases, flow dynamics is studied from flow visualisations through LIF imaging experiments. The performance of these techniques is compromised by the divergences between refractive indices of two different liquids. This problem is overcome by matching the refractive index using calcium chloride.

Figure 3.10 illustrates a flowchart of the process design to prepare model fluids with a specific viscosity ratio, which could be applied in LIF studies. This block diagram could be used as a method to achieve the desired physical properties. In optical imaging techniques, two liquids should have the same refractive indices according to the viscosity ratio previously specified. The empirical expressions demonstrated in the last

sections are referred in Figure 3.10, having each one a specific contribution to the design of model fluids.

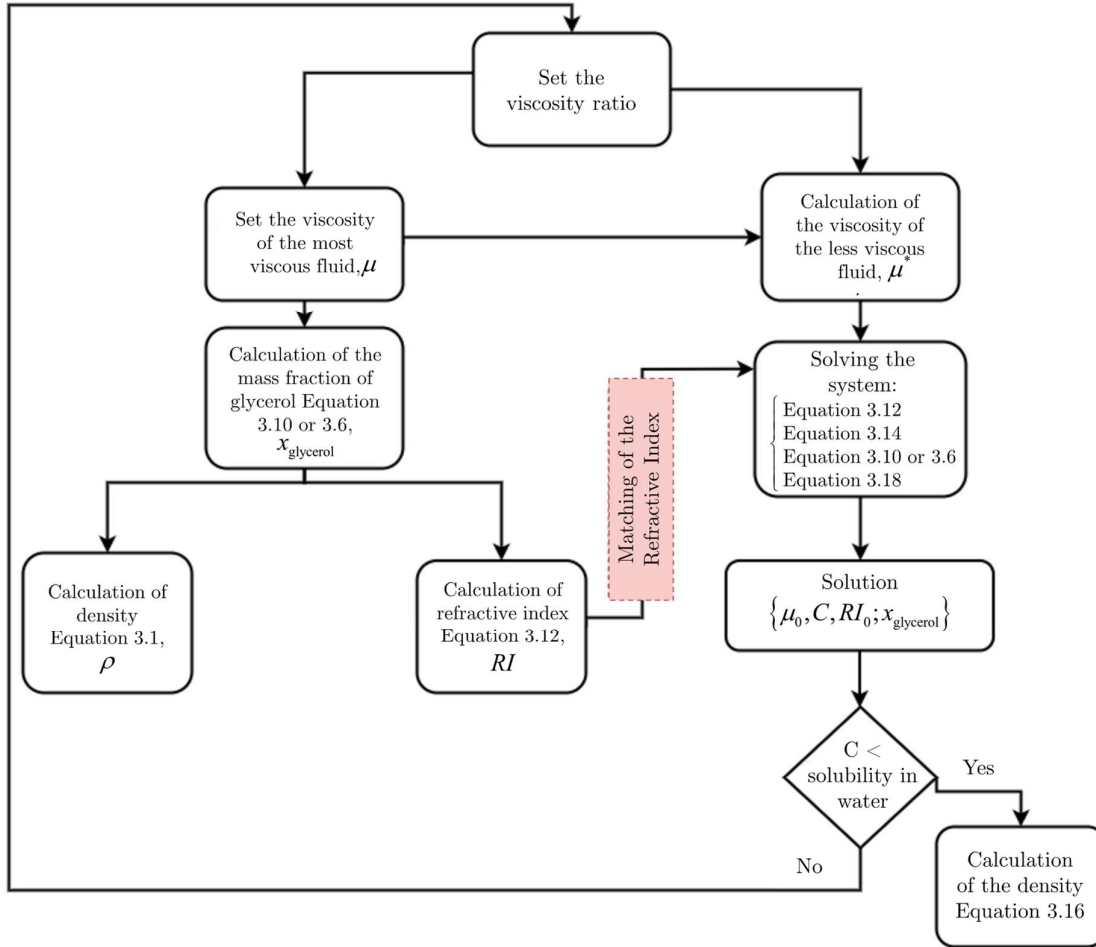


Figure 3.10 Flowchart for the design of fluids in flow phenomena studies.

3.3 Reactive Tracers for Mixing Studies

LIF experiments were introduced as a flow visualisation technique in the 70s by Dewey (1976); Owen (1976); Liu et al. (1977). This technique consists in the injection of a fluorescent tracer into the flow which will be excited by a laser. The dye absorbs the energy emitted by the laser and then re-emits a portion of that energy as fluorescence. Fluorescence can be optically measured and used to determine some properties of flow,

such as the concentration field (Liu et al., 2009). This technique has the advantage that requires low quantities of dye to visualise the flow patterns.

Tracer is typically an organic fluorescent dye soluble in water. Fluorescein and rhodamine (Rhodamine 6G and Rhodamine B) are the most common LIF dyes. Fluorescein (a.k.a. uranine or disodium acid) is particularly sensitive to pH (Walker, 1987). Rhodamine B (a.k.a. Rhodamine 610) and Rhodamine 6G (a.k.a. Rhodamine 590) are relatively insensitive to pH, whereas the temperature sensibility was reported by Sakakibara et al. (1993) and Kuzkova et al. (2014).

In this section, fluorescein and rhodamine B (RhB) are the two selected reactive tracers in LIF experiments. Fluorescein is used as a marker in an acid-base reaction because its fluorescence is sensitive to the pH of the reaction medium. Variations in fluorescence will identify the pH changes in the reaction course. Thus, differences in the fluorescence emission enable tracking the reactive fronts, which correspond to the regions controlled by the small scale mixing, mainly at the molecular scale (micromixing).

A second test-reaction using RhB is also tested in this work. A redox reaction system will promote the oxidation of RhB organic tracer, and the variation of emission wavelength. This test-reaction will enable the quantification of the micromixing extension in flow phenomena studies.

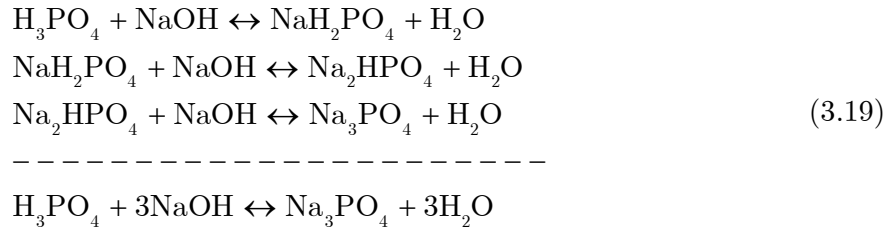
Tests on the performance of these two tracers will contribute to the implementation of reactive LIF technique on mixing studies in continuous reactors with industrial applications, such as in opposed jets mixers. The performance of this technique as a method for the visualisation of mixing dynamic was tested in T-Jet mixers, as described in Chapter 5.

3.3.1 Experimental Section

3.3.1.1 Test-Reactions

The first test-reaction studied in this work was an acid-base reaction. The hypothesis of a reaction between a strong acid and strong base was first considered. The first preliminary test was conducted for a reaction between hydrochloric acid, HCl, and sodium hydroxide, NaOH, according to Lehwald et al. (2012, 2010b, 2010a). The typical strong acid - strong base titration curve, which is given by the pH of analyte versus the volume of NaOH, shows that pH changes slowly at first and rapidly at the points close to the equivalence point (pH=7), and then it slows again. The extreme sensibility of pH affects the results reproducibility during the detection of the tracers fluorescence.

The second preliminary test was conducted for a reaction between phosphoric acid, which is a polyprotic acid, and NaOH. The titration curve of a weak acid and a strong base is smoother than the strong acid – strong base curve. This fact enables to easily detect the increase in pH and the respective change in fluorescence emission. The acid-base test-reaction system used is given by

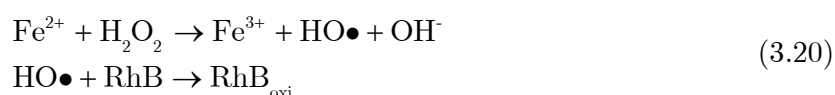


As most of acid-base reactions, the reaction scheme in Equation (3.19) is quasi-instantaneous, and thus the kinetic rate constant is $k \rightarrow \infty$. This is a good feature for flow visualisation because it ensures that the reaction takes place within the residence time.

Fluorescein is the tracer used in this test-reaction (Equation (3.19)). When fluorescein is excited by a laser, the emission intensity of fluorescein depends on the local pH.

When an acid stream, containing fluorescein, is mixed with a base stream, the local pH modification and respective changes on the emission intensity of mixture can be used for monitoring the neutralisation reaction kinetics.

The second test-reaction studied in this work uses Fenton's reaction to quench the fluorescence signal, so that the reactive mixing process can be recorded quantitatively (Liu et al., 2009). Fenton's reaction is a redox reaction which is induced by the coupling of iron, Fe^{2+} , and hydrogen peroxide, H_2O_2 ,



In this approach, a fluorescence tracer RhB is dissolved in one or both streams to be mixed, being oxidised with the hydroxyl radical ($\text{HO}\bullet$) (Equation (3.20)). The vanishing of RhB enables the assessment of the reaction kinetics based on the relationship between emission and fluorophore concentration.

3.3.2 Experimental Procedure – Study of the Test-Reactions

The concentrations of reagents in the reaction scheme were set from preliminary studies. In the acid-base reaction, the concentration of H_3PO_4 was defined according to the best balance between operational costs and the pH values for fluorescence detection. Based on that, the H_3PO_4 concentration of 0.100 M was prepared, and the concentration of NaOH was defined from the H_3PO_4 :NaOH titration curve, $[\text{NaOH}]=0.165$ M at pH=7.

For Fenton's reaction, different concentrations of H_2O_2 and Fe were tested according to the vanishing rate of RhB. For higher concentrations of Fe and H_2O_2 , the oxidation rate is higher, and simultaneously it is observed the formation of iron sludge as the results of the conversion of Fe^{2+} to Fe^{3+} . For lower concentrations, the reaction course is slower, and there is a decrease in the production of iron sludge. From that results, the concentrations used was 2 % H_2O_2 (wt./v) and 0.010 M Fe^{2+} .

The suitable operating conditions to quantify mixing from these two test-reactions were tested in an SX.18MV Reaction Analyzer Stopped-Flow (SF) apparatus from Applied Photophysics. An ozone-free xenon lamp (cut off at 250 nm) was used as a light source. The excitation wavelength was controlled by a monochromator, connected to the sample handling unit optical cell through a light guide. The sample handling unit consisted of two drive syringes whose plungers are moved by a pneumatic ram. Downstream of the driving syringes, the reagents are set in contact in the 10 μ L mixing chamber and flow down through a 20 μ L optical cell, which consisted of a silica square tube of 10 mm length. A photomultiplier tube (PMT) is installed in a normal position to the optical cell (optical pathlength is 2 mm) to detect the absorbance or the emission intensity, according to the chosen operating mode. PMT converts the light into an electrical signal to determine the absorbance or the fluorescence (emission intensity).

The absorption spectra of fluorescein and RhB were determined from PMT in a wavelength range from 250 to 700 nm. However, PMT used does not measure the wavelength emitted by the tracers, and so the emission peak is not estimated in this work. The excitation peak was predicted from the absorption spectrum, and then this value was compared to the one in the literature. The comparison of both values validates the method.

The set of experimental conditions was designed aiming to assess the conditions under which these reactions could be efficiently used as test-reactions for mixing studies. The experimental conditions are summarised in Table 3.4.

Solutions with different concentrations of RhB and fluorescein were prepared, and the absorption spectrum (from 250 to 700 nm) was determined in SF for each concentration (Essays F1 and RhB1 in Table 3.4). The excitation peak for each tracer was determined from the absorption spectrum.

These methods are later implemented and tested in opposed jet mixers using a pulsed Nd:YAG laser. Karasso and Mungal (1997) used a Nd:YAG laser to test the

relationship between the emission intensity and the concentration of fluorescein for an excitation wavelength of 532 nm. The limit of linearity concentration is 10 mg L⁻¹ for fluorescein. However, Karasso and Mungal (1997) reported that the fluorescence intensities at this concentration range are too low for imaging. Therefore, the response of fluorescein was tested for higher concentrations in F2 (Table 3.4).

Table 3.4 Experimental conditions of the experiments conducted in the SF for both test-reactions studied

Essay	Objective	C [mg.L ⁻¹]	pH	Time of measurements
F1	Absorption Spectrum	4; 20	7	Immediately after preparation
F2	Linearity dynamic range of fluorescence	4 - 30	7	Immediately after preparation
F3	pH effect on emission	20	2-12	Immediately after preparation
F4	Fluorophore stability	20	2	Immediately after preparation and 24h after preparation
RhB1	Absorption Spectrum	0.5		Immediately after preparation
RhB2	Fluorophore stability	0.5		Immediately after preparation and 24h after preparation

For RhB, the linearity range for an excitation wavelength of 532 nm has already been reported by Mortensen et al. (2004). Thus, the dependence between the concentration of RhB and its fluorescence was not determined experimentally.

The spectra readings were repeated after 24 hours to assess whether the ageing of the reagents caused any spectra changes would limit the usability of the method within that period. This period represents the preparation of the reagents from one workday to the following (Essays F4 and RhB2 – Table 3.4).

For the acid-base reaction, an additional parameter was studied, which is the relationship between pH and fluorescence. Fluorescein solutions were prepared at different pH, and the emission spectra were determined (Essay F3 – Table 3.4).

3.3.3 Results

3.3.3.1 Acid-base Test-Reaction

The absorption spectrum relates the excitation wavelength and the absorbance of the molecules of the fluorescent tracer. Figure 3.11 shows the absorption spectra of fluorescein for an excitation wavelength from 200 to 700 nm for two distinct concentrations 4 mg L^{-1} and 20 mg L^{-1} . The excitation peak of this dye is near 485 nm for both concentrations, which is in agreement with the value in the literature (Coppeta and Rogers, 1998).

The emission peak was not determined because the equipment used does not measure the emission wavelength. However, the literature points to an emission peak of 514 nm, and a red tail that continues to 640 nm (Coppeta and Rogers, 1998).

The successful implementation of this technique in flow phenomena studies requires the selection of suitable working conditions. The laser should have an emission peak near the excitation peak of fluorescein (485 nm).

Fluorescein is frequently combined with an Ar-ion laser for quantitative LIF imaging experiments in flow phenomena studies (Koochesfahani, 1984; Koochesfahani and Dimotakis, 1986). The efficient excitation of fluorescein molecules occurs at 488 nm line of an argon-ion laser. Calibration curves showed that there is a linear relationship

between the fluorescence and the dye concentration, which is the desired behaviour. This result is in agreement with the Beer-Lambert law, which relates the absorbance and the properties of the absorbing species, such as the concentration of species.

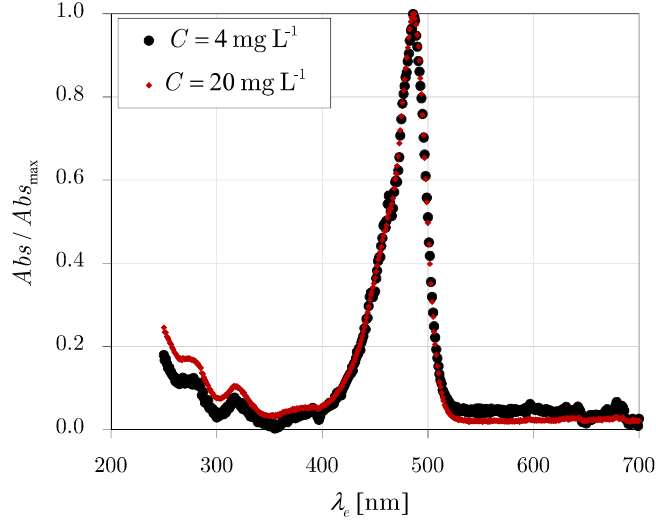


Figure 3.11 Absorption spectra of fluorescein for an excitation wavelength from 200 to 700 nm for 4 mg/L and 20 mg/L in H_3PO_4 0.100 M + NaOH 0.165 M medium, pH = 7.

Karasso and Mungal (1997) tested the combination of fluorescein with a pulsed Nd:YAG laser. Nd:YAG is a powerful laser, which enables to achieve a significant temporal resolution and is easily implemented in performing 2D images. Nd:YAG laser used by Karasso and Mungal (1997) operates at 532 nm. The absorption spectrum of fluorescein (Figure 3.11) shows that the absorption has a very deficient value for an excitation wavelength of 532 nm. Karasso and Mungal (1997) started to test the linearity between the fluorescence and the dye concentration for Nd:YAG laser. The results reported a linear region up to 10 mg L^{-1} . Then, higher concentrations of fluorescein were tested to achieve the same signal level obtained with the Ar-ion laser. Results showed that the signal calibrations violate the Beer-Lambert law and a non-linearity of fluorescence versus local excitation intensity is detected likewise. Therefore, the combination of fluorescein and Nd-YAG laser will bring problems in the image post-processing and the respective quantification from the relationship between the

concentration and fluorescence. However, this combination could naturally be used for any qualitative imaging or flow visualisation.

Since Nd:YAG laser is widely used in fluid mechanics literature, further studies on emission intensity for higher concentrations of fluorescein are addressed in this chapter. The fluorescence of fluorescein was measured for a concentration range between 4 and 30 mg L⁻¹. Figure 3.12 shows the electric potential difference versus the concentration of fluorescein at four excitation wavelengths: 350, 488, 500 and 532 nm. There is a proportional relationship between the electric potential difference measured in PMT and the emission intensity.

The emission intensity displays a linear trend ($R^2 > 0.97$) with fluorescein concentration up to at least 30 mg L⁻¹ for all tested excitation wavelengths, as shown in Figure 3.12. The large values of emission intensity are detected at $\lambda_e = 488$ nm, which corresponds to the peak in absorption spectra (Figure 3.11). For $\lambda_e = 532$ nm, the electric potential difference is low, and so weak fluorescence will be emitted in a range up to 30 mg L⁻¹. However, the performance of an Nd-YAG Laser ($\lambda_e = 532$ nm) in reactive LIF method using an acid-base reaction and fluorescein is tested in Chapter 5 using a T-Jet mixer. Note that this combination of fluorescein and Nd-YAG Laser must only be used for qualitative imaging.

For the capture of images using a Nd:YAG laser, a narrow-band filter is usually placed in front of the camera lens to only capture the images of the region emitting at fluorescence wavelengths. As the emission peak of fluorescein is approximately 510 nm, the narrow-band filter used in this method may filter the wavelengths in a range >500 nm empowering the capture of the emission wavelengths of fluorescein and filtering the light of laser.

The influence of pH on emission intensity of fluorescein is also determined adding NaOH solution to H₃PO₄. Figure 3.13 shows the electric potential difference detected

for fluorescein versus pH at four excitation wavelengths, 350, 488, 500 and 532 nm. As observed from the variations of electric potential difference, the fluorescein emits for pH above 3 and reaches its maximum emission at $\text{pH} \approx 8$. For pH between 5 and 8 the curve sharply increases, and so the maximum sensitivity of emission depends on local pH and the reaction course. These results corroborate the findings of Kola and Amataj (2006) and Lehwald et al. (2010). The curves displayed in Figure 3.13 overlaps the pH range where the $\text{H}_3\text{PO}_4\text{:NaOH}$ titration curve is smooth, enabling the detection of small differences of mixing degree at local scale.

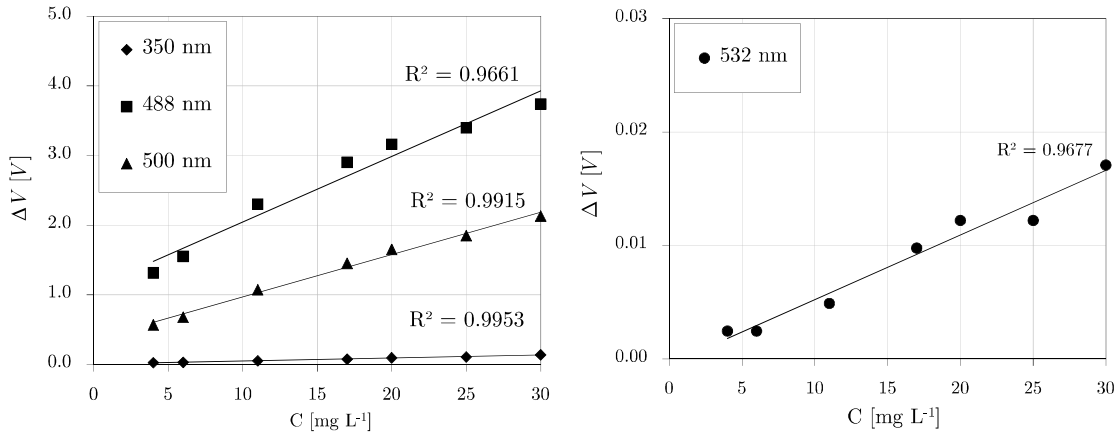


Figure 3.12 Electric potential difference for fluorescein for different concentrations at different excitation light wavelengths in H_3PO_4 0.100 M + NaOH 0.165 M medium, $\text{pH} = 7$.

These results showed that qualitative measurements of mixing employing this test-reaction could be conducted for concentrations of fluorescein up to $30 \text{ mg}\cdot\text{L}^{-1}$ with Nd:YAG laser, under excitation wavelengths in a range from 475 to 532 nm. Adopting 0.100 M H_3PO_4 , 0.165 M NaOH (for $\text{pH}=7$) and $C = 20 \text{ mg L}^{-1}$ as suitable conditions, the implementation costs of this method would be around 64 € m^{-3} . The titration inside the mixing chamber decreases the risk of accidents, which makes this method more promising.

Figure 3.14 shows the normalised electrical potential difference versus the excitation wavelength for fresh fluorescein and the repetition of this test one day later. Ageing of

reagents did not change the emission intensity and so, reagents ageing does not prevent the use of this test-reaction within a 24 h period, which is another encouraging feature of this method.

The implementation of this reaction scheme coupled to the analysis of fluorescence emission variations could be used as a method for the visualisation of reactive fronts in continuous reactors. This method would enable to quantify the goodness of mixing from the quantification of the interfacial area generation between the two liquids being mixed.

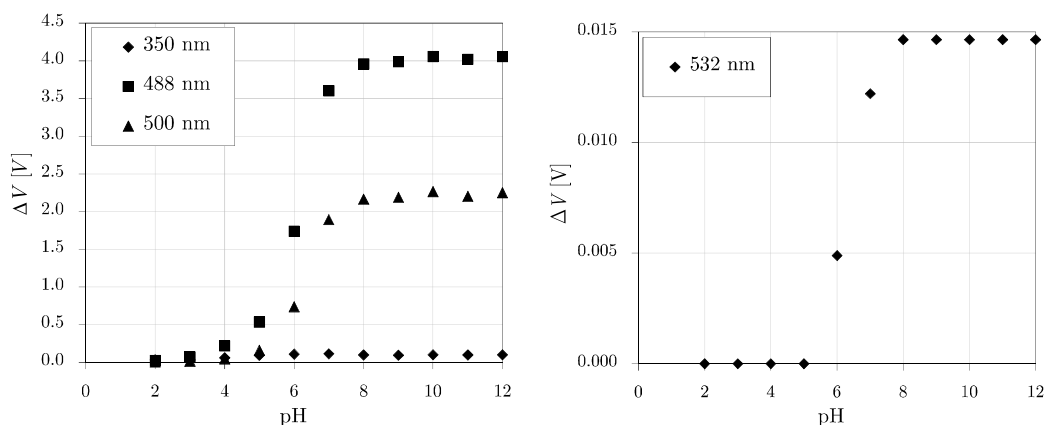


Figure 3.13 Influence of pH on electric potential difference for fluorescein, for 20 mg L^{-1} fluorescein solution at 25°C .

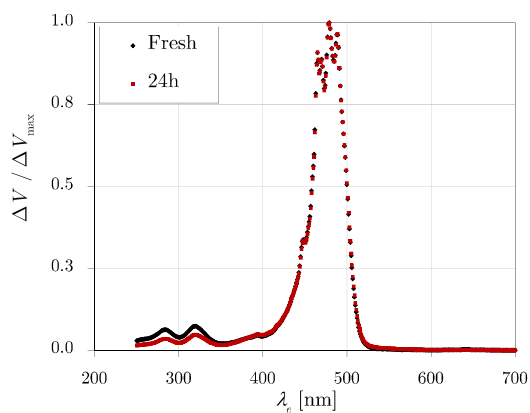


Figure 3.14 Electric potential difference associated to fluorescein versus the excitation wavelength for $20 \text{ mg} \cdot \text{L}^{-1}$ solution in H_3PO_4 0.100 M + NaOH 0.165 M medium, immediately after preparation and 24 h later.

3.3.3.2 Fenton Test-Reactions

RhB was used as a fluorescent tracer for Fenton's reaction. The absorption spectrum shows the relation between the excitation wavelength and the absorbance of RhB molecules. Figure 3.15 shows the absorption spectrum of RhB for an excitation wavelength from 200 to 700 nm and a concentration of 0.5 mg L^{-1} at 20°C . The excitation peak of this dye is approximately 550 nm for both concentrations, which is in agreement with the value in the literature (Coppeta and Rogers, 1998). According to Crimaldi (2008), the absorption spectrum is broad enough to be excited in a range from 514.5 to 532 nm.

Coppeta and Rogers (1998) detected the emission spectrum of RhB and the respective emission peak, which occurs at 580 nm.

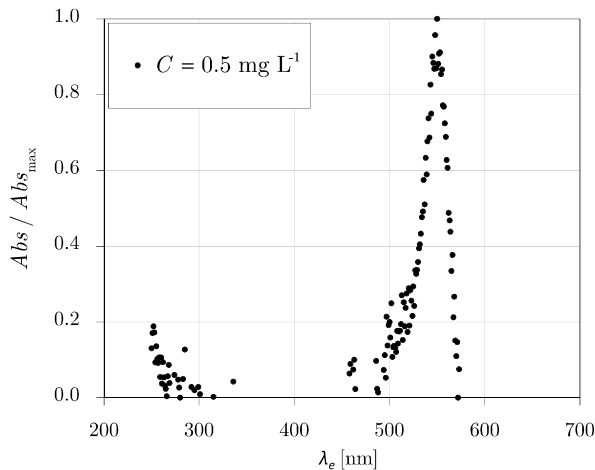


Figure 3.15 Absorption spectra of RhB for an excitation wavelength from 200 to 700 nm for 0.5 mg L^{-1} at 20°C .

The absorption spectrum shows that RhB molecules absorb strongly at 532 nm and thus Nd:YAG laser is suitable to this method. Mortensen et al. (2004) determined the calibration curve for RhB concentration and fluorescence intensity using Nd:YAG laser. Results identify a linear region for the local fluorescence and the local emission intensity up to 0.6 mg L^{-1} . As expected, the local fluorescence decreases with the concentration

of RhB, so the oxidation of RhB during the reaction course promotes the absence of fluorescence. The implementation of Fenton's reaction permits the flow visualisation and the identification of reaction regions, which are detected from the vanishing of the RhB fluorescence. The linearity between the RhB concentration and the fluorescence observed with Nd:YAG laser makes this method suitable for quantitative imaging.

When a pulsed Nd:YAG laser is combined with RhB and Fenton's reactions, a narrow-band filter should be placed in front of the camera lens to only capture the wavelength emitted by RhB. As mentioned in the literature, the emission peak of RhB is 580 nm, so the narrow-band filter used in this method may filter the wavelengths in a range > 540 nm empowering the capture of the emission wavelengths of RhB and filtering the light of the laser.

Considering 2 % H_2O_2 (wt./v) and 0.010 M Fe^{2+} concentrations (less than half the concentrations reported in the cited works), and using RhB in both streams, the ageing of reagents did not cause changes in the emission spectrum that would prevent the handling of this test-reaction within a 24 h period. The non-ageing for 24 h is an encouraging feature of this method.

In the implementation of this method for the assessment of micromixing, the temperature should be controlled since the fluorescence of RhB is very sensitive to temperature (Sakakibara et al., 1993).

The implementation costs of this method at such conditions would be as high as 405 € m^{-3} , which is a negative point of this method. This cost estimative takes into account the use of analytical grade chemicals which are associated to higher purchase costs than the reagents for industrial use. Therefore, the feasibility of this method at industrial scales is related to lowering the implementation costs in relation to the experiments at lab scale. These reagents at industrial quantities and grades, particularly H_2O_2 , will enable to perform this method at less than a tenth of the cost.

Other two disadvantages are associated to the implementation of Fenton's reaction as a reactive LIF method:

- Conversion of Fe^{2+} to Fe^{3+} during the Fenton's reaction course. It results in the production of an iron sludge that may settle and could cause negative impacts on the mixing equipment used.
- Formation of oxygen leads to bubbles in the flow, making it difficult to visualise the reactive fronts. The generation of oxygen is described by



3.4 Conclusions

In this chapter, non-reactive model fluids and reactive tracers are designed to be applied in flow phenomena visualisations.

The non-reactive fluids were aqueous solutions of glycerol with calcium chloride. An increase in the concentration of calcium chloride dehydrated is related to an increase in refractive index, density and viscosity. Refractive index grows linearly with the concentration of calcium chloride dehydrated, and no significant differences are reported for an increase of 10 K in temperature. On the other hand, viscosity increases exponentially with the concentration of calcium chloride dehydrated. Expressions based on experimental data are proposed for the calculation of the physical properties of aqueous solutions of glycerol and calcium chloride dehydrated. Final analysis from results was lastly presented, and a flowchart was drawn to describe the design of model fluids in visualisation studies of non-reactive flows.

In the second section of this chapter, the performance of reactive tracers is reported to be applied for flow imaging. Two test reactions were considered in this chapter: acid-base reaction with a pH tracer, fluorescein; and Fenton's reaction with RhB as a tracer that is oxidised in the reaction region. This method enables the visualisation of mixing since the proper conditions for the chemical system are set.

Ar-ion laser is the best suitable laser for quantitative measurements of mixing with fluorescein. But, Nd:YAG laser could also be used as an alternative to Ar-ion laser, whereas the tracer concentration and/or the laser intensity must be relatively increased. These changes make the fluorescence response to the concentration of fluorescein not valid according to Beer-Lambert Law. Therefore, the combination of fluorescein and Nd:YAG laser could not be used for the quantification of imaging; however, it could be used for flow visualisation.

Regarding Fenton's reaction, suitable conditions to employ this test-reaction would be RhB concentration up to $0.6 \text{ mg}\cdot\text{L}^{-1}$, 2 % H_2O_2 (wt./v) and 0.010 M aqueous solution of Fe^{2+} (as FeSO_4 , for economic benefit). A pulsed Nd:YAG laser is suitable for this method according to RhB absorption spectrum.

The aforementioned methodologies are tested in the following chapters for fundamental mixing studies in continuous reactors.

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4 Mixing Mechanisms in Confined Impinging Jets Mixers

4.1 Introduction and State of the Art

Confined Impinging Jets (CIJ) mixers are highly efficient mixing devices, which consists of a semi-confined cylindrical mixing chamber having two directly opposed injectors near the closed top of the chamber and an open outlet (Lee et al., 1980; Tucker and Suh, 1980; Wood et al., 1991; Johnson et al., 1996; Johnson, 2000a,b; Johnson and Wood, 2000; Sultan et al., 2013).

One of the main industrial application for this technology is the PU processing in RIM machines that was patented by Krauss-Maffei in 1970 (Keuerleber and Pahl, 1970). The most recent industrial developments in this technology were reviewed by Volpato and Fiorentini (2012) from the Cannon Group. The first studies on mixing in RIM processes took place in late 70s early 80s at MIT (Malguarnera and Suh, 1977; Tucker and Suh, 1980) and University of Minnesota (Ritcher and Macosko, 1978; Lee et al., 1980).

In a typical RIM process, two organic monomer viscous streams are initially mixed in a CIJ mixing chamber, and then the mixture of monomers is rapidly discharged into a mould where most of the polymerisation occurs. The monomers are firstly heated to ensure the low viscosity, passing through a recirculation circuit to ensure the temperature uniformity. The injection in the mixing chamber occurs through high pressure injection pistons, which are filled with the reacting fluids at the stoichiometric ratio. Modern RIM machines have been set up with rotary piston pumps, or gear pumps. The main advantage of these metering devices over injection pistons is its continuous operation mode. Rotary piston pumps can operate up to 200 bar, which enables to replace the metering pistons technology for a wide range of applications.

In the CIJ mixing chamber, the two heated monomers are mixed to achieve scales usually smaller than $50\text{ }\mu\text{m}$ (Ranz, 1986). After the discharging into the mould, the polymeric mixture turns into solid material, and then it is removed from the mould. RIM machines are typically used in polyurethanes processing. However, other polymers can also be produced, such as polyureas, polyamides, polyesters and dicyclopentadiene. In the particular case of the production of polyurethanes in RIM machines (PU-RIM processing), the polymer is formed by the reaction of polyol and isocyanate.

In systems with low diffusion and fast reaction as in PU-RIM processing, the mixing process plays an important role on the effective performance of this device because it controls the chemical reaction and thus the mechanical properties of the final polymer (Tucker and Suh, 1980). CIJ mixers in RIM machines have become a popular mixing device for PU processing because the alternatives, as high-speed rotative mixers or other static mixers, do not enable such fast mixing times ($< 10\text{ ms}$) with auto-cleaning incorporated add-ons, such as cleaning pistons. CIJ mixers for mixing of viscous fluids operate in a range of viscosity values between 10 to $1000\text{ mPa}\cdot\text{s}$ at high velocities, $v \sim 5\text{ m s}^{-1}$, of the monomers jet streams.

CIJ mixers have also been used in other applications. An optimised geometry is required according to their applications, and different configurations of the cavity above the injector axis and the outlet have been proposed for an effective mixing (Siddiqui et al., 2009; Icardi et al., 2011a). CIJ mixers have been used for precipitation of nanoparticles (Lince et al., 2009), generally at turbulent flow regimes, and so the modelling of chemical reaction generally resorts to turbulence models (Feng et al., 2005; Liu and Fox, 2006; Gavi et al., 2007a; Gavi et al., 2007b; Liu et al., 2009; Icardi et al., 2011a; Icardi et al., 2011b).

The wide range applications of CIJ mixers and the role of mixing in these devices motivated several research teams to make comprehensive research works on mixing dynamics (Unger and Muzzio, 1999; Johnson and Wood, 2000; Johnson and Prud'homme, 2003; Lince et al., 2009; Li et al., 2010).

4.1.1 Effective Mixing in CIJ mixers

A typical CIJ mixer in RIM process has a mixing chamber diameter of $3 \leq D \leq 10$ mm, which is 3 or 4 times the inlet nozzles, whose diameter is $1 \leq d \leq 3$ mm (Lee et al., 1980). A sketch of a typical CIJ mixer is displayed in Figure 4.1. The main characteristic of this mixer is the directly opposed injectors, from where two high speed-jets issue.

Studies point out that the injection of two streams at high speed, from 1 m s^{-1} to 100 m s^{-1} , is the necessary condition for the formation of dynamic flow structures in the chamber that promote the engulfment of fluids and the effective mixing (Malguarnera and Suh, 1977; Ritcher and Macosko, 1978; Lee et al., 1980; Tucker and Suh, 1980).

Malguarnera and Suh (1977) defined for the first time, the dimensionless parameters with a significant impact on mixing. The Reynolds number is an important operational parameter, and it is defined at the injectors as

$$\text{Re} = \frac{\rho v_{\text{inj}} d}{\mu} \quad (4.1)$$

where v_{inj} is the average velocity at injectors calculated by the flow rate divided by the injector area, $v_{\text{inj}} = Q_{\text{inj}} / A_{\text{inj}}$, d is the diameter of injectors, ρ and μ are the density and viscosity of fluid respectively. Industrial practice for RIM processes stipulates that the operational Reynolds number for good mixing must be above 100. Nevertheless, this topic has been studied by several authors since 1980.

Mixing in CIJ mixing chambers have been studied from flow visualisations using: tracer and PLIF images (Lee et al., 1980; Tucker and Suh, 1980; Sandell et al., 1983; Johnson et al., 1996; Johnson and Wood, 2000; Fonte et al., 2015); laser Doppler anemometry measurements of the average velocity distribution and oscillations of the jets impingement point (Johnson and Wood, 2000; Teixeira et al., 2005; Santos et al., 2009); particle image velocimetry (PIV) (Santos et al., 2008; Icardi et al., 2011a; Fonte et al., 2016) and particle tracking velocimetry (Unger et al., 1998; Zhao and Brodkey, 1998a; Zhao and Brodkey, 1998b). Numerical studies using CFD tools have also contributed for a further understanding of the mixing dynamics in CIJ mixers (Nakamura and Brodkey, 2000; Liu and Fox, 2006; Marchisio et al., 2006; Gavi et al., 2007a; Gavi et al., 2007b; Gavi et al., 2008; Marchisio et al., 2008; Lince et al., 2009; Santos et al., 2009; Gavi et al., 2010; Icardi et al., 2011b).

These studies report two distinct flow regimes, the segregated and the chaotic flow regime, at symmetric flow conditions, i.e. when both injected fluids have the same flow rate, physical properties, and the opposed injectors have equal diameters (Lee et al., 1980; Tucker and Suh, 1980; Johnson et al., 1996; Johnson, 2000b; Santos et al., 2008; Santos et al., 2009).

Figure 4.1 shows PLIF images of mixing of a jet dyed with rhodamine, represented by the white liquid, and a clear jet that corresponds to the dark liquid. The experimental

work regarding this visualisation of mixing in CIJ mixers was reported in Fonte et al. (2015) as well as more detailed results from PLIF experiments. Other authors obtained similar results with PLIF images in CIJ mixers (Li et al., 2015).

Figure 4.1a shows the segregated flow regime at $Re = 103$, which is characterised by the fact that each side of the mixing chamber contains mainly one of the fluids. So, the fluid streams flow from the injector to the outlet in each side of the mixing chamber, being delimited by the segregation plane. This plane coincides with the mixing chamber axis and is normal to the inlet axis. The typical scales at this condition correspond to half of the mixing chamber diameter, which is $3 \leq D \leq 10$ mm, far too larger than the final scale for polymerisation reaction in RIM machines, $1 \mu\text{m}$ (Ranz, 1986). This means that the segregated flow regime is not the condition for effective mixing in RIM machines.

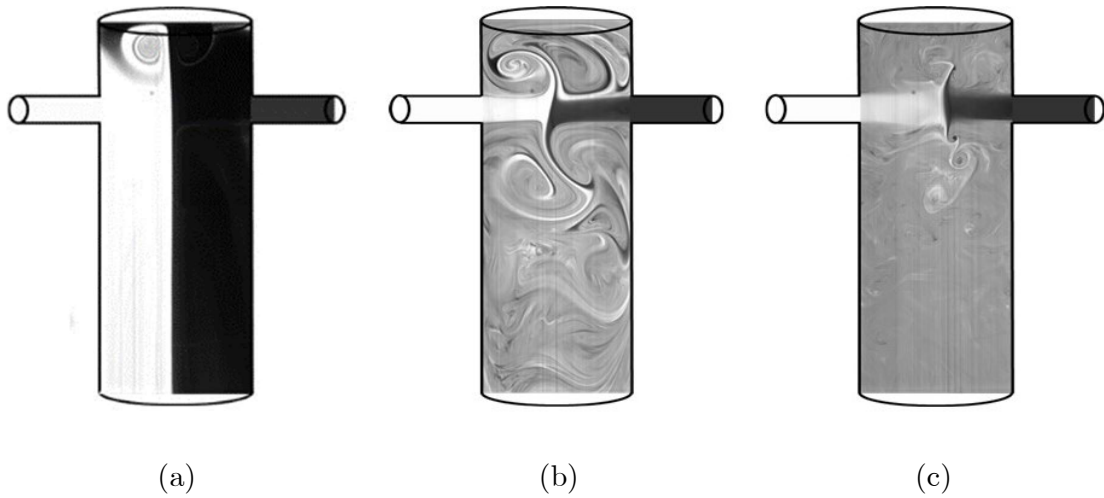


Figure 4.1 Sketch of CIJ mixing chamber framing concentration fields from PLIF images for (a) $Re=103$; (b) $Re=111$ and (c) $Re=505$.

Figure 4.1b and Figure 4.1c show the PLIF images for chaotic flow regimes, at $Re = 111$ and $Re = 505$, respectively. At $Re = 111$, the clear and dark coloured jets are impinged at the mixing chamber axis. Both jets are spread radially, forming vortices up and down the jets contact point. The engulfment of streams by vortices is caused by the

orientation of each liquid in the perpendicular direction to the main flow (Fonte et al., 2011). In Figure 4.1b, only one plane is visualised, but actually, the fluids are radially spread through a 3D squeezed fluid structure, resembling a pancake as described by Wood et al. (1991). The pancake formation enables the increase of the contact area from $\pi d^2 / 4$ to $\pi D^2 / 4$ promoting then the formation of vortices around the jets (Unger et al., 1998; Zhao and Brodkey, 1998a; Nakamura and Brodkey, 2000; Santos et al., 2009). The vortices formed downstream the jets, with half of the mixing chamber diameter, extend in a vortex street over the mixing chamber height, which is commonly known by the mixing zone. Downstream this zone, fluids are further stretched by a fully developed laminar flow, having a parabolic profile, as clearly visualised from Figure 4.1b.

At larger Reynolds numbers, see Figure 4.1c, vortices formed near the jets impingement region homogenise both fluid streams and thus PLIF images become very homogeneous around the inlet jets.

The dynamic flow visualisations for $103 < \text{Re} < 111$ reported in Fonte et al. (2015) showed that the onset of the impingement point oscillation does not necessarily correspond to the transition from segregated to chaotic flow regime. Instabilities at the interface are observed at conditions where the chaotic flow is not yet well-established. However, mixing at chaotic flow regime is fully controlled by the vortices formation and the impingement point oscillations. The relationship between the vortices formation and the oscillations of jets at the impingement point was defined by Erkoç et al. (2007) and Santos et al. (2009).

The onset of the chaotic flow regimes is a necessary condition for the efficient operation of CIJ mixers, as shown in Figure 4.1. Reynolds number at injectors is a key parameter for this, as also described by Malguarnera and Suh (1977), Lee et al. (1980) and Tucker and Suh (1980). There is a critical Reynolds number that marks the transition to the transient flow regime. Flow visualisations in cylindrical CIJ mixers point to a critical

Reynolds number between 110 and 150 (Tucker and Suh, 1980; Wood et al., 1991; Santos et al., 2009; Fonte et al., 2015).

Other operational conditions also play a crucial role in CIJ mixing dynamics. The main requirement for mixing is the balance of opposed jets, which means that the contact between fluids, also called jets impingement point, has to occur at the centre of the mixing chamber (Johnson, 2000a,b; Erkoç et al., 2007; Fonte et al., 2015,2016; Gomes et al., 2016). The quantification of mixing of similar fluids presented by Fonte et al. (2015) clearly shows that the effective mixing occurs for a flow rate ratio $r_s = 1$, and mixing is compromised by deviations of $\pm 10\%$ in the flow rate ratio.

The inertia of jets also has an impact on mixing dynamics. This was analysed in terms of Froude number, which is a dimensionless number that relates the flow inertia and the body forces (Santos et al., 2002; Santos et al., 2010). These results showed that even for the same ratio of inertial and viscous forces, i.e. $Re = \text{constant}$, there is a lower limit for the inertial forces defined by Froude number. The lowest Froude number that compromises the effective mixing corresponds to fluids in water viscosity range, at least for the RIM machines dimensions.

In conclusion, the three key parameters for the onset of the chaotic flow regime in CIJ mixing chambers are the critical Reynolds number, $Re > 110$ (see Figure 4.1), the balancing of jets and Froude number must be greater than for water conditions.

4.1.2 Kinematics of Mixing in CIJ Mixers

In the self-sustainable chaotic flow regime, mixing is promoted by stretching and folding of the two liquids streams, as described in the classical framework of mixing in chaotic flows (Ottino et al., 1979). In these mixing devices, due to the short residence time inside the mixing chamber (10 to 100 ms for RIM machines), the molecular diffusion does not occur significantly, prevailing the advection mechanisms. For these conditions, the mixing process can be described by the location of the interface, which

is stretched by the mixing structures. These mixing mechanisms promote the formation of a one-dimensional lamellar structure, where all lamellae are oriented in the same direction (Lee et al., 1980; Ottino, 1982; Ottino, 1989; Wood et al., 1991; Muzzio et al., 2000). Muzzio et al. (2000) reported that the local lamellar structure is oriented according to the direction of the maximum stretching rate, naming this property as asymptotic directionality.

Figure 4.2 shows a PLIF image of the chaotic flow regime in CIJ mixers, where it is observed that the thickness of the two initial segregated fluid streams, S , is reduced by advection mechanisms.

In RIM machines and in most fast-reactive systems, the thinning of fluid lamellae must proceed down to smaller scales than those in which diffusion can complete the mixing at molecular level, in a shorter period than the reaction time (Lee et al., 1980). In a typical RIM machine, the final striation thickness has to be of the order of $10\text{ }\mu\text{m}$ to guarantee that the polymerisation process is chemically controlled.

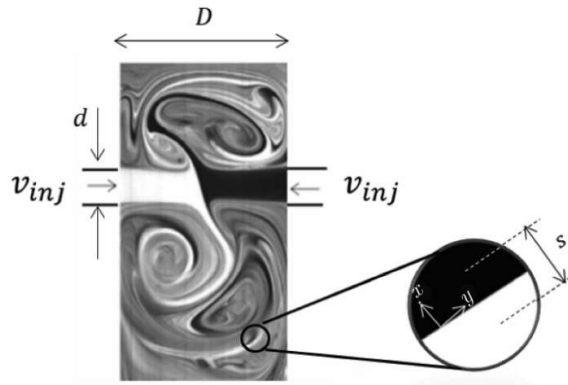


Figure 4.2 PLIF image of impingement mixing of a binary mixture.

Lee et al. (1980), Tucker and Suh (1980) and Baldyga and Bourne (1983) proposed different models to estimate the average striation thickness, S , in the lamellar structure formed in a RIM machine CIJ mixers. The model proposed by Lee et al. (1980) is based on the fact that thinning of lamellae is two-dimensional, and this is caused by

incompressible stretching of fluid elements. This model defines a coordinate system, x and y , at the interface of the fluid streams being mixed. This Lagrangian approach to the coordinates referential is shown in Figure 4.2. From these considerations, they obtained

$$\frac{s}{d} = \left(1 + \frac{\text{Re}^2 \nu \tau_{\text{MZ}}}{2d^2} \right)^{-1/2} \quad (4.2)$$

where Re is the Reynolds number given by Equation (4.1), ν is the kinematic viscosity and τ_{MZ} is the average residence time in the mixing zone. The average residence time in the mixing zone for impingement of two cylindrical streams in a cylindrical chamber was defined by Lee et al. (1980) as

$$\tau_{\text{MZ}} = \frac{nD^3}{(1 + r_s^{-1})\nu d \text{Re}} \quad (4.3)$$

where r_s is the volumetric flow rate ratio between the two jets, and nD is the distance from the top of the mixing chamber until the point where the dynamic mixing occurs, observed to be $nD \sim 2D$ to $3D$ (Kolodziej et al., 1986). Equation (4.2) describes the decreasing of the average striation thickness of the fluid laminae, s , since the instant that they are formed in the jets impingement point until they flow out from the mixing zone after the time τ_{MZ} . The striation thinning described by this model depends on the Reynolds number at injectors, the injector diameter and the physical properties of the fluid streams. This model is only valid for chaotic flow regimes where the mechanism for mixing is the stretching of the interface between fluids with corresponding interfacial area generation and striation thickness thinning.

On the other hand, Tucker and Suh (1980) assumed that impingement mixing is fully turbulent. They assumed a Kolmogorov isotropic turbulence description where the striation thickness is determined by Kolmogorov scale, $\lambda_k = (\nu^3 / \varepsilon)^{1/4}$. From dimensional considerations, Tucker and Suh (1980) obtained

$$s \propto \frac{d}{\text{Re}^{3/4}} \quad (4.4)$$

Baldyga and Bourne (1983) predicted a reduction of scales in the light of statistical theory of turbulent diffusion combined with an exponential residence time distribution of the fluid inside the mixing zone. They considered isotropic and homogeneous turbulent flow at the top of the mixing chamber, and defined the striation thickness as,

$$\frac{s}{s_0} = 0.76E \left(1 + 2.30 \frac{n^{4/3} \Gamma_{\text{MZ}}^2 \left(1 + r_s^{-3} \right)^{2/3} \left(\frac{D}{d} \right)^4}{E^{4/3} (1 + r_s^{-1})^2} \right)^{-1/4} \quad (4.5)$$

here s_0 is the initial striation thickness, E is the proportional factor in the equation $s_0 = Ed$, n is the number of mixing chamber diameters over which turbulent mixing occurs, Γ_{MZ} is the dimensionless time given by $\Gamma_{\text{MZ}} = t / \tau_{\text{MZ}}$. The initial striation thickness, s_0 , is taken as the injectors diameter, $s_0 \sim d$, and thus E is of order 1.

4.2 CIJ Mixer Geometry

CIJ mixers used in this work have typical dimensions of those used in industrial RIM machines. Figure 4.3 shows a sketch of a CIJ mixer, which consists of a semi-confined cylinder with height $H = 50$ mm and diameter $D = 10$ mm. The two opposed injectors, which are two pipes intersecting the CIJ mixing chamber perpendicularly, are placed at $h = 5$ mm from the mixing chamber closed top. Two geometries with different injectors diameters were tested in this chapter. Table 4.1 summarises the geometries used, where d_1 is the diameter of jet 1 and d_2 is the diameter of jet 2. The opposed jets of Chamber 1 have the same diameter and Chamber 2 is asymmetric, thus $d_1 \neq d_2$.

The geometries listed in Table 4.1 were used in the experimental setup and in CFD simulations.

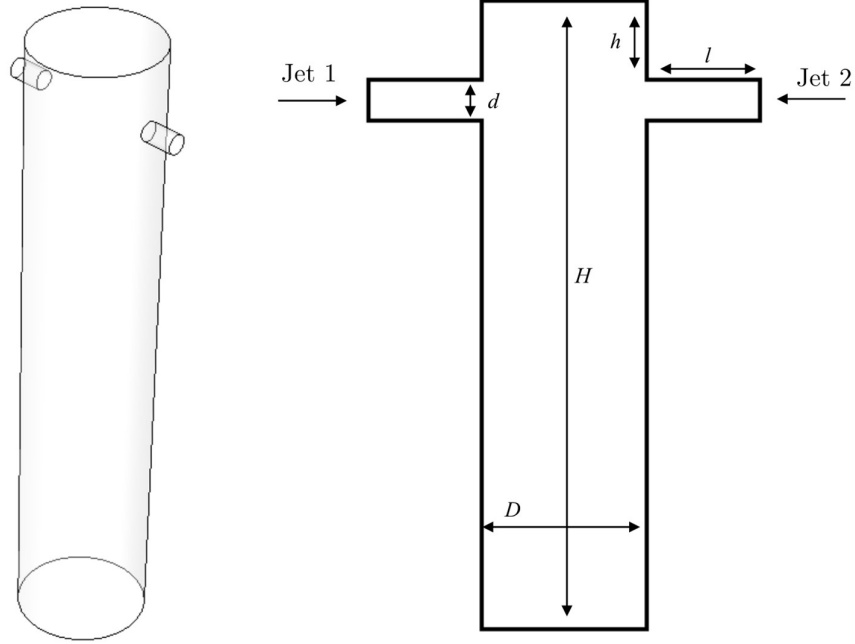


Figure 4.3 Geometry of experimental and CFD models of CIJ mixers.

Table 4.1 Geometrical parameters of the CIJ mixers.

Chamber No.	$D(\text{mm})$	$d_1(\text{mm})$	$d_2(\text{mm})$
1	10	1.5	1.5
2	10	1.5	1.9

4.3 Part I: Fully Resolved Modelling and Simulation of Micromixing

The flow of reactant fluid streams in the CIJ mixing chamber is described by the decrease of the striation thickness and also by a set of complex interactions between molecular diffusion, chemical reaction and fluid mechanics. Ottino et al. (1979) were the first to describe a mixing model which balances the description of reaction, diffusion and deformation from a Lagrangian point of view. Kusch et al. (1989) applied this

mixing model to CIJ mixers using the striation thickness evolution proposed by Lee et al. (1980) for laminar flow conditions. The numerical results from the mixing model were validated from experimental data of competitive-consecutive azo-coupling reaction where the working fluids had the same physical properties of water.

The actual conditions in RIM machines differ from the experimental work of Kusch et al. (1989) where water was used as working fluid. This motivated the experimental work of Nunes et al. (2012), where the micromixing test reaction of Bourne et al. (1990) was implemented according to the best knowledge on the conditions that promote the chaotic mixing in CIJ mixers. These conditions for chaotic flow regimes are viscous fluids that ensure adequate dynamics of the flow at low Re and the balance of jets. The working fluids used in Nunes et al. (2012) are 20 times more viscous than water. This aimed at narrowing the gap from experiments to industrial RIM machines, where for typical Reynolds numbers (from 100 to 500), jets velocities and corresponding Froude numbers are larger and passage times shorter than the ones occurring in water based experimental setups.

Micromixing promotes the homogenisation of species at molecular scales, and so the chemical reactions may proceed, guaranteeing the production of the desired products. A theoretical methodology is presented to describe the micromixing in CIJ mixers using a lamellar model that considers the dynamics of striation thinning and diffusion at the interface of the fluids. A lamellar micromixing (LM) model based on mixing evolution functions was applied to simulate chemical reactions, similar to that one proposed by Ottino et al. (1979). This model was solved using striation thickness data from the models proposed by Lee et al. (1980) and Baldyga and Bourne (1983) and then compared with the experimental data from Nunes et al. (2012). The experimental work of Nunes et al. (2012) used micromixing test reactions in a viscosity range close to polymer processing applications, and so this data is closer to the actual applications than data obtained with water as working fluid (Kusch et al., 1989). The main issue with the application of the modelling developed in Ottino et al. (1979) is getting the

right description of the stretching field. The model from Lee et al. (1980) assumes the thinning of lamellae is two-dimensional and this is caused by incompressible stretching of fluid elements, i.e. uses the description of the kinematics of mixing in chaotic flows. The model of Baldyga and Bourne (1983) is based on the statistical description of scales in turbulent flows.

4.3.1 Lamellar Micromixing Model

A complete mechanistic micromixing model describes molecular diffusion, chemical reaction and fluid mechanics in a mixing device. The model presented in this thesis considers that reaction and diffusion do not affect the fluid properties inside the CIJ mixing chamber. This is applied to the micromixing test reaction of Bourne et al. (1990) because the chemical reaction does not significantly change the properties of fluids. This consideration is also valid in RIM machines. In RIM process, there are viscosity changes with reaction, heat release and adiabatic temperature rise, which is often in the 100 °C range. However, the changes of fluid properties take place only when the mixture is discharged into the mould. This occurs because the residence time in the RIM CIJ mixers ($\tau_{\text{CIJ}} \sim 10 \text{ ms}$) is not sufficient for the reaction to take place.

The lamellar micromixing model was introduced in late 1970s early 1980s and describes the evolution of chemical species concentration in space and time between two liquids being mixed into a lamellar structure (Ottino et al., 1979; Ranz, 1979; Ottino, 1980). This model takes into account the stretching of the interface between two fluids and the respective increase of the interfacial area. As given from Fick's law, the ultimate mass transfer mechanism is solely diffusion, but now in a warped space. The warping is determined by the dynamics of mixing in chaotic flows and portrayed by the stretching of the fluids interface which is proportional to the thinning of the mixing lamellar structures. For this micromixing model, the coordinate system, x and y is set up at the interface of two fluids. Figure 4.2 shows the proper colocation of the

coordinate system at the interface between the two fluids, A and B. From these assumptions, the conservation equation of species i is

$$\frac{\partial C_i}{\partial t} + (\mathbf{D}:\mathbf{m})x \frac{\partial C_i}{\partial x} = D_i \frac{\partial^2 C_i}{\partial x^2} + R_i \quad (4.6)$$

where $\mathbf{D}$ is the stretching tensor and $\mathbf{n}$ is the normal direction of the interface, which corresponds to the direction of the mass transfer (Ottino, 1982). The stretching function is given by $\alpha(\mathbf{X}, t) = -(\mathbf{D}:\mathbf{m})$ which corresponds to the rate of expansion or contraction around the particle $\mathbf{X}$ (Ottino et al., 1979).

The convective term of Equation (4.6) can be eliminated by a change of variables. The position x is transformed as $\xi^* = x / s(t)$ and time t as $\Gamma = t / t_D$, where $s(t)$ is the striation thickness evolution and t_D is the characteristic diffusion time. From this change of variables, the species conservation equation takes the form

$$\frac{\partial C_i}{\partial \Gamma} = \left(\frac{s_0}{s(\Gamma)} \right)^2 \frac{\partial^2 C_i}{\partial \xi^{*2}} + t_D R_i \quad (4.7)$$

4.3.2 Application to Experimental Data

LM model was applied to the same operational conditions of the experimental work in Nunes et al. (2012), where the micromixing process in a pilot RIM machine was studied using a test reaction system. The experimental setup is described in Nunes et al. (2012). The setup consists of a mixing chamber and two injectors drilled in a single plexiglass block. A geometry similar to Chamber 1 was used for these experiments. The mixing chamber has a diameter $D = 10$ mm, a height $H = 50$ mm and a headspace $h = 5$ mm. Two opposed cylindrical injectors with a diameter $d_1 = d_2 = 1.50$ mm are placed at 5 mm from the mixing chamber closed top. Each injector is fed through a tank with a pump. At the outlet of the mixing chamber, the fluid is discharged into a transparent mould.

The test reaction system carried out by Nunes et al. (2012) is the simultaneous coupling of 1-naphtol, A_1 , and 2-naphtol, A_2 , with diazotised acid, B, (Bourne et al., 1990)



The experiments were performed injecting the limiting reactant, diazotised acid, B, from one injector while the other injector delivered 1-naphtol, A_1 , and 2-naphtol, A_2 . The working conditions are symmetric, i.e. same viscosity, density and flow rate in both injectors. The density of reactants corresponds to the density of water, $\rho = 1000 \text{ kg m}^{-3}$, at $\theta = 293.15 \text{ K}$.

The experiments were carried out using aqueous solutions with $\mu = 20 \text{ mPa} \cdot \text{s}$ at $20 \text{ }^\circ\text{C}$. Rheolate 255 was used as a thickener to achieve the desired viscosity. Baldyga and Bourne (1999), Bourne et al. (1985) and Gholap et al. (1994) concluded that the amount of Rheolate 255 added to reactant solutions does not affect the kinetics parameters: $k_1 = 14 \times 10^3 \text{ m}^3 \text{mol}^{-1} \text{s}^{-1}$, $k_2 = 2.56 \text{ m}^3 \text{mol}^{-1} \text{s}^{-1}$ and $k_3 = 95 \text{ m}^3 \text{mol}^{-1} \text{s}^{-1}$ at $\theta = 293.15 \text{ K}$ (Nunes et al., 2012). These kinetic constants mean that the first reaction in Equation (4.8) is much faster than the second one and even than the third one. This results on the maximum yield of R when the injected reactants, A_1 and B, are completely mixed in a shorter time than the second reactional step.

Since the reactant B is the limiting reactant, Nunes et al. (2012) measured the product distribution from the fraction of reactant B that is converted to S and Q, i.e. from the reaction selectivities. The selectivities X_Q and X_S depend on the reactant combination and they are defined as,

$$X_s = \frac{2C_s}{C_R + C_Q + 2C_s} \quad (4.9)$$

$$X_Q = \frac{C_Q}{C_R + C_Q + 2C_s} \quad (4.10)$$

The final products concentrations, C_R , C_Q and C_s , achieved in Nunes et al. (2012) can be compared with the numerical simulation results obtained from LM model by solving a PDE system for each species. When the LM model is applied to the test reaction system of Bourne et al. (1990) (Equation (4.8)), a system of six PDEs results,

$$\begin{cases} \frac{\partial A_1}{\partial \Gamma} = \eta^2(\Gamma) \frac{\partial^2 A_1}{\partial \xi^{*2}} - Da A_1 B \\ \frac{\partial A_2}{\partial \Gamma} = \eta^2(\Gamma) \frac{\partial^2 A_2}{\partial \xi^{*2}} - Da \varepsilon_2 A_2 B \\ \frac{\partial B}{\partial \Gamma} = \eta^2(\Gamma) \frac{\partial^2 B}{\partial \xi^{*2}} - Da (\beta_1 A_1 B + \beta_1 \varepsilon_1 B R + \beta_2 \varepsilon_2 A_2 B) \\ \frac{\partial R}{\partial \Gamma} = \eta^2(\Gamma) \frac{\partial^2 R}{\partial \xi^{*2}} + Da (A_1 B - \varepsilon_1 B R) \\ \frac{\partial S}{\partial \Gamma} = \eta^2(\Gamma) \frac{\partial^2 S}{\partial \xi^{*2}} + Da \varepsilon_1 B R \\ \frac{\partial Q}{\partial \Gamma} = \eta^2(\Gamma) \frac{\partial^2 Q}{\partial \xi^{*2}} + Da \varepsilon_2 \frac{\beta_2}{\beta_1} A_2 B \end{cases} \quad (4.11)$$

where $A_1 = C_{A_1} / C_{A_{1,0}}$, $B = C_B / C_{B,0}$, $A_2 = C_{A_2} / C_{A_{2,0}}$, $R = C_R / C_{A_{1,0}}$, $S = C_s / C_{A_{1,0}}$, $Q = C_Q / C_{A_{1,0}}$, $\eta = s_0 / s(\Gamma)$, $\beta_1 = C_{A_{1,0}} / C_{B,0}$, $\beta_2 = C_{A_{2,0}} / C_{B,0}$, $\varepsilon_1 = k_2 / k_1$ and $\varepsilon_2 = k_3 / k_1$. $Da = t_D / t_R$ is the Damköhler number and $t_R = C_{A_{1,0}} / (k_1 C_{A_{1,0}} C_{B,0})$ is the reaction time.

Equation (4.11) describes the changes of molar fraction of each species in the normal direction of the interface when a lamellar structure is formed by the impingement of the reactants in the CIJ mixing chamber. Reagent B is injected from one injector and, A_1 and A_2 are injected from the other one, so the initial mixing conditions correspond to the complete initial segregation of reagents,

$$\Gamma = 0, \quad A_1 = A_2 = H(\xi^*); B = H(-\xi^*); R = Q = S = 0 \text{ for } \xi^* = [-0.5, 0.5] \quad (4.12)$$

where $H(\xi^*)$ is a Heaviside function, which coincides with the mixing chamber axis. The boundary conditions correspond to the gradient of concentrations at the boundaries of a single stria, $\xi^* = -0.5$ and 0.5 , which is equal to 0,

$$\Gamma > 0, \quad \frac{\partial A_1}{\partial \xi^*} = \frac{\partial A_2}{\partial \xi^*} = \frac{\partial B}{\partial \xi^*} = \frac{\partial R}{\partial \xi^*} = \frac{\partial Q}{\partial \xi^*} = \frac{\partial S}{\partial \xi^*} = 0 \text{ for } \xi^* = \pm 0.5 \quad (4.13)$$

The PDE system, Equation (4.11), was solved using an algorithm developed in Matlab based on the PDE solver pdepe. This solver uses the finite element method (FEM) to solve initial-boundary value problems for parabolic-elliptic PDEs.

The initial concentrations $(C_{A_1,0}, C_{B,0}, C_{A_2,0})$ set as initial conditions of LM model correspond to half of the concentration in the feed concentrations summarised in Table 4.2. Table 4.2 also shows the stoichiometric ratios, $\gamma_{A_1} = C_{A_1,0} / C_{B,0}$ and $\gamma_{A_2} = C_{A_2,0} / C_{B,0}$ for each experiment and the respective reaction time, t_R . This set of working conditions corresponds to the experimental plan carried out by Nunes et al. (2012). The first two experiments, #1 and #2, were performed to evaluate the reproducibility of the experimental method. In experiments from #1 to #4, A_1 and B concentrations were kept constant, and A_2 concentration was decreased in order to study the micromixing at different γ_{A_2} values and reaction times. In experiments from #5 to #7, lower concentrations of A_1 were tested for longer reaction times.

4. Mixing Mechanisms in Confined Impinging Jets

Table 4.2 List of experiments with respective feed reactant concentrations, values of γ_{A_1} and γ_{A_2} and reaction time (Nunes et al., 2012)

Experiments	Reactant concentration in the feed	γ_{A_2}	γ_{A_1}	t_R (ms)
Exp #1 and #2	$C_{A_1}^{\text{feed}} = 1.1 \text{ mol m}^{-3}$ $C_{A_2}^{\text{feed}} = 6.6 \text{ mol m}^{-3}$ $C_B^{\text{feed}} = 1.0 \text{ mol m}^{-3}$	6	1.1	21
Exp #3	$C_{A_1}^{\text{feed}} = 1.1 \text{ mol m}^{-3}$ $C_{A_2}^{\text{feed}} = 3.3 \text{ mol m}^{-3}$ $C_B^{\text{feed}} = 1.0 \text{ mol m}^{-3}$	3		
Exp #4	$C_{A_2}^{\text{feed}} = 1.1 \text{ mol m}^{-3}$ $C_{A_1}^{\text{feed}} = 1.1 \text{ mol m}^{-3}$ $C_B^{\text{feed}} = 1.0 \text{ mol m}^{-3}$	1		
Exp #5	$C_{A_1}^{\text{feed}} = 0.24 \text{ mol m}^{-3}$ $C_{A_2}^{\text{feed}} = 1.44 \text{ mol m}^{-3}$ $C_B^{\text{feed}} = 0.2 \text{ mol m}^{-3}$	6	1.2	105
Exp #6	$C_{A_1}^{\text{feed}} = 0.24 \text{ mol m}^{-3}$ $C_{A_2}^{\text{feed}} = 0.72 \text{ mol m}^{-3}$ $C_B^{\text{feed}} = 0.2 \text{ mol m}^{-3}$	3		
Exp #7	$C_{A_1}^{\text{feed}} = 0.24 \text{ mol m}^{-3}$ $C_{A_2}^{\text{feed}} = 0.24 \text{ mol m}^{-3}$ $C_B^{\text{feed}} = 0.2 \text{ mol m}^{-3}$	1		

The diffusion coefficient, D_m , used in the numerical calculations, was estimated from data presented in the literature. According to Stokes-Einstein equation, the diffusion coefficient decreases with the increasing of the fluid viscosity. So, the diffusion coefficient was estimated, considering that the diffusivity is less than the characteristic diffusivity in water. According to Delgado and Guedes de Carvalho (2001), the diffusivity of naphthol in water is $D_m = 1.04 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at $\theta = 293.15 \text{ K}$. Therefore, the influence of the diffusional coefficient was studied in the range between $1.04 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

LM model was simulated using the model of Lee et al. (1980) (Equation (4.2)) or the model of Baldyga and Bourne (1983) (Equation (4.5)) to estimate the striation thickness evolution, $\eta = s_0 / s(\Gamma)$, which is taken in account in the first term of the right-hand side of Equation (4.11). The initial striation thickness, s_0 , is equal to the diameter of injectors, $s_0 \sim d$. When the model of Baldyga and Bourne (1983) is used, the length of the mixing chamber where chaotic mixing occurs has to be specified. According to Kolodziej et al. (1982), the most active mixing region in CIJ mixers is around the jets impingement point up to a distance of D to $3D$ from the mixing chamber top. Therefore, the term nD in the model of Baldyga and Bourne (1983) is $nD = 2D$. Table 4.3 summarises the lamellar model parameters used in numerical calculations.

Table 4.3 List of lamellar model parameters

$d = s_0 = 1.50 \text{ mm}$	$n = 2$	$k_1 = 14 \times 10^3 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$D = 10 \text{ mm}$	$r_s = 1$	$k_2 = 2.56 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$\mu = 20 \text{ mPa} \cdot \text{s}$	$\rho = 1000 \text{ kg m}^{-3}$	$k_3 = 95 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$

4.3.3 Results and Discussion

First, the LM model was solved using the striation thickness function proposed by Lee et al. (1980). This function is only valid for chaotic flow regimes that occur for $\text{Re} > 150$

(Santos et al., 2008). LM model was solved for the initial working conditions presented in Table 4.2 and for Reynolds numbers ranging from 150 to 700. The final products concentrations obtained from the LM model give the selectivity X_Q (Equation (4.10)).

Figure 4.4 shows the selectivity X_Q as a function of Reynolds number for experiments #1 and #2 of Table 4.2 and the corresponding predictions using Lee et al. (1980) model for three different diffusion coefficient values, $D_m = 1.04 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $D_m = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $D_m = 1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. This figure illustrates the sensibility of the LM model to the diffusion coefficient.

The selectivity X_Q decreases with the Reynolds number, as shown in Figure 4.4. This means that when the Reynolds number is increased, the microscale homogenisation becomes faster and so the conversion of B favours the reactions with faster kinetics, resulting in the decrease of the formation of Q and S. From Figure 4.4, it is also observed that LM model is quite sensitive to the diffusion coefficient chosen. The diffusion coefficient $D_m = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ gives the best estimation of the actual diffusivity. Based on this observation, the diffusional coefficient $D_m = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ was set in the following LM model simulations.

The LM model numerical validation comprised the analysis of time and space discretisation scales effect on X_Q curve. The range of studied parameters showed no influence on the LM model results. Therefore, the same number of intervals in time discretisation, $n_t = 500$, and in space discretisation, $n_x = 500$, were set in all LM model simulations.

Nunes et al. (2012) used the average X_Q curve obtained from experiments #1 and #2 as the base case for comparison with the results of experiments #3 and #4 of Table 4.2. The difference between experiments #2, #3 and #4 is the initial naphthol ratios, γ_{A_2} . Figure 4.5 shows X_Q as a function of Reynolds number for these experimental conditions and the corresponding predictions using the striation function

of Lee et al. (1980). The experimental data is well described by the lamellar micromixing model mainly for $Re > 200$. Experiment #3 presents a small deviation from the LM model; however, the numerical results are within the uncertainty associated to the experiments. At lower Reynolds number or larger ratios of concentrations, the condition that all the limiting reagent was consumed is more difficult to guarantee, at the sampling point in the centre of the CIJ outlet. So, these points are generally more prone to experimental deviations.

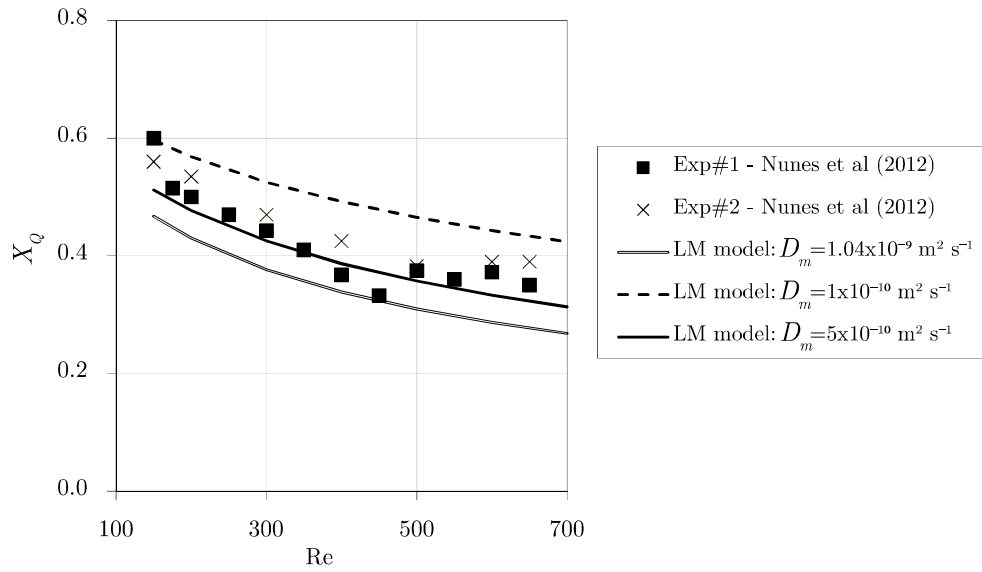


Figure 4.4 Product distribution obtained from experimental results (Nunes et al., 2012) and from LM model using the model defined by Lee et al. (1980) for the following experimental conditions:

$$C_{B,0} = 0.5 \text{ mol m}^{-3} \text{ and for a diffusional coefficient range between } D_m = 1.04 \times 10^{-9} - 1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}.$$

Figure 4.6 shows X_Q as a function of Reynolds number for experiments #5, #6 and #7, associated to longer reaction times, and the corresponding simulations using the model of Lee et al. (1980). The concentrations of reactants decreased in experiments #5, #6 and #7. From Figure 4.6, it is observed that the LM model gives a good prediction of experiments #5 to #6 within the uncertainty associated to the experiments. However, a small deviation is observed for experiment #7 model for $Re > 300$. For this range of Reynolds numbers, the selectivity obtained from

experimental data is $X_Q \sim 0$, which may be related to the concentration detection threshold of the experimental method.

Figure 4.5 and Figure 4.6 show the good agreement between experimental data and LM model results, which means that the model proposed by Lee et al. (1980) gives an accurate estimation for the reduction of the striation thickness in CIJ mixing chamber. Moreover, the LM model accurately predicts the experimental data when the diffusion coefficient is $D_m = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, see Figure 4.5 and Figure 4.6. Therefore, this value is a good estimation for the actual diffusivity.

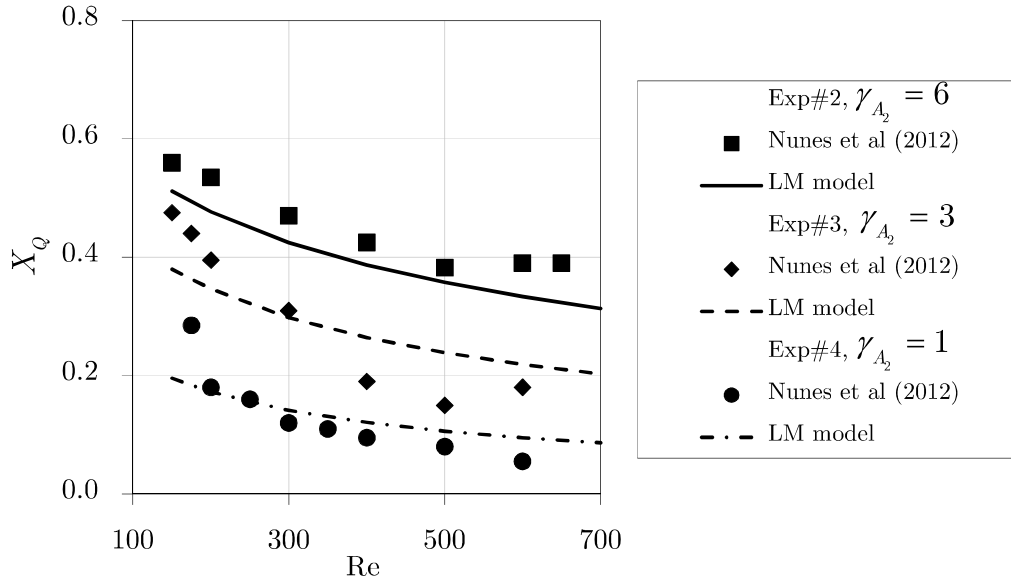


Figure 4.5 Product distribution obtained from experimental results (Nunes et al., 2012) and from LM model using the model defined by Lee et al. (1980) for the following experimental conditions:

$$C_{B,0} = 0.1 \text{ mol m}^{-3}, \gamma_{A_1} = 1.1, t_R \sim 21 \text{ ms} \text{ and different values of } \gamma_{A_2}.$$

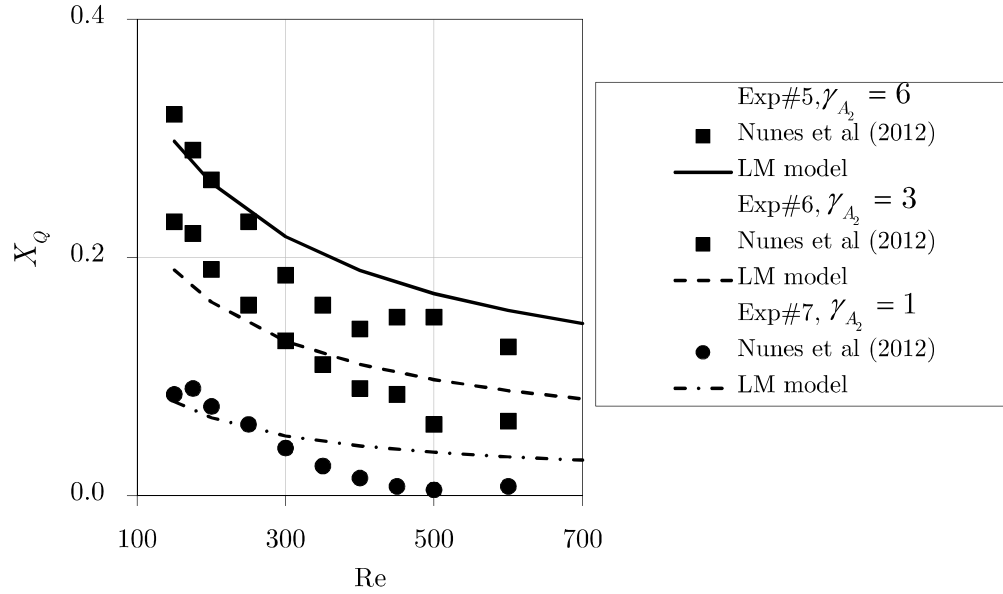


Figure 4.6 Product distribution obtained from experimental results (Nunes et al., 2012) and from LM model using the model defined by Lee et al. (1980) for the following experimental conditions:

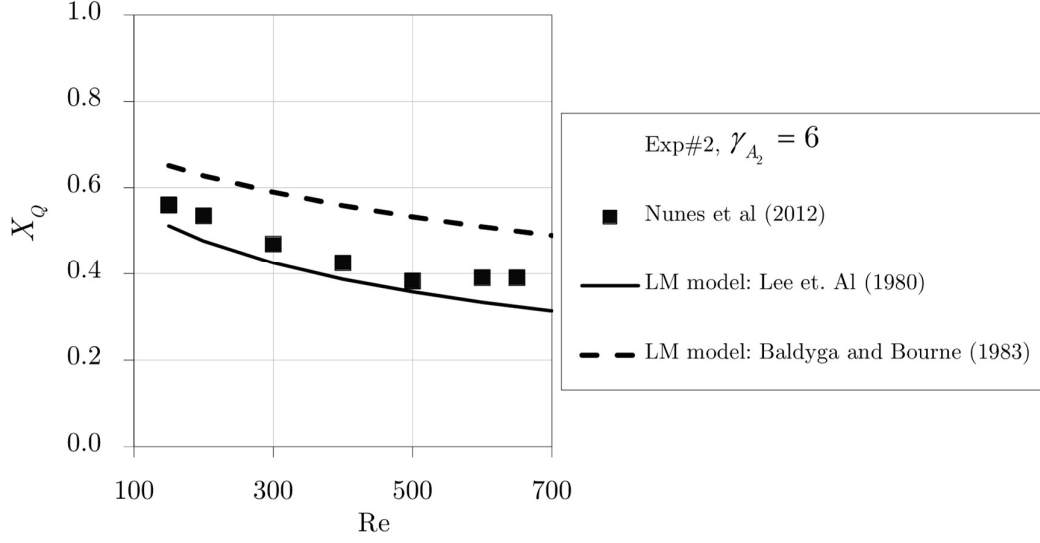
$$C_{B,0} = 0.1 \text{ mol m}^{-3}, \gamma_A = 1.2, t_R \sim 105 \text{ ms} \text{ and different values of } \gamma_{A_2}.$$

A second analysis was made by solving the LM model using the striation thickness function proposed by Baldyga and Bourne (1983). This striation function is based on the statistical theory of turbulent diffusion.

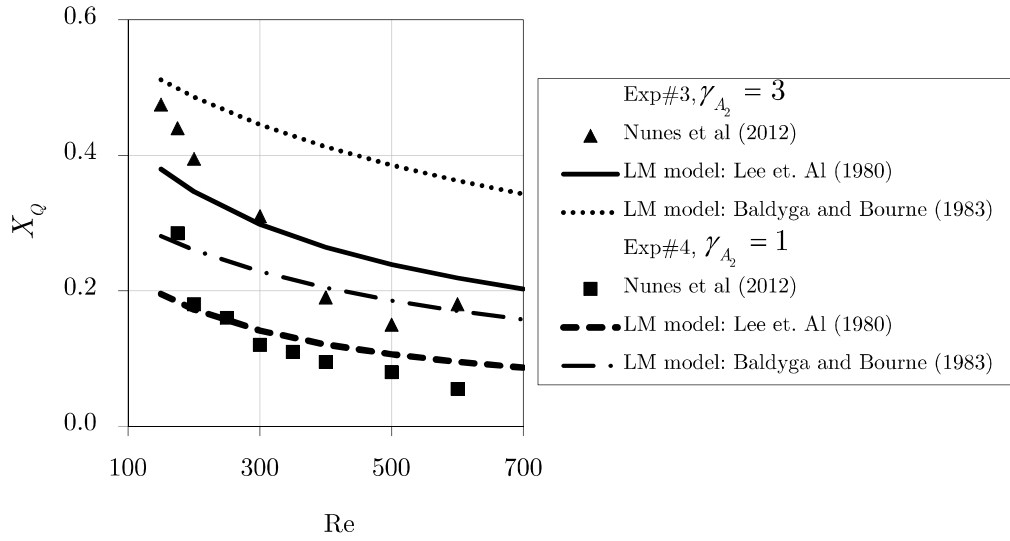
The solutions of LM model according to the striation functions of Baldyga and Bourne (1983) and Lee et al. (1980) are shown in Figure 4.7 for experiments #2 to #4. Experiment #2 data is in Figure 4.7a and experiments #3 and #4 in Figure 4.7b. For experiments #2 to #4, the model from Lee et al. (1980) clearly makes a better description of the experimental results (Figure 4.7).

For higher Reynolds numbers, $Re > 500$, dynamic mixing structures, characteristic of turbulent flow, are formed. For these conditions, the model of Baldyga and Bourne (1983), which is based on turbulence assumption, will most likely describe better the experimental data. Figure 4.7a and Figure 4.7b actually show that the LM results using the Baldyga and Bourne (1983) striation function and experimental data for $Re \gg 500$

are in agreement. However, further experimental data for larger Reynolds numbers would be required to demonstrate this.



(a)



(b)

Figure 4.7 Product distribution obtained from experimental results (Nunes et al., 2012) and from LM model using the model defined by Lee et al. (1980) and Baldyga and Bourne (1983):experiments (a) 2 and (b) 3 and 4.

In conclusion, the striation thickness function proposed by Lee et al. (1980) gives the best estimation of the striation thickness evolution for Reynolds numbers at which the self-sustainable laminar chaotic flow regime is fully established, $200 < \text{Re} < 600$. This presents the definite proof that, from micromixing data, the flow in the studied range of Reynolds numbers for CIJ mixers is laminar. Thus, the mechanism of mixing in CIJ mixers is the stretching of the interface between fluids as described in chaotic mixing for laminar flows (Ottino et al., 1979).

The striation thickness distribution in CIJ mixer was also compared with the models of Lee et al. (1980) and Baldyga and Bourne (1983) in Fonte (2012). The striation thickness distribution was estimated from the stretching of the particles injected in the mixing chamber (Fonte, 2012). The striation thickness of a particle initially at position $\mathbf{X}$ can be estimated from

$$s(\mathbf{X}, t) = (\sqrt{3}\lambda(\mathbf{X}, t))^{\frac{1}{2}} s_0 \quad (4.14)$$

where the initial striation thickness is close to the injector's diameters, $s_0 \approx d$.

Fonte (2012) compared the average striation thickness obtained from 3D CFD simulations for $100 < \text{Re} < 300$ and the striation thickness functions presented in the literature: model introduced by Lee et al. (1980) (Equation (4.2)), the model of Baldyga and Bourne (1983) (Equation (4.5)) and the model of Tucker and Suh (1980) (Equation (4.4)). Results show that, at the Reynolds numbers range between 100 and 300, the order of magnitude of the average striation scale is close to the values predicted by Lee et al. (1980). So, this observation is in agreement with the results of LM model presented in this section.

Therefore, the validation of Lee et al. (1980) assumption from the striation thickness evolution, shows that the flow in the studied range of Reynolds number for CIJ mixers is laminar and the mechanism of mixing is the stretching of the interface as described in chaotic mixing in laminar flows.

The validation of the model of Lee et al. (1980) as the best prediction of the stretching field in CIJ mixers also shows that the relevant information of mixing is two-dimensional. Hereupon, it would be expected that the information exported from 2D and 3D CFD models describe the formation of lamellar structures likewise. In the following section, CFD simulations well-established in the literature are used to determine the stretching histories, and then 2D and 3D results will be faced to validate the premise regarding the 2D mixing information in CIJ mixers.

4.3.4 Validation of 2D Micromixing Flow Nature

2D and 3D CFD results of CIJ mixers have been compared since the beginning of this century (Santos et al., 2002; Santos, 2003; Santos et al., 2009). These works report that the main differences between the two models are: dissipation of vortices from the inlet to the outlet occurs faster in 3D models; in 3D simulations, the vortices street involves the two streams within a distance equal to the mixing chamber diameter, and in 2D models, the vortices evolve through a longer distance. Nevertheless, the 2D model describes the most important flow features in CIJ mixers. Segregated and chaotic flow regimes are captured by 2D simulations, and the oscillation frequency of jets impingement point and vortices formation rate are identical in both models (Santos et al., 2009).

Numerical studies indicate that 3D CIJ mixing information may be easily captured from a 2D CFD model, and thus mixing studies may be run from simplified geometries (Santos et al., 2002; Santos, 2003; Santos et al., 2009). Although the comparison between 2D and 3D model is well-established in the literature, the 2D information of the lamellar structure obtained from 2D CFD models has never been faced with 3D CFD simulations. Data in the literature was used to compare the stretching histories from 2D and 3D simulations.

Fonte (2012) described the mixing length scales and stretching properties of the flow from 3D CFD simulations. A method is thus introduced to determine the stretching

histories undergone by a fluid element in a 3D CIJ mixing chamber, that was later published in Brito et al. (2020). The flow stretching was studied from a Lagrangian approach by tracking the position and deformation of a spherical element in the flow. A cluster of 172 particles was injected in the transient 3D CFD simulations from each injector (Fonte, 2012). The particles were tracked by the integration of advection, $d\mathbf{x}/dt = \mathbf{u}(x, t)$ where $\mathbf{u}$ is the velocity vector and t is the flow time, up to the instant when the first injected particle leaves the chamber. The particles are passive elements which have the same physical properties of the fluid, thus not perturbing the flow. Each particle position was calculated integrating the advection equation with a sixth order Runge-Kutta scheme available in Fluent. The position of particles, velocity components and velocity gradient were imported from the CFD simulation.

The deformation was estimated from an algorithm implemented in Matlab. For this, the deformation gradient tensor $\mathbf{F}$ is computed from the position of particles, $\mathbf{F}(\mathbf{X}, t) = d\mathbf{x}(\mathbf{X}, t) / d\mathbf{X}$, where $\mathbf{F}$ can be obtained from $d\mathbf{F}/dt = (\nabla\mathbf{u})^T \cdot \mathbf{F}$. The initial condition is $\mathbf{F}(t=0) = \mathbf{I}$ wherein $\mathbf{I}$ is the identity tensor (Ottino, 1980). Locally, the deformation of the element is given by

$$\lambda = \sqrt{\mathbf{C}:\mathbf{M}\mathbf{M}} \quad (4.15)$$

where $\mathbf{M}$ is calculated by $\mathbf{M} = d\mathbf{X} / |d\mathbf{X}|$ and $\mathbf{C}$ is the right Cauchy-Green deformation tensor, which is $\mathbf{C}(t) = \mathbf{F}(t) \cdot \mathbf{F}(t)^T$. Equation (4.15) describes the local stretching of an element of fluid. For $0 < \lambda < 1$, the system is compressed, while for $\lambda > 1$ it is stretched.

The 3D CFD domain in Fonte (2012) consists of a cylinder with a diameter $D = 10$ mm and a height $H = 50$ mm. Two cylindrical injectors, with a diameter $d_1 = d_2 = 1.5$ mm (Chamber 1 in Table 4.1) and a length of 2.5 mm, issue into the cylindrical chamber at 5 mm from the top. The axis of the two opposed jets is coincident and perpendicular

to the mixing chamber axis. Figure 4.8 shows the average stretching, $\langle \lambda \rangle$, determined from the 3D simulation at $Re = 300$, which was calculated from

$$\langle \lambda(t / \tau) \rangle = \frac{1}{np} \sum_{i=1}^{np} \lambda_i(t / \tau_{CIJ}) \quad (4.16)$$

where np is the number of injected particles and τ_{CIJ} is the mean residence time of the mixing chamber, which is given by

$$\tau_{CIJ} = \frac{D^2 H}{2v_{inj} d^2} \quad (4.17)$$

wherein v_{inj} is the velocity at injectors. For these working conditions, $\tau_{CIJ} = 0.3$ s.

Figure 4.8 also gives a description of the stretching features in 3D CIJ mixers. The average stretching increases nearly exponentially with time for $Re = 300$. At this flow regime, the dynamics structures enhance the mixing of the two streams delivered through the two opposed injectors. The exponential increase of the average stretching with time is actually a feature of chaotic flows (Aref and Tryggvason, 1984).

The mixing dynamics in CIJ mixers were also described at $Re = 300$ from a 2D CFD simulation in Matos et al. (2018). The 2D domain consists of a longitudinal cut of the 3D geometry with the same dimensions of the chamber in Fonte (2012). The same methodology described in 3D model was used to determine the average stretching. A cluster of 172 particles was injected through each injector, and the position of each particle, velocity components and velocity gradient were imported from CFD simulations. The stretching average is determined using the algorithm mentioned above.

The average particle stretching determined from both models is in Figure 4.8. The stretching histories in 2D and 3D flow domains are coincident. This is the final evidence

that the 3D mixing information of CIJ mixing is completely captured from 2D simulations and so the relevant information in CIJ mixers is two dimensional.

The most important conclusion from these results stems from the fact that the mixing information in 3D CIJ mixers can be determined from simplified geometries, that consists of a longitudinal cut of the 3D geometry, making this study less time-consuming, in terms of computing time.

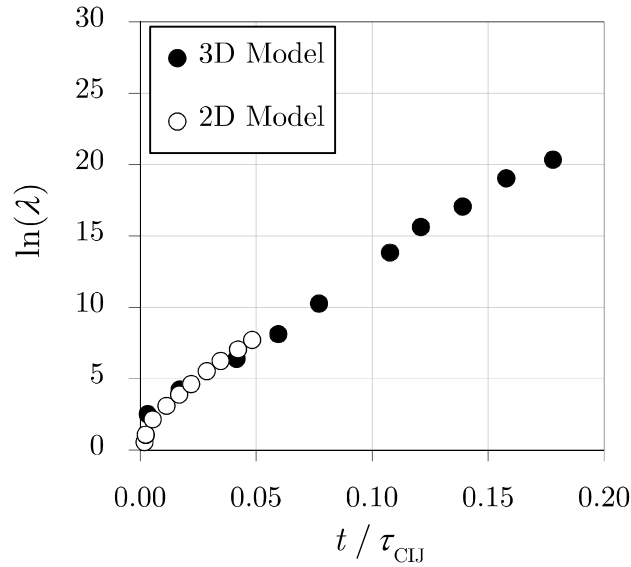


Figure 4.8 Average particle stretching at $Re=300$ calculated from 3D (Fonte, 2012) and 2D models.

As a final remark, LM model enables the fully resolved simulation of a complex chemical reaction system in CIJ mixers coupling the flow dynamics and the micromixing scales. This model must assume the stretching field described by Lee et al. (1980) considering then stretching occurs in the plane of the lamellae. Results indicate that the model gives a complete picture of chemical synthesis down to the nanoscales of molecules accounting the macroscales of flow distribution and the microscales of mixing. This brings an alternative to the 3D CFD simulations with the complete description of physics of a chemical process, which, most of the times, is out-of-reach for modern computers. Considering typical values for diffusivity of liquids,

$D_m = 10^{-9} \text{ m}^2 \text{ s}^{-1}$, in micro/milli-reactors with micromixing times around $t_{\text{micromixing}} = 0.1 \text{ s}$, the length scale of micromixing is within the order of $\Delta x = 10$ to $1 \text{ }\mu\text{m}$. CFD simulation of such a reactor with volumes of 50 cm^3 would require more than 10^{11} cells, a value that is orders of magnitude larger than usual reasonable values for CFD simulations. Therefore, LM model bridges the micromixing information and the macroscale of flow distribution, delivering information to the nanoscale.

Some results presented in this section were already published in Brito et al. (2020).

4.4 Part II: Mixing Dynamics of Dissimilar Fluids in CIJ Mixers – Influence of Flow Imbalance and Inlet Reynolds number

Mixing in CIJ mixers has been widely studied from flow visualisation. The main works that contributed most for the research on mixing dynamics in CIJ mixers are listed in Table 4.4. All these works were performed at symmetric flow rates.

The chaotic flow regime in CIJ mixers, which is the operation regime in industrial applications, has only been observed at symmetric conditions. This assumption does not represent the mixing dynamics in the most important range of industrial applications. For instance, in PU RIM processes, the two reactive monomers have different viscosities, which differ according to each formulation. The typical viscosities are in the $0.1 \text{ Pa} \cdot \text{s}$ range for isocyanate and $1 \text{ Pa} \cdot \text{s}$ for polyols. An example is Baydur 425 MR, a high-density polyurethane produced by the Polyurethanes Division of Bayer, which is a mixture of polymeric diphenylmethane diisocyanate (PMDI) ($0.2 \text{ Pa} \cdot \text{s}$) and a formulated polyether polyol system ($1.6 \text{ Pa} \cdot \text{s}$).

This work shows the ability to operate CIJ mixers at chaotic flow regimes with dissimilar fluids, i.e. having different physical properties. Furthermore, the critical Reynolds number for the onset of the chaotic regime is also identified from flow visualisations.

Table 4.4 List of flow visualisations in CIJ mixers.

Reference	D (mm)	d (mm)	Experimental Technique	Conclusions
Lee et al. (1980)	3.18	1	Density variation of the injected solutions	An intense motion of the fluid is registered at the impingement point.
Tucker and Suh (1980)	22	9.5	Ink tracer	An intensive mixing occurs for $Re > 150$ until a value of 1000, where no further improvements are reported.
Sandell et al. (1983)	52	9.5	Tracer – thymol blue (pH indicator)	Continuous and significant improvement in mixing quality occurs up to $Re = 400$.
Wood et al. (1991)	25.4	2.38	Polystyrene particles ($\bar{d} = 100 \mu\text{m}$)	A flow structure, like a pancake, is centred at the intersection of the mixing chamber and injectors axes. The onset of the oscillations and the respective instability of the jets were detected for $Re > 150$.
Johnson and Wood (2000)	20	2	Dye, fluorescent dye, tracer particles	At $Re = 90$, the interface of the two fluids begins to oscillate, and an unsteady flow structure is formed at $Re \sim 150$.

Table 1.4 List of flow visualisations in CIJ mixers (concluded)

Reference	D (mm)	d (mm)	Experimental Technique	Conclusions
Unger et al. (1998)	89	13	PLIF	A modified mixing chamber is used where the two jets do not impinge directly. The calculation of striation thickness shows that it decreases from $Re = 150$ to $Re = 300$.
Bierdel and Piesche (2001)	10	1	Coloured Tracer	Mixing patterns were studied at two flow regimes: from $Re = 50$ to $Re = 150$.
Santos et al. (2009)	10	1.5	PIV	Flow oscillations are detected below the critical Reynolds number that marks the onset of chaotic mixing. Increase of Re promotes greater instabilities. The actual transition to chaotic flow regime was visualised at $Re = 120$, where the intensity of the oscillations was doubled.
Fonte et al. (2015)	10	1.5	PLIF	The best mixing quality is achieved for balanced flow conditions, i.e. equal flow rates at injectors. This means that the impingement point has to be at the centre of the mixing chamber.

4.4.1 Experimental Methods and Experimental Setup

Experiments were run in an acrylic CIJ mixer having the same dimensions of Chambers 1 and 2 described in Table 4.1. CIJ mixing chamber was drilled and cut in a single Plexiglas block with dimensions $150 \times 40 \times 47.5$ mm. The aligned injectors were precisely drilled in the block, horizontally from one side to the other at 5 mm from the mixing chamber head. The transparency feature of this block enables to visualise the flow inside of the mixing chamber.

The injectors have a length of $40d$, ensuring a fully developed laminar velocity profile at the inlet of the mixing chamber. This chamber with a height of 50 mm is connected to a cylindrical mould with a diameter of 15 cm and a height of 8 cm. The mould guarantees a parallel flow at the outlet of the mixing chamber, minimising any hydrodynamic influence at the outlet boundary condition.

The description of CIJ mixers experimental setup is well-established in Santos et al. (2008), Nunes et al. (2012), Fonte et al. (2015) and Fonte et al. (2016). Figure 4.9 shows a schematic representation of the experimental setup and the respective photographs of the incorporated parts are in Figure 4.10. The flow dispensing system is composed of two lines that transport the fluids from the pressurised tank (number 1 in Figure 4.9 and Figure 4.10b) to the mixing chamber. Each line has a gear pump with a variable speed motor, a ROTA-Yokogawa Coriolis mass flow meter (model RCCS33 M01A1SH) (number 2 in Figure 4.9, Figure 4.10c and Figure 4.10e), and a needle valve to tune the flow rate (number 3 in Figure 4.9 and Figure 4.10e). The pressurisation of tanks helps to prevent inherent flow perturbations originated by pump operation. The relative errors associated to this system are related to the $\pm 0.05 \text{ g s}^{-1}$ precision of the Coriolis mass flow meters in range from 1.2 g s^{-1} to 14.1 g s^{-1} . Thus, the relative errors of the experiments are between 4% and 0.4%.

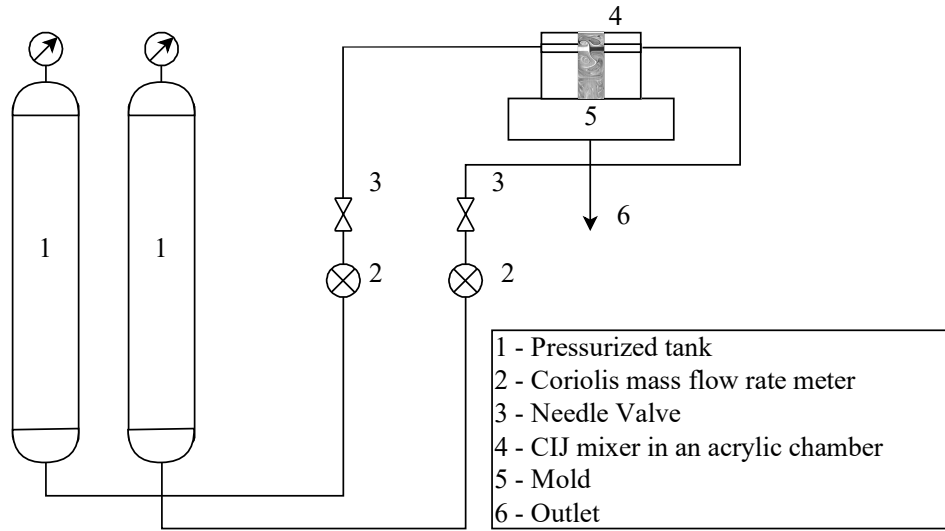


Figure 4.9 Schematic representation of CIJ experimental setup.



Figure 4.10 Photographs of CIJ experimental setup (a) full experimental setup; (b) pressurised tanks; (c) Coriolis flow meters screen; (d) CIJ mixer; (e) needle valves and Coriolis flow meter.

PLIF experimental technique was used to characterise the flow field in CIJ mixers. The schematic representation of this technique is in Figure 4.11. A laser sheet illuminates a plan of the transparent mixing chamber, cutting it through the injectors (numbers 5 and 7 in Figure 4.11). For the flow visualisation, one of the fluids is dyed with a marker, and the other is a clear liquid. The doped fluid is fluorescent, emitting light at a different wavelength from the laser. Thus, an image of the flow is made filtering the laser wavelength. The result is a PLIF image that maps the tracer in the laser sheet

plan. The fluorescent light emitted by the dyed fluid is proportional to the local concentration of the fluorescent marker, enabling to visualise the flow structures formed in this plane. The concentration scalar field may be assessed from the spatial distribution of fluorescence captured by PLIF images, providing a qualitative and quantitative analysis of the system.

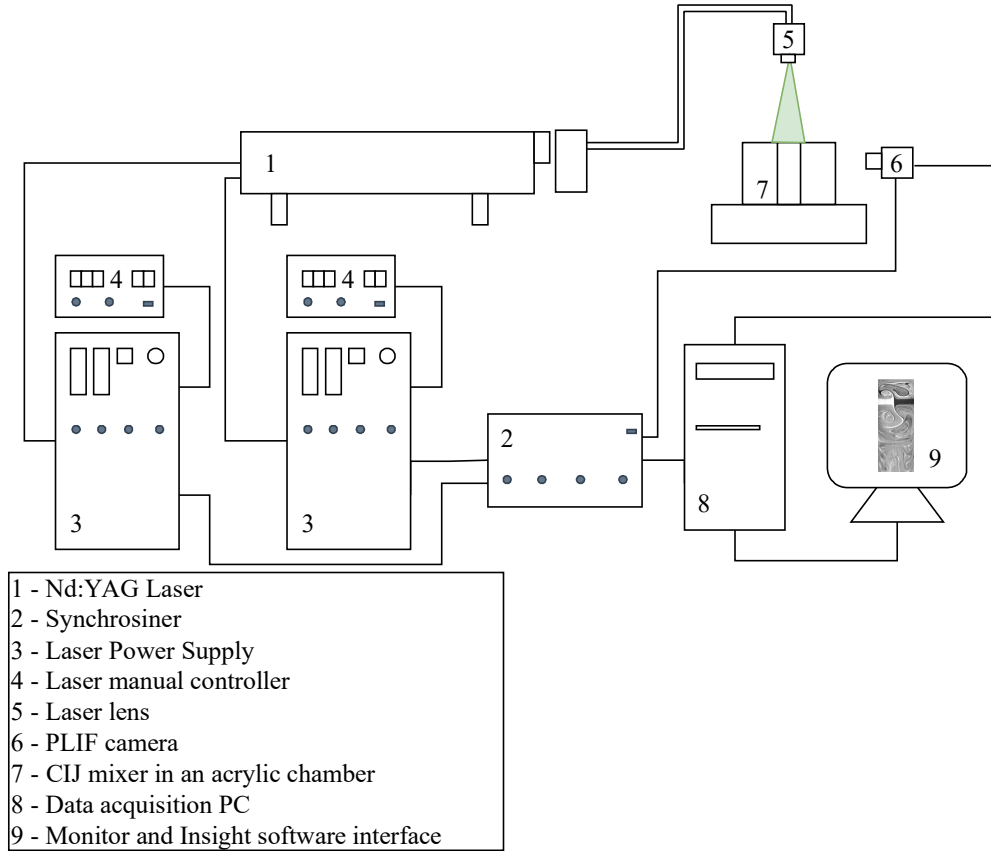


Figure 4.11 Schematic representation of the PLIF technique.

The laser sheet was generated in a Nd:YAG laser from Litron Lasers[®] (Nano L 50-100) with an emission peak at 532 nm (number 1 in Figure 4.11). This laser emits 4 ns pulsed beams with a maximum energy of 400 mJ/pulse at a maximum of 100 Hz. The laser beam is emitted from the top of the mixing chamber being transported through a TSI light arm (Model 610015), which consists of an articulated tube with internal reflecting mirrors. At the outlet of the light arm, the laser beam is spread in a sheet with a -15 mm cylindrical lens and focused with 500 mm spherical lens (number 5 in

Figure 4.11). The TSI light arm is placed at a distance of 50 cm from the mixing chamber head producing a sheet with less than 1 mm of thickness.

The fluorescent tracer used in this work was rhodamine 6G that has the maximum absorption of light close to 525 nm and emits fluorescence at 555 nm (Crimaldi, 2008). PLIF images were acquired with a light orange glass filter (545 nm) in front of the digital CCD camera filtering possible reflections of the laser light (number 6 in Figure 4.11). The lens and camera used were respectively an AF Micro-Nikkor 60 mm f/2.8D and a TSI model 630157 that captures 1192×1600 pixels images at a maximum frame rate of 30 Hz. The frames acquired by CCD camera were transferred to a computer through a frame grabber (TSI model 600067). This camera was placed in front of the mixing chamber to capture the illuminated plane of the mixing chamber, as shown in number 6 in Figure 4.11.

The concentration of rhodamine 6G used was $C_{\text{Rhodamine6G}} = 3.5 \times 10^{-4} \text{ g L}^{-1}$, as recommended in the literature (Sultan et al., 2012). This concentration corresponds to the linear region from the plot rhodamine concentration versus the fluorescence intensity in Sultan et al. (2012).

The number of acquired images was chosen according to the working conditions. For segregated flow regimes, 50 frames were acquired, and 100 frames were set for chaotic flow regime. The exposure time for the image capturing is controlled from a TSI synchroniser (model 610035) (number 2 in Figure 4.11) to avoid induced blurring. The image acquisition was made with TSI Insight 3GTM software installed in a Dell Precision 690 PC with a dual core Intel Xeon CPU at 2.33 GHz and 2 GB of RAM (numbers 8 and 9 in Figure 4.11).

The working fluids in this work are glycerol solutions that were designed according to the method proposed in the diagram of Figure 3.11. Table 4.5 summarises the physical properties of the working fluids. Three viscosity ratios were performed: 2, 5 and 9. The more viscous solution, MV fluid, was designed from the determination of the mass

fraction of glycerol according to Equation (3.10). Then, the less viscous fluid, LV fluid was prepared from the matching of refractive index setting previously according to the viscosity ratio (see Figure 3.11). Calcium chloride was used to match the refractive indices. The final fluid viscosities are listed in Table 4.5, as well as the respective concentration of calcium chloride.

The viscosity of fluids was checked from rheological tests performed in rheometer Anton Paar MCR 92 SN8247897. The density of each liquid and the temperature was measured from a Coriolis mass flow meter. The refractive index was checked at 25 °C using a digital ABBE Refractometer (AB-R-100D).

Table 4.5 Working fluids for mixing of dissimilar fluids in CIJ mixers.

Viscosity ratio	μ	ρ	θ [K]	$C_{\text{CaCl}_2 \cdot \text{H}_2\text{O}}$ [kg m ⁻³]	RI
2	$\mu_{\text{LV}} = 20 \text{ mPa} \cdot \text{s}$ $\mu_{\text{MV}} = 40 \text{ mPa} \cdot \text{s}$	$\rho_{\text{LV}} = 1176 \text{ kg m}^{-3}$ $\rho_{\text{MV}} = 1208 \text{ kg m}^{-3}$	293.15	187	$RI = 1.445$
5	$\mu_{\text{LV}} = 9.2 \text{ mPa} \cdot \text{s}$ $\mu_{\text{MV}} = 47.8 \text{ mPa} \cdot \text{s}$	$\rho_{\text{LV}} = 1339 \text{ kg m}^{-3}$ $\rho_{\text{MV}} = 1215 \text{ kg m}^{-3}$	291.85	790	$RI = 1.447$
9	$\mu_{\text{LV}} = 9.1 \text{ mPa} \cdot \text{s}$ $\mu_{\text{MV}} = 81.1 \text{ mPa} \cdot \text{s}$	$\rho_{\text{LV}} = 1371 \text{ kg m}^{-3}$ $\rho_{\text{MV}} = 1217 \text{ kg m}^{-3}$	292.15	1000	$RI = 1.464$

4.4.2 Experimental Results

4.4.2.1 Effect of Reynolds Number on Mixing

The effect of Reynolds number was described from the balance of two dissimilar fluids at the mixing chamber axis. For this, the flow rate of the MV fluid stream is set at a

constant Reynolds number, and then the LV fluid is adjusted in order to get the impingement point at the centre of the mixing chamber, which is the necessary condition for the mixing of similar fluids at chaotic flow regime. The viscosity ratio in CIJ experiments was defined according to $(\mu_1 / \mu_{LV}) : (\mu_2 / \mu_{LV})$, wherein the indices 1 and 2 correspond to the jets 1 and 2 in Figure 4.3.

For a viscosity ratio 2:1, four fixed Reynolds numbers of MV fluid stream were tested: 50, 100, 125 and 150. The geometry used in these experiments was Chamber 1, $d_1 = d_2 = 1.5$ mm (Table 4.1). The MV fluid dyed with rhodamine (white fluid) was injected from the left side injector, jet 1, and the LV fluid (dark fluid) through the right side injector, jet 2. Figure 4.12 to Figure 4.15 show the PLIF images, obtained at the plane defined by the mixing chamber and injectors axes, for the mixing of two dissimilar fluids: $\mu_1 = 40$ mPa $\cdot$ s and $\mu_2 = 20$ mPa $\cdot$ s, at $Re_1 = 50$, $Re_1 = 100$, $Re_1 = 125$ and $Re_1 = 150$.

PLIF images for a viscosity ratio 2:1 show the flow dynamics and the formation of mixing structures for each working condition:

- For $Re_1 = 50$ (Figure 4.12), the MV fluid (white fluid) is continuously injected through the left side injector, and the right side injector delivers the LV fluid (dark fluid). Both streams flow from the injector to the outlet without being mixed, and thus the flow field patterns remain segregated. A vortex is formed in the left side of the chamber, but an efficient mixing between liquid streams is not promoted. Therefore, the interfacial area created between fluid is invariant and corresponds to the mixing chamber axis. At this working condition, the mixing is only promoted by the molecular diffusion at the interface;
- For $Re_1 = 100$ (Figure 4.13), the flow regime is steady and similar to the segregated flow regime obtained for symmetric flow conditions. The right-hand side jet, $Re_2 = 197$, is above the critical Reynolds number that onsets chaotic flow regimes at symmetric flow conditions, $Re_c > 150$; however, a vortex street

issuing from the jets impingement point, which is the signature mark of chaotic flow regimes, is not formed. A small perturbation is observed at the interface, which is caused by small-amplitude convective waves. This observation was also visualised by Santos et al. (2008) for symmetric flow conditions, evidencing once again that the oscillation onset occurs at lower Re values than those marking the transition between segregated and chaotic flow regime;

- For $Re_1 = 125$ (Figure 4.14), the flow patterns are similar to those described for $Re_1 = 100$ (Figure 4.13). Figures show that vortices are formed upstream the impingement point in each side of the mixing chamber, and convective waves are still generated at the interface;
- The increase of Reynolds number to $Re_1 = 150$ (Figure 4.15) promotes the development of a self-sustainable oscillatory and periodic regime, similar to that reported for symmetric flow conditions (Unger et al., 1998; Zhao and Brodkey, 1998a; Nakamura and Brodkey, 2000; Santos et al., 2009; Fonte et al., 2015). The opposite jets are impinged at the mixing chamber axis and spread radially forming a sort of a flow pancake as seen from previous works with symmetric flow conditions (Wood et al., 1991; Unger et al., 1998; Nakamura and Brodkey, 2000). These vortices around the right-hand side jet are clear in Figure 4.15, where a streak of white and dark fluid is seen issuing from the jets impingement point upwards and then being bent into the inside of a spiral pattern. Similar pattern is observed downwards, although not so clearly. In this work, the top part of the mixing chamber is only imaged, and so the structure of the mixture in the downward runner is not seen. The pattern of the mixture formed by fluids in the upper part of the CIJ mixers, from the closed top down to a distance D from the top, is the same imaged for symmetric CIJ mixers operation (Fonte et al., 2011). After this mixing region, a thin lamellar structure of both fluids interlaid is formed.

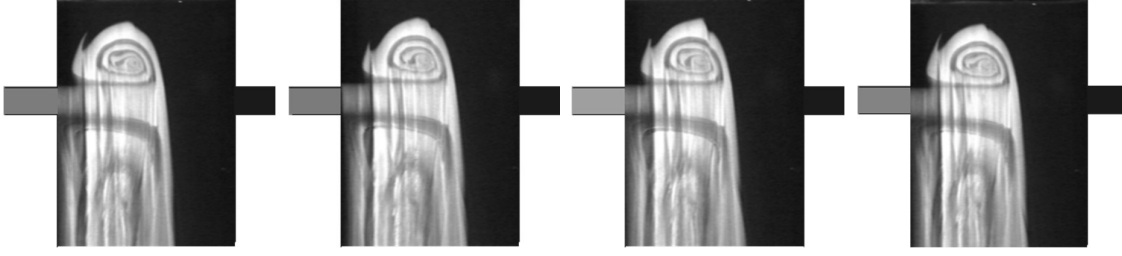


Figure 4.12 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 2:1: $\mu_1 = 40 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 20 \text{ mPa} \cdot \text{s}$, at $\text{Re}_1 = 50$ and $\text{Re}_2 = 124$, using Chamber 1.

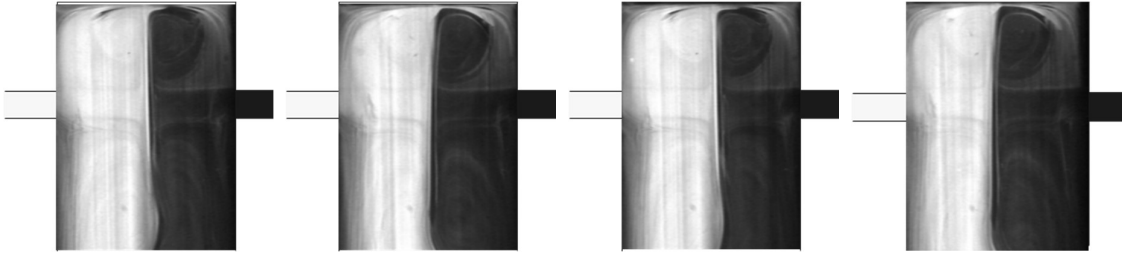


Figure 4.13 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 2:1: $\mu_1 = 40 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 20 \text{ mPa} \cdot \text{s}$, at $\text{Re}_1 = 100$ and $\text{Re}_2 = 197$, using Chamber 1.

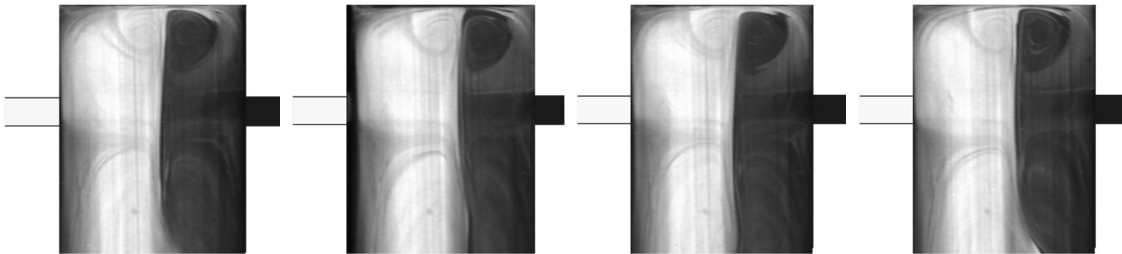


Figure 4.14 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 2:1: $\mu_1 = 40 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 20 \text{ mPa} \cdot \text{s}$, at $\text{Re}_1 = 125$ and $\text{Re}_2 = 246$, using Chamber 1.

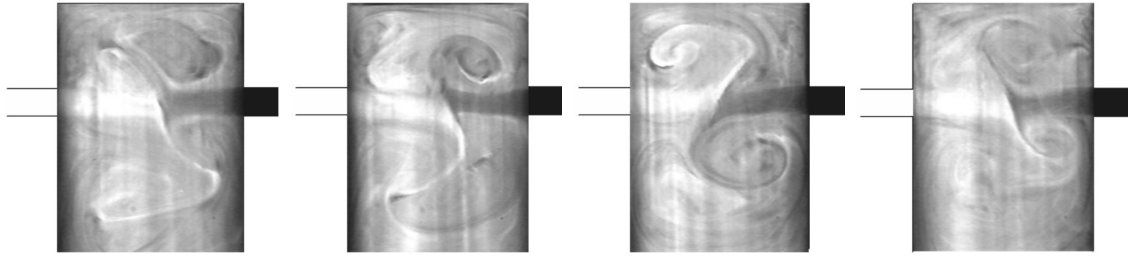


Figure 4.15 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 2:1: $\mu_1 = 40 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 20 \text{ mPa} \cdot \text{s}$, at $\text{Re}_1 = 150$ and $\text{Re}_2 = 295$, using Chamber 1.

The same flow visualisations were reported for other viscosity ratios. For a viscosity ratio 1:5, the LV fluid was injected from the left side injector, jet 1 (dark fluid) and the MV fluid dyed with rhodamine through the right side injector, jet 2 (white fluid). The respective viscosity and density are listed in Table 4.5, and the geometrical parameters correspond to Chamber 1.

Four working conditions were tested for this viscosity ratio. The Reynolds number of the MV liquid stream was set at 50, 66, 70 and 78 and the LV liquid stream was then adjusted in order to balance both jets. Figure 4.16 to Figure 4.19 show the PLIF images, obtained at the plane defined by the mixing chamber and injectors axes, for mixing of two dissimilar fluids: $\mu_1 = 9.2 \text{ mPa} \cdot \text{s}$ and $\mu_1 = 47.8 \text{ mPa} \cdot \text{s}$, at $\text{Re}_2 = 50$, $\text{Re}_2 = 66$, $\text{Re}_2 = 70$ and $\text{Re}_2 = 78$. These images show:

- For $\text{Re}_2 = 50$ (Figure 4.16), the flow has a typical behaviour of a segregated flow regime even at $\text{Re}_1 = 165$. The light pathlines observed in these images are caused by undissolved microparticles of rhodamine. This is a result of a poor homogeneity of the inlet streams that it ends up being quite useful to visualise the pathlines of each liquid stream. From this flow feature, a vortex downstream of the impinging jet is clearly observed in the right side of the mixing chamber as well as in the right side of the headspace. Although not easily visualised from these images, the same mixing structures should be formed at the left side of

the mixing chamber, because it is the necessary condition to reach a steady flow regime. The presence of these structures on the left side of the chamber will be detected later from CFD simulations in Section 4.5. Although the formation of dynamic structures is observed in each side of the mixing chamber, the flow remains segregated, and the interface between flows still roughly coincides with the mixing chamber axis. This interface exhibits a slight curvature which was reported as a possible steady-state solution for symmetric flow conditions from 2D simulations in Santos et al. (2010);

- For $Re_2 = 66$ (Figure 4.17), the two fluid streams remain segregated and small-amplitude convective waves are observed at the interface between the two fluids. This observation is in agreement with the flow visualisations for symmetric flow conditions (Santos et al., 2008) and for viscosity ratio 2:1. These oscillations are not yet enough to promote the engulfment of both fluids;
- Increasing the Re at MV jet, the onset of the chaotic flow regime is reached. Chaotic flow regime is observed for $Re_1 = 250$ and $Re_2 = 70$, as shown in Figure 4.18. Oscillations are observed at the impingement point, ensuring the engulfment of the two liquid streams and the stretching of the interface between fluids. The chaotic regime dynamics for this viscosity ratio presents similar flow patterns to that in symmetric flow conditions (Figure 4.1) and even for a viscosity ratio 2:1 (Figure 4.15). Figure 4.18 shows that vortices engulf the fluids until a distance of approximately $2D$ from the top of the mixing chamber, and from this point, the flow is fully developed laminar. These observations are in agreement with Fonte et al. (2011), who observed a parabolic velocity profile at the outlet of the mixing chamber from PIV visualisations for symmetric flow conditions;
- As Re increases, thinner lamellar structures are observed from the flow images. For $Re_1 = 303$ and $Re_2 = 78$ (Figure 4.19), fewer mixing structures are visually detected comparing to Figure 4.18 ($Re_1 = 250$ and $Re_2 = 70$). This is associated to a faster laminae thicknesses reduction, that immediately upon the opposed

jets contacting render the two fluids homogeneous. Thus, the two impinging jets are hardly visible in the almost homogeneous concentration field. At these flow conditions, there is an increase in the mixing degree.

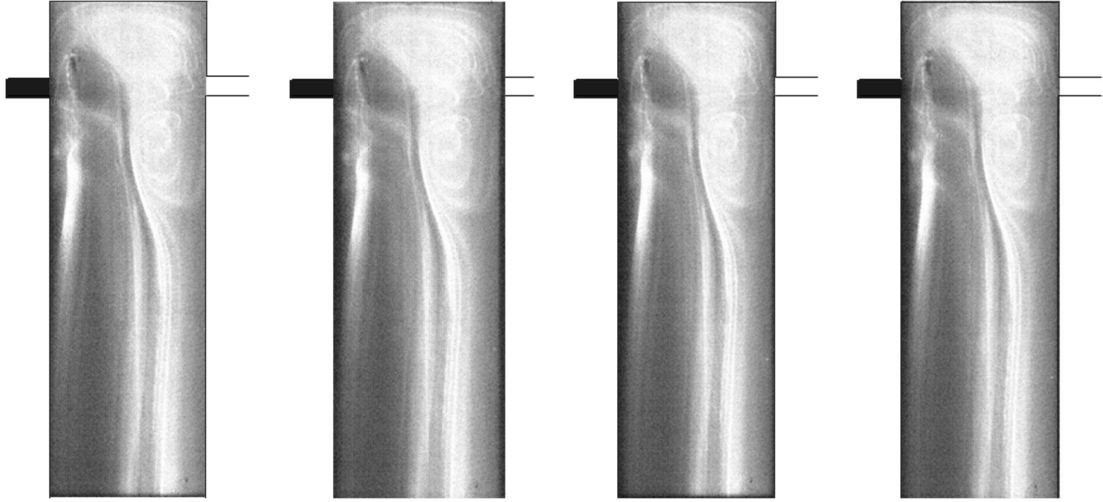


Figure 4.16 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:5: $\mu_1 = 9.2 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 47.8 \text{ mPa} \cdot \text{s}$, at $\text{Re}_1 = 165$ and $\text{Re}_2 = 50$, using Chamber 1.

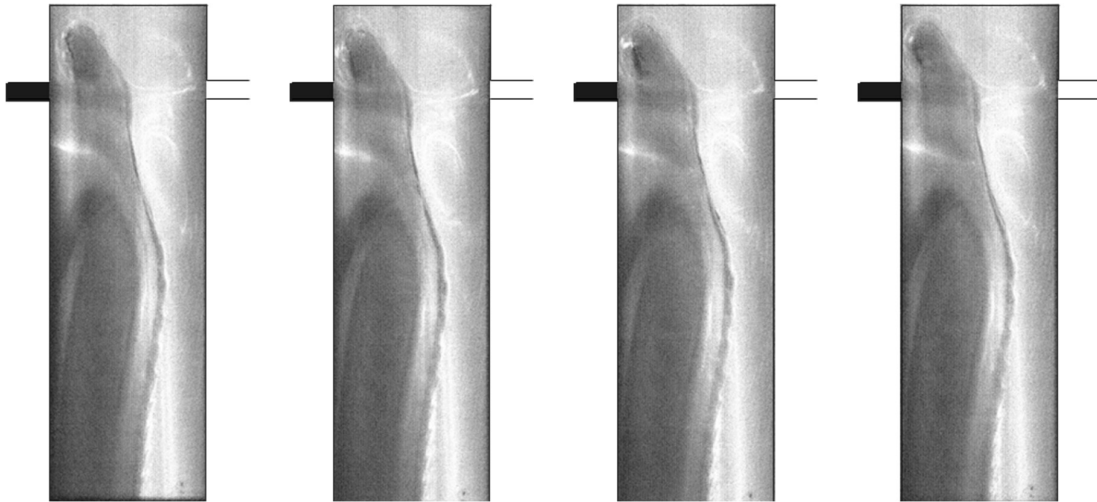


Figure 4.17 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:5: $\mu_1 = 9.2 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 47.8 \text{ mPa} \cdot \text{s}$, at $\text{Re}_1 = 238$ and $\text{Re}_2 = 66$, using Chamber 1.

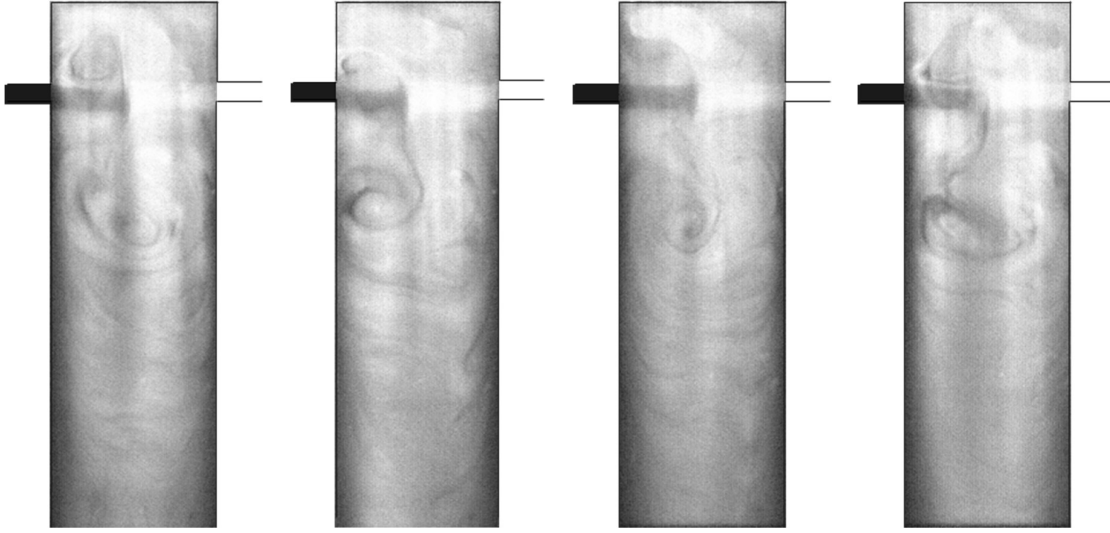


Figure 4.18 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:5: $\mu_1 = 9.2 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 47.8 \text{ mPa} \cdot \text{s}$, , at $\text{Re}_1 = 250$ and $\text{Re}_2 = 70$, using Chamber 1.

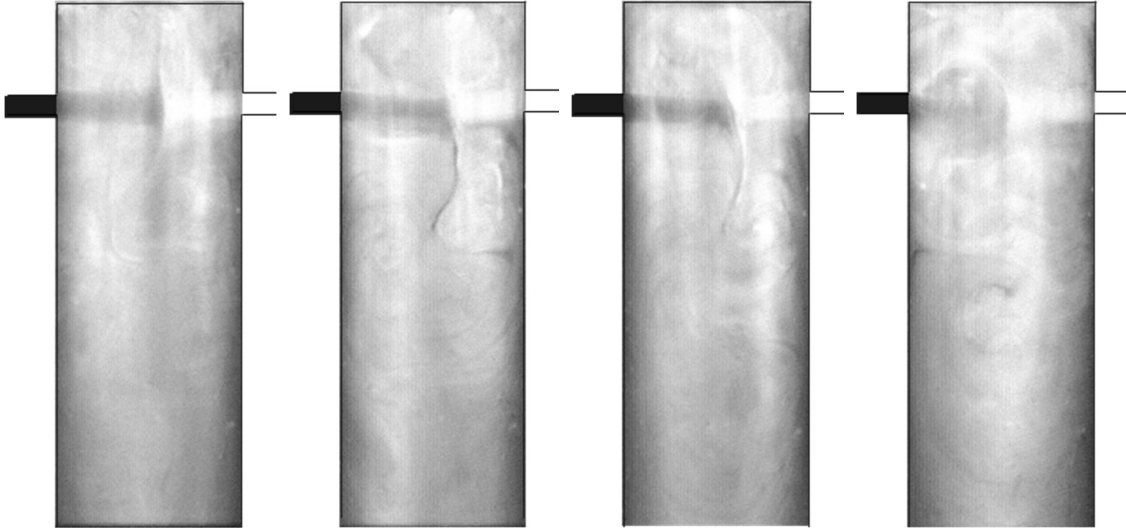


Figure 4.19 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:5: $\mu_1 = 9.2 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 47.8 \text{ mPa} \cdot \text{s}$, , at $\text{Re}_1 = 303$ and $\text{Re}_2 = 78$, using Chamber 1.

The viscosity ratio of 1:9 is also addressed in this chapter. The viscosity of the LV fluid is $\mu_1 = 9.1 \text{ mPa} \cdot \text{s}$, and the MV fluid is $\mu_2 = 81.1 \text{ mPa} \cdot \text{s}$, as summarised in Table 4.5.

The LV fluid was injected through jet 1 with $d_1 = 1.5$ mm, and the MV fluid dyed with rhodamine was injected through jet 2 with $d_2 = 1.5$ mm. Figure 4.20 to Figure 4.22 are the 2D concentration fields for the following Re conditions: $Re_2 = 45$, $Re_2 = 47$ and $Re_2 = 60$. These images show:

- At $Re_2 = 45$ (Figure 4.20), the flow has a typical segregated behaviour. The light lines that correspond to rhodamine microparticles enable to visualise the flow pathlines of the MV fluid. A vortex is formed downstream the impingement point at the right side of the mixing chamber, and another one is formed in the left side of the mixing chamber, although it is not so visible. A small perturbation seems to occur next to the interface, which is clearly observed from the light lines;
- At $Re_2 = 47$, Figure 4.21 shows that the flow is still segregated, but the oscillations at the interface are more evident. At this condition, the balance of jets occurs at a Re_{LV} of approximately five times Re_{MV} . This figure also shows that the pancake formation suffers a higher deviation from the mixing chamber axis to the headspace's left-hand side, compared to the previous cases. The sideward pancake formation promotes the creation of a larger vortex at the right side of the mixing chamber headspace;
- At $Re_2 = 60$, there is the onset of the self-sustainable chaotic flow, as shown in Figure 4.22. At this condition, the LV fluid has a Reynolds number seven times higher than at MV jet. The impingement point is easily observed from PLIF images, but the reduction of the lamellae structures is not so easily visualised due to the lack of sharpness of these images. These results show that the CIJ mixers are able to promote the efficient mixing of fluid with a viscosity ratio 1:9;

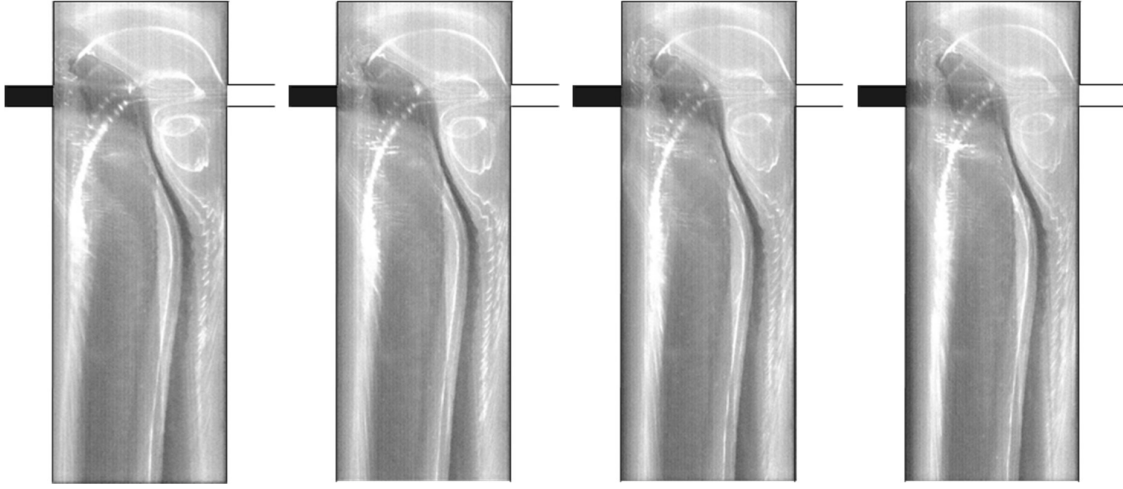


Figure 4.20 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:9: $\mu_1 = 9.1 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 81.1 \text{ mPa} \cdot \text{s}$, at $\text{Re}_1 = 244$ and $\text{Re}_2 = 45$, using Chamber 1.

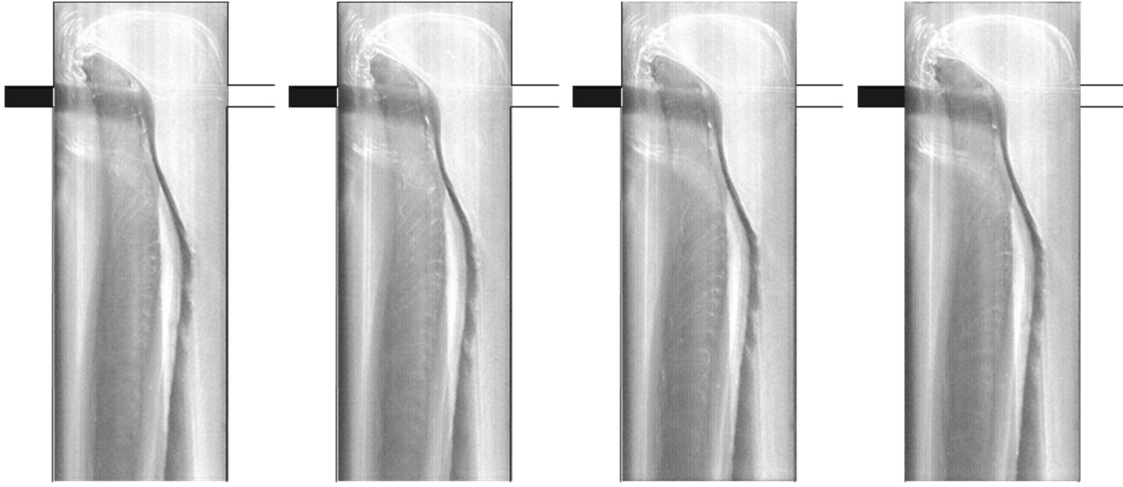


Figure 4.21 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:9: $\mu_1 = 9.1 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 81.1 \text{ mPa} \cdot \text{s}$, at $\text{Re}_1 = 263$ and $\text{Re}_2 = 47$, using Chamber 1.

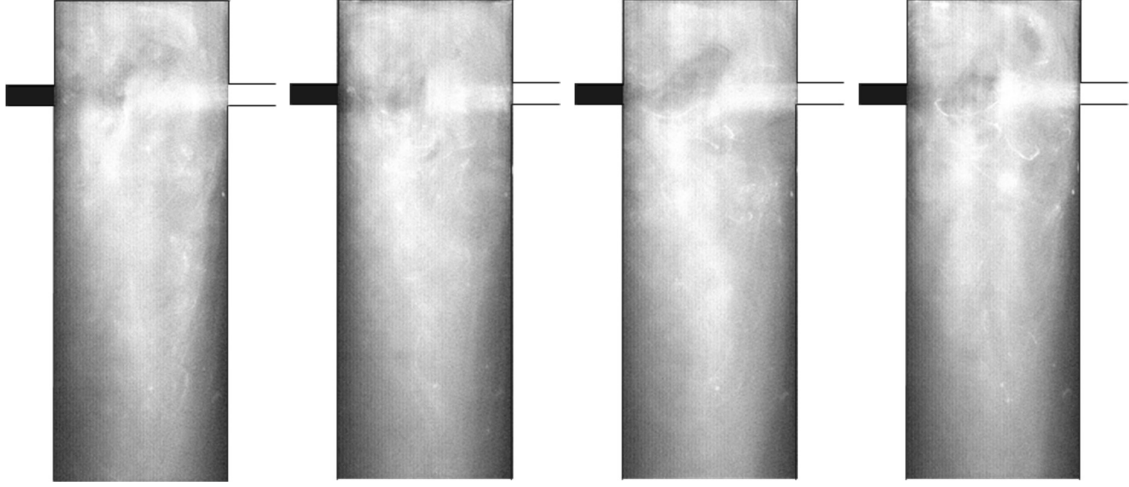


Figure 4.22 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:9: $\mu_1 = 9.1 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 81.1 \text{ mPa} \cdot \text{s}$, , at $\text{Re}_1 = 404$ and $\text{Re}_2 = 60$, using Chamber 1.

Table 4.6 summarises the conditions where the chaotic flow regimes were registered according to the previous PLIF images. The MV fluid sets the transition between flow regimes because smaller Re number is required for the engulfment of liquid streams. For viscosity ratio 2:1, the chaotic flow regime is detected at $\text{Re}_{\text{MV}} = 150$ and $\text{Re}_{\text{LV}} = 295$; for viscosity ratio 1:5, the same regime is visualised at $\text{Re}_{\text{MV}} = 70$ and $\text{Re}_{\text{LV}} = 250$; for 1:9, the chaotic regime is observed at $\text{Re}_{\text{MV}} = 60$ and $\text{Re}_{\text{LV}} = 404$. This means that the critical Reynolds number defined by the MV fluid may take any value $50 < \text{Re}_{\text{MV},c} < 150$ to ensure the self-sustainable chaotic flow regime. This characteristic Reynolds number is lower than the one set for symmetric flow conditions ($100 < \text{Re}_c < 150$) (Fonte et al., 2015).

Other authors have pointed out that the onset of mixing in CIJ mixers is determined from the conditions of MV fluid stream (Malguarnera and Suh, 1977; Nguyen and Suh, 1985). This evidence was generated from RIM experiments with actual reactive polymerisation system. Nevertheless, in these works, the jets balancing was not guaranteed, and the onset of mixing was observed indirectly from parameters as the

adiabatic temperature rise. This is the first work that addresses the onset of chaotic flow regimes in CIJ mixers for mixing of dissimilar fluids.

Table 4.6 Conditions for chaotic flow regime reported from PLIF images.

Viscosity ratio	μ	ρ	Re	r_s
2:1	$\mu_{LV} = 20 \text{ mPa}\cdot\text{s}$	$\rho_{LV} = 1176 \text{ kg m}^{-3}$	$\text{Re}_{LV} = 295$	$r_s = 1.02$
	$\mu_{MV} = 40 \text{ mPa}\cdot\text{s}$	$\rho_{MV} = 1208 \text{ kg m}^{-3}$	$\text{Re}_{MV} = 150$	
1:5	$\mu_{LV} = 9.2 \text{ mPa}\cdot\text{s}$	$\rho_{LV} = 1339 \text{ kg m}^{-3}$	$\text{Re}_{LV} = 250$	$r_s = 0.69$
	$\mu_{MV} = 47.8 \text{ mPa}\cdot\text{s}$	$\rho_{MV} = 1215 \text{ kg m}^{-3}$	$\text{Re}_{MV} = 70$	
1:9	$\mu_{LV} = 9.1 \text{ mPa}\cdot\text{s}$	$\rho_{LV} = 1371 \text{ kg m}^{-3}$	$\text{Re}_{LV} = 404$	$r_s = 0.76$
	$\mu_{MV} = 81.1 \text{ mPa}\cdot\text{s}$	$\rho_{MV} = 1217 \text{ kg m}^{-3}$	$\text{Re}_{MV} = 60$	

The flow rate ratios, r_s , for the onset of the chaotic flow regime are also listed in Table 4.6, according to each condition. The flow rate ratio was calculated from

$$r_s = \frac{\rho_1 d_1^2 v_{\text{inj},1}^2}{\rho_2 d_2^2 v_{\text{inj},2}^2} \quad (4.18)$$

The flow rate ratios in Table 4.6 show that $r_s = 1$ is not the condition that ensures the balance of jets. For high viscosity ratios, the balance occurs for $r_s \neq 1$. These results also indicate that the density ratio between jets, which is approximately 1 (Table 4.6), will not have an impact on the flow regime. Actually, this feature would not be so marked because the CIJ mixer is placed at the vertical position in the experimental setup.

The 2D concentration fields captured from the plane defined by the mixing chamber and injectors axes could be processed for qualitative flow analysis. Nevertheless, the lack of the precision in the visualisation of the lamellae evolution, more pronounced for

higher viscosity ratios (e.g. Figure 4.22), does not enable quantitative analysis, e.g. the estimation of the scale of segregation or the intensity of segregation.

4.4.2.2 Effect of the Imbalance of Jets on Mixing

The assessment of the imbalance of jets on mixing was performed by setting constant the Reynolds number of the MV fluid and changing the flow rate at LV jet. The displacement of the jets impingement point will be then observed at the mixing chamber. Fonte et al. (2015) reported that the jets impingement point displacement from the mixing chamber axis is proportional to the kinetic energy feeding rate ratio of the opposed jets, given by

$$\phi_K = \frac{\rho_1 d_1^2 v_{\text{inj},1}^3}{\rho_2 d_2^2 v_{\text{inj},2}^3} \quad (4.19)$$

The experimental conditions in this work are thus presented as a function of ϕ_K .

The conditions studied in this chapter were: viscosity ratio 2:1 using Chamber 1, viscosity ratio 1:5 using Chambers 1 and 2 and viscosity ratio 1:9 using Chamber 1.

Viscosity Ratio 2:1 – Chamber 1

For a viscosity ratio 2:1, four fixed Reynolds number at MV jet were tested 50, 100, 125 and 150. The white fluid is the MV fluid dyed with rhodamine and was injected from jet 1. The black fluid is the LV fluid, and was delivered by the right-hand side injector, jet 2. Figure 4.23 to Figure 4.26 show the PLIF images, obtained at the plane defined by the mixing chamber and injectors axes, for a viscosity ratio 2:1 at $\text{Re}_1 = 50$, $\text{Re}_1 = 100$, $\text{Re}_1 = 125$ and $\text{Re}_1 = 150$, and using Chamber 1, $d_1 = d_2$ (Table 4.1).

PLIF images in Figure 4.23 are obtained for $\text{Re}_1 = 50$ and ϕ_K goes from 0.1 to 10. When $\phi_K = 0.1$, the deviation of the left white jet towards the mixing chamber top is clear. This jet then circles around the opposed jet making this white liquid to appear

bellow the dark jet. In the CIJ mixing chamber headspace, only one large vortex is observed. When the flow rate of the right jet decreases, corresponding to $\phi_K = 0.2$, the jets impingement point is slightly shifted to the right, although the fluid from the left injector is still pushed into the left side of the chamber. The white jet is not deviated around the CIJ top walls as in Figure 4.23c, and so white fluid is now more confined into a single side of the mixer. Enough white fluid is being transported to the opposite side to create thin laminas that highlight the vortices on the right side of CIJ chamber. In a narrow range of kinetic rate ratios that correspond to $0.5 < \phi_K < 2$ (Figure 4.23c to Figure 4.23e), the jets impingement point is close to the mixing chamber axis. The flow patterns are similar to the ones observed for the steady-state flow regime obtained for CIJ mixers with jets having equal flow rates and viscosities. Note that figure for $\phi_K = 0.5$ corresponds to the experimental conditions of Figure 4.12.

Figure 4.24 shows the PLIF images for $Re_1 = 100$. The same overall flow behaviour described for the $Re_1 = 50$ is also observed for the $Re_1 = 100$. The main difference is the increase of the flow patterns instability when $\phi_K = 0.1$ and $\phi_K = 0.2$. For the cases $\phi_K = 0.1$ and $\phi_K = 0.2$, the right-hand side jet Reynolds numbers are 423 and 336, respectively, and at these ranges the jets upon impinging the opposed wall have some dynamic behaviours. For balanced flows, such as in Figure 4.24d, where the Reynolds numbers are $Re_1 = 100$ and $Re_2 = 197$ that corresponds to the conditions of Figure 4.13, the flow regime is steady and similar to the steady flow regimes obtained for equal fluids and flow rates, although the right-hand side jet is clearly above the critical Reynolds number for symmetric conditions.

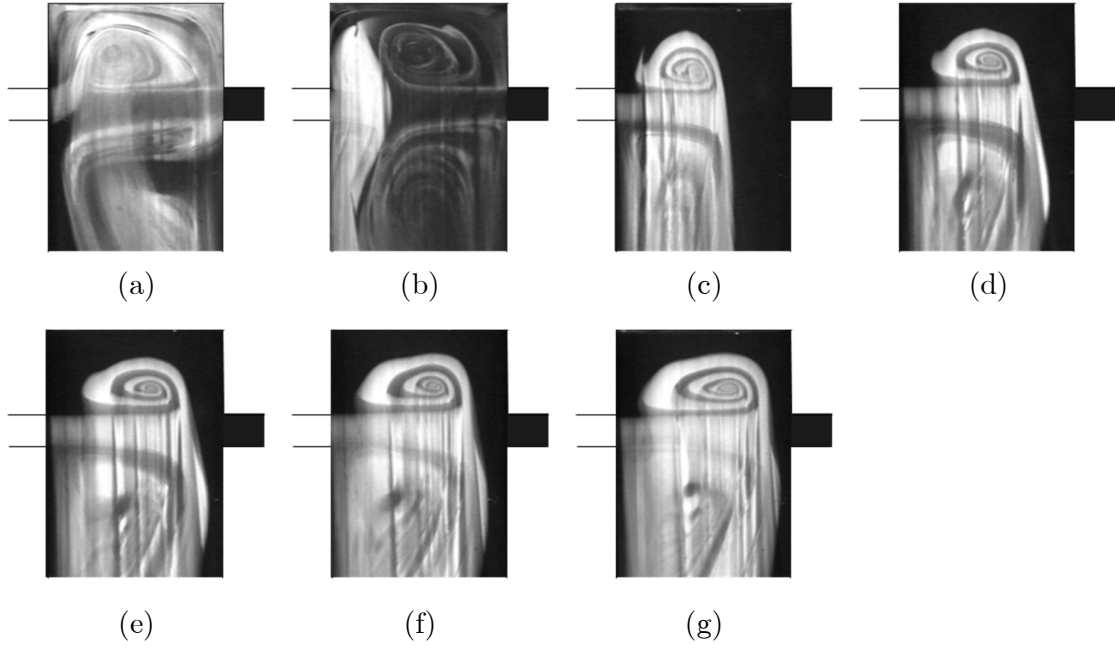


Figure 4.23 PLIF images for viscosity ratio 2:1 of fluid 1, $\mu_1 = 40 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 20 \text{ mPa} \cdot \text{s}$, at $\text{Re}_1 = 50$ using Chamber 1 and at (a) $\phi_K = 0.1$ ($\text{Re}_2 = 212$); (b) $\phi_K = 0.2$ ($\text{Re}_2 = 168$); (c) $\phi_K = 0.5$ ($\text{Re}_2 = 124$); (d) $\phi_K = 1$ ($\text{Re}_2 = 98$); (e) $\phi_K = 2$ ($\text{Re}_2 = 78$); (f) $\phi_K = 5$ ($\text{Re}_2 = 57$) and (g) $\phi_K = 10$ ($\text{Re}_2 = 46$).

PLIF experiments were also run in Chamber 1 for larger Reynolds numbers than 100, namely for $\text{Re}_1 = 125$ and $\text{Re}_1 = 150$. PLIF images at these conditions are displayed in Figure 4.25 and Figure 4.26, respectively. For these cases, ϕ_K values were set in the range $0.2 \leq \phi_K \leq 5$. At $\text{Re}_1 = 125$, the flow patterns are similar to those described for $\text{Re}_1 = 100$, see Figure 4.25. In Figure 4.26c, at $\phi_K = 1$, the flow is no longer the steady-state segregated flow, and the formation of self-sustainable chaotic regime promotes the formation of a lamellar structure by the continuous stretching and folding of fluids from two streams. For this condition, the flow rate ratio is $r_s = 1.01$. A more detailed description of the chaotic flow regime seen in Figure 4.26c was already made in Section 4.4.2.1 from the visualisation of Figure 4.15.

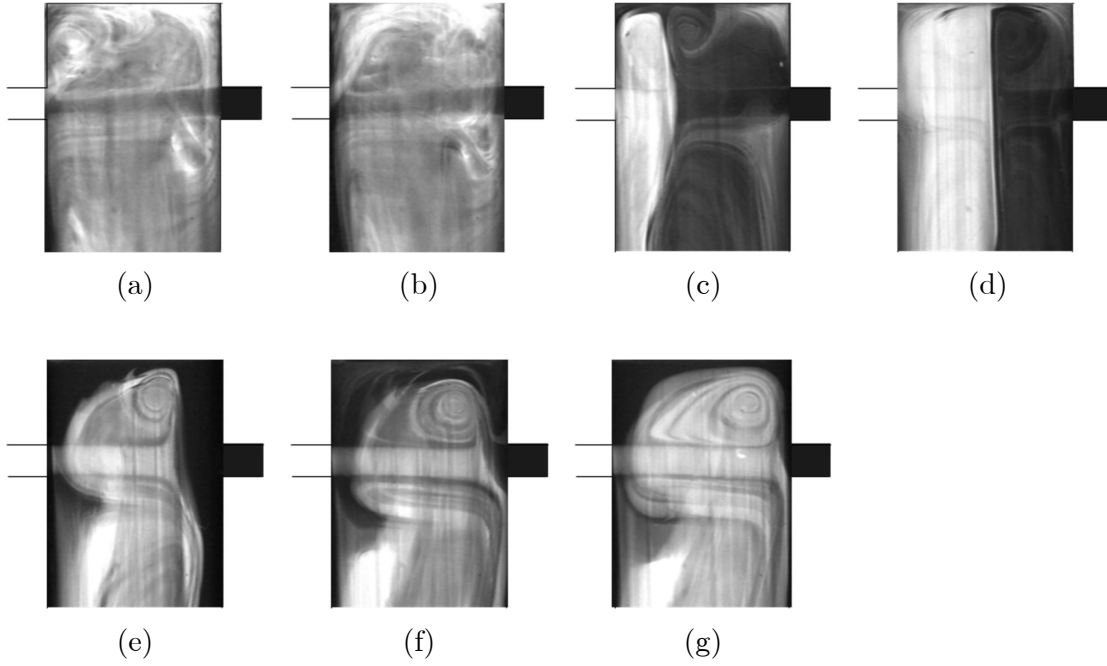


Figure 4.24 PLIF images for viscosity ratio 2:1 of fluid 1, $\mu_1 = 40 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 20 \text{ mPa} \cdot \text{s}$, at $\text{Re}_1 = 100$ using Chamber 1 and (a) $\phi_K = 0.1$ ($\text{Re}_2 = 423$); (b) $\phi_K = 0.2$ ($\text{Re}_2 = 336$); (c) $\phi_K = 0.5$ ($\text{Re}_2 = 248$); (d) $\phi_K = 1$ ($\text{Re}_2 = 197$); (e) $\phi_K = 2$ ($\text{Re}_2 = 156$); (f) $\phi_K = 5$ ($\text{Re}_2 = 115$) and (g) $\phi_K = 10$ ($\text{Re}_2 = 91$).

Figure 4.26c shows the ability of CIJ mixers to mix two dissimilar fluids with a viscosity ratio 2:1 when the opposite jets are balanced. For dissimilar fluids, the critical Reynolds number marking the onset of chaotic flow regimes is given by the jet with the lower Reynolds number, which is in the range of values known for CIJ mixers operating at symmetric conditions.

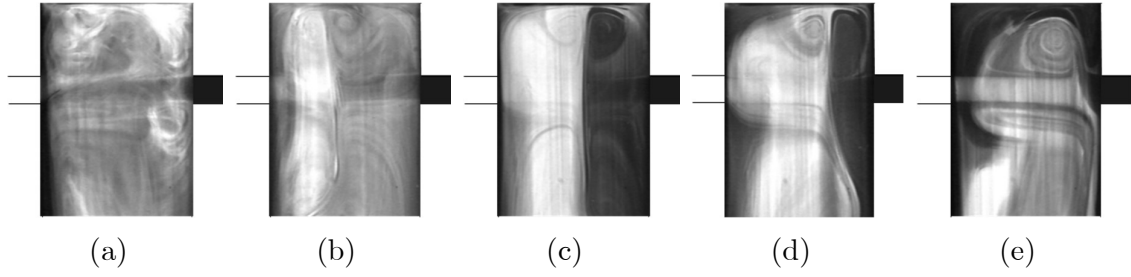


Figure 4.25 PLIF images for viscosity ratio 2:1 of fluid 1, $\mu_1 = 40 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 20 \text{ mPa} \cdot \text{s}$, for $\text{Re}_1 = 125$ using Chamber 1 and at (a) $\phi_K = 0.2$ ($\text{Re}_2 = 420$); (b) $\phi_K = 0.68$ ($\text{Re}_2 = 279$); (c) $\phi_K = 1$ ($\text{Re}_2 = 246$); (d) $\phi_K = 2$ ($\text{Re}_2 = 195$) and (e) $\phi_K = 5$ ($\text{Re}_2 = 144$).

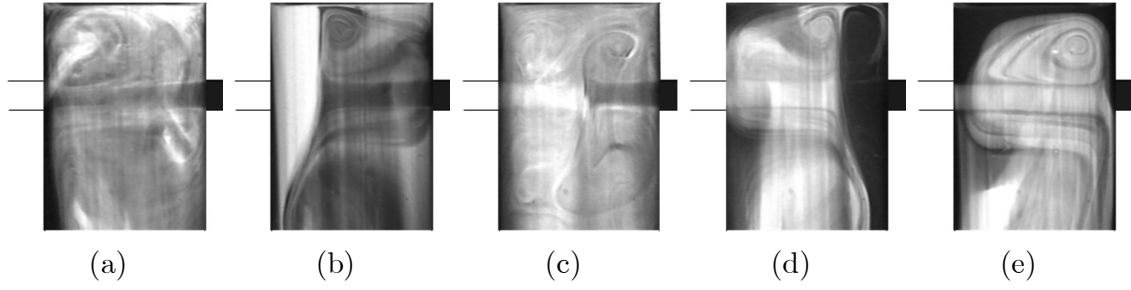


Figure 4.26 PLIF images for viscosity ratio 2:1 of fluid 1, $\mu_1 = 40 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 20 \text{ mPa} \cdot \text{s}$, for $\text{Re}_1 = 150$ using Chamber 1 and at (a) $\phi_K = 0.2$ ($\text{Re}_2 = 504$); (b) $\phi_K = 0.5$ ($\text{Re}_2 = 371$); (c) $\phi_K = 1$ ($\text{Re}_2 = 295$); (d) $\phi_K = 2$ ($\text{Re}_2 = 234$) and (e) $\phi_K = 5$ ($\text{Re}_2 = 172$).

Viscosity Ratio 1:5 – Chamber 1

For a viscosity ratio 1:5, three fixed Reynolds number at MV jet were tested: 50, 66 and 70. LV fluid was injected through the left-hand side injector and MV fluid dyed with rhodamine through the right-hand side injector. Figure 4.27 to Figure 4.29 show the PLIF images, obtained at the plane defined by the mixing chamber and injectors axes, for a viscosity ratio 1:5 at $\text{Re}_2 = 50$, $\text{Re}_2 = 66$ and $\text{Re}_2 = 70$ using Chamber 1.

PLIF images in Figure 4.27 are obtained for a fixed $\text{Re}_2 = 50$ and ϕ_K goes from 0.07 to 0.64. The studied range of ϕ_K is narrower than for a viscosity ratio 2:1, but it permits to observe the complete shifting of the jets impingement point through the entire mixing chamber. This means that the two jets system is more sensitive to the flow rate

ratios for higher viscosity ratio. When $\phi_K = 0.07$, the black jet is pushed by the white fluid to the top wall of the mixing chamber. This is caused by the higher flow rate at MV jet. For $\phi_K = 0.10$, small perturbations are created at the interface in the headspace of the mixing chamber. However, no further mixing dynamics are observed.

Further increase in Re_{LV} promotes the displacement of the impingement point to the right side of the mixing chamber. The balance of jets occurs in a range $0.18 < \phi_K < 0.42$ ($0.55 < r_s < 0.73$), and at these conditions, the flow is steady and segregated, as also shown in Figure 4.16. It is also observed that a larger vortex is formed upstream the injectors axis at the right side of the mixing chamber, creating a deviation of the pancake to the left side of the chamber upstream the impingement point.

For $\phi_K > 0.42$, an upper vortex in the headspace of the chamber is created and engulfs the white and dark fluids.

For a fixed $Re_2 = 66$ (Figure 4.28), ϕ_K was studied in a range between 0.17 and 1.12. The increase of ϕ_K is associated to the rise of the dark jet flow rate and the displacement of the impinging jet point from left to right. Images clearly show that the balance of jets occurs for $\phi_K \approx 0.28$ (Figure 4.28b), and the flow rate ratio is $r_s = 0.68$. For lower ϕ_K values, MV fluid pushes the dark fluid towards the left sidewalls, shifting then the impingement point to the left-hand side of the mixing chamber. For higher ϕ_K values, the jets point impingement is shifted to the right, and upper vortices are formed in the mixing chamber. These dynamic structures promote the engulfment of the two fluids streams in the headspace of the chamber.

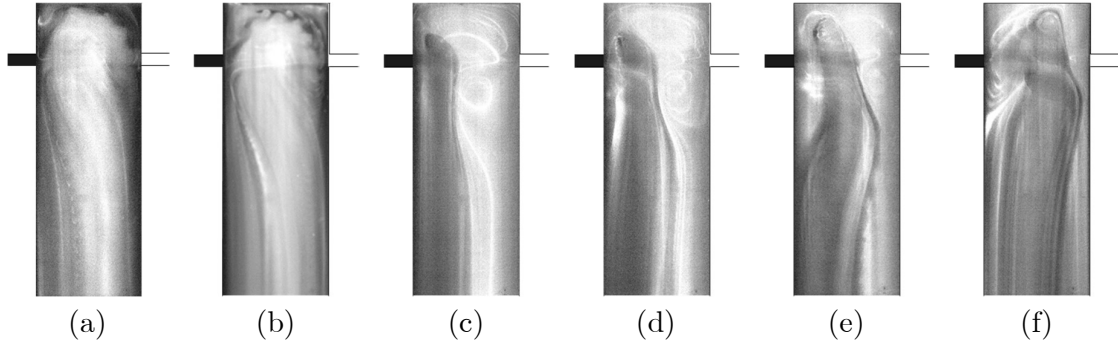


Figure 4.27 PLIF images for a viscosity ratio 1:5 of fluid 1, $\mu_1 = 9.2 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 47.8 \text{ mPa} \cdot \text{s}$, at $\text{Re}_2 = 50$ using Chamber 1 and at (a) $\phi_K = 0.07$ ($\text{Re}_1 = 114$); (b) $\phi_K = 0.10$ ($\text{Re}_1 = 125$); (c) $\phi_K = 0.18$ ($\text{Re}_1 = 154$); (d) $\phi_K = 0.20$ ($\text{Re}_1 = 154$); (e) $\phi_K = 0.42$ ($\text{Re}_1 = 211$); (f) $\phi_K = 0.64$ ($\text{Re}_1 = 248$).

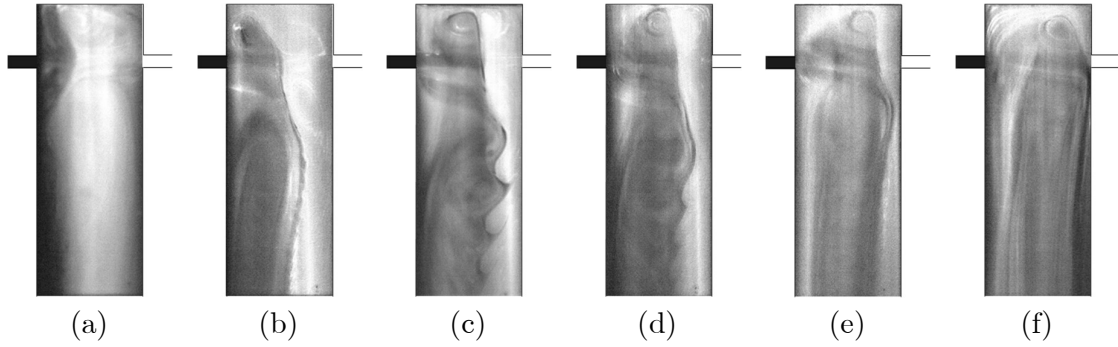


Figure 4.28 PLIF images for a viscosity ratio 1:5 of fluid 1, $\mu_1 = 9.2 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 47.8 \text{ mPa} \cdot \text{s}$, at $\text{Re}_2 = 66$ using Chamber 1 and at (a) $\phi_K = 0.17$ ($\text{Re}_1 = 201$); (b) $\phi_K = 0.28$ ($\text{Re}_1 = 238$); (c) $\phi_K = 0.38$ ($\text{Re}_1 = 267$); (d) $\phi_K = 0.45$ ($\text{Re}_1 = 279$); (e) $\phi_K = 0.66$ ($\text{Re}_1 = 321$); (f) $\phi_K = 1.12$ ($\text{Re}_1 = 380$).

The ϕ_K range studied for a fixed $\text{Re}_2 = 70$ goes from 0.08 to 0.73 (Figure 4.29). At very low ϕ_K as $\phi_K = 0.08$, it is observed a perturbation at the interface when the dark jet is deflected towards the headspace, which is also visualised for lower Re_2 (e.g. Figure 4.27b). When the two jets are still imbalanced, small oscillations are created downstream the impingement point, as shown in Figure 4.29b, and upper vortices are created in the headspace of the chamber. However, self-sustainable chaotic flow regime only onsets for balanced flow conditions, at $\phi_K \approx 0.27$ and $r_s \approx 0.62$ (Figure 4.29c). At

this condition, the fluid streams are engulfed, and the generated lamellar structure of fluids are clearly stretched over the mixing chamber. The chaotic flow regime is also observed at $\phi_K = 0.41$, but the mixing is quite more efficient at the centre of the chamber ($\phi_K = 0.27$) because vortices are able to engulf both fluids over the entire chamber.

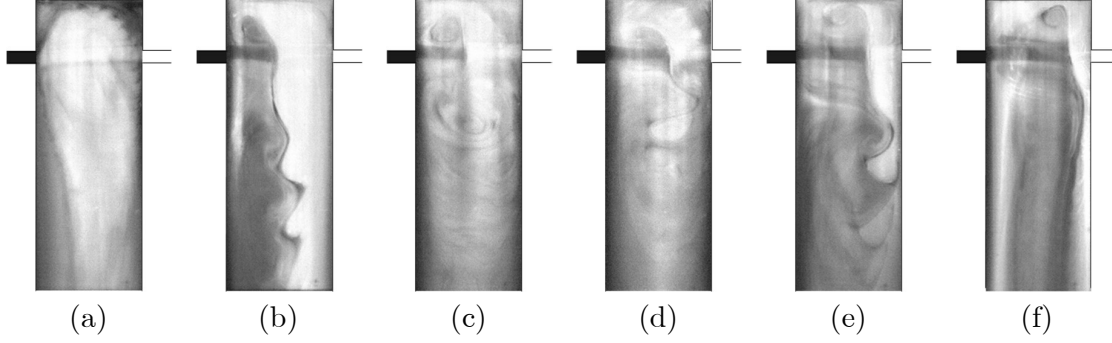


Figure 4.29 PLIF images for a viscosity ratio 1:5 of fluid 1, $\mu_1 = 9.2 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 47.8 \text{ mPa} \cdot \text{s}$, at $\text{Re}_2 = 70$ using Chamber 1 and at (a) $\phi_K = 0.08$ ($\text{Re}_1 = 168$); (b) $\phi_K = 0.24$ ($\text{Re}_1 = 243$); (c) $\phi_K = 0.27$ ($\text{Re}_1 = 250$); (d) $\phi_K = 0.41$ ($\text{Re}_1 = 289$); (e) $\phi_K = 0.47$ ($\text{Re}_1 = 303$); (f) $\phi_K = 0.73$ ($\text{Re}_1 = 350$).

Results for a viscosity ratio 1:5 show that the mixing quality is highly affected by the balance of jets as a consequence of the displacement of the impinging jets from the mixing chamber axis. The conditions for the balance of jets corresponds to $r_s < 1$, due to the dissimilarities of fluids viscosities.

Viscosity Ratio 1:9 – Chamber 1

Figure 4.30 to Figure 4.32 show randomly chosen images of the concentration fields for viscosity ratio 1:9 at selected values of ϕ_K . A fixed Reynolds number was set in the MV liquid stream, $\text{Re}_2 = 45$, $\text{Re}_2 = 47$ and $\text{Re}_2 = 56$ and using Chamber 1. MV fluid dyed with rhodamine was injected from jet 2 and LV fluid through jet 1.

The fixed Reynolds number $\text{Re}_2 = 45$ (Figure 4.30) was studied for a range of ϕ_K between 0.16 and 0.64. The balance of jets occurs at $\phi_K \approx 0.18$, which corresponds to $r_s = 0.54$. Figure 4.30a and Figure 4.30b show that a relative deviation of 11% in ϕ_K , in relation to the larger value, promotes a strong shifting of the jets impingement point

position. This means that for higher viscosity ratios, small changes in the flow rate ratio result in a strong deviation of the jets impingement point, affecting the effective performance of mixing in CIJ mixers. The shifting of the pancake at the impingement point to the left side of the headspace is still more pronounced, mainly for lower ϕ_K values, compared to that observed for viscosity ratio 1:5. At $\phi_K = 0.64$, the contact point is diverted to the right side of the mixing chamber and vortices are created in the headspace.

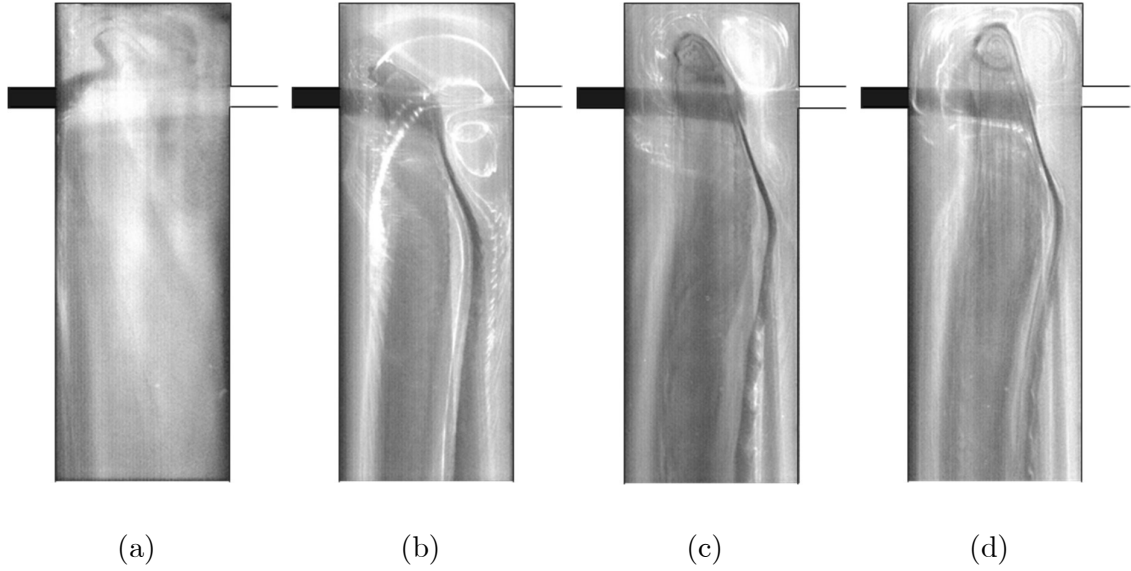


Figure 4.30 PLIF images for a viscosity ratio 1:9 of fluid 1, $\mu_1 = 9.1 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 81.1 \text{ mPa} \cdot \text{s}$, for $\text{Re}_2 = 45$ using Chamber 1 and at (a) $\phi_K = 0.16$ ($\text{Re}_1 = 235$); (b) $\phi_K = 0.18$ ($\text{Re}_1 = 244$); (c) $\phi_K = 0.35$ ($\text{Re}_1 = 302$); (d) $\phi_K = 0.64$ ($\text{Re}_1 = 379$).

For $\text{Re}_2 = 47$ (Figure 4.31), four ϕ_K values were set 0.15, 0.19, 0.33 and 0.39. These images show that a slight change in ϕ_K has a strong impact on the jets impingement point position, causing large displacements from the centre. The balance of the opposed jets occurs at $\phi_K \approx 0.18$, which corresponds to $r_s = 0.55$. Nevertheless, at these conditions, it is not possible to achieve the self-sustainable chaotic flow regime.

Concentration field images for a $Re_2 = 56$ are displayed in Figure 4.32 for a ϕ_K range from 0.16 and 0.40. The jets impinging jets position is at the centre of the mixing chamber at $\phi_K \approx 0.24$ and $r_s \approx 0.60$.

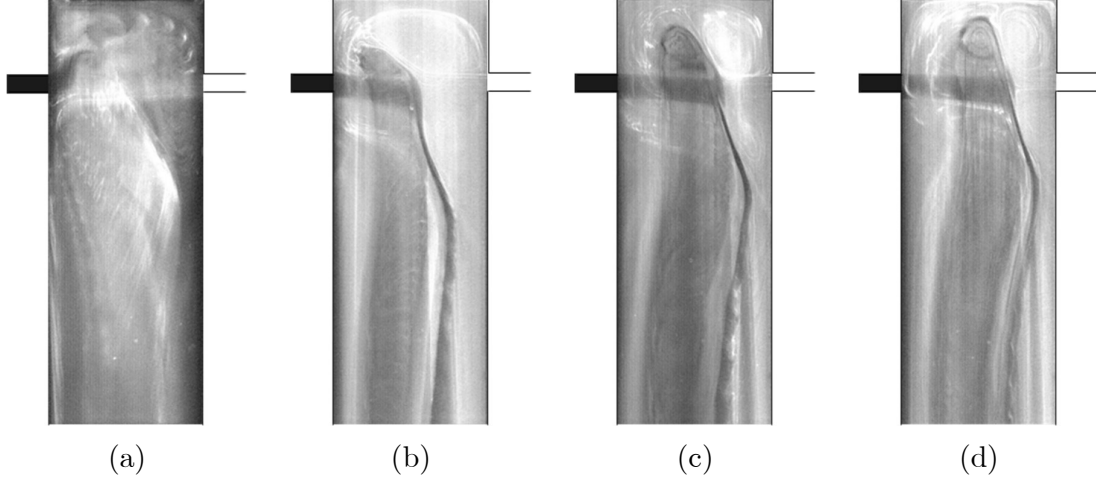


Figure 4.31 PLIF images for a viscosity ratio 1:9 of fluid 1, $\mu_1 = 9.1 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 81.1 \text{ mPa} \cdot \text{s}$, for $Re_2 = 47$ using Chamber 1 and at (a) $\phi_K = 0.15$ ($Re_1 = 242$); (b) $\phi_K = 0.19$ ($Re_1 = 263$); (c) $\phi_K = 0.33$ ($Re_1 = 314$); (d) $\phi_K = 0.39$ ($Re_1 = 332$).

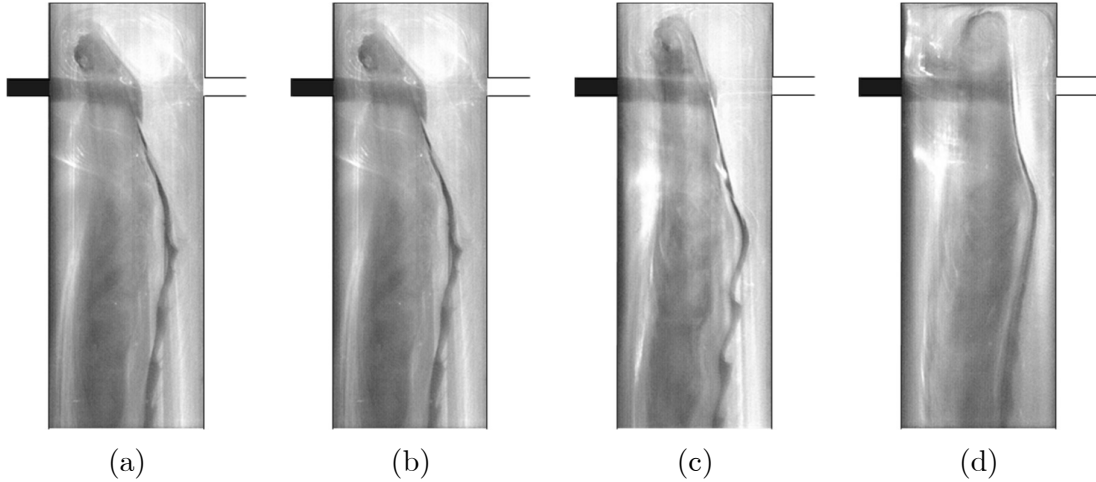


Figure 4.32 PLIF images for a viscosity ratio 1:9 of fluid 1, $\mu_1 = 9.1 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 81.1 \text{ mPa} \cdot \text{s}$, for $Re_2 = 56$ using Chamber 1 and at (a) $\phi_K = 0.16$ ($Re_1 = 292$); (b) $\phi_K = 0.24$ ($Re_1 = 338$); (c) $\phi_K = 0.30$ ($Re_1 = 365$); (d) $\phi_K = 0.40$ ($Re_1 = 401$).

The shifting of the impingement point position over the injectors axis at chaotic flow regime is not presented in this chapter for a viscosity ratio 1:9. Nevertheless, the balance conditions to the onset of the self-sustainable chaotic flow regime were captured in Figure 4.22, at $Re_1 = 404$ and $Re_2 = 60$. Images in Figure 4.22 indicate that the balance of jets is the key condition for the onset of effective mixing.

Viscosity Ratio 1:5 – Chamber 2

Flow dynamics for a viscosity 1:5 was also studied using another CIJ geometry that corresponds to Chamber 2 in Table 4.1. This geometry is characterized by different injector diameters, $d_1 = 1.5$ mm and $d_2 = 1.9$ mm. In these experiments, the LV fluid (dark fluid) is injected through jet 1 and the MV fluid dyed with rhodamine (white fluid) through jet 2 with a larger diameter. The physical properties of each stream are $\mu_{LV} = 9.5$ mPa · s, $\rho_{LV} = 1339$ kg m⁻³, $\mu_{MV} = 48.0$ mPa · s and $\rho_{MV} = 1285$ kg m⁻³.

Experiments were tested at $Re_2 = 46$ and $Re_2 = 71$. The white jet was then adjusted for four ϕ_K values for each condition. Figure 4.33 and Figure 4.34 show the PLIF images for $Re_2 = 46$ and $Re_2 = 71$ respectively, and for a ϕ_K range between 0.17 and 0.76. The flow remains segregated at both conditions, and no mixing dynamics are generated in the CIJ mixing chamber.

Flow patterns in Figure 4.33 and Figure 4.34 are similar to those observed in Chamber 1 (Figure 4.27 and Figure 4.28). In both cases, the formation of a large vortex at the right side of the headspace diverges the pancake to the opposite side for low kinetic energy feeding rate ratios. For higher ϕ_K values, a more pronounced vortex engulfs both streams in the headspace. For these cases, it is observed that the white fluid flows from jet 2 and then appears next to the left sidewalls. This will be analysed later from CFD simulations in Section 4.5.

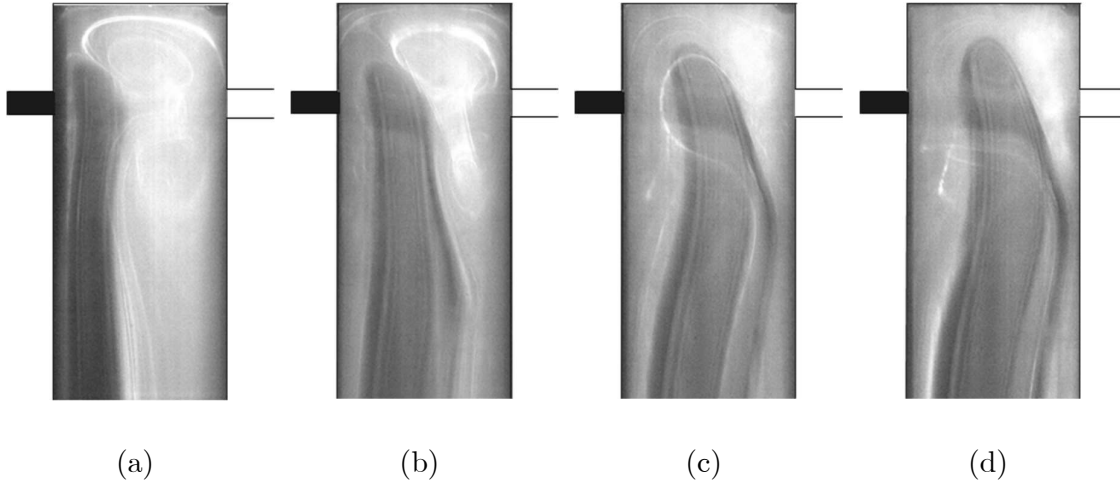


Figure 4.33 PLIF images for a viscosity ratio 1:5 of fluid 1, $\mu_1 = 9.5 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 48.0 \text{ mPa} \cdot \text{s}$, at $\text{Re}_2 = 46$ using Chamber 2 and at (a) $\phi_K = 0.17$ ($\text{Re}_1 = 123$); (b) $\phi_K = 0.35$ ($\text{Re}_1 = 156$); (c) $\phi_K = 0.61$ ($\text{Re}_1 = 183$); (d) $\phi_K = 0.76$ ($\text{Re}_1 = 213$).

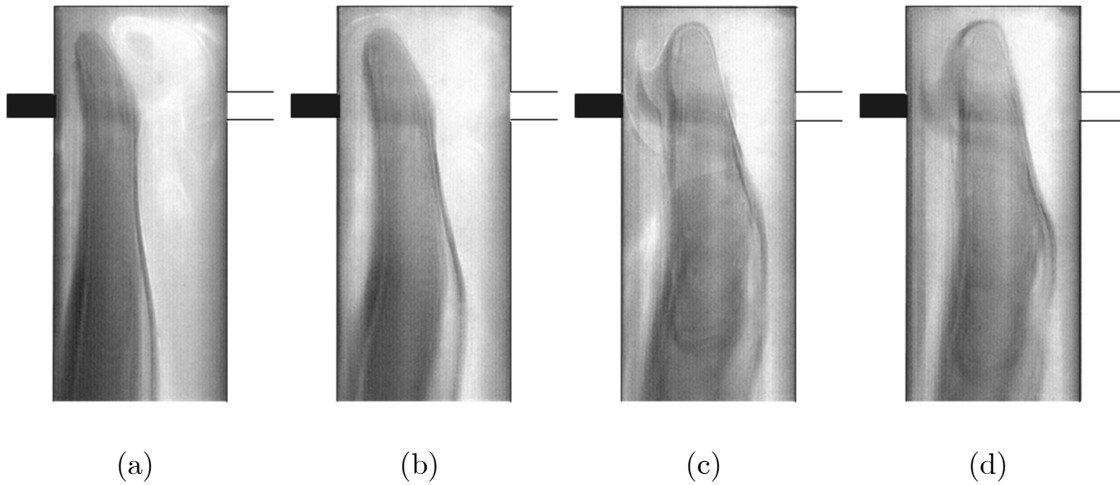


Figure 4.34 PLIF images for a viscosity ratio 1:5 of fluid 1, $\mu_1 = 9.5 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 48.0 \text{ mPa} \cdot \text{s}$, at $\text{Re}_2 = 71$ using Chamber 2 and at (a) $\phi_K = 0.41$ ($\text{Re}_1 = 258$); (b) $\phi_K = 0.51$ ($\text{Re}_1 = 272$); (c) $\phi_K = 0.66$ ($\text{Re}_1 = 297$); (d) $\phi_K = 0.74$ ($\text{Re}_1 = 309$).

Images of the self-sustainable chaotic flow regime were acquired at $\text{Re}_1 = 350$ and $\text{Re}_2 = 86$ in Chamber 2 for a viscosity ratio 1:5, as shown in Figure 4.35. These images

show the Reynolds number of MV fluid clearly sets the efficient mixing, and the balance of the jets is the crucial condition for effective mixing in CIJ mixers.

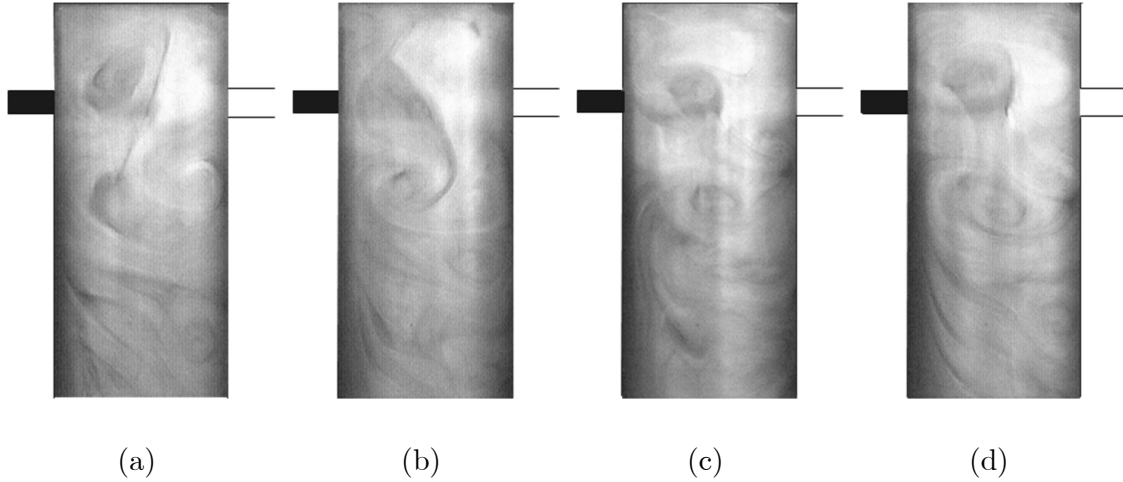


Figure 4.35 Instantaneous 2D concentration fields at the top of the mixing chamber for Chamber 2 and a viscosity ratio 1:5: $\mu_1 = 9.5 \text{ mPa} \cdot \text{s}$, and fluid 2, $\mu_2 = 48.0 \text{ mPa} \cdot \text{s}$, at $\text{Re}_1 = 350$ and $\text{Re}_2 = 86$.

Experimental results presented in this thesis clearly show that CIJ mixers are able to efficiently mix fluids with different viscosities at non-unitary flow rate ratios. The operation at chaotic flow regime is a necessary condition for CIJ mixers efficient operation, and the jets Reynolds number is the key parameter (Malguarnera and Suh, 1977; Lee et al., 1980; Tucker and Suh, 1980). The balance of jets also plays an important role in the onset of the self-sustainable chaotic flow; this has been clearly demonstrated by Fonte et al. (2015) for symmetric flow conditions. These results indicate that mixing in CIJ mixers running at laminar flow regimes with dissimilar fluids, is largely dependent on keeping and maximizing the natural chaotic oscillation of the two jets at the impingement point, as observed for similar fluids in Fonte et al. (2015).

The operation of CIJ mixers at balanced flow conditions is of utmost importance in the industry, for instance, in processes involving polymerisation reactions. The imbalance

of jets results in an inefficient mixing and polymer formation close to the inlet nozzles, bringing clogging problems due to the fast polymerization.

Results on mixing of dissimilar fluids with viscosity ratio of 2 were already published in Brito et al. (2018).

4.5 Part III: Impingement Point Interaction for Effective Mixing

The operation at chaotic flow regimes is of the utmost importance in applications, such as RIM machines, where the monomers must be mixed into a thin enough lamella for reaction to be only limited by diffusion after the mixing chamber (Ranz, 1986). The onset of chaotic flow regime in CIJ mixers strongly depends on the adequate conditions to promote the impinging jets oscillation, and the formation of dynamic structures that ensures the engulfment of the two liquid streams injected in CIJ mixers.

The critical Reynolds number that marks the transition between the segregated flow regime and the self-sustainable chaotic flow regime has a strong impact on effective mixing. However, even for a Reynolds number higher than the critical one, distinguishing physical properties of liquid streams or small deviation in the flow rate cause poor mixing. This was clearly shown by Fonte et al. (2016) for similar fluids and in the last section for dissimilar fluids.

The description of the contact point between streams becomes imperative to the design of RIM processes. Fonte et al. (2016) developed the elastic analogue model, which describes the impingement of jets in a CIJ mixer, which accounts the geometrical mixer parameters and the fluid physical properties of fluids. The validation of this model was made for ratios of flow rate and different geometrical parameters (Fonte et al., 2016), but never for mixing of dissimilar fluids. The validation of this model enables to use it on the design of CIJ mixers with directly opposite jets, impinging at mixing chamber axis, for fluids with different viscosities.

In this thesis, the prediction of the opposed jets impingement point position is extended to the case of dissimilar fluids comprising a viscosity ratio range between 2 and 9. Three models able to describe the jets impingement point position are presented in this section. The elastic analogue model proposed by Fonte et al. (2016), and two new models are also introduced in this chapter. One is based on the balance of kinetic energy at the impingement point position, and the other considers the equilibrium of the linear momentum of jets at the contact point. The validation of the model applicability for dissimilar fluids is based on 3D CFD simulations validated from the PLIF experimental data described in the previous section.

4.5.1 Models for Impingement Point Prediction

4.5.1.1 Analogue Elastic Model

Flow visualisations in Fonte et al. (2015) report a dramatic effect of r_s for mixing of similar fluids. For the maximum deviation from $r_s = 1$ of 15%, the jets are completely pushed into one of the injectors, creating a great clogging problem in industrial RIM machines due to the fast polymerization next to the inlet nozzles. Alternative techniques to make CIJ mixers operation more robust are based on the control of the static pressure difference between the opposed jets (Erkoç et al., 2007; Gomes et al., 2016), which enables to control the jets balancing in real time. This technology is not yet introduced in commercial RIM machines and would not overcome the limitation associated to the mixing of fluids with different flow rates.

Figure 4.36 shows a schematic drawing of 2D CIJ mixers. This sketch illustrates the impingement point position in the mixing chamber.

Fonte et al. (2016) described the impingement point position assuming that the jets act as springs of equal force $F = kl$, where k is the spring constant and l is the spring length variation. The model gets its name, elastic analogue model, from the spring analogy. The variation of the potential energy of each jet is proportional to the jets

displacement from the mixing chamber axis, $\Delta E_p = kl^2$. Thus, the potential energy of each jet is determined from the length of each jet, l_1 and l_2 , as illustrated in Figure 4.36. The ratio of the opposed jets potential energy is proportional to the ratio of the jets kinetic energy rate, $\dot{E}_{K,1} / \dot{E}_{K,2} = l_1 / l_2$, and so the jets impingement point displacement is proportional to the kinetic energy feeding rate ratio of the opposed jets (Equation (4.19)).

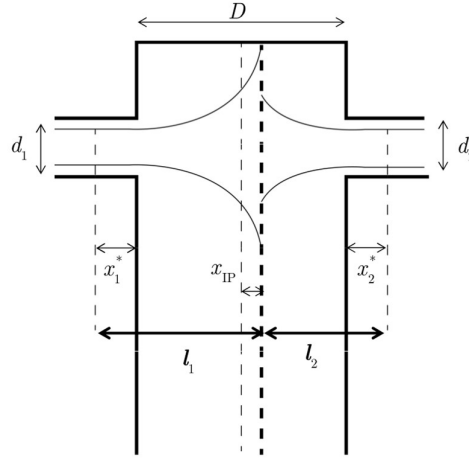


Figure 4.36 Sketch of the impingement point in the front view CIJ mixing chamber and the respective representation of x_1^* , x_2^* , D , d_1 , d_2 , l_1 , l_2 and x_{IP} .

Fonte et al. (2016) introduced a correction for the energy dissipation in each jet using the model of a narrow axisymmetric jet (NAJ) due to viscous effects. The axial velocity of jets according to the NAJ model is,

$$v(x, r) = \frac{3J}{8\pi\mu x} \left[1 + \frac{1}{4} \left(\frac{C_{\text{int}} r}{x} \right)^2 \right]^{-2} \quad (4.20)$$

where J is the fed jet momentum rate, $J = (\pi / 3) \rho v_{\text{inj}}^2 d^2$, C_{int} is an integration constant $C_{\text{int}} = \sqrt{3\rho J / (16\pi\mu^2)}$, r is the radial coordinate and x is the axial coordinate. NAJ model introduces viscosity related terms, namely the jets Reynolds numbers, in the elastic analogue model for the prediction of the jets impingement point

displacement from the mixing chamber axis, x_{IP} (see Figure 4.36). Considering NAJ, the jets impingement point position relation (l_1 / l_2) is given by

$$\frac{\dot{E}_{K,1}}{\dot{E}_{K,2}} = \frac{l_1}{l_2} = \frac{\int_0^\infty \nu_1(l_1, r)^3 2\pi\rho_1 r dr}{\int_0^\infty \nu_2(l_2, r)^3 2\pi\rho_2 r dr} = \sqrt{\phi_K \frac{\text{Re}_1 d_1}{\text{Re}_2 d_2}} \quad (4.21)$$

NAJ model assumes a momentum source, represented by x_1^* and x_2^* in Figure 4.36, that is placed at a distance $x^* = \text{Re} d / 20$ (Fonte et al., 2016) before the inlet, and so

$$\frac{D / 2 + x_{\text{IP}} + x_1'}{D / 2 + x_{\text{IP}} + x_2'} = \sqrt{\phi_K \frac{\text{Re}_1 d_1}{\text{Re}_2 d_2}} \quad (4.22)$$

where x_{IP} is the jets impingement point displacement. From the dimensionless impingement point position as shown in Figure 4.36, $\xi = x_{\text{IP}} / (D / 2)$, and considering $x^* = \text{Re} d / 20$, Equation (4.22) results in

$$\xi = \frac{\sqrt{\phi_K \frac{\text{Re}_1 d_1}{\text{Re}_2 d_2}} \left(1 + \frac{\text{Re}_2 d_2}{10 D} \right) - \left(1 + \frac{\text{Re}_1 d_1}{10 D} \right)}{\sqrt{\phi_K \frac{\text{Re}_1 d_1}{\text{Re}_2 d_2}} + 1} \quad (4.23)$$

Equation (4.23) enables to design CIJ mixers for mixing at non-unitary flow rate ratios, $r_s \neq 1$, by changing the diameter of the nozzles so that $\xi = 0$. The full derivation of the model, the validation, and the application to the design of CIJ mixers with $r_s \neq 1$ for similar fluids was made in Fonte et al. (2016).

The elastic analogue model, Equation (4.23), accounts the differences in the fluid viscosities that indicate the viscosity also plays a role in the jets equilibrium condition. The differences of the viscosities for liquids are taken into account in the Reynolds number term (Re_1 and Re_2) of Equation (4.23).

4.5.1.2 Kinetic Energy Model

A new model is here introduced for the description of the impingement point position in CIJ mixing chambers. This model considers that the kinetic energy of both jets at the impingement point (at $r = 0$ and $l = [l_1, l_2]$) are balanced. Hereupon, the equilibrium between the kinetic energy at the impingement point is determined considering a Lagrangian entity belonging to each jet,

$$\rho_1 v_{\text{inj},1}^2(l_1, r = 0) = \rho_2 v_{\text{inj},2}^2(l_2, r = 0) \quad (4.24)$$

where $v_{\text{inj},1}$ and $v_{\text{inj},2}$ are the velocities at impingement point position described by the NAJ model (Equation (4.20)).

The point source of momentum assumed by the NAJ model corresponds to the position in the injector where the axial velocity, $u(x, r = 0)$, is equal to the maximum velocity achieved in the injector. Considering a fully developed parallel parabolic velocity profile along the injectors and equalizing to the NAJ model, the point source is $x^* = \text{Re } d / 16$.

The replacement of $v_{\text{inj},1}(l_1, r = 0)$ and $v_{\text{inj},2}(l_2, r = 0)$ by the NAJ model in Equation (4.24) results in

$$\rho_1 \left(\frac{3J_1}{8\pi\mu_1 l_1} \right)^2 = \rho_2 \left(\frac{3J_2}{8\pi\mu_2 l_2} \right)^2 \quad (4.25)$$

According to Figure 4.36, the expression for each jet length, l_1 and l_2 , can be rewritten as a function of the momentum sources, x_1^* and x_2^* , and the impingement point position, x_{IP} , as

$$\begin{cases} l_1 = x_1^* + \frac{D}{2} + x_{\text{IP}} \\ l_2 = x_2^* + \frac{D}{2} - x_{\text{IP}} \end{cases} \quad (4.26)$$

The jet lengths can be rewritten in Equation (4.25) according to Equation (4.26), where x_1^* and x_2^* are the source points given by $x^* = \text{Re} d / 16$,

$$\frac{\rho_1^{1/2} J_1}{\mu_1 \left(\frac{D}{2} + x_{IP} + \frac{\text{Re}_1 d_1}{16} \right)} = \frac{\rho_2^{1/2} J_2}{\mu_1 \left(\frac{D}{2} - x_{IP} + \frac{\text{Re}_2 d_2}{16} \right)} \quad (4.27)$$

From Equation (4.27), a dimensionless impingement point position $\xi = x_{IP} / (D / 2)$ can be estimated according to

$$\xi = \frac{\left[\frac{\rho_1^{1/2}}{\rho_2^{1/2}} \phi_M \frac{\mu_2}{\mu_1} \right] \left(1 + \frac{\text{Re}_2 d_2}{8 D} \right) - \left(1 + \frac{\text{Re}_1 d_1}{8 D} \right)}{\frac{\rho_1^{1/2}}{\rho_2^{1/2}} \phi_M \frac{\mu_1}{\mu_2} + 1} \quad (4.28)$$

where $\phi_M = J_1 / J_2$ is the momentum rate ratio of jets. In Equation (4.28), ξ can take values from -1 to 1 because the jets contact in the chamber are bounded by walls and cannot expand up to the position of the momentum source points, which are place at the injectors.

The kinetic energy model described in Equation (4.28) considers that the impingement point position is fully described by the balance of kinetic energy of two passive particles at the jets contact point. This model also accounts the viscosity of fluids, considered in Re_1 and Re_2 , and the geometrical parameters of CIJ mixers. The main difference between the elastic analogue model and kinetic energy model stems from the fact that the first one assumes the balance of the kinetic energy rate of both jets from an analogy to two springs. In contrast, the second one refers to the equilibrium of the kinetic energy from two particles at the impact point position.

4.5.1.3 Momentum Model

A new approach is also introduced for the prediction of the impingement point position. The momentum model is based on the balance of the linear momentum of two particles,

issued from opposed jets, at the impingement point, i.e. at $r = 0$ and $l = [l_1, l_2]$. This balance is described by

$$\rho_1 v_{\text{inj},1}(l_1, r = 0) = \rho_2 v_{\text{inj},2}(l_2, r = 0) \quad (4.29)$$

where $v_{\text{inj},1}$ and $v_{\text{inj},2}$ are predicted by the NAJ model (Equation (4.20)), enabling to rewrite Equation (4.29) as

$$\rho_1 \left(\frac{3J_1}{8\pi\mu_1 l_1} \right) = \rho_2 \left(\frac{3J_2}{8\pi\mu_2 l_2} \right) \quad (4.30)$$

The dimensionless impingement position, $\xi = x_{ip} / (D / 2)$, can be estimated by replacing the jet lengths defined in Equation (4.26) and the source point, $x^* = \text{Re } d / 16$. So, Equation (4.30) results in

$$\xi = \frac{\left[\frac{\rho_1}{\rho_2} \phi_M \frac{\mu_2}{\mu_1} \right] \left(1 + \frac{\text{Re}_2}{8} \frac{d_2}{D} \right) - \left(1 + \frac{\text{Re}_1}{8} \frac{d_1}{D} \right)}{\frac{\rho_1}{\rho_2} \phi_M \frac{\mu_1}{\mu_2} + 1} \quad (4.31)$$

The momentum model described in Equation (4.31) predicts the impingement point from the balance of the linear momentum of a Lagrangian entity belonging to each jet at the impingement point position.

The difference between the kinetic energy model (Equation (4.28)) and the momentum model (Equation (4.31)) is in the density ratio term. In Equation (4.28), the term is $\sqrt{\rho_1 / \rho_2}$ while, in Equation (4.31), this term is ρ_1 / ρ_2 . Therefore, the validation of models is only verified for high density ratios.

A sensibility analysis of models is presented in this thesis enabling to set the working range of validity for each one.

4.5.2 3D CFD model

The ability of the analogue elastic model (EAM), the kinetic energy model (KEM) and the momentum model (MM) to describe the mixing of two dissimilar fluids in CIJ mixing chamber was validated from 3D CFD simulations and from the experimental data presented in Section 4.4.

4.5.2.1 Governing Equations and Boundary Conditions

The three viscosity ratio conditions presented in Section 4.3.4 (2:1, 1:5 and 1:9) were simulated in this section from CFD simulations. Table 4.7 summarizes the working and boundary conditions tested in CFD simulations. The geometrical parameters of Chamber 1 and Chamber 2 mentioned in Table 4.7 are described in Table 4.1. Re_{MV} in Table 4.7 was set according to the conditions used for PLIF experiments in order to directly compare CFD results and PLIF data.

In Cases 1 and 2 in Table 4.7, the density of liquid streams was set as $\rho_{MV} = \rho_{LV} = 1000 \text{ kg m}^{-3}$. In fact, the density measured in Coriolis flow meter showed that there is a deviation of 3% in the density of liquids, $\rho_{MV} = 1208 \text{ kg m}^{-3}$ and $\rho_{LV} = 1176 \text{ kg m}^{-3}$, which do not have a significant effect on the jets balancing. In Cases 3, 4 and 5, the density was set in 3D CFD simulations using exactly the same value measured in Coriolis flow meter. Case 6 is a hypothetical condition which does not correspond to any experimental condition in the previous section. The high density ratio between jets in Case 6 results in significant differences in the density term of the kinetic energy and momentum models (Equation (4.28) and Equation (4.31)). So, the simulation with these conditions enables to distinguish the behaviour described by each model.

Table 4.7 Working and boundary conditions imposed in CFD simulations.

Case	Viscosity Ratio	Physical Properties	Chamber	Re_{MV}
1	2:1	$\mu_{LV} = 20 \text{ mPa} \cdot \text{s}; \rho_{LV} = 1000 \text{ kg m}^{-3}$ $\mu_{MV} = 40 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1000 \text{ kg m}^{-3}$	1	50
2	2:1	$\mu_{LV} = 20 \text{ mPa} \cdot \text{s}; \rho_{LV} = 1000 \text{ kg m}^{-3}$ $\mu_{MV} = 40 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1000 \text{ kg m}^{-3}$	1	100
3	1:5	$\mu_{LV} = 9.2 \text{ mPa} \cdot \text{s}; \rho_{LV} = 1339 \text{ kg m}^{-3}$ $\mu_{MV} = 47.8 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1215 \text{ kg m}^{-3}$	1	50
4	1:5	$\mu_{LV} = 9.5 \text{ mPa} \cdot \text{s}; \rho_{LV} = 1339 \text{ kg m}^{-3}$ $\mu_{MV} = 48.0 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1285 \text{ kg m}^{-3}$	2	45
5	1:9	$\mu_{LV} = 9.1 \text{ mPa} \cdot \text{s}; \rho_{LV} = 1371 \text{ kg m}^{-3}$ $\mu_{MV} = 81.1 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1217 \text{ kg m}^{-3}$	1	45
6	1:5	$\mu_{LV} = 9.5 \text{ mPa} \cdot \text{s}; \rho_{LV} = 100 \text{ kg m}^{-3}$ $\mu_{MV} = 48.0 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1000 \text{ kg m}^{-3}$	2	50

In CFD simulations, the velocity profile of jets was set through a Fluent User Defined Function (UDF). A parabolic velocity profile, normal to each injector, is defined for each inlet as

$$v(r) = 2v_{inj} \left(1 - 4 \frac{r^2}{d^2} \right) \quad (4.32)$$

where r is the distance from the injector axis to the wall, v_{inj} is the average velocity at the inlet and d is the diameter of the injector.

At CIJ mixer walls, no slip conditions were set, and at the outlet, a uniform value was set for pressure. CIJ mixers geometry was discretised with a mesh of 2×10^6 nodes. The mesh cells are predominantly hexahedral.

The flow was simulated using the Finite Volume software package ANSYS/Fluent to solve the continuity equation,

$$\nabla \cdot \mathbf{u} = 0 \quad (4.33)$$

and the Navier-Stokes equation,

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u} \quad (4.34)$$

where p is the pressure and $\mathbf{u}$ is the velocity vector. In addition, since two fluids were considered, the mass transfer was also simulated using the convection-diffusion equation,

$$\rho \left(\frac{\partial C_A}{\partial t} + \mathbf{u} \cdot \nabla C_A \right) = D_m \nabla^2 C_A \quad (4.35)$$

where C is the concentration of species A, in this case A being fluid 1 or 2, and D_m is the diffusivity. In CFD simulations, D_m was set as $10^{-9} \text{ m}^2 \text{ s}^{-1}$. Simulations were run at steady state, which is in agreement with the PLIF images at these working conditions.

For the numeric simulation of the flow a pressure-based solver was used, with the SIMPLEC pressure-velocity coupling scheme. For the spatial discretization, Second Order UPWIND was used. The simulations were performed for steady state, setting all variables to zero as initial condition.

4.5.2.2 Results and Discussion

Figure 4.37 and Figure 4.38 show the mass fraction maps of two fluids in the frontal plane defined by the mixing chamber and injectors axes. The mass fraction maps were obtained from 3D CFD simulations for the mixing of fluids with $\mu_1 = 40 \text{ mPa} \cdot \text{s}$ and $\mu_1 = 20 \text{ mPa} \cdot \text{s}$. The MV fluid is injected through the left side injector and corresponds to the blue fluid in mass fraction maps. Jet 2 delivers the LV fluid, displayed as a white fluid in CFD simulations. The left-hand side Reynolds number was initially set at $\text{Re}_1 = 50$ in Figure 4.37 (Case 1 in Table 4.7), and at $\text{Re}_1 = 100$ in Figure 4.38 (Case 2 in Table 4.7), i.e. clearly in the steady-state range of Reynolds numbers. The right hand side jet flow rate is varied from a flow rate ratio of $r_s = 0.46$ and $\phi_K = 0.1$, Figure 4.37a and Figure 4.38a, to $r_s = 2.15$ and $\phi_K = 10$, Figure 4.37i and Figure 4.38i.

In Figure 4.37a for $\text{Re}_1 = 50$ and $\phi_K = 0.1$, where the opposite jet has $\text{Re}_2 = 215$, it can be seen the white jet flowing from the right-hand side almost into the opposite injector. Fluid issuing from the left injector is directed towards the close top of the mixing chamber where a large vortex filled of white fluid makes the blue fluid flow close to the chamber walls. In a 3D movement not displayed in the imaged plane, the blue fluid circles to the down part of the white jet, issuing from the right-hand side injector. Nevertheless, the mixing dynamics is quite weak with the lower flow rate component flowing close to the chamber walls, regions of weaker flow dynamics. These overall flow patterns are consistent with the description of PLIF images in Figure 4.23.

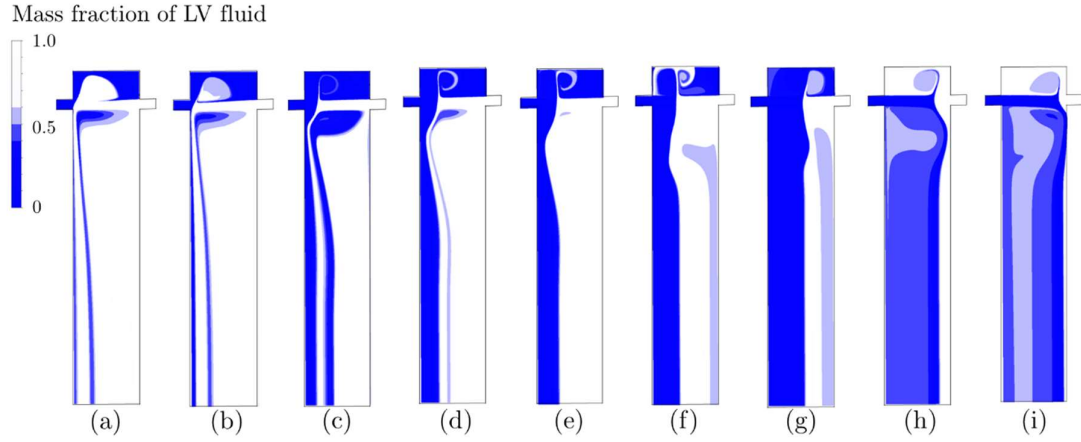


Figure 4.37 Mass fraction of MV fluid (blue colour, left side), $\mu_1 = 40 \text{ mPa} \cdot \text{s}$, being mixed with LV fluid (white colour, right side), $\mu_2 = 20 \text{ mPa} \cdot \text{s}$, (viscosity ratio 2:1) from CFD simulations for $\text{Re}_1 = 50$ and (a) $\phi_K = 0.1$ ($\text{Re}_2 = 215$); (b) $\phi_K = 0.2$ ($\text{Re}_2 = 171$); (c) $\phi_K = 0.5$ ($\text{Re}_2 = 126$); (d) $\phi_K = 0.67$ ($\text{Re}_2 = 114$); (e) $\phi_K = 0.77$ ($\text{Re}_2 = 109$); (f) $\phi_K = 1$ ($\text{Re}_2 = 100$); (g) $\phi_K = 2$ ($\text{Re}_2 = 79$); (h) $\phi_K = 5$ ($\text{Re}_2 = 58$) and (i) $\phi_K = 10$ ($\text{Re}_2 = 46$).

Figure 4.39 shows pathlines for the case $\text{Re}_1 = 50$ and $\phi_K = 0.1$, where the pathlines issuing from left injector are black while for the opposite injector, grey and ticker pathlines are used. CIJ mixers in Figure 4.39a are displayed in a view where the injector corresponding to the left-hand side in Figure 4.37, is now the one in the front left position of the mixer. In Figure 4.39b and Figure 4.39c, the relative position of the injectors is kept, Figure 4.39b is a front view, the same as Figure 4.37a, and Figure 4.39c is a view from the CIJ mixers closed top. The pathlines show the 3D patterns of the flow that transport the fluid from the CIJ headspaces, above the jets, to immediately downstream the jets. The right-hand side jet is clearly dominant and impinges on the opposite side of the CIJ mixer. After impinging on the opposite side of the CIJ mixer, fluid from the dominant jet spreads radially, and around this jet, a large vortex occupying all the headspace of the CIJ is formed. This vortex makes the blue fluid to circulate close to the CIJ walls, and also drags some portions of blue fluid making it to flow around the white jet and transports this blue fluid downwards the jets.

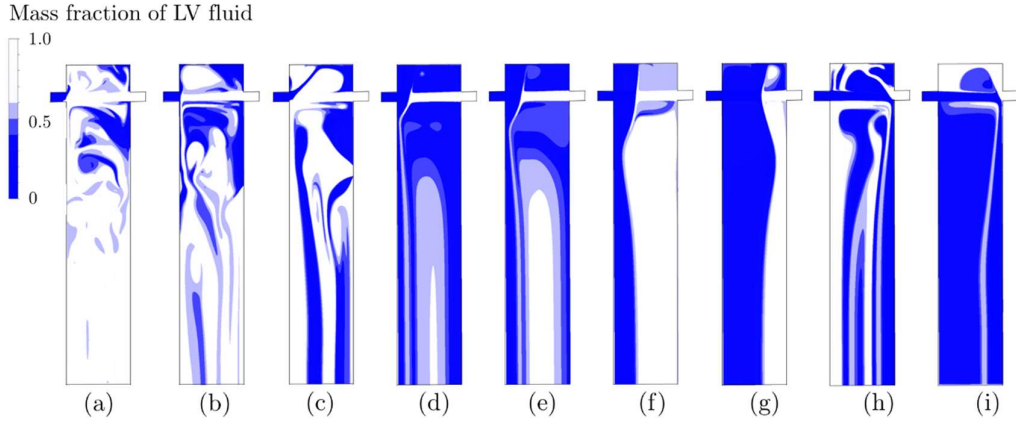


Figure 4.38 Mass fraction of MV fluid (blue colour, left side), $\mu_1 = 40 \text{ mPa} \cdot \text{s}$, being mixed with LV fluid (white colour, right side), $\mu_2 = 20 \text{ mPa} \cdot \text{s}$, (viscosity ratio 2:1) in Chamber 1 from CFD simulations for $\text{Re}_1 = 100$ and (a) $\phi_K = 0.1$ ($\text{Re}_2 = 431$); (b) $\phi_K = 0.2$ ($\text{Re}_2 = 342$); (c) $\phi_K = 0.5$ ($\text{Re}_2 = 252$); (d) $\phi_K = 0.67$ ($\text{Re}_2 = 229$); (e) $\phi_K = 0.77$ ($\text{Re}_2 = 218$); (f) $\phi_K = 1$ ($\text{Re}_2 = 200$); (g) $\phi_K = 2$ ($\text{Re}_2 = 159$); (h) $\phi_K = 5$ ($\text{Re}_2 = 117$) and (i) $\phi_K = 10$ ($\text{Re}_2 = 93$).

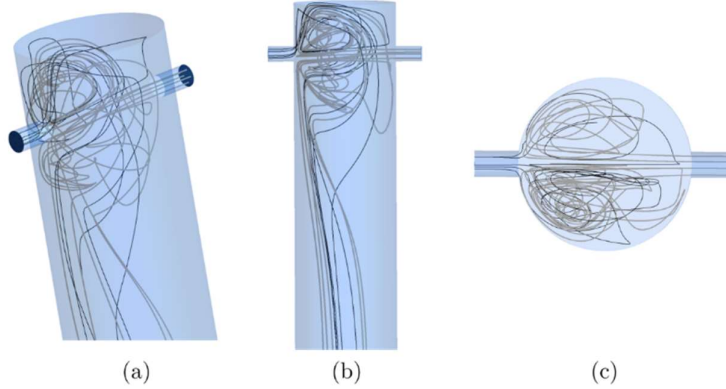


Figure 4.39 Path lines from 3D CFD simulation for $\text{Re}_1 = 50$ and $\phi_K = 0.1$ and $\mu_1 = 40 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 20 \text{ mPa} \cdot \text{s}$ (viscosity ratio 2:1).

Decreasing the right-hand side jet flow rate, Figure 4.37b and Figure 4.37c, to $r_s = 0.585$ and $r_s = 0.794$ ($\phi_K = 0.2$ and $\phi_K = 0.5$), shows the impingement point of the jets moving slightly towards the mixing chamber axis. The blue jet is not completely pushed towards the mixing chamber top, but even so, it is squeezed into the mixing chamber walls. Although the blue jet is now penetrating further into the mixing chamber, it is

still flowing next to the wall. These flow patterns, where the jets impinge quite close to one inlet nozzle, are quite prone to clogging in RIM processes, due to the formation of a polymer directly at the nozzles of the CIJ mixers. Figure 4.40b and Figure 4.40c show the pathlines for these simulations, from where it is seen the jets impinging slightly further from the left nozzle than in $\phi_K = 0.1$ (Figure 4.40a). The deflection of the left hand side jet is kept in this range $\phi_K = 0.1$ to 0.5.

When ϕ_K is close to one, $0.67 < \phi_K < 2$, the jets impinge at central positions of the CIJ mixer, without one of the jets overtaking the other. This corresponds to a limited range of flow rate ratios $0.88 < r_s < 1.3$, which highlights the process of extreme dependence on the flow rate ratio control (Erkoç et al., 2007). This was also observed from CFD simulations, and the same observations are directly applied to the PLIF data. When the fluids have different viscosities, 2:1, the impingement point at $\phi_K = 1$ is no longer coincident with the mixing chamber axis, although it is close to it. This was also verified from the PLIF images in Figure 4.23. The pathlines in Figure 4.40 also show the impinging of the jets close to the mixing chamber axis in the range $0.67 < \phi_K < 2$. Although there is the equilibrium of jets, the flow in the runner is not completely symmetric, and so the tracer maps differ from the PLIF images reported by Fonte et al. (2015).

Further decreasing the right jet flow rate to $\phi_K = 2$ and $\phi_K = 10$ creates flow patterns that were previously described for $\phi_K = 0.1$ and $\phi_K = 0.2$, but now with the blue jet overtaking the white one. The dominant blue jet for $\phi_K = 10$ is at $Re_1 = 50$, while in $\phi_K = 0.1$, the dominant jet Reynolds number was at $Re_2 = 215$. This causes no meaningful difference in the flow patterns because the dominant phenomenon in these cases is the stabilization of the flow by the effect of the wall of the CIJ mixers, where the dominant jet impacts and dissipates its energy.

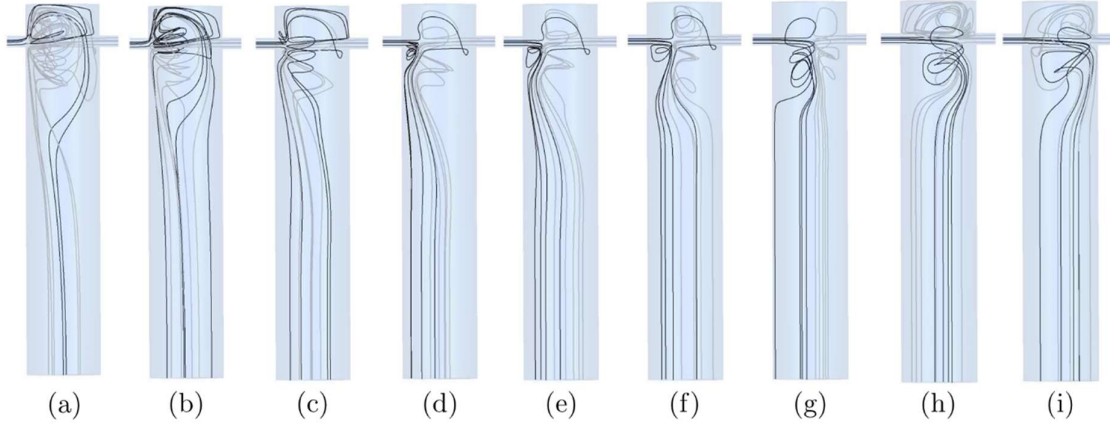


Figure 4.40 Pathlines from 3D CFD simulations for $Re_1 = 50$, $\mu_1 = 40 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 20 \text{ mPa} \cdot \text{s}$ (viscosity ratio 2:1) in Chamber 1, and (a) $\phi_K = 0.1$ ($Re_2 = 431$); (b) $\phi_K = 0.2$ ($Re_2 = 342$); (c) $\phi_K = 0.5$ ($Re_2 = 252$); (d) $\phi_K = 0.67$ ($Re_2 = 229$); (e) $\phi_K = 0.77$ ($Re_2 = 218$); (f) $\phi_K = 1$ ($Re_2 = 200$); (g) $\phi_K = 2$ ($Re_2 = 159$); (h) $\phi_K = 5$ ($Re_2 = 117$) and (i) $\phi_K = 10$ ($Re_2 = 93$).

For $Re_1 = 100$, Figure 4.41 shows similar effect of ϕ_K on the jets impingement point position. The main difference from $Re_1 = 50$ to $Re_1 = 100$ cases is the increase in flow instability, which has particular importance for smaller ϕ_K values, e.g. $\phi_K = 0.1$, where the dominant blue jet Reynolds number is $Re_2 = 431$. This was also observable from PLIF images in Figure 4.24. The large vortex in the CIJ mixers headspace occurring for $\phi_K = 0.1$ and $Re_1 = 50$ that was setting the distribution of blue fluid to downstream positions is no longer identified. Instead, some unstable flow patterns are promoting interactions between blue and white, although the blue fluid is mainly kept close to the walls. The instability flow at $Re_1 = 100$ and $\phi_K = 0.1$ is promoted by the impingement of the jet with more kinetic energy into the wall. Nevertheless, the jets are not being directly engulfed by vortices, as in a generalised chaotic flow that would promote fast mixing of two fluids. This increase in flow instability is also clear from pathlines in Figure 4.41 that are becoming increasingly random.

Further decrease in the flow rate of the right-hand side jet results that the jets impingement point moves towards the mixing chamber axis, particularly in the range of $0.77 < \phi_K < 2$. The decrease of the Reynolds number at right side injector makes these

flow patterns more stable and similar to the ones already described for Figure 4.37 and Figure 4.39. Similarly to the cases where $Re_1 = 50$, for $Re_1 = 100$ the jets are not impinging at the mixing chamber axis when $\phi_K = 1$. Larger Reynolds numbers where the flow becomes dynamic were not simulated.

Figure 4.42 and Figure 4.43 show the mass fraction contour maps and the pathlines in the axial plane defined by the mixing chamber and injectors axes obtained from 3D CFD simulations for the mixing of fluids with a viscosity ratio 1:5, $\mu_1 = 9.2 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 47.8 \text{ mPa} \cdot \text{s}$. LV and MV liquid streams were delivered according to the conditions set in PLIF experiments. The left-hand side injector, jet 1, delivers the LV fluid (white fluid) while the MV fluid (blue fluid) is injected through jet 2. In Figure 4.43, the dark lines correspond to the MV fluid and the grey lines to the LV fluid.

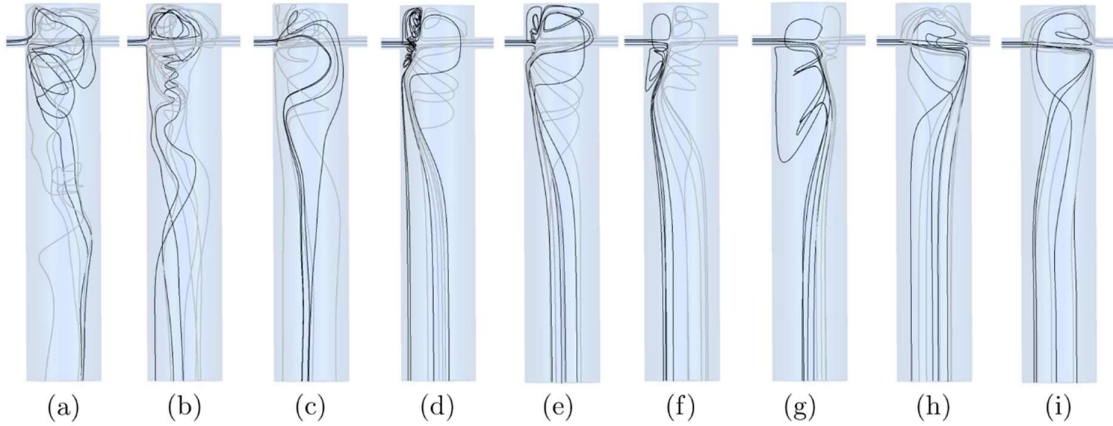


Figure 4.41 Pathlines from 3D CFD simulations for $Re_1 = 100$, $\mu_1 = 40 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 20 \text{ mPa} \cdot \text{s}$ (viscosity ratio 2:1) in Chamber 1, and (a) $\phi_K = 0.1$ ($Re_2 = 431$); (b) $\phi_K = 0.2$ ($Re_2 = 342$); (c) $\phi_K = 0.5$ ($Re_2 = 252$); (d) $\phi_K = 0.67$ ($Re_2 = 229$); (e) $\phi_K = 0.77$ ($Re_2 = 218$); (f) $\phi_K = 1$ ($Re_2 = 200$); (g) $\phi_K = 2$ ($Re_2 = 159$); (h) $\phi_K = 5$ ($Re_2 = 117$) and (i) $\phi_K = 10$ ($Re_2 = 93$).

The Reynolds number of right-hand side injector (MV fluid) is kept constant at $Re_2 = 50$. The ϕ_K range was set according to the one calculated from the PLIF images. The right-hand side jet flow rate is varied from a flow rate ratio of $r_s = 0.45$ and

$\phi_K = 0.1$, Figure 4.42a and Figure 4.43a, to $r_s = 2$ and $\phi_K = 2$, Figure 4.42e and Figure 4.43e. These conditions were summarized in Table 4.7 (Case 3).

In Figure 4.42a for $Re_2 = 50$ and $\phi_K = 0.1$ ($Re_1 = 129$), the white fluid flows towards the close top of the mixing chamber where a large vortex filled of blue fluid makes the white fluid flow close to the chamber walls. The mixing dynamics is quite weak at these conditions, as also observed from PLIF images in Figure 4.27b.

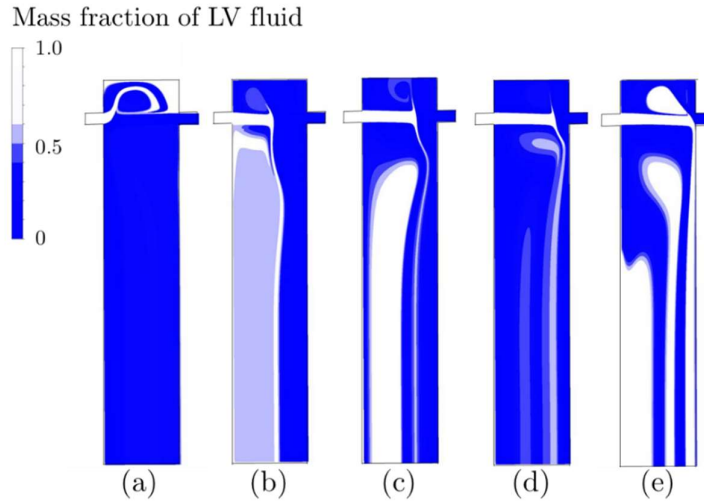


Figure 4.42 Mass fraction of LV fluid (white colour, left side), $\mu_1 = 9.2 \text{ mPa} \cdot \text{s}$, being mixed with MV fluid (blue colour, right side) in Chamber 1, $\mu_2 = 47.8 \text{ mPa} \cdot \text{s}$ (viscosity ratio 1:5), in Chamber 1 from CFD simulations for $Re_2 = 50$ and (a) $\phi_K = 0.1$ ($Re_1 = 129$); (b) $\phi_K = 0.2$ ($Re_1 = 162$); (c) $\phi_K = 0.5$ ($Re_1 = 220$); (d) $\phi_K = 1$ ($Re_1 = 278$); (e) $\phi_K = 2$ ($Re_1 = 350$).

Further increase of the Reynolds number of jet 1 promotes shifting the jets impingement point to the right-hand side of the mixing chamber. For $0.2 < \phi_K < 0.5$ ($0.57 < r_s < 0.77$), the jets impinge at the central position of CIJ mixing chamber. The same observations can be made from PLIF images, Figure 4.27c to Figure 4.27e. Again, these results indicate that the jets impingement point position is no longer at $\phi_K = 1$ for viscosities ratios larger than the unity.

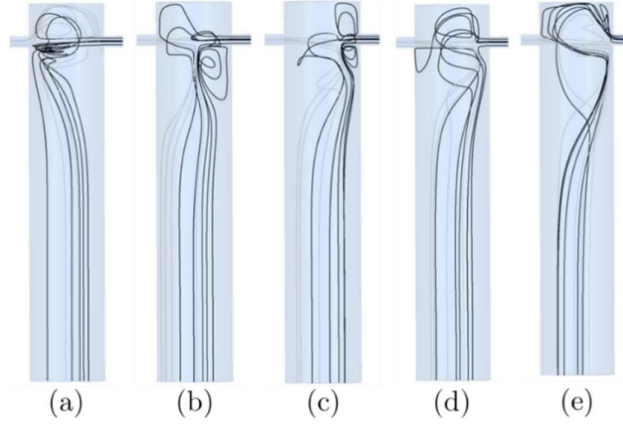


Figure 4.43 Pathlines from 3D CFD simulations for $Re_2 = 50$, $\mu_1 = 9.2 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 47.8 \text{ mPa} \cdot \text{s}$ (viscosity ratio 1:5), in Chamber 1 and (a) $\phi_K = 0.1$ ($Re_1 = 129$); (b) $\phi_K = 0.2$ ($Re_1 = 162$); (c) $\phi_K = 0.5$ ($Re_1 = 220$); (d) $\phi_K = 1$ ($Re_1 = 278$); (e) $\phi_K = 2$ ($Re_1 = 350$).

For conditions when the jets are injected close to the mixing chamber axis, two upper vortices (Figure 4.42b and Figure 4.43b) are formed above the jets, and downstream the jets, making both streams flow side by side towards the outlet. The overall flow regime closely resembles the steady-state flow regime. For $\phi_K > 0.5$, contour maps also show that a vortex is created by the white fluid, deviating the blue fluid close to the top wall of the chamber. This behaviour is quite similar to the one obtained to low ϕ_K values.

CFD simulations for viscosity ratio 1:5 ($\mu_1 = 9.5 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 47.8 \text{ mPa} \cdot \text{s}$) were performed in Chamber 2, and the working conditions are described in Table 4.7 (Case 4). Figure 4.44 and Figure 4.45 show the mass fraction contour maps and the pathlines at these conditions. LV fluid (white fluid in Figure 4.44 and grey lines in Figure 4.45) is injected from the left side injector, $d_1 = 1.5 \text{ mm}$, and MV fluid (blue fluid in Figure 4.44 and dark lines in Figure 4.45) through the right side injector, $d_2 = 1.9 \text{ mm}$. The Reynolds number at jet 2 was set as constant at $Re_2 = 45$, which corresponds to one of the conditions performed in PLIF experiments, Section 4.4.2. The flow rate at jet 1 was changed according to $0.2 < \phi_K < 5$ ($0.42 < r_s < 1.23$).

At $\phi_K = 0.2$, a vortex is created upstream the jets impingement point with white fluid. From the pathlines (Figure 4.45a), it is observed that the MV fluid (dark lines) is recirculating in the right side of the mixing chamber. This is also observed from PLIF images, but in that case, from light streaks, i.e., particles of rhodamine in the MV liquid stream, which were observed in the right side of the chamber headspace (Figure 4.33a). The increasing of Re_1 number approaches the conditions where the opposed jets are balanced. The impingement point is at the central position for approximately $\phi_K = 0.33$ and $r_s = 0.5$, which is in agreement with experimental data (Figure 4.33b).

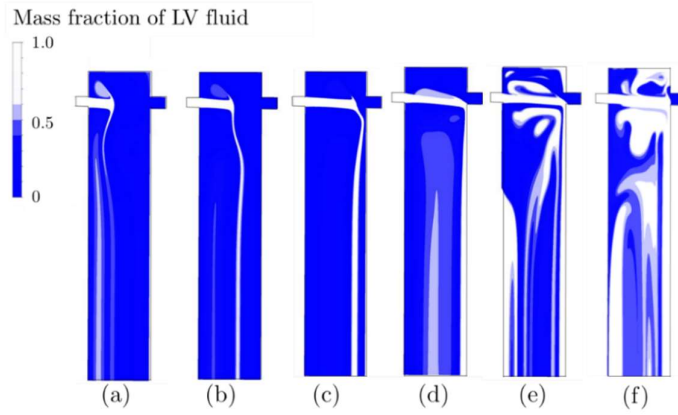


Figure 4.44 Mass fraction of LV fluid (white colour, left side), $\mu_1 = 9.5 \text{ mPa} \cdot \text{s}$, being mixed with MV fluid (blue colour, right side), $\mu_2 = 48 \text{ mPa} \cdot \text{s}$ (viscosity ratio 1:5), in Chamber 2 from CFD simulations for $Re_2 = 45$ and (a) $\phi_K = 0.2$ ($Re_1 = 126$); (b) $\phi_K = 0.33$ ($Re_1 = 150$); (c) $\phi_K = 1$ ($Re_1 = 216$); (d) $\phi_K = 1.25$ ($Re_1 = 233$); (e) $\phi_K = 2$ ($Re_1 = 272$); (f) $\phi_K = 5$ ($Re_1 = 369$).

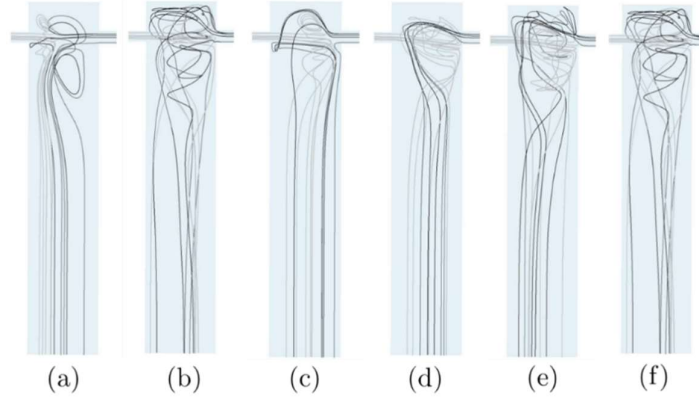


Figure 4.45 Pathlines from 3D CFD simulations for $Re_2 = 45$, $\mu_1 = 9.5 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 48 \text{ mPa} \cdot \text{s}$ (viscosity ratio 1:5), in Chamber 2 and (a) $\phi_K = 0.2$ ($Re_1 = 126$); (b) $\phi_K = 0.33$ ($Re_1 = 150$); (c) $\phi_K = 1$ ($Re_1 = 216$); (d) $\phi_K = 1.25$ ($Re_1 = 233$); (e) $\phi_K = 2$ ($Re_1 = 272$); (f) $\phi_K = 5$ ($Re_1 = 369$).

The shifting of the impingement point to the right pushes the MV fluid to the top of the mixing chamber, and the LV fluid remains enclosed in a region downstream the injectors axis, as clearly shown in Figure 4.44e. The pathlines in Figure 4.45e, show that the MV fluid (dark lines), after pushed to the top of the mixing chamber, flows next to the left sidewall. This is also clearly observed in PLIF images (Figure 4.33c), where the fluid dyed with rhodamine flows in the left-hand side of the mixing chamber.

At $\phi_K = 5$, the blue fluid in Figure 4.44f is completely crushed by the white fluid, and the impingement point occurs next to the nozzle of jet 2.

For a viscosity ratio 1:9, the MV fluid was set at $Re_2 = 45$ as described in Table 4.7. These conditions correspond to the PLIF images in Figure 4.30. Figure 4.46 and Figure 4.47 show the mass fraction contour maps and the pathlines, respectively, when the LV fluid (white fluid) is injected through the left side injector, jet 1, and the MV fluid (blue fluid) through the jet 2. Re at jet 2 was set at $Re_2 = 45$, and then Re_1 was changed according to $0.2 < \phi_K < 1.4$ ($0.8 < r_s < 1.1$).

The jets impinging position is at the centre of the chamber for $0.2 < \phi_K < 0.5$ ($0.6 < r_s < 0.8$), as shown in Figure 4.46 and Figure 4.47. PLIF images (see Figure 4.30b

and Figure 4.30c) also indicate that the central position of the impingement point is at $0.18 < \phi_K < 0.35$. On the other hand, pathlines in Figure 4.47a and Figure 4.47b show that a vortex is created downstream the jets in the right side of the mixing chamber mainly composed of the MV fluid (dark lines). This is also observed in Figure 4.30b and Figure 4.30c where light lines (rhodamine particles in the MV fluid) are clearly engulfed in the same region.

Further increase in Re_1 (Figure 4.46c to Figure 4.46e) promotes the shifting of the impact point to the right side of the mixing chamber, pushing the MV fluid to the headspace.

CFD results are in agreement with PLIF images. The experimental and numerical data indicate that the impingement point position is strongly sensible to ϕ_K and, for viscosity ratio range from 2 to 9, the impact point is no longer at $\phi_K = 1$.

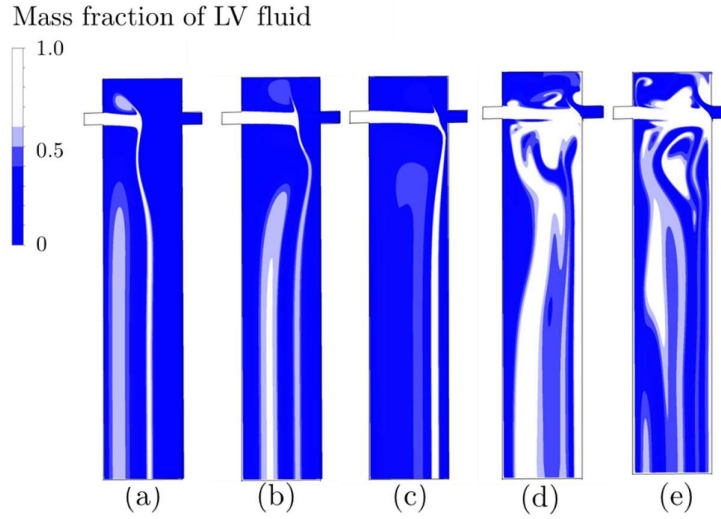


Figure 4.46 Mass fraction of LV fluid (white colour, left side), $\mu_1 = 9.1 \text{ mPa} \cdot \text{s}$, being mixed with MV fluid (blue colour, right side), $\mu_2 = 81.1 \text{ mPa} \cdot \text{s}$ (viscosity ratio 1:9), in Chamber 1 from CFD simulations for $Re_2 = 45$ and (a) $\phi_K = 0.2$ ($Re_1 = 253$); (b) $\phi_K = 0.5$ ($Re_1 = 344$); (c) $\phi_K = 1$ ($Re_1 = 433$); (d) $\phi_K = 1.2$ ($Re_1 = 461$); (e) $\phi_K = 1.4$ ($Re_1 = 488$).

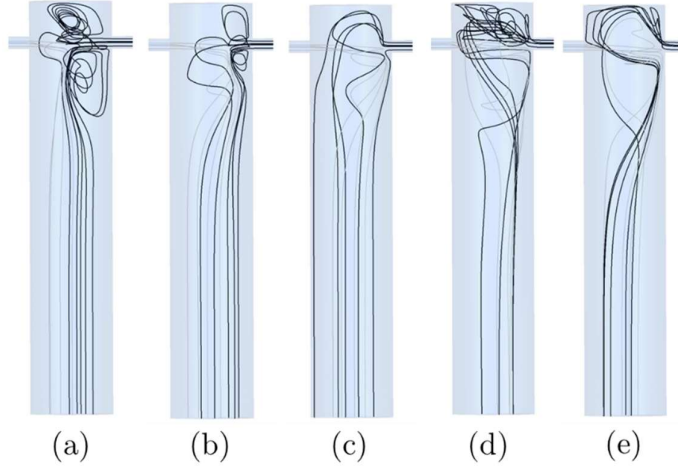


Figure 4.47 Pathlines from 3D CFD simulations for $Re_2 = 45$, $\mu_1 = 9.1 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 81.1 \text{ mPa} \cdot \text{s}$ (viscosity ratio 1:9), in Chamber 1 and (a) $\phi_K = 0.2$ ($Re_1 = 253$); (b) $\phi_K = 0.5$ ($Re_1 = 344$); (c) $\phi_K = 1$ ($Re_1 = 433$); (d) $\phi_K = 1.2$ ($Re_1 = 461$); (e) $\phi_K = 1.4$ ($Re_1 = 488$).

4.5.3 Model Validation from Experimental and CFD Results

The jets impingement point position is estimated in this thesis from PLIF and CFD results, validating EAM, KEM and MM. The contact point was determined in CFD simulation from the axial velocity profile along the injectors axis, which was extracted from the simulation results. The jets impingement position corresponds to the point where the axial velocity is $v(x_{IP}, r=0) = 0$. The ξ value is also determined from PLIF images plotting the value of the colour at each pixel along the line defined from the injectors axis. Therefore, the contact point of both jets is marked by a steep gradient in this plot.

For mixing similar fluids, EAM has been already validated by Fonte et al. (2016), and a good agreement between EAM, experimental and numerical data is achieved. The validity of KEM and MM for similar conditions is here examined. Figure 4.48 shows the dimensionless impinging point in the mixing chamber for mixing of similar fluids, $\mu_1 = \mu_2 = 20 \text{ mPa} \cdot \text{s}$, at $Re_1 = 50$. In Figure 4.48a, the experiments were run in Chamber 1 where $d_1 = d_2 = 1.5 \text{ mm}$ (Table 4.1) and in Figure 4.48b, the experiments

were run in a chamber where $d_1 = 1.9$ mm and $d_2 = 1.9$ mm, i.e. the same geometry of Chamber 2, but mirrored (Table 4.1). PIV and CFD results were reported by Fonte et al. (2016) and used to compare both models. Very slight differences between both models are registered for similar fluids, meaning that EAM, KEM and MM can be used to design CIJ mixers working with similar fluids.

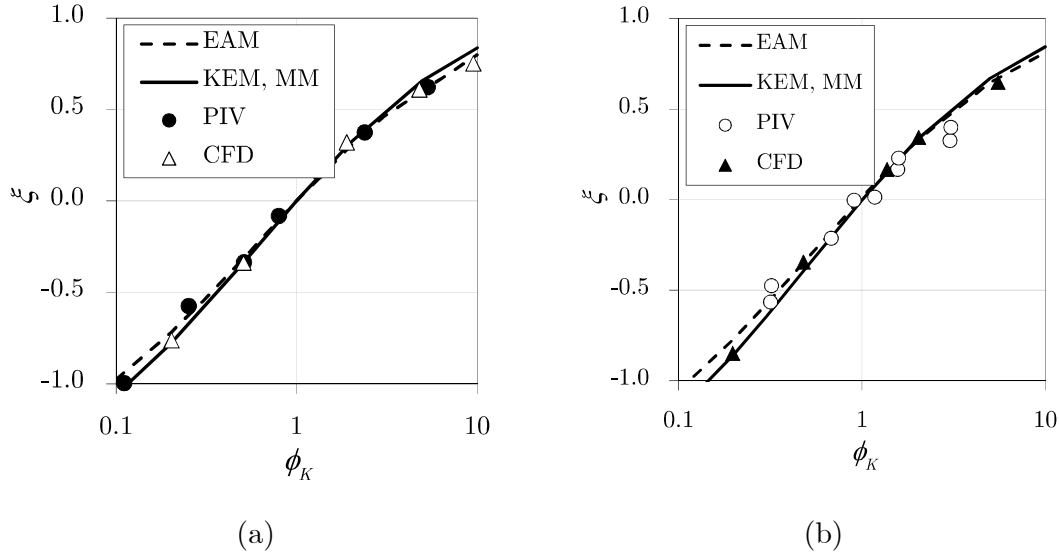


Figure 4.48 Non-dimensional impingement point position from the elastic analogue model (EAM), kinetic energy model (KEM), momentum model (MM), CFD results (Fonte et al., 2016) and PIV data (Fonte et al., 2016) as a function of the jets kinetic energy rate for similar fluids at $Re_1 = 50$ and using (a) Chamber 1 and (b) mirrored Chamber 2.

Further validation of EAM, KEM and MM is made for viscosity ratios larger than unity. Figure 4.49 and Figure 4.50 show the plots of the normalised displacement of the jets impingement point from the mixing chamber axis, ξ , as a function of the jets kinetic energy rate ratio, ϕ_K , (Figure 4.49a and Figure 4.50a) and Re number at jet 2 (Figure 4.49b and Figure 4.50b) in Chamber 1 and for a viscosity ratio 2:1. In Figure 4.49, the Reynolds number at jet 1 was set at $Re_1 = 50$ and at $Re_1 = 100$ in Figure 4.50. These plots clearly show that the position of jets is extremely sensitive to ϕ_K values ((Figure 4.49a and Figure 4.50a), and the balancing condition is no longer

at $\phi_K = 1$. This is affected by the fact that $Re_1 \neq Re_2$ at the equilibrium conditions, as shown in Figure 4.49b and Figure 4.50b, that slightly offsets $\xi=0$.

Figure 4.49 and Figure 4.50 give a direct comparison between models (EAM, KEM and MM), CFD and PLIF data. The position of the impingement point for a viscosity ratio 2:1 is clearly more predictable from the balance of kinetic energy (Equation (4.28)) and the linear momentum (Equation (4.34)) than by the elastic analogue model, particularly in this validity range $0.1 < \phi_K < 10$. The prediction of ξ given by KEM and MM are coincident because CIJ mixer is operating at symmetric flow conditions in terms of density ratios.

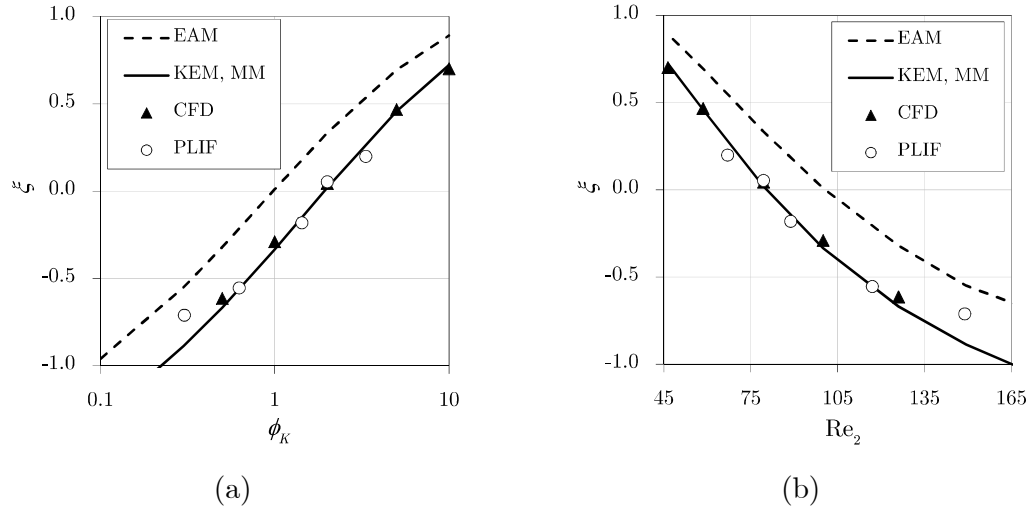


Figure 4.49 Non-dimensional impingement point position from the elastic analogue model (EAM), kinetic energy model (KEM), momentum model (MM), CFD results and PLIF data for mixing of fluids with a viscosity ratio 2:1, $\mu_1 = 40 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 20 \text{ mPa} \cdot \text{s}$ at $Re_1 = 50$ and using Chamber 1 versus (a) the jets' kinetic energy rate; (b) the Reynolds number at jet 2.

Figure 4.50 shows that the fitting of KEM and MM to the experimental data is not as good as for CFD results. This may be caused by the flow rate ratio deviation during the experimental running, which can lead to a deviation of up to 30 % in ϕ_K . However, since CFD simulation results, KEM and MM are completely coincident, these models can be validated as a design tool for these working conditions.

Figure 4.51 shows the fitting of models to PLIF and CFD data for conditions of Case 3 (Table 4.7). These results provide experimental and numerical validation of KEM and MM for mixing of fluids with a viscosity ratio 1:5 in Chamber 1, namely at $Re_2 = 50$. On the other hand, EAM does not predict the displacement of the impingement point in the mixing chamber. Note that, in Figure 4.49 and Figure 4.50, EAM overpredicts PLIF and CFD data, while, in Figure 4.51, this model underpredicts the results. This involves the definition of the injection of fluids in CIJ mixer. For viscosity 2:1, MV fluid is injected through jet 1, and for viscosity 1:5, the corresponding stream is delivered from jet 2.

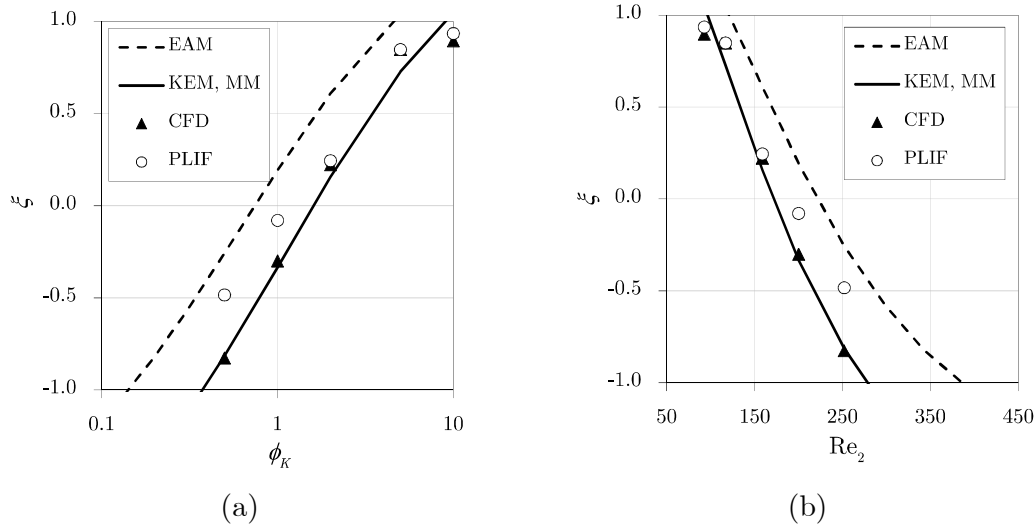


Figure 4.50 Non-dimensional impingement point position from the elastic analogue model (EAM), kinetic energy model (EAM), momentum model (MM); CFD results and PLIF data for mixing of fluids fluids with a viscosity ratio 2:1, $\mu_1 = 40 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 20 \text{ mPa} \cdot \text{s}$ at $Re_1 = 100$ and using Chamber 1 versus (a) the jets' kinetic energy rate; (b) the Reynolds number at jet 2.

Case 3 considers that the density ratio of streams is approximately $\rho_1 / \rho_2 = 1$, and so KEM and MM give the same description of ξ , as observed in Figure 4.51.

Figure 4.51b shows the displacement of ξ as a function of Re_1 . This plot could be a useful tool for the prediction of the balance conditions in CIJ mixers. The validation

of KEM and MM from PLIF and CFD results give an estimation of the conditions for $\xi = 0$, that occurs at $Re_1 = 165$ and $Re_2 = 50$.

EAM, KEM and MM also take into account the geometrical parameters of CIJ mixing chamber. Validation of these models was then extended to the asymmetric mixing chamber, Chamber 2. Figure 4.52 shows the impingement point position described by EAM, KEM, MM, CFD simulations and PLIF data for $Re_2 = 45$ when two fluids with a viscosity ratio 1:5 are mixed in Chamber 2, $d_1 = 1.5$ mm and $d_2 = 1.9$ mm. PLIF experiments corroborate the CFD results and provide validation of the ability of KEM and MM to predict the contact point of jets in asymmetric chambers. The similarities between KEM and MM results of the density ratio of streams is approximate $\rho_1 / \rho_2 = 1$, making both expressions (Equations (4.28) and (4.31)) numerically equal.

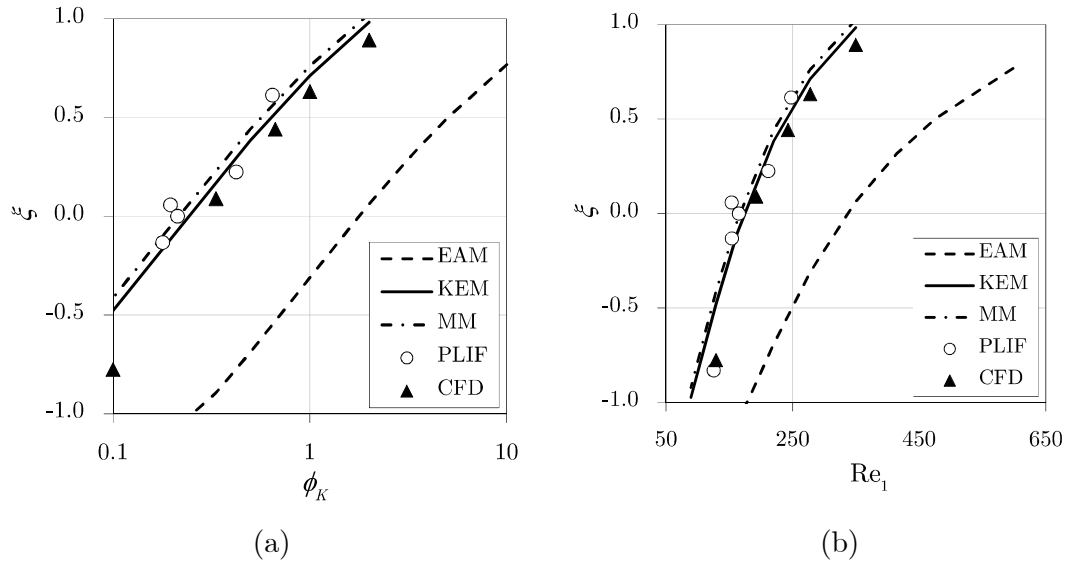


Figure 4.51 Non-dimensional impingement point position from the elastic analogue model (EAM), kinetic energy model (KEM), momentum model (MM), CFD results and PLIF data for mixing of fluids fluids with a viscosity ratio 1:5, $\mu_1 = 9.2$ mPa $\cdot$ s and $\mu_2 = 47.8$ mPa $\cdot$ s at $Re_2 = 50$ and using Chamber 1 versus (a) the jets' kinetic energy rate; (b) the Reynolds number at jet 1.

There are small deviations of the numerical and experimental data from KEM and MM; however, Figure 4.52 clearly shows that data is quite more predictable from these

models than from the elastic analogue model. Figure 4.52b shows that the working conditions for the central position of the impingement point position is at $Re_1 = 165$ and $Re_2 = 45$.

Figure 4.53 displays the impingement point position as a function of ϕ_K and Re of jet 1 for mixing of two streams with a viscosity ratio 1:9, $\mu_1 = 9.1 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 81.1 \text{ mPa} \cdot \text{s}$, at $Re_2 = 45$ in Chamber 1. KEM and MM are approximately coincident and give a good prediction of PLIF and CFD data comparing with EAM.

The impingement point at $\phi_K = 1$ is no longer coincident with the mixing chamber axis and, the balance of jets at the centre of the chamber occurs at $Re_1 = 200$ and $Re_2 = 45$, as observed from Figure 4.53b.

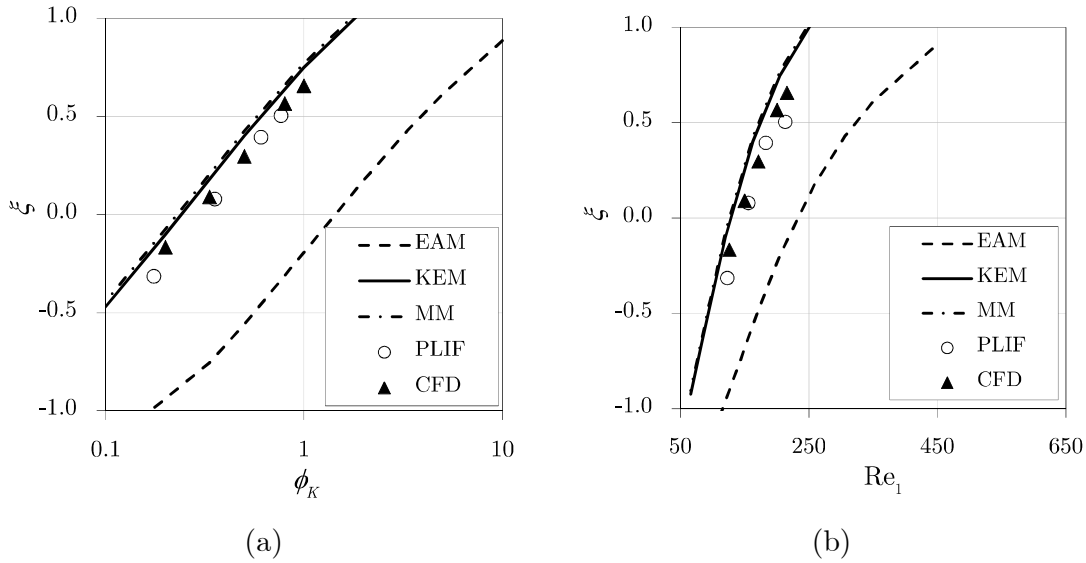


Figure 4.52 Non-dimensional impingement point position from the elastic analogue model (EAM), kinetic energy model (KEM), momentum model (MM), CFD results and PLIF data for mixing of fluids fluids with a viscosity ratio 1:5, $\mu_1 = 9.5 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 48 \text{ mPa} \cdot \text{s}$ at $Re_2 = 45$ and using Chamber 2 versus (a) the jets' kinetic energy rate; (b) the Reynolds number at jet 1.

These results (Figure 4.49 to Figure 4.53) provide clear evidence that KEM and MM is the alternative to EAM for viscosity ratios larger than the unity. EAM has only been

validated for similar fluids (Fonte et al., 2016), and its prediction is poor for mixing of dissimilar fluids in CIJ mixers. Nevertheless, the working conditions studied in this work are not enough to demonstrate the differences between KEM and MM. The full validation of the best prediction of impingement point requires the simulation of an extreme condition for high-density ratio, permitting the distinction of both models. Although these conditions do not have any envisioned industrial application, 3D CFD simulations were performed for a density ratio 1:10, a viscosity ratio of 1:5 and using an asymmetric CIJ mixing chamber, $d_1 \neq d_2$. This corresponds to Case 6 in Table 4.7. The Reynolds number at jet 1 was set as constant, $Re_1 = 45$.

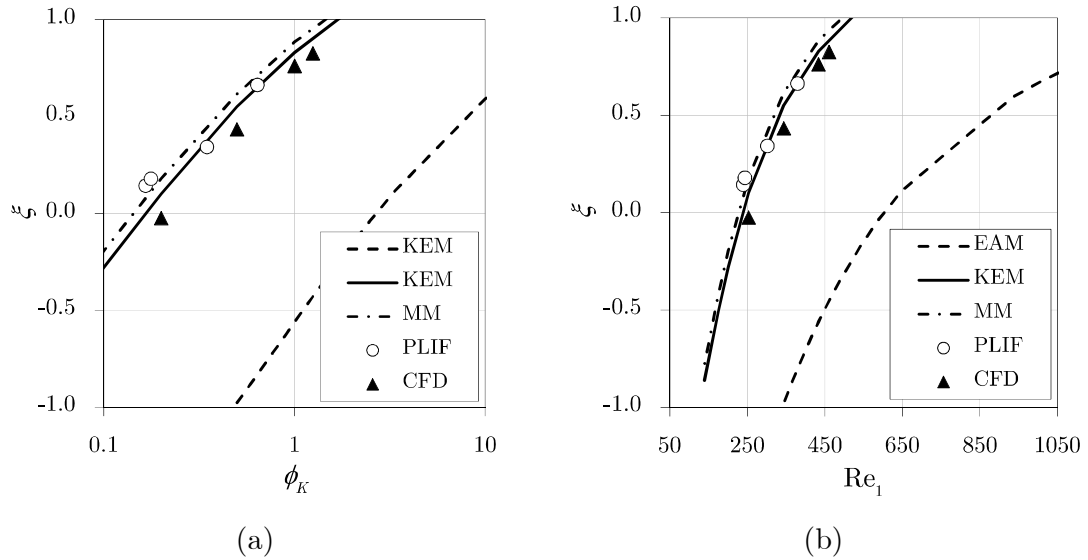


Figure 4.53 Non-dimensional impingement point position from the elastic analogue model (EAM), kinetic energy model (KEM), momentum model (MM), CFD results and PLIF data for mixing of fluids fluids with a viscosity ratio 1:9, $\mu_1 = 9.1 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 81.1 \text{ mPa} \cdot \text{s}$ at $Re_2 = 45$ and using Chamber 1 versus (a) the jets' kinetic energy rate; (b) the Reynolds number at jet 1.

Figure 4.54 shows the impingement point position as a function of jets kinetic energy (Figure 4.54a) and Reynolds number at jet 1 (Figure 4.54b) for conditions of Case 6. The great difference in densities enables to distinguish the three models and conclude that KEM is the model that gives the best prediction of experimental and CFD data.

This means that the shifting of the impingement point in CIJ mixer is exclusively given by the balance of the kinetic energy at the contact point between jets.

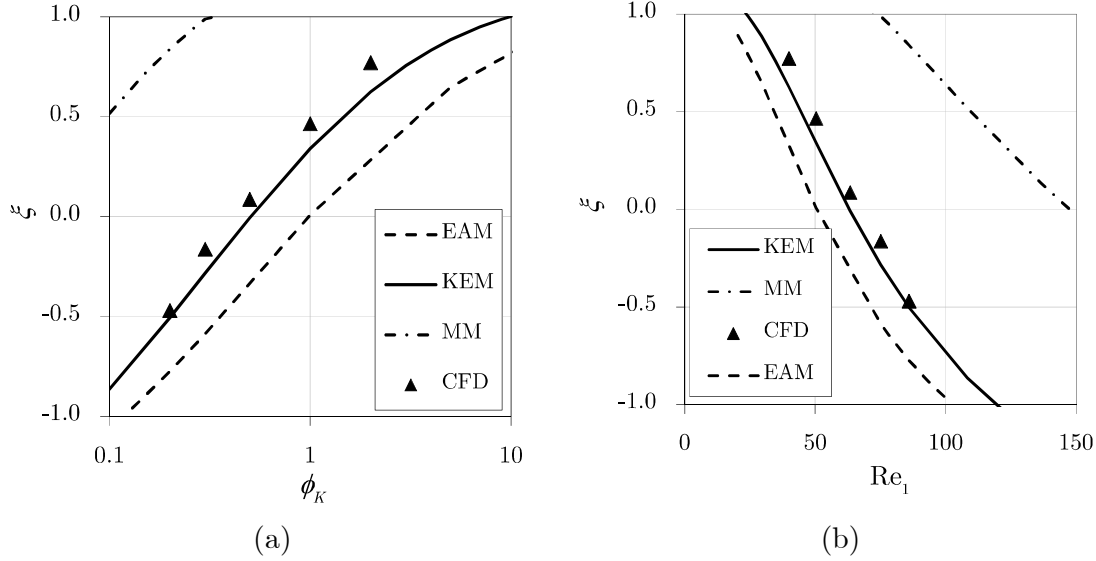


Figure 4.54 Non-dimensional impingement point position from the elastic analogue model (EAM), kinetic energy model (KEM), momentum model (MM), CFD results and PLIF data for mixing of fluids with a viscosity ratio 1:5, $\mu_1 = 9.5 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 48 \text{ mPa} \cdot \text{s}$, and densities $\rho_1 = 100 \text{ kg m}^{-3}$ and $\rho_2 = 1000 \text{ kg m}^{-3}$, at $Re_2 = 45$ and using Chamber 2 versus (a) the jets' kinetic energy rate; (b) the Reynolds number at jet 2.

Table 4.8 summarizes the models that described each working condition studied in this thesis. These models were validated in a particular range of a viscosity ratio from 1 to 9 and a density ratio from 1 to 10. EAM only fits the experimental and numerical results for similar fluids, but this model does not fit experiments with fluids with different viscosities. This indicates that the balance of kinetic energy fluxes of opposed jets is not the necessary condition that implies the central position of jets impingement point (Fonte et al., 2016). MM predicts the tendency and the actual position of the jets impingement point for similar fluids and fluids with different viscosities and similar densities. However, for high-density ratios, MM does not predicts ξ . KEM gives the full prediction of the impingement point position, ensuring a good estimation for similar and dissimilar fluids using asymmetric mixing chambers.

Table 4.8 Summary of the validity range of each model.

Viscosity Ratio	Physical Properties	Chamber	Models
1:1	$\mu_{LV} = 20 \text{ mPa} \cdot \text{s}; \rho_{LV} = 1000 \text{ kg m}^{-3}$ $\mu_{MV} = 20 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1000 \text{ kg m}^{-3}$	1; 2	EAM, KEM, MM
2:1	$\mu_{LV} = 20 \text{ mPa} \cdot \text{s}; \rho_{LV} = 1000 \text{ kg m}^{-3}$ $\mu_{MV} = 40 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1000 \text{ kg m}^{-3}$	1	KEM, MM
2:1	$\mu_{LV} = 20 \text{ mPa} \cdot \text{s}; \rho_{LV} = 1000 \text{ kg m}^{-3}$ $\mu_{MV} = 40 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1000 \text{ kg m}^{-3}$	1	KEM, MM
1:5	$\mu_{LV} = 9.2 \text{ mPa} \cdot \text{s}; \rho_{LV} = 1339 \text{ kg m}^{-3}$ $\mu_{MV} = 47.8 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1215 \text{ kg m}^{-3}$	1	KEM, MM
1:5	$\mu_{LV} = 9.5 \text{ mPa} \cdot \text{s}; \rho_{LV} = 1339 \text{ kg m}^{-3}$ $\mu_{MV} = 48.0 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1285 \text{ kg m}^{-3}$	2	KEM, MM
1:9	$\mu_{LV} = 9.1 \text{ mPa} \cdot \text{s}; \rho_{LV} = 1371 \text{ kg m}^{-3}$ $\mu_{MV} = 81.1 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1217 \text{ kg m}^{-3}$	1	KEM, MM
1:5	$\mu_{LV} = 9.5 \text{ mPa} \cdot \text{s}; \rho_{LV} = 100 \text{ kg m}^{-3}$ $\mu_{MV} = 48.0 \text{ mPa} \cdot \text{s}; \rho_{MV} = 1000 \text{ kg m}^{-3}$	2	KEM

The studied validation range partially describes the industrial applications of CIJ mixer considered in this thesis. In PU-RIM processing, polyol and isocyanate have a density of 1100 kg m^{-3} and 1200 kg m^{-3} , and a viscosity of 200 to $1000 \text{ mPa} \cdot \text{s}$ and $30 \text{ mPa} \cdot \text{s}$, respectively (Lee et al., 1980). In the production of mayonnaise, the aqueous stream

and oil have approximately densities of 984 kg m^{-3} and 1000 kg m^{-3} and viscosities of $0.1 \text{ mPa} \cdot \text{s}$ and $60 \text{ mPa} \cdot \text{s}$, respectively.

The validation of KEM assesses a full control of the impinging point position in the mixing chamber. This model takes into account the geometrical parameters and the physical properties of both liquid streams. Experiments in CIJ mixers operating at chaotic flow regime can be designed estimating from KEM the conditions for the effective mixing: $\xi = 0$ and $\text{Re}_{\text{MV}} > 150$ (for cases with dissimilar fluids). The geometry of CIJ mixing chamber and the physical properties of fluids would be the input variables in the kinetic energy model.

4.6 Part IV: Product Development in CIJ Mixers

The most common application of CIJ mixers is as a mixing device in RIM machines. Nevertheless, other industrial processes integrate CIJ mixers in their plants, and usually, with adapted geometries. In this section, CIJ mixers are addressed as a mixing technology in two distinct processes: PU processing and mayonnaise production.

In industrial processes where mixing is fully controlled, product development is initially carried in lab devices where the mixing scales can be screened, and then the formulation recipes are tested in pilot machines. This thesis brings a contribution with a new formulation method using rotational devices for the screening of the mixing scales at lab scale (Chapter 2). In the first part of this section (Section 4.6.1), experiments in plate-plate or cone-plate rheometers are designed to mimic the mixing scales in CIJ mixers for PU-RIM processes.

Section 4.6.2 focuses on the second stage of product development, which is the formulation tests in pilot machines. The design tools introduced in the last section are applied to predict the conditions for effective mixing. The case study addresses the production of mayonnaise in CIJ mixers with typical dimensions in industrial processes.

4.6.1 PD Case-Study 1: PU Production at Lab-scale using Rotational Devices

A formulation process is here implemented in plate-plate or cone-plate rheometers as a methodology for high throughput material development. This method is quite useful to determine the exact evolution of mixing scales in chemical processes. CIJ mixers in PU-RIM processes are set as the case study for the implementation of this methodology for product development.

CIJ mixing chamber in RIM machines operates at production rates from 10 to 100 kg min⁻¹. Furthermore, the actual mixing conditions in CIJ mixers have an impact on the final mechanical properties of products made in RIM machines. This was reported in previous works on PU processing (Lee et al., 1980; Kolodziej et al., 1982; Nguyen and Suh, 1985; Kolodziej et al., 1986; Gomes et al., 2016), and the assessment of micromixing from tests reactions (Kusch et al., 1989; Nunes et al., 2012; Brito et al., 2020). Product development for RIM machines is generally made with actual production conditions in pilot machines, making the formulations screening a lengthy process. Typically, the operations involved in setting the new raw materials for a formulation testing, include thermostabilizing, tank cleaning and filling, and this whole process may take longer than one hour. The development of a methodology for the pre-screening of RIM formulations in plate-plate or cone-plate devices accelerates the development of new products with the advantage of decreasing quantities of testing raw materials from the scale of kilograms to grams.

In PU-RIM process, a stream would be an isocyanate and the other a polyol. The top left sketch in Figure 4.55a, shows a cross-view in the normal direction to the injectors axis of a typical CIJ mixer and the bottom right sketch of Figure 4.55a is the front view.

As shown in Figure 4.55b and Figure 4.55c, the impingement of the two monomers in the mixing chamber promotes the formation of a pancake at the point where liquids contact, as observed by Wood et al. (1991). Effective mixing occurs due to the

stretching of the interface between fluids, and thus the formation of a lamellar structure composed of two monomers. The relevant information of the ensemble of fluid layers is 2D and therefore, the rheometric flow could be used to mimic the mixing structures formed in CIJ mixers. Thus, the mixing conditions in a plate-plate or cone-plate rheometer have been studied to ensure that the 2D information of the lamellar structure is replicated in CIJ mixers.

Figure 4.55b to Figure 4.55d show PLIF images of concentration fields for different mixing conditions at the same conditions of Fonte et al. (2015): $d_1 = d_2 = 1.5 \text{ mm}$, $D = 10 \text{ mm}$ and fluids were glycerol aqueous solutions with $\mu = 20 \text{ mPa} \cdot \text{s}$ and $\rho = 1180 \text{ kg m}^{-3}$.

Figure 4.55b and Figure 4.55c show the mixing of a dyed stream (white fluid) issuing from left-hand side, and a clear stream (dark fluid) delivered through the right-hand side. A dashed line represents the injectors axis in the figure. Figure 4.55b displays a segregated flow regime, with clear and dyed stream flowing side by side. Figure 4.55c is obtained at the onset of the chaotic flow regime, which corresponds to the operating condition to mix the two liquid streams in RIM machines. Detailed analysis of flow regimes in CIJ mixers from PLIF and other visualization techniques is well-established in the literature (Santos and Sultan, 2013; Fonte et al., 2015; Li et al., 2015; Shi et al., 2015; Brito et al., 2018).

For the exact screening of the 2D information, the evolution of the lamellar structure was assessed in each region of the mixing chamber working at chaotic flow regime. The three regions identified from PLIF images are: in the contact point between jets where a pancake is formed, in the mixing zone where a vortex street is formed and in a region downstream where a fully developed laminar flow is generated.

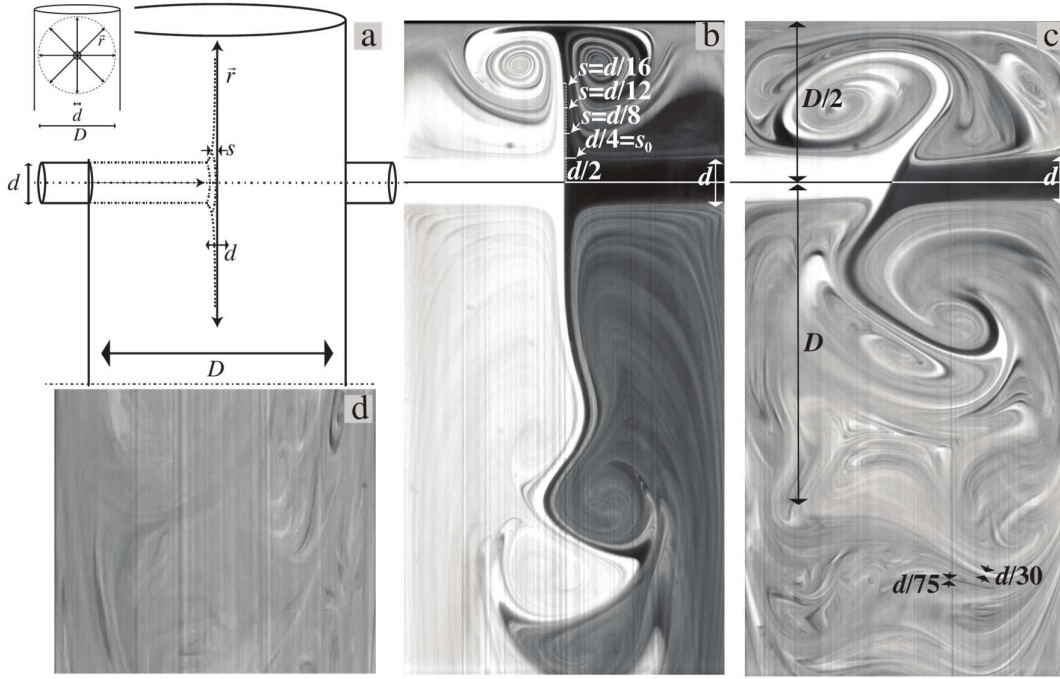


Figure 4.55 Analysis of mixing scales in CIJ mixers (a) sketch of CIJ mixers and main flow paths; (b) from PLIF images for segregated flow regime, $Re = 104$; (c) at the flow regime transition to self-sustainable chaotic flow regime; (d) PLIF image at downstream position $> 5D$ from the jets impingement point (Fonte et al., 2015).

The segregated flow regime images are useful for the analysis of the initial contact of the two flow streams because the interfaces are clear. When the two opposed jets impinge in CIJ mixers, they spread radially, forming a pancake like structure (Wood et al., 1991). The flow spreading occurs nearly without deceleration of the injection velocity in the mixing chamber, v_{inj} , following a pattern that is schematically depicted in Figure 4.55a from two views. The scale analysis starts at a radial distance of $d/2$ from the jets impingement point (Figure 4.55b). Considering that the jets inlet velocity is v_{inj} , each inlet flow rate is $Q_{inj} = v_{inj} \pi d^2 / 4$. The implementation of the mass conservation to the ring around the jet at $r = d/2$ results

$$Q_{inj} = v_{inj} 2\pi r(t) s \quad (4.36)$$

where $r(t)$ and s are the radial direction and the striation thickness, respectively, which are represented in Figure 4.55a. Considering that the striation thickness is s_1 at $r = d/2$, $s_1 = d/4$ from Equation (4.36). This position is illustrated in Figure 4.55b. Assuming that the velocity does not decrease in the pancake (Santos et al., 2008; Santos et al., 2009), the striation thickness decreases with the radius as,

$$\frac{s(t)}{s_1} = \frac{d}{2r(t)} \quad (4.37)$$

Considering an element in the pancake interface, the dependence of the particle position with the time is $t = r(t) / v_{\text{inj}}$. This results in

$$\frac{s(t)}{s_1} = \frac{d}{2v_{\text{inj}}t} \quad (4.38)$$

At the end of the pancake spreading ($r(t) = D/2$), the striation is $s_2 / s_1 = d / D$ according to Equation (4.37), where index 2 in s_2 stands for the striation thickness at the end of the pancake.

The segregated flow regime was used to illustrate the initial thinning of the raw materials, but the mixing efficiency in this regime is not sufficient for industrial fast polymerization processes. For PU processing, the operation must occur at chaotic flow regime, where after the initial thinning of the raw materials, further mixing occurs by engulfment in vortices that are formed around the inlet jets. These vortices are clear from Figure 4.55c, and extend through a distance of approximately half a mixing chamber diameter, $D/2$. The shedding frequency of these vortices is given by the velocity oscillations frequency at the jets impingement point that is widely reported in the literature (Wood et al., 1991; Santos et al., 2009; Li et al., 2011; Li et al., 2015; Shi et al., 2015). A typical value for this shedding frequency is Strouhal number of $St \approx 0.06$ (Santos et al., 2009; Gonçalves et al., 2017). The vortex shedding frequency is $\phi_v = St v_{\text{inj}} / d$, corresponding to an average period of shearing in these flow

structures of $T = 1 / \phi_v$. These vortices radius is $D/4$ with average velocity in the periphery of v_{inj} , and thus the shear rate in radial direction of these vortices is $\dot{\gamma} = 4v_{inj} / D$. Considering that the fluids strias are oriented in the angular direction in these vortices, as can be seen from Figure 4.55c, a pure shear flow could be used as a good approximation of the flow dynamics in CIJ mixers. So, the striation thinning in this region is,

$$\frac{s(t)}{s_2} = \frac{1}{\sqrt{1 + \dot{\gamma}t^2}} = \frac{1}{\sqrt{1 + \left(\frac{4v_{inj}}{D}\right)^2 t^2}} \quad (4.39)$$

The final striation thickness can be determined from the average shedding period of these vortices, $t = T = 1 / \phi_v$. The resulting striation thickness is,

$$\frac{s_3}{s_2} = \frac{1}{\sqrt{1 + \frac{16d^2}{St^2 D^2}}} \quad (4.40)$$

where the index 3 in s_3 is the striation thickness after the mixing region with vortex shedding.

After the engulfment region, the vortices are rapidly involved in the region defined by an approximate parabolic flow profile where the average shear rate is $\dot{\gamma} = 2v_{mean} / D$ (Figure 4.55d). The mean velocity, v_{mean} , is determined by the mass conservation between the inlet and the outlet and so $v_{mean} = 2v_{inj} d^2 / D^2$. Considering a pure shear flow in this region, the striation thickness rate is,

$$\frac{s(t)}{s_3} = \frac{1}{\sqrt{1 + \frac{16v_{inj}^2 d^4}{D^6} t^2}} \quad (4.41)$$

The striation thinning rate in CIJ mixers can be matched to that of a plate-plate device from its angular velocity, as listed in Table 4.9. The striation thickness evolution and the respective plate angular velocity are plotted in Figure 4.56, where different values of angular velocity correspond to markedly different regions in CIJ mixers. The CIJ mixer considered for the calculations has a length of $5D$, and injectors diameter of $d_1 = d_2 = 1.5 \text{ mm}$, a mixing chamber diameter of $D = 10 \text{ mm}$, and inlet velocity of $v_{\text{inj}} = 4 \text{ m s}^{-1}$. The corresponding plate-plate analysis was made for an $R_p = 10 \text{ cm}$ and $h_p = d / 4 = 0.345 \text{ mm}$.

Table 4.9 Mixing scales length evolution in CIJ mixers and related evolution on plate-plate devices.

	CIJ mixers	Period	Plate-Plate angular velocity
Pancake shearing	$\frac{s(t)}{s_1} = \frac{d}{2v_{\text{inj}}t}$	$\frac{d}{2v_{\text{inj}}} \leq t \leq \frac{D}{2v_{\text{inj}}}$	$\omega(t) = \frac{h}{R_p} \sqrt{\left(\frac{2v_{\text{inj}}t}{d}\right)^2 - 1}$
Engulfing vortices	$\frac{s(t)}{s_2} = \frac{1}{\sqrt{1 + \left(\frac{4v_{\text{inj}}}{D}\right)^2 t^2}}$	$\frac{D}{2v_{\text{inj}}} \leq t \leq \frac{d}{Stv_{\text{inj}}}$	$\omega(t) = \frac{4v_{\text{inj}}h_p}{DR_p}$
CIJ mixers runner	$\frac{s(t)}{s_3} = \frac{1}{\sqrt{1 + \frac{16v_{\text{inj}}^2 d^4}{D^6} t^2}}$	$\frac{d}{Stv_{\text{inj}}} \leq t$	$\omega(t) = \frac{4d^2 v_{\text{inj}} h_p}{D^3 R_p}$

The final striation in the plot of Figure 4.56 is $s = 0.01s_0 \approx 3.5 \text{ }\mu\text{m}$. Depending on the path of different fluid elements, the striation thickness varies. So, the sampling of annular sections of the final material properties at different mixing histories can be obtained from a single test.

The final striation in the plate-plate depends on the material being analysed. Data on small scale interfacial phenomena in PU synthesis shows that in the $10 \text{ }\mu\text{m}$ range there

are other “mixing” mechanisms besides convection (Wickert et al., 1987; Machuga et al., 1988). So, for the PUs case, there is evidence that a final striation of $10 \mu\text{m}$ is enough for material synthesis aiming fast product development.

An interesting fact from the analysis of Figure 4.55 is that in RIM machines, the topology, i.e. the relative position of the injection of streams, also plays a major role on the evolution of mixing scales. Different topologies of the fluid interface are associated to different flow regimes. An analogy between the topology set in the plate-plate geometry in Chapter 2 and CIJ mixers flow regimes can be done: Topology 1, that is when the two fluids are initially placed side-by-side in the rotational devices, corresponds to chaotic flow regimes, where there is the formation of vortices that reduce the distance between streams; Topology 2, where the fluids are initially placed one on top of the other, corresponds to the segregated flow regime where the interface between two phases is preserved without any change. Although the segregated flow regime has vortices engulfing fluids, these vortices are placed in opposite sides of the mixing chamber failing in this way to engulf fluid from both jets.

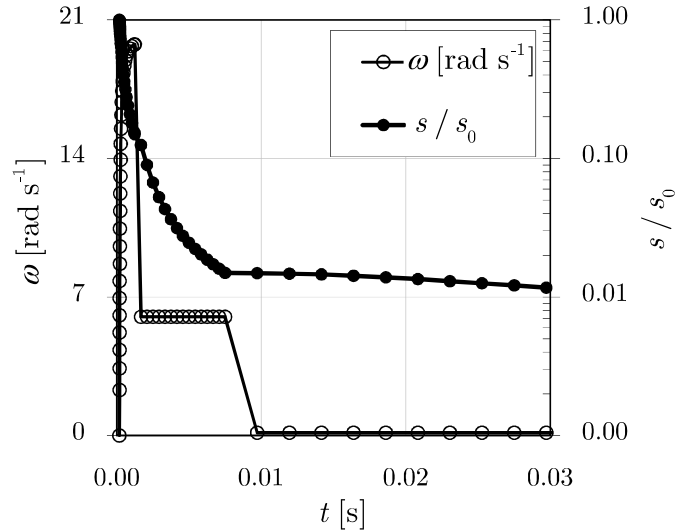


Figure 4.56 Shear thinning profile (s/s_0) in CIJ mixer for a RIM process ($v_{\text{inj}} = 4 \text{ m s}^{-1}$, $d = 1.5 \text{ mm}$ and $D = 10 \text{ mm}$) and a matched profile in a plate-plate device ($R_p = 10 \text{ cm}$, $h = d/4$) and respective plate angular velocity (ω).

4.6.2 PD Case-Study 2: Mayonnaise Production in CIJ Pilot Machines

Emulsification is widely carried out in the food, cosmetics, paints and pharmaceuticals industries. Emulsification process typically occurs under turbulent flow regime, for example, in high-shear devices or from colloidal milling; through high-pressure homogenization or micro fluidization; or ultrasound.

In the food industry, the emulsification processes commonly occur by mechanical agitation in high shear devices, which are usually used in batch or inline configurations (Rodgers, 2016). The taste, texture, colour and appearance are features that are related to the efficient mixing of ingredients during its production (Rodgers, 2016). The quality of these characteristics has gained importance because it often meets customer satisfaction.

In high shear devices, the quality consistency of emulsions is not an easily controllable process, because it strongly depends on the local shear field. Uniform shear conditions in the entire mixing volume are not ensured due to the formation of dead zones in reactors.

The quality of emulsions is commonly characterized in terms of the droplet size and droplet size distribution. The hydrodynamics conditions, the process time scales and the interfacial properties are the features that have a larger influence on the droplet breakup and coalescence.

The droplet breakup is mostly affected by the shear level and the absorption of emulsifier at the interface. The deformation and break of droplets must occur within the eddy lifetime, wherein the inertial stresses in eddies overcome the viscous stress within. Therefore, the droplets deformation and the respective droplet breakup only occurs when the inertial stresses overcome the restoring viscous and interfacial forces.

The droplet coalescence consists of the collision of droplets and its agglomeration. In turbulent dynamics, the droplets collide due to the velocity fluctuation and gradient.

Therefore, the coalescence depends on the eddy life, collisions rate, the deformation of droplets and the contact time.

The quality of emulsions is strongly affected by the emulsifier stability because it depends on its nature and concentration. The production of emulsions can take place under an emulsifier-poor regime or an emulsifier-rich regime. In emulsifier-poor regime, the collision of droplets at turbulent flow regimes promotes the coalescence of drops. In emulsifier-rich regime, the interface is rapidly stabilized, but the final droplet size depends on the droplet breakup at turbulent flow conditions (Tripodi et al., 2019a).

The droplets coalescence is also influenced by the increase of the effective viscosity of the emulsion, making the process of shearing arduous (Siddiqui and Norton, 2012). So, the droplet coalescence can be easily manipulated from hydrodynamics and the droplet interface features.

CIJ mixers are addressed in this thesis as an alternative to high-shear devices in emulsification processes. CIJ mixers have a huge potential for the emulsification process due to its large throughputs, in a range up to 100 kg min^{-1} , combined with the high energy efficiency for mixing of liquid streams (Tripodi et al., 2019a). This occurs because the full inlet power is focused and dissipated at the contact point of opposed jets.

Siddiqui and Norton (2012), Tripodi et al. (2019a) and Tripodi et al. (2019b) have used CIJ mixers for emulsification. These works injected a pre-emulsion of oil and water in CIJ mixing chamber and then reported the droplet size and droplet size distribution. One step emulsion, by direct injection of oil through one injector and water from the opposite one, has never been done.

Siddiqui and Norton (2012) were the first authors to relate the droplet size and the flow conditions in jet mixers. The highest shear conditions for higher jet flow rate and Reynolds numbers are related to smallest droplets size. Different emulsifiers with

different molecular weights were also studied in Siddiqui and Norton (2012). It was reported that the mean droplet sizes are a feature of the emulsifier.

Pickering emulsions were also tested in CIJ mixers by Tripodi et al. (2019b) where the emulsifier used was Tween 20-silica. For this, pre-emulsions were prepared with different ratios of oil and water stabilised with Tween 10-silica. The droplet size was reduced by the recirculation under fixed flow rates of jets.

In this chapter, CIJ mixers are used as a continuous process for the production of oil and water emulsions, where oil and water are injected as opposed jets. The two main goals of this work are:

- The implementation of KEM as a design tool for efficient CIJ mixers, operating at chaotic flow regimes. This is a direct application of opposed jets mixers in the development of new products;
- Validation of CIJ emulsification process, injecting the two phases directly from opposed injectors. The validation is done from the comparison of the performance at the same conditions in a batch configuration.

4.6.2.1 Experiments

4.6.2.1.1 Experimental Setup and Working Conditions

The emulsification process is divided into two steps: a batch process, which is a preliminary study to determine the ideal conditions to get stable emulsion and a continuous process in CIJ mixers. KEM, described in Equation (4.28), is used to determine the working conditions for efficient mixing in CIJ mixers. The chamber geometry and the physical properties of fluids are the input variables to predict the conditions for the central position of the impingement point, $\xi=0$.

Mayonnaise is an oil-in-water emulsion with a typical recipe of approximately 80% of vegetable oil, 12% of water and 3% of egg yolk that is used as an emulsifier (Kerkhofs

et al., 2011). Modifications in the mayonnaise recipe were made in this work. An emulsion with an oil/water ratio of 60%/40% (in volume) was prepared, and lecithin was the emulsifier. Lecithin is the protein in the egg yolk able to stabilize the interface. The raw materials used to prepare the emulsion were sunflower oil purchased by a local retailer and tap water. The soybean lecithin with 90% of purity was supplied by Alfa Aesar (J61675-30).

The mass fraction of lecithin in emulsions was determined according to its hydrophilic-lipophilic (HBL) index. HBL index measures the hydrophilic and lipophilic behaviour, which are related to the water-loving and the fat-loving, respectively. HBL is scaled from 1 to 20 that classifies the ability of emulsifiers to produce oil/water (o/w) or water/oil (w/o) emulsions (Cabezas et al., 2016). In o/w emulsions, the oil is the dispersed phase, and the water is the continuous phase. In w/o emulsion, water is the dispersed phase and oil is the continuous phase. High HBL values are associated to hydrophilic emulsifiers, i.e., they have more affinity to water and, the emulsifiers with affinity with oil have low HBL values. Therefore, emulsifiers with HBL values lower than 6 tend to form w/o emulsions and those, whose HBL values are between 8 and 16, form o/w emulsions.

Lecithins generally cover a large range of HBL values. The mass fractions for o/w emulsions is 1-5% (wt./wt. of fat) and w/o emulsions is 5-10% (wt./wt. of fat) (List, 2015). This data is useful for the stability analysis of emulsions in the following sections.

In this thesis, the stability of o/w emulsions is assessed during the emulsification using different mass fractions of lecithin. The viscosity of both phases is an input variable in KEM. And so, rheological tests were performed to measure the exact viscosity of each stream using a rheometer Anton Paar MCR 92 SN8247897. The sunflower oil is a Newtonian fluid and has a viscosity of $\mu_{\text{oil}} = 57.8 \text{ mPa} \cdot \text{s}$. Aqueous solutions of lecithin were prepared for a mass fraction range from 3% to 10%. The flow curves were plotted for a shear rate range from 100 to 600 s^{-1} , as Figure 4.57 shows. Within this range,

dispersion with 3% wt./wt. behaves approximately as a Newtonian fluid. On the other hand, the dispersions with 4% wt./wt., 5% wt./wt. and 10% wt./wt. of lecithin behave as shear-thinning fluids, i.e. the viscosity decreases with the shear rate. Flow curves also show that for larger mass fraction of lecithin, the viscosity increases.

The mass fraction of emulsifier is typically presented as the mass of the emulsifier in the total mass of the emulsion, i.e. $m_{\text{emulsifier}} / (m_{\text{water}} + m_{\text{oil}} + m_{\text{emulsifier}})$. Therefore, the 60/40% o/w emulsions prepared from 3%, 4%, 5% and 10% wt./wt. of aqueous solutions of lecithin corresponds to emulsions of 1.3%, 1.7%, 2.1% and 3.4% wt./wt. of lecithin, respectively.

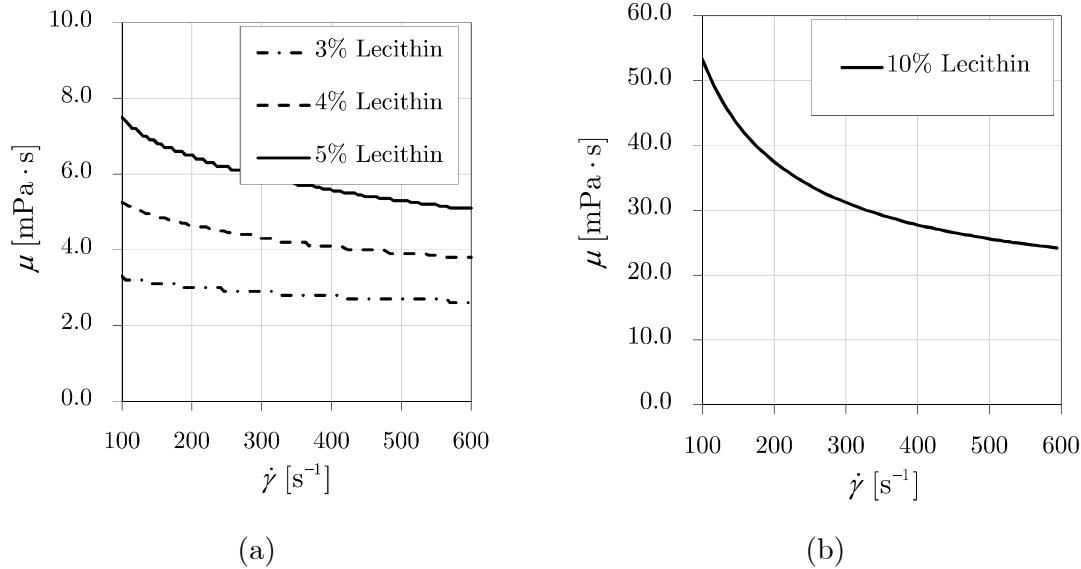


Figure 4.57 Flow curves of lecithin dispersions in water with (a) 3%, 4% and 5% of lecithin; (b) 10% of lecithin.

In continuous CIJ mixers, the mixing of sunflower oil and the aqueous solution of lecithin occurs from the impingement in the mixing chamber of the two phases as high-speed jets. The geometry used in this work corresponds to Chamber 1 in Table 4.1: $D = 10 \text{ mm}$ and $d_1 = d_2 = 1.5 \text{ mm}$. According to the study on mixing of dissimilar fluids in CIJ mixers (Section 4.4), the two main conditions for the onset of the chaotic flow regime and effective mixing are:

- Reynolds number of the MV liquid stream has to be higher than 100;
- The impingement point position must be at the central position of the mixing chamber.

Based on this, two operation conditions were tested: $Re_{oil} = 150$ and $Re_{oil} = 200$, where Re_{oil} is the Reynolds number at the injector from where sunflower is injected.

In the first stage of this work, mayonnaise is produced as in a typical batch process, slowly adding the oil to the water phase under intensive agitation producing then the o/w emulsion. A high-speed dispersing and homogenizing device (MICCRA Homogenizer Disperser D-9) was used to promote the mixing of oil and water. For this, lecithin is previously added to water using a magnetic stirrer, and then sunflower oil is gradually added to water using a pump at 240 rpm.

The objective of the preliminary performance of a batch process stems from the fact that the shear rate conditions in CIJ mixer have to be mimicked in the high-speed dispersion and homogenization device. The shear rate in CIJ mixers can be estimated from the characteristic deformation in each region:

- At the impingement point: Previous works (Fonte, 2012; Gomes, 2014) reported from CFD contour maps that the highest deformation region is at the contact point between jets. The norm of the rate of strain tensor can be determined by $1/2(\mathbf{D}:\mathbf{D})^{1/2} = \dot{\gamma}_{inj}\varpi$, where $\dot{\gamma}_{inj}$ is the strain experienced by the fluid at the injectors' walls ($\dot{\gamma}_{inj} = 8\mu Re/(\rho d^2)$) and ϖ is a non-dimensional rate of strain. CFD results in Fonte (2012) showed that $\varpi = 1$ at the impingement point.
- In pancake shearing: The typical shear rates can be estimated equalizing Equation (4.38) to $s/s_1 = 1/\sqrt{1+(\dot{\gamma}t)^2}$ and thus $\dot{\gamma} = \sqrt{4v_{inj}^2/d^2 - 1/t^2}$ for $\frac{d}{2v_{inj}} \leq t \leq \frac{D}{2v_{inj}}$.

- In engulfing vortices region: A pure shear flow is considered, and the vortices radius is $D/4$ with average velocity in the periphery of v_{inj} . The shear rate in the radial direction is $\dot{\gamma} = 4v_{inj} / D$.
- At CIJs runner: The shear rate is formed by a parabolic profile and so $\dot{\gamma} = 4d^2 v_{inj} / D^3$.

The high-speed homogenizer is based on the rotor-stator device, which consists of a fast-spinning inner rotor and a stationary outer stator. The shear rate in rotor-stator devices is determined by $\dot{\gamma} = RPM \pi r_r h_{r/s}^{-1} / 30$, where RPM is the rotor speed in rpm, r_r is the rotor radius and $h_{r/s}$ is the distance between the rotor and stator. The homogenizer has a speed scale between 11 000 and 39 000 rpm, a distance between the rotor and stator of 0.5 mm and a rotor radius of $r_r = 6.25$ mm.

Table 4.10 summarizes the deformation at each region in CIJ mixers and the respective rotor speed to replicate the same stretching regions in the batch process. The rotor speed was determined by equalizing both shear rate expressions for high-speed homogenizer and the continuous mixer. The period of time was defined according to Table 4.9, and the residence time was determined from Equation (4.17).

For $Re_{oil} = 150$ and $Re_{oil} = 200$, all regions, except at the impingement point, the respective rotor speeds are under the working range of the high-speed homogenizer. In this sense, the lowest shear rate condition in the homogenizer (11 000 rpm) was set in the batch process.

Table 4.10 Deformation conditions in CIJ mixers and high-speed homogenizer.

$\text{Re}_{\text{oil}} = 150$			
Region	Period [ms]	$\dot{\gamma}$ [s^{-1}] (CIJ mixer)	RPM [rpm] (high-speed homogenizer)
Impingement Point	$0 \leq t \leq 0.18$	33054	25251
Pancake Shearing	$0.18 < t < 1.21$		$0 < RPM < 6269$
Engulfing Vortices	$1.21 \leq t < 6.05$	2479	1894
CIJ mixers runner	$6.05 \leq t < 269$	37	28
$\text{Re}_{\text{oil}} = 200$			
Region	Period [ms]	$\dot{\gamma}$ [s^{-1}] (CIJ mixer)	RPM [rpm] (high-speed homogenizer)
Impingement Point	$0 \leq t \leq 0.09$	44072	33668
Pancake Shearing	$0.09 < t < 0.61$	$0 < \dot{\gamma} < 10893$	$0 < RPM < 8321$
Engulfing Vortices	$0.61 \leq t < 3.03$	3305	2525
CIJ mixers runner	$3.03 \leq t < 134$	74	57

4.6.2.1.2 Emulsions Stabilization

The first stabilization analysis was made from the observation of samples for more than four days. This measuring time is not ideal for the typical study on the production of emulsions. However, the main objective is the comparison of the droplet size formed in CIJ mixers and batch processes. In this work, it is important that the emulsions are stable for a few hours that will enable to characterize the emulsion. The separation of two phases is the result of emulsions destabilization, which can be the result of excess or the lack of emulsifier.

The type of emulsion (o/w emulsion or a w/o emulsion), is classified from the drop test. For this, a drop of emulsion is added to a container with oil and to another one with water. If the continuous phase is water (o/w emulsion), a drop will be formed when added to oil and disperse when added to water. If the continuous phase is oil (w/o emulsion), a drop will be formed in the water container, and it will disperse in the oil container. The drop test is the easiest way to characterize the type of emulsions rapidly.

4.6.2.1.3 Droplet Size Measurements

The comparison between batch and continuous processes was made from the measurement of the droplet size from microscope images, which were taken from the samples collected during the experiments. A Microscope ZEISS coupled with an Axiocam 105 colour camera was used to observe the oil droplets. For imaging treatment, ZEN proprietary software is used with the ZEISS microscope. The effective measurement of the droplet size was made with Image J using the analysis particle tools. In this image processing, the image scale has to be set, and the images are converted to a binary colour scale. The circularity of the droplets was imposed as a condition for the pattern recognition algorithm, which generates a list with all droplets recognized from the optical microscope image. The mean diameter is calculated from the list of droplet diameters generated with Image J.

4.6.2.2 Batch Process – Results and Discussion

The first characterization test, concerning the behaviour of emulsions, was made from the drop test. Figure 4.58 shows the drop tests carried out for emulsions with 4.1%, 2.1%, 1.7% and 1.3% wt./wt. of lecithin. The dispersion of a drop is observed when added to water, so the emulsions are oil-in-water. The opposite effect is observed by adding to oil.

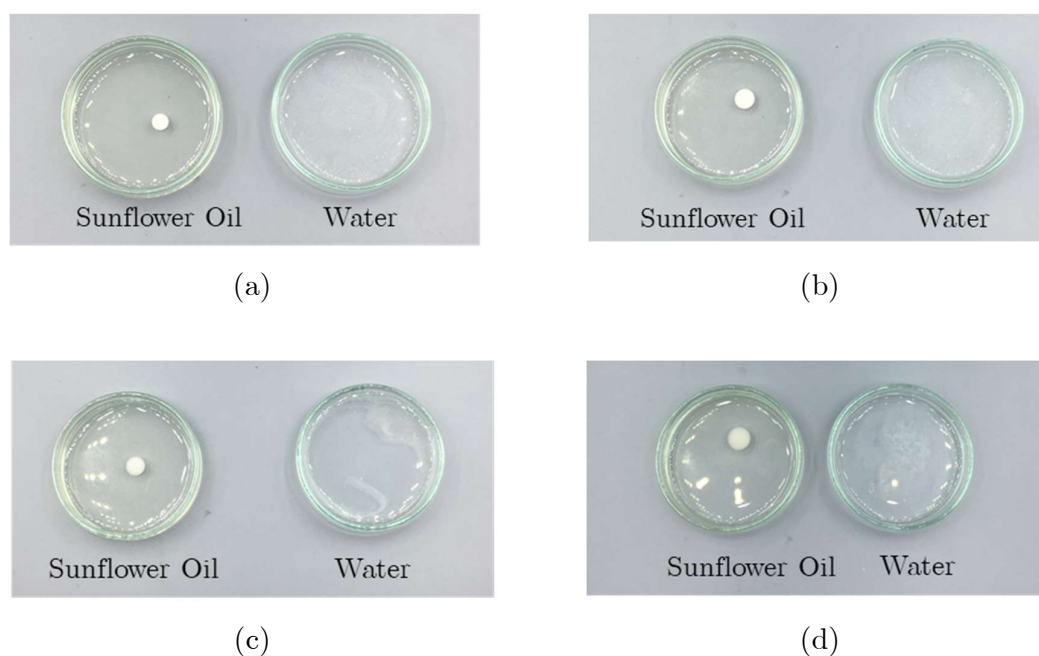


Figure 4.58 Drop Tests for o/w emulsions made with the rotor-stator mixer for different mass fractions of lecithin (a) 1.3%; (b) 1.7%; (c) 2.1% and (d) 4.1%.

The stabilization of emulsions over six days was visually assessed by the homogeneity or separation of oil and aqueous phases with time in glass bottles. Figure 4.59 shows images of different stabilization stages of o/w emulsions with different mass fraction of lecithin. The mass fraction of lecithin of 1.3% (wt./wt.) is not enough to get stable emulsions (Figure 4.59a and Figure 4.59b). One day after, the interface between both phases is clearly observed in Figure 4.59a, and two phases are distinguished: a dark yellow phase and a lighter yellow phase. Figure 4.59c and Figure 4.59d show that emulsions with 1.7% lecithin (wt./wt.) still lack emulsifier, and so after one day, the emulsion is unstable. This is clear from the visualisation of the interface between both phases. For a concentration of 2.1% lecithin (wt./wt.), in Figure 4.59e and Figure 4.59f, the emulsion is still unstable after one day. Increasing the mass fraction of lecithin to 4.1% (wt./wt.), the emulsion is stable for at least six days (Figure 4.59g to Figure 4.59i). This result is in agreement with the literature, where it is claimed that

the lecithin is a suitable emulsifier for o/w emulsions for a mass fraction of 5-10% (wt./wt.) of fat (List, 2015).

Therefore, experimental data show that 4.1% lecithin (wt./wt.) is the ideal concentration to obtain a stable emulsion for a longer time. However, for this concentration of lecithin, the fluid has a behaviour that approaches a shear-thinning fluid. This feature has to be taken into account for the design of the emulsification process in CIJ mixers. Furthermore, the amount of lecithin required in the continuous process, due to the high throughput of continuous experiments, makes these preliminary tests quite unpractical to undertake in CIJ mixers at chaotic flow regimes.

Figure 4.60 shows microscope and the respective image post-processing of o/w emulsions for the different concentrations of lecithin: 1.3%, 1.7%, 2.1% and 4.1% (wt./wt.) on Day 0. The droplets in Figure 4.60 corresponds to oil, and the continuous phase is water. In these four images, it is observed big and small droplets of oil, that means oil droplets were coalescing, which is the result of the instability of emulsions.

The microscope images post-processing in Image J enables to determine the mean oil drops diameter on Day 0. The mean diameter of oil droplets was calculated in terms of number. For a solution of 1.3% lecithin (wt./wt.), the mean diameter is $\bar{d} = 21.92 \pm 47.33 \mu\text{m}$, $\bar{d} = 12.35 \pm 14.40 \mu\text{m}$ for 1.7% lecithin (wt./wt.), $\bar{d} = 6.00 \pm 9.05 \mu\text{m}$ for 2.1% lecithin (wt./wt.) and $\bar{d} = 13.75 \pm 13.45 \mu\text{m}$ for 4.3% lecithin (wt./wt.).



Figure 4.59 Stabilization analysis of o/w emulsions made with the rotor-stator mixer, for different mass fraction of lecithin (a) 1.3% on Day 0; (b) 1.3% on Day 1; (c) 1.7% on Day 0; (d) 1.7% on Day 1; (e) 2.1% on Day 0; (f) 2.1% on Day 1; (g) 4.1% on Day 0; (h) 4.1% on Day 1; (i) 4.1% on Day 6.

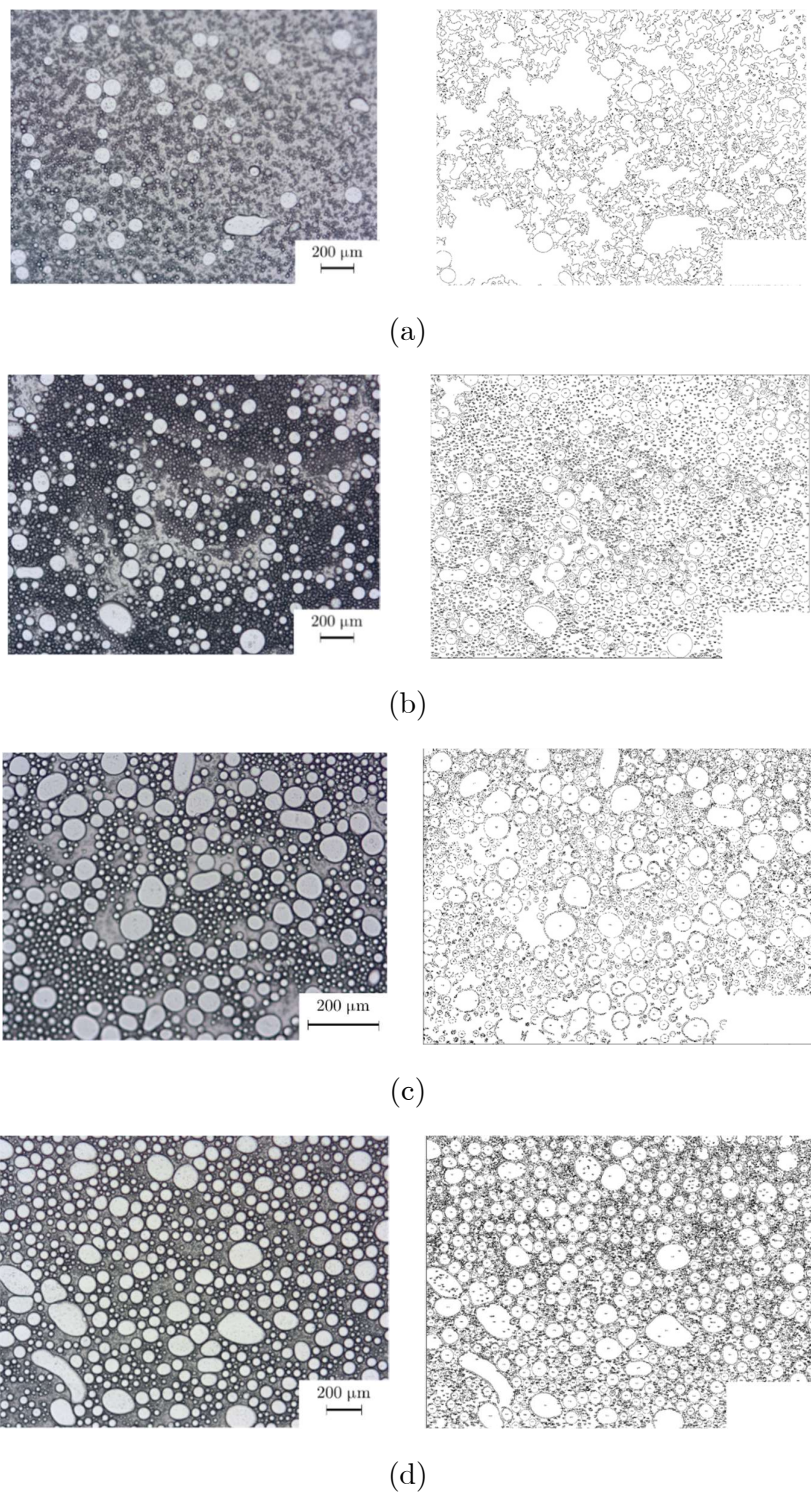


Figure 4.60 Microscope images of o/w emulsions and respective image post-processing in Image J, made with the rotor-stator mixer on Day 0 at (a) 1.3%; (b) 1.7%; (c) 2.1% and (d) 4.1%.

The analysis of particle size distribution can be assessed from the probability density function of the diameter of droplets. The probability density function, pdf, of the diameter of droplets is determined from

$$\Pr(d_{\text{oil}}) = \frac{n_{\text{samples}} \big|_{d_i \leq d_{\text{oil}} \leq d_i + \Delta d}}{n_{\text{samples}} \Delta d} \quad (4.42)$$

where $n_{\text{samples}} \big|_{d_i \leq d_{\text{oil}} \leq d_i + \Delta d}$ is the number of particles belonging to the interval $d_i \leq d_{\text{oil}} \leq d_i + \Delta d$, n_{samples} is the total number of samples and Δd is the width of each scale in the probability density function.

Figure 4.61 shows the probability density function of the diameter of oil droplets. For all cases, the larger probability is in the bin between 0 and $10 \mu\text{m}$.

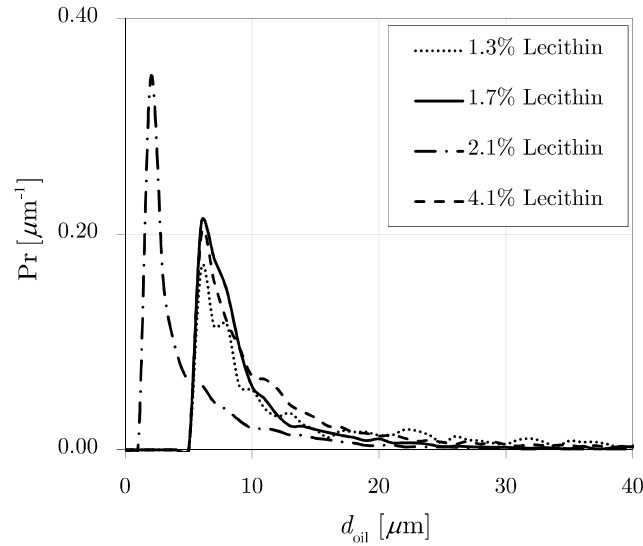


Figure 4.61 Probability density function of diameter of oil droplets for the three o/w emulsions, made with the rotor-stator mixer.

Emulsions produced with a solution of 2.1% lecithin (wt./wt.) have smaller mean diameters of droplets and standard deviations. This is also shown in Figure 4.61, where the greatest probability is identified for smaller drops of oil. Nevertheless, the control of the stability from the visualization of the phases interface shows that the emulsion

with 4.1% of lecithin (wt./wt.) promotes the best stabilization times. This result is in agreement with the literature, where is claimed that the lecithin is suitable for an o/w emulsions with 5-10% (wt./wt.) of fat (List, 2015).

4.6.2.3 Continuous Process using CIJ mixers – Results and Discussion

The ability of CIJ mixers to produce o/w emulsions was tested using an aqueous solution with 3% of lecithin (wt./wt.). Although the emulsion is clearly unstable for this concentration of lecithin, it is stable enough to analyse samples immediately after being produced, i.e. on Day 0. As the main goal of this work is the demonstration of the ability of CIJ mixers to produce o/w emulsions, the behaviour of emulsions with 3% of lecithin (wt./wt.) was considered reasonable. The reasons for not performing the experiment with 10% of lecithin were: the behaviour of this dispersion as a shear-thinning fluid, which must be taken into account in KEM; the requirement of large amounts of lecithin due to the high throughput in these mixing devices.

The working conditions were set according to the previous studies on mixing of dissimilar fluids in CIJ mixers. Based on this, the Reynolds number at the oil jet was $Re_{oil} = 150$ and $Re_{oil} = 200$. The Reynolds number of the aqueous stream was determined from KEM. So, as the contact point between jets must be at the centre of the mixing chamber ($\xi=0$), Re_{water} has to be 2658 (for $Re_{oil} = 150$) and 3771 (for $Re_{oil} = 200$), considering the geometrical parameters of Chamber 1 (Table 4.1). The physical properties used for the prediction of Re_{water} were measured from rheological tests (Figure 4.57a) and from the density first estimated from literature data and then checked in the Coriolis flowmeter. The experimental setup in this work was already described in Figure 4.9 and Figure 4.10.

Figure 4.62 shows the microscope images, and the respective image post-processing of o/w emulsions stabilized with 1.3% of lecithin (wt./wt.) for the two working conditions. The determination of the mean diameter of the oil drops was made from the image

post-processing, $\bar{d} = 13.93 \pm 12.91 \mu\text{m}$ at $\text{Re}_{\text{oil}} = 150$ and $\bar{d} = 13.55 \pm 12.13 \mu\text{m}$ at $\text{Re}_{\text{oil}} = 200$.

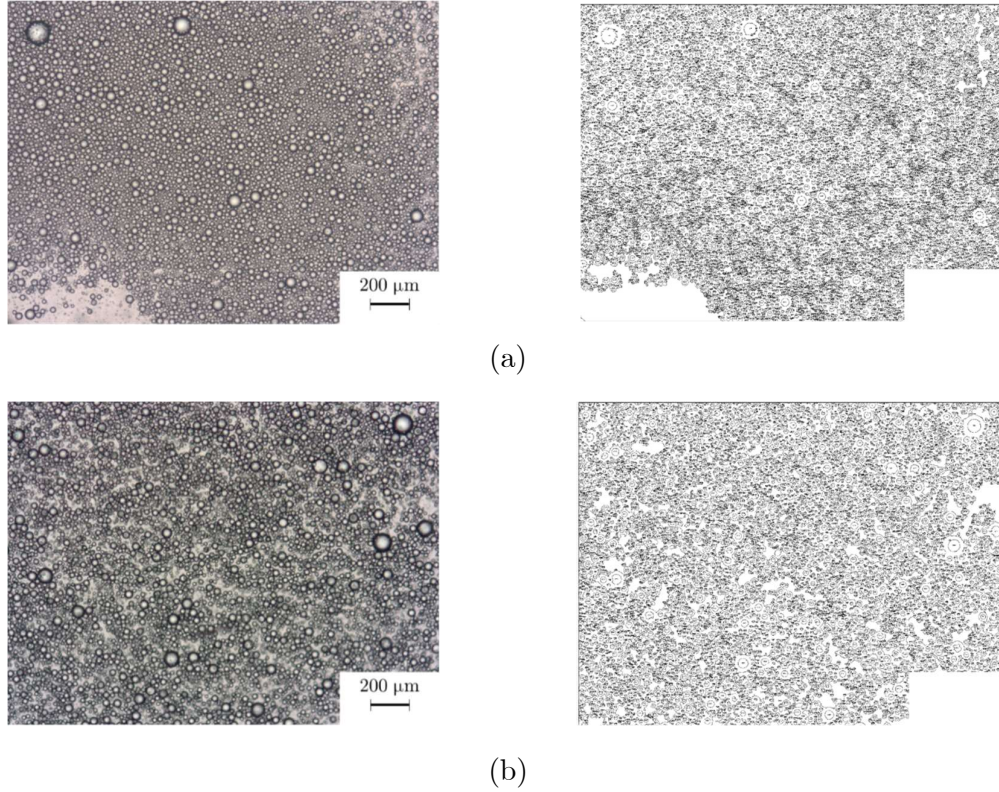


Figure 4.62 Microscope images and the respective image post-processing in Image J of o/w emulsions with 1.3% produced in CIJ mixers at (a) $\text{Re}_{\text{oil}} = 150$ and (b) $\text{Re}_{\text{oil}} = 200$.

Figure 4.62 also shows that CIJ mixer can produce quite homogeneous emulsions compared with the batch production (Figure 4.60a). Table 4.10 shows that in CIJ mixers, liquids undergo lower deformation than in the batch process ($\text{RPM} = 11000 \text{ rpm}$), except at the impingement point where the respective rotor speeds are 16834 for $\text{Re}_{\text{oil}} = 150$ and 33668 for $\text{Re}_{\text{oil}} = 200$. Nevertheless, the deformation at the impingement point in the continuous process is higher than in the high-speed homogeniser, promoting a better droplet size distribution (Figure 4.62). This is evidence that the full inlet power focused and dissipated at the jets contact point is the key to high energy efficiency in CIJ mixers.

The probability density function of the diameter of oil droplets produced in CIJ mixers is in Figure 4.63 for $Re_{oil} = 150$ and $Re_{oil} = 200$. Microscope images were taken on Day 0 because these emulsions are quite unstable. Note that smaller droplets are formed in CIJ mixers, and so that large amounts of emulsifier would be required to stabilize this system. This means that the behaviour of emulsions over time is not the same than in the batch process.

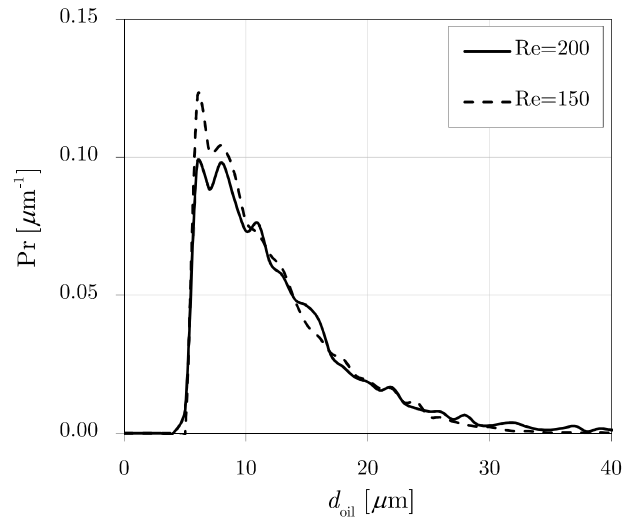


Figure 4.63 Frequency function of the mean diameter of the oil droplets of o/w emulsions with 1.3% produced in CIJ mixers.

Table 4.11 shows the comparison between the mean diameter produced in batch and continuous processes (CIJ mixers) for the same working conditions (1.3% of lecithin). Results are in the same order of magnitude, and so the continuous reactors can efficiently mix two liquid streams. This makes the implementation of opposed jets in an emulsification process a promising solution for industrial plants.

Table 4.11 Mean diameter of oil droplets in the batch process and continuous process (CIJ mixers).

Batch Process	Continuous Process
$\bar{d} = 21.92 \pm 47.33 \mu\text{m}$	$\text{Re} = 150 : \bar{d} = 12.93 \pm 12.91 \mu\text{m}$
	$\text{Re} = 200 : \bar{d} = 13.55 \pm 12.13 \mu\text{m}$

4.7 Conclusions

This chapter was divided into four parts: Part I - the development of a lamellar model to describe the micromixing in CIJ mixers; Part II - analysis of mixing dynamics for mixing of dissimilar fluids; Part III - the development of models to predict the impingement point position; Part IV - two examples of product development in CIJ mixers: first example is the screening of mixing scales in rotational devices and application of this to RIM-PU process, and the second case is the design of a process in CIJ mixers at pilot scale.

The analysis of the lamellar microstructure generated by impinging jets flows, with application to RIM machines, is presented in Part I. A lamellar micromixing model was solved using striation thickness data from the models proposed by Lee et al. (1980) and Baldyga and Bourne (1983) and compared with the experimental data from Nunes et al. (2012). The data from the striation thickness models were compared to the deformation undergone by material elements in CIJ mixers obtained from CFD simulations and using particle tracking approaches.

Results from the LM model show that the striation thickness function proposed by Lee et al. (1980) gives the best estimation of the striation thickness evolution for a range of Reynolds number $200 < \text{Re} < 600$. The description of the micromixing from the LM model and the respective validation enables the use of the LM model as a design tool for reactive processes based on CIJ technology.

3D CFD simulations show a nearly exponential increase of the average stretching of fluid elements with time for $Re > 110$, which is a feature of chaotic flows. These results indicate that smaller striation thicknesses of the liquid streams at the outlet of the mixing chamber are observed with increasing Reynolds numbers. The striation thickness reduction obtained from CFD simulations is in agreement with the model of Lee et al. (1980).

The model proposed by Lee et al. (1980) is based on the balance of mechanical energy in the CIJ mixing chamber and assumes that all energy injected in the mixing chamber is used in the generation of the interfacial area between fluids. The validation of Lee et al. (1980) assumption from micromixing data, clearly shows that CIJ mixers make a very efficient transfer of the jets kinetic energy into mixing.

These conclusions also present the definite proof that the flow in the studied range of Reynolds numbers in CIJ mixers is laminar. The mechanism of mixing in CIJ mixers is the stretching of the interface between the two fluids as described in chaotic mixing for laminar flows.

CIJ mixers are able to mix dissimilar fluids of different viscosities, under a chaotic flow regime that is characterised by the generation of vortices that engulf both fluids, forming a structure of thin lamellae. This was demonstrated in Part II. The necessary condition for the onset of this mixing flow regime is the balance of the opposed jets, i.e. the jets impingement point must be located at the mixing chamber axis. PLIF experiments clearly indicate that the critical Reynolds number able to onset the chaotic flow regime is defined by the more viscous fluid inlet jet. Experiments with viscosity ratios from 2 to 9 showed that the critical Reynolds number defined by the MV fluid may take any value $Re_{MV,c} > 150$, that ensures the self-sustainable chaotic flow regime. The increase of the Reynolds number above 120 in LV fluid streams promotes instabilities in the MV liquid stream at lower Re values. Results with external stimuli have shown that it is possible to onset chaotic flows below the transition Reynolds numbers, namely in opposed jets (Li et al., 2013b,a; Shi et al., 2015; Li et al., 2016).

The other parameter that plays a critical role in the onset of chaotic flow regime is the balance of jets. Results in Part II show that the CIJ mixers running in the laminar mixing of dissimilar fluids, is focused on keeping and maximizing the natural chaotic oscillation of the two opposed jets impingement point, as observed for similar fluids (Fonte et al., 2015).

In Part III, three models were considered to describe the shifting of the impingement point position in the mixing chamber. The elastic analogue model predicts the tendency and actual position of the jets impingement point, with particular accuracy for Reynolds numbers of industrial relevance, above 150. The kinetic energy model predicts the contact point between jets from the balance of the kinetic energy of two Lagrangian entities belonging to each stream at the impingement point. The momentum model considers the equilibrium between the linear momentum of two entities in each fluid. Experimental and numerical results enabled to validate the range of validity of each model. The elastic analogue model only predicts the mixing of similar fluids. The momentum model is able to estimate the contact point for similar conditions and for mixing of fluids with different viscosities (validity range from 2 to 9) and similar densities (density ratio of approximately 1). The kinetic energy model is the one with a wider range of application, because it is able to predict even the mixing of similar fluids as the mixing of fluids with quite different density and viscosity ratios. This means that the balance of two opposed jets is totally described by the equilibrium of the kinetic energy at the impingement point. PLIF results and CFD simulations of a CIJ mixer validated the kinetic energy model as a design tool for mixing of dissimilar fluids in CIJ mixers.

Two stages of product development in CIJ mixers are described in Part IV. The first stage consists of mimicking the mixing scales formed in CIJ mixers using rotational devices able to produce the same scales. The application of the rotational device as a product development procedure to an actual reactive polymerization industrial process was made for a case study, the RIM process. For the full control of testing conditions in rotational devices, the mixing conditions are related to industrial processing, which enables direct process scale-up from this product development procedure. Three distinct regions in CIJ mixers were identified according to the shear rate differences in each

region. These conditions were defined in the rotational devices in order to obtain the same mixing scales.

The second case of product development in CIJ mixers is the testing of working conditions for effective mixing of two phases, oil and an aqueous phase. The case study in this work was the production of mayonnaise, i.e. oil/water emulsion. The experiments were designed from the kinetic energy model introduced in Part III. The efficiency of the mayonnaise production was validated from a batch process. These experiments prove that CIJ mixers are able to produce emulsions injecting the two phases directly as opposed jets.

4.8 References

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5 Mixing Mechanisms in T-Jets Mixers

5.1 Introduction and State of the Art

T-Jets reactors are prismatic opposed-jets mixers that have become even more common due to the wide spreading of microreactors in industrial applications. The intensification of the industrial performance of T-Jets mixers resulted in the increase of publications on this topic after 2000. One of the most common industrial applications of T-Jets mixers is the production of nanoparticles from a continuous process (Masala and Seshadri, 2004; Schikarski et al., 2016). The main advantage of conducting nanoparticle production in T-Jets reactors is the controlled particle size distribution that is much influenced by the mixing mechanisms in the opposed jets reactor.

More recently, these impinging jets have been applied in other industrial processes to increase its mixing performance, such as, in combustion, gasification, absorption, extraction and drying (Wang et al., 2012; Luo et al., 2013; Niemann et al., 2014; Tsaoulidis et al., 2018).

A classical T-Jets mixer has a T-shaped geometry and consists of a prismatic mixing chamber having two directly opposed prismatic injectors near the closed top of the chamber at an angle of 90° with the chamber. Jets inlet channels generally extend through the complete depth of the mixer, preventing the radial spreading of the jets and the formation of a pancake contrarily to the flow dynamics in CIJ mixers. This is the main difference between CIJ and T-Jets mixers.

In the present thesis, the geometry used consists of two opposed prismatic jets with a cavity above the jets inlet, commonly named as headspace, h , as shown in Figure 5.1. This cavity is not a common design feature of T-Jets mixers in other published works. However, it has a fundamental role in the formation of vortices, which ensures the generation of the jets auto-oscillation (Santos et al., 2002; Santos et al., 2010). This configuration was introduced, for the first time, by Sultan et al. (2012), and more recently, Tu et al. (2015) and Li et al. (2016) have performed their experiments in T-Jets mixers with headspace. The specific role of this cavity is demonstrated later in this chapter.

In T-Jets reactors, two liquid streams are fed through the opposed jets, and the mixing occurs in the mixing chamber. Mixing of streams is promoted by the injection of two jets, ensuring the decrease of the thickness of the inlet streams, which initially have the same dimensions of the injectors. The fact that the jets with reactants are directly contacted to each other results in high concentrations, which is a key factor for the control of product properties from chemical reactions. This particularly noticeable in the case of nanoparticles properties, where supersaturation control plays a key role. The mixing mechanisms in T-jet reactors are actually quite similar to those in CIJ mixers, where the main mechanisms is a vortex street that sheds from the jets impingement point towards the outlet. After the fluid streams undergo a flow field with high shear rates, the mixture will leave the mixing chamber through an open outlet.

The characteristic dimensions of T-Jets are also illustrated in Figure 5.1: the width of the mixing chamber, W , the width of injectors, w , the depth of the mixing chamber, e , the mixing chamber height, H , and the headspace of the mixing chamber, h . In this work, jets 1 and 2 are defined according to Figure 5.1.

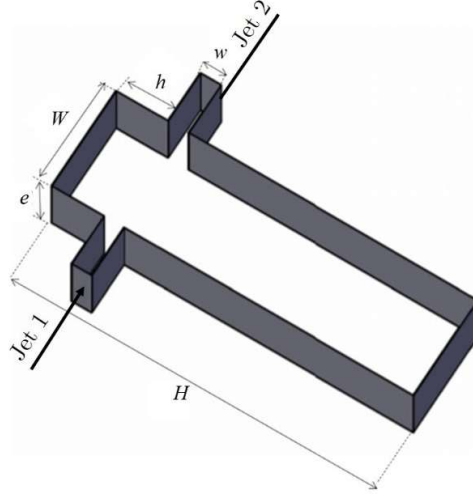


Figure 5.1 Sketch of the T-Jets geometry (scale is not the same of the actual device) .

The definition of flow regimes in T-Jet mixers is a much more arduous task than in CIJ mixers. Many studies show that mixing and flow dynamics in the mixing chamber depend on the operating conditions, which are mostly associated to Reynolds number. Nevertheless, other works also show that geometrical parameters have a strong impact on convective flow patterns. Therefore, Reynolds number is not the only variable that contributes to the onset of dynamic flow regimes, making the process of defining the flow regimes in T-Jets mixers much more complex than in CIJ mixers. The flow regime in T-Jet mixers depends on the momentum ratio of the jets, the chamber-to-injector width or chamber width-to-depth ratios and the jets Reynolds number, which is defined as (Sultan et al., 2012)

$$\text{Re} = \frac{\rho v_{\text{inj}} w}{\mu} \quad (5.1)$$

where ρ and μ are the density and the viscosity, respectively, and v_{inj} is the velocity at the injector. Some authors recurrently define the Reynolds number at injectors, i.e., hydraulic Reynolds number, as

$$Re_{Hjet} = \frac{\rho v_{inj} d_{Hjet}}{\mu} \quad (5.2)$$

where v_{inj} is the superficial velocity at the injector, ρ and μ are the density and viscosity of fluids, respectively, and d_{Hjet} is the hydraulic diameter of the injector, which is given by

$$d_{Hjet} = \frac{2we}{(w + e)} \quad (5.3)$$

5.1.1 Mixing Dynamics – Influence of Reynolds Number

Previous works have reported different flow regimes that resulted from different combinations of operational and geometrical parameters. The flow visualisations have been based on advanced optical techniques as micro-Particles Image velocimetry (μ -PIV) and micro-Laser Induced Fluorescence (μ -IF) (Kockmann et al., 2003; Engler et al., 2004; Hoffmann et al., 2006; Ait Mouheb et al., 2012). CFD simulations have also contributed to a description of flow dynamics in T-Jets mixers (Bothe et al., 2006). From these visualisations, two main flow regimes are distinguished: steady at low Re and unsteady regimes at high Re, according to Mariotti et al. (2018). Three stages in steady regimes were identified: stratified, vortex and engulfment flow regime. These regimes are not detected for all geometrical parameters, and some of them are restricted for specific geometries. A detailed description of stratified, vortex and engulfment flow regimes is then described:

- Segregated or stratified flow regime – in this regime, each side of the mixing chamber contains mainly one of the fluids. Figure 5.2a and Figure 5.2b, which are reprinted from Soleymani et al. (2008), show the pathlines of this flow regime

from two different views. The fluid stream flows from the inlets to the outlet delimited by the segregation plane that coincides with the mixing chamber axis and is normal to the injectors axes (Soleymani et al., 2007; Bothe et al., 2008; Sultan et al., 2012; Mariotti et al., 2018). Table 5.1 shows the experimental and numerical results at this condition reported in Mariotti et al. (2018). Mariotti et al. (2018) defined that the working range for segregated flow regime is $Re_{Hjet} < 80$, which is in agreement with Figure 5.2a and Figure 5.2b (Soleymani et al., 2007);

- Vortex (steady symmetric) flow regime – this regime is characterised by the formation of a Dean vortex in each side of the mixing chamber, as shown from the pathlines in Figure 5.2c and Figure 5.2d (Soleymani et al., 2008). These vortices are characterised by a helicoidal movement of each liquid flow stream, and their rotation axis is aligned with the mixing chamber axis preserving the flow symmetry. This is also observable from figures in Table 5.1. At the plane defined by the mixing chamber and injector axes, the flow patterns are similar to the stratified flow regime. The distinction between stratified and vortex flow regime is made from the pathlines (Soleymani et al., 2008) or the isosurfaces (Mariotti et al., 2018), where a double pair of vertical structures are clearly visualised. At this flow regime, the mixing only occurs by diffusion at the interface between the two Dean vortices (Soleymani et al., 2007; Bothe et al., 2008; Soleymani et al., 2008; Sultan et al., 2012; Mariotti et al., 2018). Mariotti et al. (2018) defined the working Re range for this regime for $80 < Re_{Hjet} < 140$, which is in agreement with the CFD results in Soleymani et al. (2007) at $Re_{Hjet} = 80$ (Figure 5.2a to Figure 5.2d);
- Steady engulfment flow regime – this regime was visualized, for the first time, by Kockmann et al. (2003). Helicoidal vortex structures are formed at the plane defined by the mixing chamber and injectors axes leading to the break of symmetry. This regime is characterised by the formation of two recirculation structures at the top of the mixing chamber that promotes the transport from

one half of the chamber to the other. The behaviour of these structures is clearly visualised from the pathlines in Figure 5.2e and Figure 5.2f (Soleymani et al., 2008) and the experimental results in Table 5.1 (Mariotti et al., 2018). The dye concentration images taken at the cross-section of the mixing chamber in Table 5.1 (Mariotti et al., 2018) enables to visualise the two fluids superimposed, and the axis of the flow rotation is parallel to the mixing chamber axis (Soleymani et al., 2007; Bothe et al., 2008; Sultan et al., 2012; Mariotti et al., 2018; Zhang et al., 2019). However, no dynamic structures at the cross-section are formed. Mariotti et al. (2018) defined the Re range for the engulfment flow regime, which is $145 < Re_{Hjet} < 220$ and Soleymani et al. (2007) visualised this flow regime at $Re_{Hjet} = 240$, which is slightly above the value registered in Mariotti et al. (2018). This difference in the definition of Re ranges stems to the fact that Mariotti et al. (2018) distinguished the steady engulfment flow regimes and the other unsteady flow regimes (unsteady periodic flow regime), narrowing the working range for the engulfment flow regimes. The unsteady periodic flow regime will be described later in this chapter.

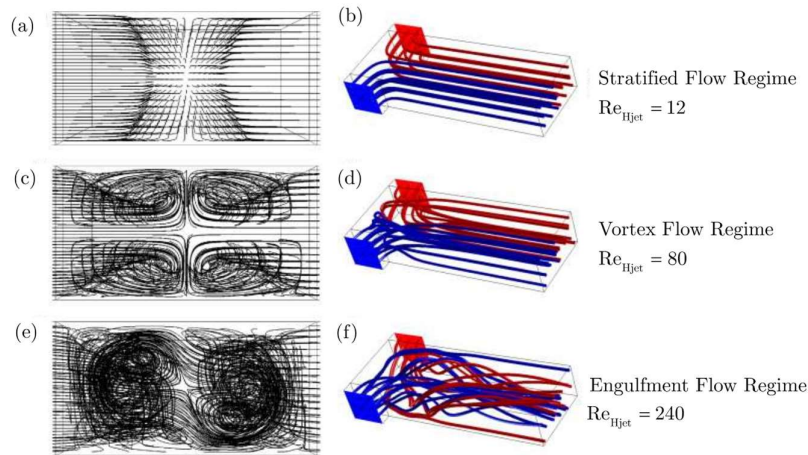
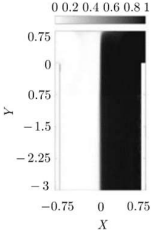
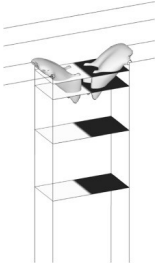
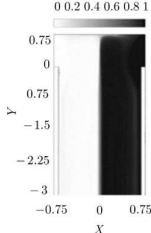
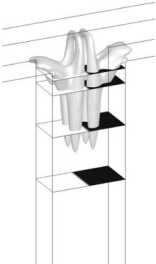
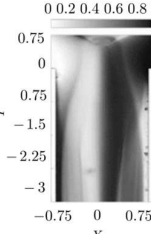
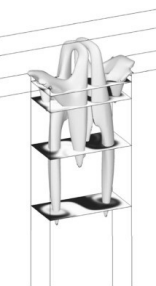
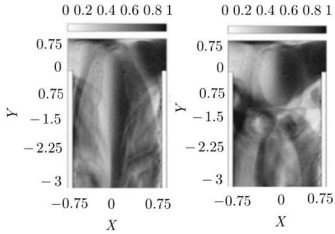
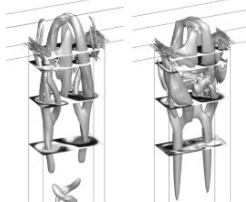
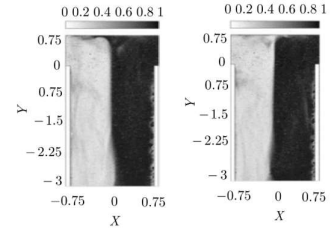
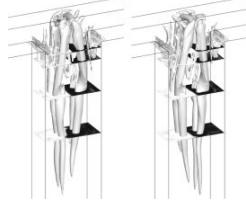


Figure 5.2 Pathlines for different flow regimes: stratified (a,b), vortex (c,d) and engulfment flow regime (e,f) obtained from CFD results from different views: the top of the mixing chamber (a,c,d) and isometric (b,d,f). Reprinted with permission from Soleymani et al. (2008).

Table 5.1 Summary of the flow regimes from experimental and CFD images. Reprinted with permission from Mariotti et al. (2018).

Flow regime	Flow visualisation	Vortical structures
Stratified flow regime $Re_{Hjet} < 80$		
Vortex flow regime $80 < Re_{Hjet} < 140$		
Engulfment flow regime $145 < Re_{Hjet} < 220$		
Unsteady periodic asymmetric regime $225 < Re_{Hjet} < 320$		
Unsteady periodic symmetric regime $325 < Re_{Hjet} < 510$		

Increasing Re , unsteady and periodic flow structures are formed in the mixing chamber. Four unsteady flow regimes were identified in T-Jets mixers, namely periodic asymmetric, periodic symmetric, chaotic and turbulent flow regime, which are characterised by:

- Periodic asymmetric flow regime – this regime is detected due to the formation of 3D vortical structures. The dynamic structures are formed at the top of the mixing chamber extending to the entire mixing chamber as two or four vortices emerging at the centre of the mixing chamber (Mariotti et al., 2018; Mariotti et al., 2019). Table 5.1 (Mariotti et al., 2018) shows experimental images of this flow regime, where periodic unsteady motions are observed. Periodic asymmetric flow regime was firstly detected from numerical simulations (Dreher et al., 2009; Minakov et al., 2012; Fani et al., 2013; Minakov et al., 2013; Andreussi et al., 2015; Galletti et al., 2017), and later the experimental corroboration was achieved by Thomas et al. (2010); Thomas and Ameel (2010); Mariotti et al. (2018); Mariotti et al. (2019); Zhang et al. (2019). This flow regime was only reported in T-Jets mixers without headspace for $225 < Re_{Hjet} < 320$ (Mariotti et al., 2018);
- Periodic symmetric flow regime – increasing Re , changes in flow patterns are observed from images in Table 5.1 (Mariotti et al., 2018). The flow seems to be steady and segregated from the front view of the mixing chamber, maintaining the double mirror in the entire length of the chamber. Nevertheless, 3D vortical structures are formed in the normal direction of the mixing chamber and injectors axes, as shown from the images in Table 5.1 (Mariotti et al., 2018). The oscillation of these structures is not enough to break the symmetric at the mixing chamber. At this flow regime, it is registered a significant decrease in the mixing degree (Mariotti et al., 2018; Mariotti et al., 2019). This regime was only observed in T-Jets mixers without headspace for $325 < Re_{Hjet} < 510$ (Mariotti et al., 2018);

- Chaotic flow regime – this flow regime is characterised by the formation of a vortex street, resembling a von Karman vortex street, consisting in the shedding of vortices from the opposed jets impingement point, which evolves throughout the mixing chamber promoting the fast mixing of the fluid streams (Sultan et al., 2012). For this regime, the formation of vortices occurs in the normal direction to the mixing chamber and injectors axes. The result is the stretching of the interface between the two liquid streams that promotes the reduction of the mixing scales. This flow regime was firstly reported from 2D CFD simulations, and later, Sultan et al. (2012) experimentally achieved this flow regime using T-Jets mixers with specific design features: with headspace at the top of the mixing chamber, the ratio W/w is larger than typical T-jets mixers, and the mixing chamber is deeper than the mixing chamber previously used. For this geometry in Sultan et al. (2012) and for a certain Re, the onset of a self-sustainable chaotic flow regime is characterised by the auto-oscillations of jets at the impingement point. The critical working condition for the onset of self-sustainable chaotic flow regimes is Re above 300 for a geometry with $W/w = 6$ and $W/e \leq 2$;
- Turbulent flow regime – for larger Re, small vortices are formed with a wide range of length scales (Schwarzer et al., 2006). The characterisation of this flow regime has only made from numerical simulations in Schwarzer et al. (2006) and Gradl and Peukert (2009). The production of nanoparticles is performed at these flow conditions by the group of Prof. Peukert at the University of Erlangen-Nürnberg (Gradl et al., 2006; Schikarski et al., 2019).

Santos and Sultan (2013) reported the mixing efficiency as the result of a reasonable balance between residence time and the formation of advective structures. In the stratified flow regime, low Re and residence time ensures the mixing by molecular diffusion. Further increasing Re, the residence time decreases, which in turn decreases the mass transfer by diffusion. When the increase in Re onsets the vortex flow regime,

the mixing efficiency increases due to the formation of dynamics flow structures, such as Dean vortices. The same is observed for the engulfment flow regime. Although these mechanisms are not so efficient as those formed in unsteady flow regimes, they are enough to offset the decrease of diffusional mechanisms due to the residence time. In unsteady flow regimes, the mixing efficiency is still promoted by the formation of vortices that stretch the fluids impinged through the two opposed jets (Engler et al., 2004; Soleymani et al., 2007; Soleymani et al., 2008; Dreher et al., 2009; Sultan et al., 2012). The increase of Re at unsteady flow regime does not mean that the mixing efficiency will increase. Mariotti et al. (2018) registered a decrease of mixing degree in the transition from the periodic asymmetric to the periodic symmetric flow regime. This fact is directly related to the topology of mixing that does not promote the formation of vortices in the normal direction of the interface. At these conditions, there is the formation of a “double mirror symmetry” in the mixing chamber, hampering the mixing degree (Mariotti et al., 2018).

5.1.2 Mixing Dynamics – Influence of Geometrical Parameters

In the last section, the flow regimes in T-Jets mixers were defined according to a specific $Re_{H_{jet}}$ range. Several authors concluded that the geometrical parameters also play an important role in mixing in T-Jets mixers, in addition to $Re_{H_{jet}}$ (Thomas et al., 2010; Shi et al., 2011; Galletti et al., 2012; Somashekar et al., 2012; Fani et al., 2013; Orsi et al., 2013a; Orsi et al., 2013b; Zhang et al., 2020). Engler et al. (2004) and Soleymani et al. (2007) were the first authors to report that the transition between flow regimes occurs at different Re for different geometries.

Literature reports the transition from steady to unsteady flow regime using different T-Jets mixers geometries (Hoffmann et al., 2006; Soleymani et al., 2008; Sultan et al., 2012; Krupa et al., 2014). A detailed analysis of the impact of each geometric parameters is presented in the following sections.

5.1.2.1 Effect of the Headspace on the Flow Dynamics

As already mentioned, the existence of headspace in T-Jets mixers is not a common design feature. This new geometry was introduced by Sultan et al. (2012) to demonstrate the existence of laminar chaotic flow regimes with jets auto-oscillation in T-Jets mixers. Later on, other works also used a similar T-Jets reactor (Krupa et al., 2014; Tu et al., 2015; Zhang et al., 2020). The main contributions using geometries with headspace in T-Jets mixers are listed in Table 5.2.

2D CFD simulations of T-Jets mixers (Santos et al., 2002; Santos et al., 2005) demonstrated that the flow is characterised by the oscillation above a certain jets Reynolds number that promotes the formation of vortex structures downstream the impingement point. These vortices are shed in a sequence of counter-rotating vortices towards the outlet, forming a vortex street throughout the mixing chamber. The frequency of oscillations of jets is directly related to the frequency of vortices formation (Santos et al., 2005). This flow regime is called the self-sustainable chaotic flow regime. Based on these numerical results, further studies to find a consistent 3D configuration able to achieve the self-sustainable chaotic flow regime were conducted by Sultan et al. (2012). Sultan et al. (2012) verified that the existence of a cavity above the injector axis promotes the formation of a vortex street that is the signature of the self-sustainable chaotic flow regime. In fact, the geometrical parameters and the operational conditions that enable the self-sustainable chaotic flow regime are $W/w = 6$, $W/e \leq 2$, $h = 2 \text{ mm}$ and $Re_{Hjet} > 300$.

Tu et al. (2014) observed the flow patterns in T-Jets mixers for different headspace lengths at $Re_{Hjet} = 412$ using two gas streams. For a geometry with $h = 0$, gases bend towards the outlet and instabilities occurs at the interface. This regime corresponds to the unsteady periodic flow regime. The increase of the headspace height from 0 to 10 mm promotes the oscillatory deflection of jets, up and down the injector axis. The concept of deflecting oscillation, which was introduced by Denshchikov et al. (1983),

consists of the oscillation of the impingement point position back and forth between the opposed injectors, switching simultaneously the jets bending to up or down positions. The deflecting oscillation is observed in geometries with $h = 10$ mm and $h = 20$ mm . Therefore, h contributes to the deflecting oscillation. This phenomenon was not observed in Sultan et al. (2012) because the T-Jets configuration has a lower value of h .

In Sultan et al. (2019), the onset of chaotic flow regime was also addressed from CFD simulations. Sultan et al. (2019) aimed at the identification of the critical parameters for the onset of this flow regime. One of the geometrical parameters considered was the free headspace in T-Jets mixers. Sultan et al. (2019) compared the pathlines at $Re_{Hjet} = 480$ using two geometries with $W/w = 6$ and $w/e = 1.5$. For geometries with a headspace $h = 2$ mm , CFD results show the formation of vortices downstream the impingement point (self-sustainable chaotic flow regime). On the other hand, for geometry with $h = 0$ mm , flow is no longer chaotic. The numerical results for $h = 2$ mm were also validated from the experimental results in Sultan et al. (2012).

Zhang et al. (2020) present one of the more recent experimental studies on the effect of geometrical parameters on the flow dynamics in T-Jets reactors. Zhang et al. (2020) defined the critical Re for this flow regime. Experiments were conducted for $W/w = 2$. The transition from segregated to steady engulfment flow regime delays with the increase of h . The unsteady asymmetric flow regime only occurs for $0 \leq h \leq 3$ mm . In addition, the Re range for unsteady asymmetric flow regime is delayed for higher values of h . For this flow regime, h has a different effect in comparison to chaotic flow regimes. In chaotic flow regimes, the lubricating role of h in the jets oscillation magnifies flow dynamics. In vortex flow regimes, the wall next to the jets causes shear instabilities that promote mixing. Once again, this evidences that the headspace has an important role in the onset of the unsteady asymmetric flow regime. This conclusion was already supported by Fani et al. (2013), who reported that the cavity at the top

of the mixing chamber is responsible by the deflection of the impingement plane and the onset of the engulfment flow regime.

Table 5.2 Summary of studies on the influence of headspace in T-Jets flow regimes.

Authors	W [mm]	W/w	W/e	h [mm]	Re_{Hjets}
Sultan et al. (2012)	6	6	1.5	2	280^{*1}
Tu et al. (2014)	40	10	1.25	0	-
	40	10	1.25	10	412^{*2}
	40	10	1.25	20	412^{*2}
Sultan et al. (2019)	6	6	1.5	0	480^{*3}
Zhang et al. (2020)	20	2	2	0	$100^{*3} \mid 200^{*4} \mid 300^{*5}$
	20	2	2	1	$120^{*3} \mid 200^{*4} \mid 300^{*5}$
	20	2	2	2	$140^{*3} \mid 200^{*4} \mid 300^{*5}$
	20	2	2	3	$150^{*3} \mid 200^{*5}$
	20	2	2	4	$150^{*3} \mid 200^{*5}$
	20	2	2	5	$150^{*3} \mid 200^{*5}$

^{*1} self-sustainable chaotic flow regime; ^{*2} deflecting oscillation; ^{*3} steady engulfment flow regime; ^{*4} unsteady asymmetric flow regime; ^{*5} unsteady symmetric flow regime.

5.1.2.2 Effect of the Width Ratio on the Flow Dynamics

Studies on free jets demonstrated that the increase of clearance between opposed jets means the increase of the jets instability (Denshchikov et al., 1978; Denshchikov et al., 1983; Li et al., 2008; Li et al., 2010; Li et al., 2011). The main contributions on the effect of ratio between the mixing chamber and the injectors widths, W/w , on the flow dynamics are listed in Table 5.3.

Denshchikov et al. (1983) visualised from free jet that the instabilities are accentuated for a separation between jets from four to six times the injector diameter. These instabilities result from the auto-oscillation of jets at the impingement point for a Re range between 100 and 500 (Denshchikov et al., 1983). Nevertheless, a ratio $W/w > 4$ is not so common in literature, as demonstrated in Table 5.3.

Hoffmann et al. (2006) studied the performance of mixing using geometries with $W/w = 4$ and $W/w = 2$. For lower W/w , the transition to the engulfment flow regime occurs at higher hydraulic Reynolds numbers, which is defined from the mixing chamber width. Chambers with larger W/w present a transition for lower Re (from 100 to 150). Soleymani et al. (2008) validated the conclusions presented by Hoffmann et al. (2006), stating that geometries with larger W/w require lower Re for the transition to the engulfment flow regime.

Sultan et al. (2012) and Krupa et al. (2014) also reported the effect of W/w on the flow transition. The mixing degree increases for larger expansion ratios, within a W/w from 1 to 6. This increasing occurs faster for larger W/w . It is also observed that geometries with $W/w > 4$ are able to operate at self-sustainable chaotic flow regime. On the other hand, for $W/w \leq 4$, the engulfment flow regime is the only flow regime achieved in this geometry. Note that the geometries used in Sultan et al. (2012) and Krupa et al. (2014) have the headspace above the injectors axis that is not a particular design feature in the previous studies.

Tu et al. (2014) studied experimentally the onset of deflecting oscillation in T-Jets reactors with two gas streams using a geometry similar to the one used in Sultan et al. (2012) and Krupa et al. (2014). The working range of W/w is from 2 to 10. For $W/w = 2$, the flow dynamics behave as in engulfment flow regime, where it is observed the oscillation of jets after a specific distance. For $W/w = 4$ and 6, the self-sustainable chaotic flow is clearly observed, being in agreement with Sultan et al. (2012). For larger W/w , $W/w = 8$ and $W/w = 10$, the deflecting oscillation is observed at the

impingement point, having a behaviour similar to the one observed for free jets in Denshchikov et al. (1983). Observations in Tu et al. (2014) showed that confined boundaries have a strong impact on the onset of the deflecting oscillation. It is observed that the jets bend towards the outlet and the oscillation of jets occurs below the injectors axis promoting the periodic switch of their directions and the vanishing of the impingement plane. This flow regime is commonly called half deflecting oscillation and has never been observed earlier because previous studies only considered geometries with $W/w \leq 4$. Therefore, the onset of the deflecting oscillation of confined opposed jets occurs for $W/w \geq 8$.

Recent studies in Zhang et al. (2020) addresses the effect of the width ratio for geometries without headspace. The transition to steady engulfment flow regimes occurs for lower Reynolds number as W/w increases. Increasing Reynolds number, the unsteady asymmetric regime onsets, and a further increase of Re enables the onset of the steady symmetric engulfment regime. The Re working range was $50 < Re_{HJet} < 400$. For $W/w > 4$ and at $Re_{HJet} < 200$, the segregated flow regime is clearly observed in the mixing chamber. For $Re_{HJet} > 200$, the unsteady asymmetric engulfment flow regime onsets. It is not observed the generation of a chaotic flow regime because this T-Jets mixers geometry does not have headspace.

In sum, W/w has a strong impact on the mixing efficiency. Small expansion ratios favour the mixing in T-Jets mixers, as for geometries with as without headspace. High expansions ratios do not promote the formation of unsteady asymmetric flow regime in geometries without headspace. On the other hand, in geometries with headspace, mixing is much more efficient at self-sustainable chaotic flow regime, i.e at $4 < W/w < 6$. The key condition for the onset of mixing dynamics is the balance between degrees of freedom for flow oscillations and shear instabilities caused by the walls.

Table 5.3 Summary of studies on the influence of W/w in T-Jets flow regimes.

Authors	W [mm]	W/w	W/e	h [mm]	Re_{Hjets}
Engler et al. (2004)	0.6	2	2	0	157
Hoffmann et al. (2006)	0.4	2	4	0	315
	0.4	4	4	0	100
Soleymani et al. (2008)	0.2	1	2	0	477
	0.8	2	2	0	141
Bothe et al. (2010)	0.2	2	2	0	186
Sultan et al. (2012)	2	1	0.5	2	400
	2	2	0.5	2	533
	2	4	0.5	2	266
Tu et al. (2014)	0.8	2	0.25	32	196
	1.6	4	0.5	32	98
	2.4	6	0.75	32	98
	3.2	8	1	32	100 ^{*1}
	4.0	10	1.25	32	100 ^{*1}
Zhang et al. (2020)	5	0.5	0.5	0	-
	10	1	1	0	150
	20	2	2	0	150 200 ^{*2}
	40	4	4	0	150 200 ^{*2}
	80	8	8	0	260

^{*1}onset of the deflection oscillation; ^{*2}onset of the unsteady engulfment flow regime

5.1.2.3 Effect of the Depth on the Flow Dynamics

The depth of the mixing chamber also influences the mixing dynamics. The main contributions on the effect of depth in T-Jets mixers are listed in Table 5.4. Hoffmann et al. (2006) demonstrated that deeper mixing chambers promote the engulfment flow regime at lower Re . Soleymani et al. (2008) defined three different steps for the behaviour of mixing chamber depth: for $W/e < 1.5$ the mixing degree increases; mixing efficiency is approximately constant for $1.5 < W/e < 2$, and the mixing degree substantially decreases for $W/e > 2$. This is directly related to the type of flow regime established. Chambers with $W/e > 2$ operate at stratified flow regime. The increase on the depth enables to operate at vortex flow regime and then at engulfment flow regime until $W/e < 1.5$. For deeper chambers, the mixing is hindered by the decrease of wall shearing. There is thus an optimal range for the depth.

Sultan et al. (2012) also studied the effect of depth in the flow dynamics. Once again, results point out that shallow mixing chambers compromise the mixing in the chamber, which is the result of a strong wall effect. The particular focus of that paper was the influence of depth on the onset of the self-sustainable flow regime. A constant W/w was used according to the conclusions presented in the last section, $W/w = 6$, which is the critical parameter for the self-sustainable chaotic flow regime. The depth was then changed from 1 to 6 mm. Experimental results show that for deeper mixing chamber ($W/e = 1$), the mixing efficiency decreases, and the optimum value of efficiency occurs for $W/e = 1.5$. The transition from steady to chaotic flow regime occurs at $Re_{Hjet} = 300$. These results were also obtained by Krupa et al. (2012) and Krupa et al. (2014), where the product distribution of a fast chemical reaction was used for the characterisation of micromixing.

Tu et al. (2014) studied the effect of depth using a T-Jets reactor with $W/w = 10$, $h = 12.5$ mm and at $Re_{Hjet} = 430$. The range of depth was $0.83 \leq W/e \leq 10$ and half-deflecting oscillation occurs for $W/e \leq 1.25$. For higher W/e , the half deflecting also

occurs at high Re numbers, e.g. for T-Jets mixers with $W/e = 10$ and $W/w = 10$, it occurs at $\text{Re}_{\text{Hjet}} = 462$.

Sultan et al. (2019) also reported from experimental results the influence of depth on the engage into a chaotic flow regime. The depths were chosen according to a range $1 < W/e < 6$ and for $W/w = 6$. The power spectra determined for $W/e = 1$ and $W/e = 1.5$ showed that $W/w = 1.5$ presents higher energy at typical frequencies, due to the large oscillation amplitude determined from the velocity at the central position of the injectors axis. So, the vortices at a chaotic flow regime are promoted by jets oscillations and the wall shearing.

Zhang et al. (2020) also reported the effect of depth in the transition to the unsteady engulfment flow regime. The vanishing of this flow regime was identified when the reactor depth increases to 2 and decreases to 0.5. These changes in the flow regimes are associated to the reduction of the mixing degree. Zhang et al. (2020) also concluded that the optimum depth of chamber is $W/e = 2$.

Tu et al. (2014) also studied a new configuration where the injectors depth does not extend throughout the entire depth of the mixing chamber. In this particular case, the mixing chamber depth is twice the injectors depth. A greater deflection of jets under these conditions is observed, compared to the case where the injectors depth extends throughout the entire chamber depth.

Table 5.4 Summary of studies on the influence of W/e in T-Jets flow regimes.

Authors	W [mm]	W/w	W/e	h [mm]	Re_{Hjets}
Engler et al. (2004)	0.6	2	2	0	157
Hoffmann et al. (2006)	0.4	2	2	0	150
	0.4	2	4	0	300
Soleymani et al. (2008)	0.1	1	1	0	278
	0.8	1	2	0	477
Bothe et al. (2010)	0.2	2	2	0	186
Sultan et al. (2012)	6	6	1	2	300
	6	6	1.5	2	160 ^{*1}
	6	6	2	2	133
	6	6	3	2	200
Tu et al. (2014)	40	10	10	20	132
	40	10	2.5	20	371
	40	10	1.25	20	412 ^{*2}
	40	10	0.83	12	428 ^{*2}
Sultan et al. (2019)	6	6	1	2	300
	6	6	1.5	2	400 ^{*1}
	6	6	2	2	450 ^{*1}
Zhang et al. (2020)ha	20	2	4	0	220
	20	2	2	0	107
	20	2	1	0	260

^{*1}onset of the deflection oscillation; ^{*2}onset of the unsteady engulfment flow regime

5.1.3 Identification Number for the Transition Flow Regimes

The transition between flow regimes is strongly affected by Re and geometrical parameters, and thus these two variables are not good identification numbers. Different attempts have been made to find a critical number that defines the transition between flow regimes. Engler et al. (2004) proposed a dimensionless number to distinguish flow regimes. This identification number relates the Kolmogorov scale, λ_K , and the mixing chamber diameter, D_H , which is calculated by $D_H = 2We / (W + e)$. The identification number defined by Engler et al. (2004) is given by

$$\frac{D_H}{\lambda_K} = \left(Eu \frac{D_H}{l_V} Re_H^3 \right)^{1/4} \quad (5.4)$$

where l_H is the ratio of control volume over the cross-sectional area of the mixing chamber, and Eu is the Euler number, which is given by

$$Eu = \frac{\Delta p}{\rho v_{\text{chamber}}^2} \quad (5.5)$$

where Δp is the pressure loss per the length from the control volume inlet to the outlet. Engler et al. (2004) defined the onset of the engulfment flow regimes for $D_H / \lambda_K = 40$.

Soleymani et al. (2008) proposed a new dimensionless number that indicates the transition from the vortex to the engulfment flow regime,

$$K = Re_{Hjet}^{0.82} \left(\frac{w}{W} \right)^{-0.79} \left(\frac{d_{Hjet}}{D_H} \right)^{-1.5} \left(\frac{W}{e} \right)^{0.15} \quad (5.6)$$

Numerical and experimental results showed the critical K to the transition between vortex and engulfment flow regime is $K_c = 100$. The definition of K_c enables to use it to optimise the geometrical parameters and the operating conditions achieving the efficient mixing performance in T-Jets mixers. The critical value of $K_c = 100$ makes a good prediction of the onset of engulfment flow regime for data of Soleymani et al.

(2008), Bothe et al. (2008), Hoffmann et al. (2006) and Engler et al. (2004). K_c was tested for mixing chambers with headspace (Sultan et al., 2012). The K_c values show no relation with the onset of dynamic flow regimes, both chaotic or engulfment, for these geometries.

5.1.4 Mixing of Binary Fluids in T-Jets Mixers

Studies on mixing of two dissimilar fluids, particularly between ethanol and water, have recently emerged in the academic community. The main reason for this interest rises from the solubility dependent bioavailability problem in drug development processes. The poor solubility of drugs in water, which results in the low availability of drugs in the target tissue, has forced the production of monodispersed drug nanoparticles. Liquid antisolvent precipitation has been demonstrated as a promising process in the pharmaceutical industry. In this process, the drug is initially dissolved in an organic solvent, such as ethanol, and later mixed with water. During the mixing of water and ethanol, supersaturation occurs due to the existence of a thermodynamic driving force, promoting the precipitation of the drug into nanoparticles. The particle size is determined by the supersaturation, which depends on the local concentration distribution, or in other words, the particle size depends on the mixing efficiency. From these findings, studies have emerged for the modelling of mixing of water and ethanol.

In the mixing of ethanol and water and in the liquid antisolvent precipitation, the viscosity and density of mixture depend on the local concentration. Therefore, the simulation of mixing dynamics has emerged before 2000. Wang et al. (2002); Jeon et al. (2003); Lin et al. (2007); Chung and Shih (2008); Ansari et al. (2010); Lin et al. (2011). Orsi et al. (2013b) started to study the best geometrical setup to optimise the mixing of water and ethanol using a simple T-shaped geometry without headspace in a Reynolds number range from 100 to 300. Experimental results show that the mixing is controlled by diffusion for $Re_{Hjet} < 100$. As ethanol is three times more viscous than water, the formation of a vortex street is delayed by a viscous layer separating the two liquid streams. Therefore, the onset of the engulfment flow regime is hampered: for

water-water system, this transition occurs at $Re_{Hjet} \approx 105$ and for water-ethanol, at $Re_{Hjet} \approx 173$, where Re_{Hjet} is defined using the water conditions for any case.

Galletti et al. (2015) further studied the mixing of binary fluids in T-Jets mixers. The mixture model presented in Galletti et al. (2015) takes into account the fluidity of mixing, which can be zero, positive or negative. A positive fluidity of mixing means that the viscosity of mixture increases, a zero fluidity of mixing corresponds to the case where the viscosity remains constant, and a negative fluidity of mixing is when the viscosity decreases. In that paper, it is observed that the critical Re for the transition from the vortex to the engulfment flow regime, decreases for positive fluidity of mixing. The critical Re is $Re_{Hjet} = 138$ for zero fluidity of mixing and $Re_{Hjet} = 89$ for positive fluidity of mixing. The same is observed for the onset of the unsteady flow regime, which is $Re_{Hjet} = 131$ for positive fluidity of mixing and $Re_{Hjet} = 180$ for zero fluidity of mixing. For negative fluidity of mixing, the onset of engulfment flow regimes occurs at lower Re than for zero fluidity of mixing ($Re_{Hjet} = 175$), due to the forces induced by the viscosity gradients. The diffusion between phases is hampered by the formation of a viscous layer at the interface between fluids.

Recently, Schikarski et al. (2016) studied the mixing of water and ethanol under complex mixing structures that are characteristic of a turbulent flow regime. Increasing Re after achieving the steady engulfment flow regime, the flow becomes time-periodic, and the unsteady flow regime is achieved. Further increase of Re results in the change of flow dynamics at $Re_{Hjet} = 500$ that behaves as in a vortex flow regime. As Re increases, the fluctuations become more intense, but only at $Re_{Hjet} \approx 1000$ the typical mixing degree obtained for $Re_{Hjet} = 450$ is again achieved.

5.2 T-Jets Mixer Geometry

In this thesis, experiments were performed with three mixers selected out of eight from the previous works. The respective geometrical parameters, such as headspace, and the

respective dimensions, are summarised in Table 5.5. All geometries used in this work have a headspace height of $h = 2 \text{ mm}$, and the chamber height of $H = 50 \text{ mm}$. The geometry selection, i.e. the combination of W/w and W/e , were based on the previous studies already published.

Table 5.5 Geometrical parameters of T-Jets mixers.

Name	W (mm)	w (mm)	e (mm)	W/w	W/e
W6w1e4	6	1	4	6	1.5
W6w1e2	6	1	2	6	3
W2w1e4	2	1	4	2	0.5

T-Jets mixers are made of aluminium and fabricated using the milling of the material with computer numerical control (CNC) milling. These mixers can be sealed in a transparent acrylic block, enabling to visualise the flow inside of the mixing chamber.

5.3 Part I: Experimental Study of Symmetric and Unsymmetric Flow Conditions in T-Jets Mixers

Several works have been emerging on mixing dynamics in T-Jets mixers. Attention has focused on the cases where both inlet streams are water, or when fluids are water and ethanol, as already mentioned in Introduction and State of the Art.

Experimental work presented in this thesis is motivated by the lack of works on mixing at self-sustainable chaotic flow regime in T-Jets mixers, considering a representative range of fluid properties ratios between the opposed streams. The first condition studied in this work was the mixing at symmetric flow conditions, i.e. when the two jets have the same physical properties and flow rates. The second case considered was the mixing at asymmetric flow conditions. In this case, the flow rate of one of the jets is kept constant, and the other was changed, offsetting the impingement point position. Model

fluids with equal refractive index were used to enable better visualisation of the mixing dynamics.

5.3.1 Experimental Methods and Setup

The description of T-Jets mixers experimental setup is well-established in Krupa et al. (2012) and Krupa et al. (2014). Figure 5.3 and Figure 5.4 show a schematic representation of the experimental setup and the respective photographs. The reagents solutions are delivered from two pressurised stainless-steel tanks, represented by the number 1 in Figure 5.3, to the T-Jets reactor, number 4 in Figure 5.3. Each line has a volumetric flow rate controller (number 2 in Figure 5.3) from Alicat Scientific model LC-200CCM-D, and a needle valve (number 3 in Figure 5.3) that ensures steady flow rates. The flow rate in each flow metering line is monitored and set by the flow rate controller using an interface program built in a Labview software (number 10 in Figure 5.3). The Labview program registers the Re at each injector using the following inputs: physical properties and geometrical parameters (W , w and e). For high viscosity ratios, the flow rate achieved from Alicat Scientific flow controllers is not enough to obtain the full range of working conditions in this work. Hereupon, in the experiments with high viscous liquid stream, a Mini Cori-flow M15 is used to control the flow rate of the more viscous liquid stream. Then, two liquid streams are fed to each injector of a T-Jets mixer. The mixer is inserted in an acrylic mono-block that is sealed with an O-ring and tightened by a replaceable transparent cover (Figure 5.4c). The respective dimensions are listed in Table 5.5.

The mixing mechanisms in T-Jets mixers are studied from PLIF images, whose experimental setup is also illustrated in Figure 5.3. The laser sheet illuminates the cross-plane of the mixing chamber (number 6 in Figure 5.3), and an image is captured by a camera (number 7 in Figure 5.3) working at an acquisition rate of 25 frames per second. Rhodamine 6G is the tracer used in this work. Sultan et al. (2012) pointed out

an ideal concentration of rhodamine of approximately $3.5 \times 10^{-4} \text{ g L}^{-1}$, which is within the linear relationship between concentration and fluorescence.

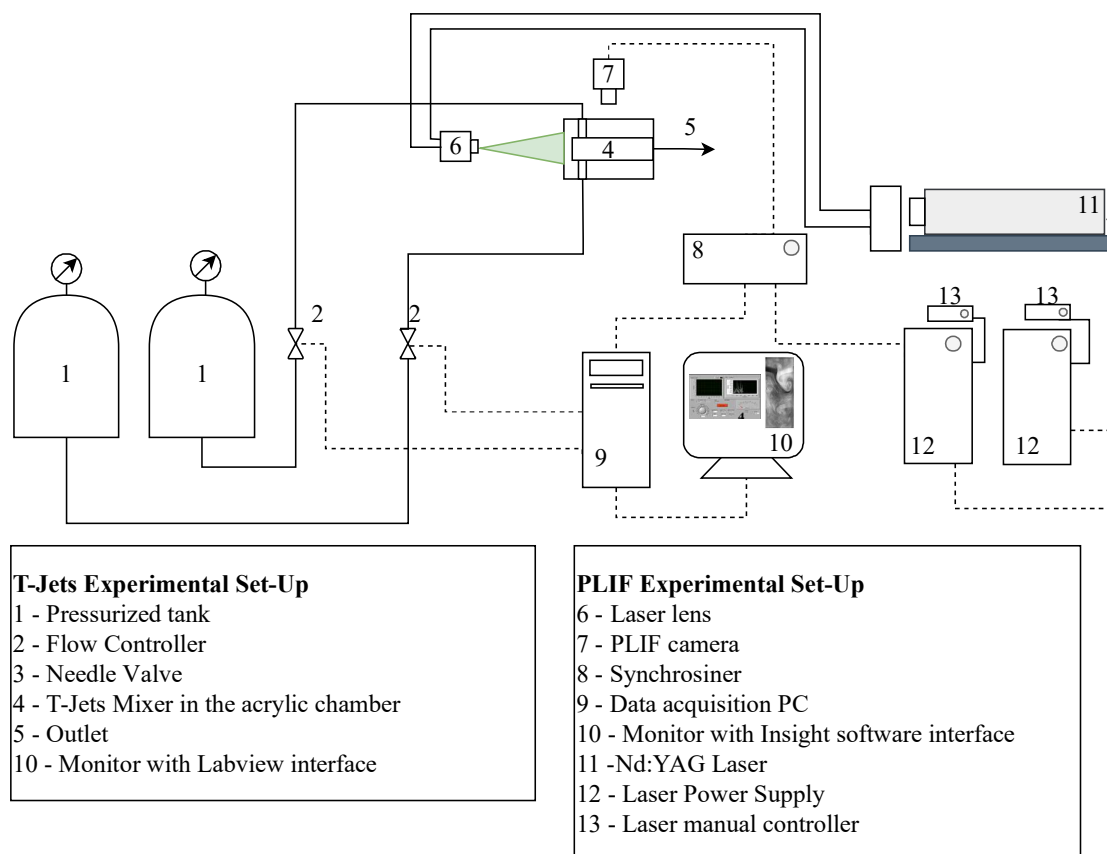


Figure 5.3 Schematic representation of T-Jets mixers and PLIF setup.

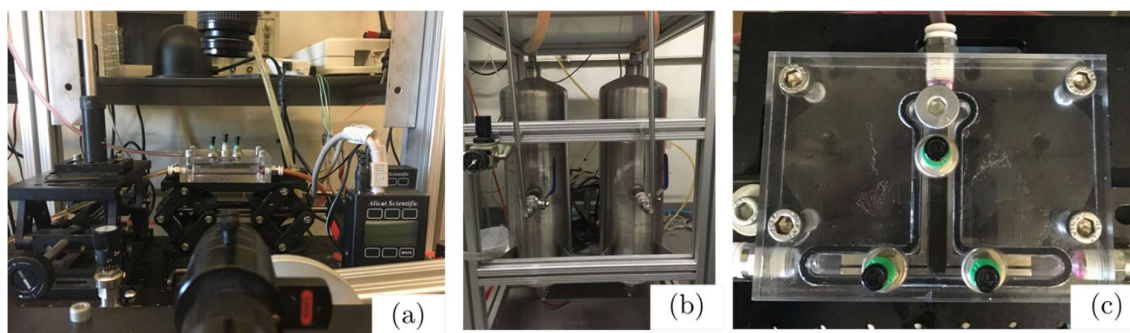


Figure 5.4 Photographs of T-Jets mixers experimental setup (a) LCD camera, laser lens and T-Jets mixer sealed in an acrylic chamber; (b) pressurised tanks; (c) T-Jets mixer enclosed in the acrylic box with a lead having a rubber O-ring.

According to Table 5.6, the mixing of similar fluids with the same properties of water is used as the base case for the comparison with the other cases (Case 0). These conditions are well-established experimentally by Hoffmann et al. (2006), Soleymani et al. (2007) and Sultan et al. (2012). However, the direct comparison at exactly the same conditions is essential to set the basis for a correct analogy of results. Then, the conditions were changed, tuning the viscosity of both streams using glycerol. The model fluids are approximately twice more viscous than water (Case 1). The mixing of dissimilar fluids is also studied in this section from the injection of different flow streams through each injector. A viscosity ratio 1:1.2 is first considered in order to perceive whether an offset of 20% on the viscosity of one of the streams affects the mixing dynamics (Case 2). A viscosity ratio 1:3 is finally tested, and the mixing dynamics are reported from PLIF images (Case 3).

The working fluids used at these conditions are glycerol solutions that were designed according to the method proposed in Figure 3.11. The more viscous solution, MV fluid, was designed from the determination of the mass fraction of glycerol according to Equation (3.10). Then, the less viscous fluid, LV fluid was prepared from the matching of the refractive index setting previously the viscosity ratio (see in Figure 3.1). Calcium chloride was used for the matching of the refractive index. The final fluid viscosity was checked from rheological tests performed in the rheometer Anton Paar MCR 92 SN8247897. The refractive index was measured at 25 °C using a digital ABBE Refractometer (AB-R-100D). The viscosity of streams, the refractive index and the respective concentration of calcium chloride are listed in Table 5.6.

Table 5.6 Working fluids for mixing of dissimilar fluids in T-Jets mixers.

Case	Viscosity Ratio	μ	ρ	θ [K]	$C_{\text{CaCl}_2 \cdot 2\text{H}_2\text{O}}$ [kg m ⁻³]	RI
0	1:1	$9.0 \times 10^{-1} \text{ mPa} \cdot \text{s}$	996 kg m^{-3}	297.15	-	-
1	1:1	$1.7 \text{ mPa} \cdot \text{s}$	1051 kg m^{-3}	298.15	-	-
2	1:1.2	$\mu_{\text{MV}} = 1.7 \text{ mPa} \cdot \text{s}$ $\mu_{\text{LV}} = 1.4 \text{ mPa} \cdot \text{s}$	$\rho_{\text{MV}} = 1046 \text{ kg m}^{-3}$ $\rho_{\text{LV}} = 1170 \text{ kg m}^{-3}$	295.15	172	1.41
3	1:3	$\mu_{\text{MV}} = 4.1 \text{ mPa} \cdot \text{s}$ $\mu_{\text{LV}} = 1.4 \text{ mPa} \cdot \text{s}$	$\rho_{\text{MV}} = 1105 \text{ kg m}^{-3}$ $\rho_{\text{LV}} = 1257 \text{ kg m}^{-3}$	295.15	259	1.39

5.3.2 Experimental Results

5.3.2.1 Effect of Reynolds Number and Geometrical Parameters on Mixing

The effect of operating Reynolds number and the geometrical parameters in mixing efficiency is studied for Cases 0, 1, 2 and 3.

5.3.2.1.1 Case 0

Figure 5.5 to Figure 5.7 show the 2D concentration field at the cross-section defined by the mixing chamber and injectors axes for conditions of Case 0 for respectively three different geometries W6w1e4, W6w1e2 and W2w1e4. The dimensions of each geometry are summarised in Table 5.5. The two fluids have the same properties of water at $\theta = 297.15 \text{ K}$, $\rho = 996 \text{ kg m}^{-3}$ (determined from Equation 3.2) and $\mu = 9.0 \times 10^{-1} \text{ mPa} \cdot \text{s}$ (determined from Equation 3.4), and were injected at symmetric flow conditions. The fluid stream injected from jet 1 was dyed with rhodamine emitting

fluorescence in the presence of a laser, and so its colour is captured from the PLIF images as white. The dark fluid corresponds to the clear fluid.

Geometry W6w1e4

Figure 5.5 shows the PLIF images at working conditions of Case 0 at $Re_{Hjet} = 90$, $Re_{Hjet} = 179$, $Re_{Hjet} = 269$ and $Re_{Hjet} = 359$. The geometry used was W6w1e4, which corresponds to the best geometrical configuration for the operation at self-sustainable flow regime. From Figure 5.5a and Figure 5.5b ($Re_{Hjet} = 90$ and $Re_{Hjet} = 179$), a pair of vortices at the top of the mixing chamber is clearly observed. The flow field is almost steady from the plane displayed, and the symmetry seems to be broken. This indicates that the geometry is operating at steady engulfment flow regime. Nevertheless, these conclusions would only be definitive from the visualisation of the closed top view. If the steady engulfment flow regime was confirmed, it would be observed a point central symmetry that would promote the dragging fluids from one half to the other. On the other hand, if the breaking of symmetry in T-Jets mixers is caused by the formation of a double pair of counter-rotating vortical structures, whose lengths are parallel to the mixing chamber, the conclusions previously made would not correspond to the reality. For that case, the regime would be denoted vortex regime. The closed top images were not captured because the actual configuration of the experimental setup is not able to capture these images.

At $Re_{Hjet} = 269$ (Figure 5.5c), it is observed the onset of mechanisms that promote the material exchange from one side to the other. At impingement point, oscillations are observed evolving to a vortex street in the entire mixing chamber. This flow is termed self-sustainable chaotic flow regime. Similar flow patterns are captured at $Re_{Hjet} = 359$ (Figure 5.5d), where it is observed the formation of vortices that promote the engulfment of two liquid streams. This figure also shows the oscillation of jets impingement point and the formation of coherent vortices downstream the jets impingement point.

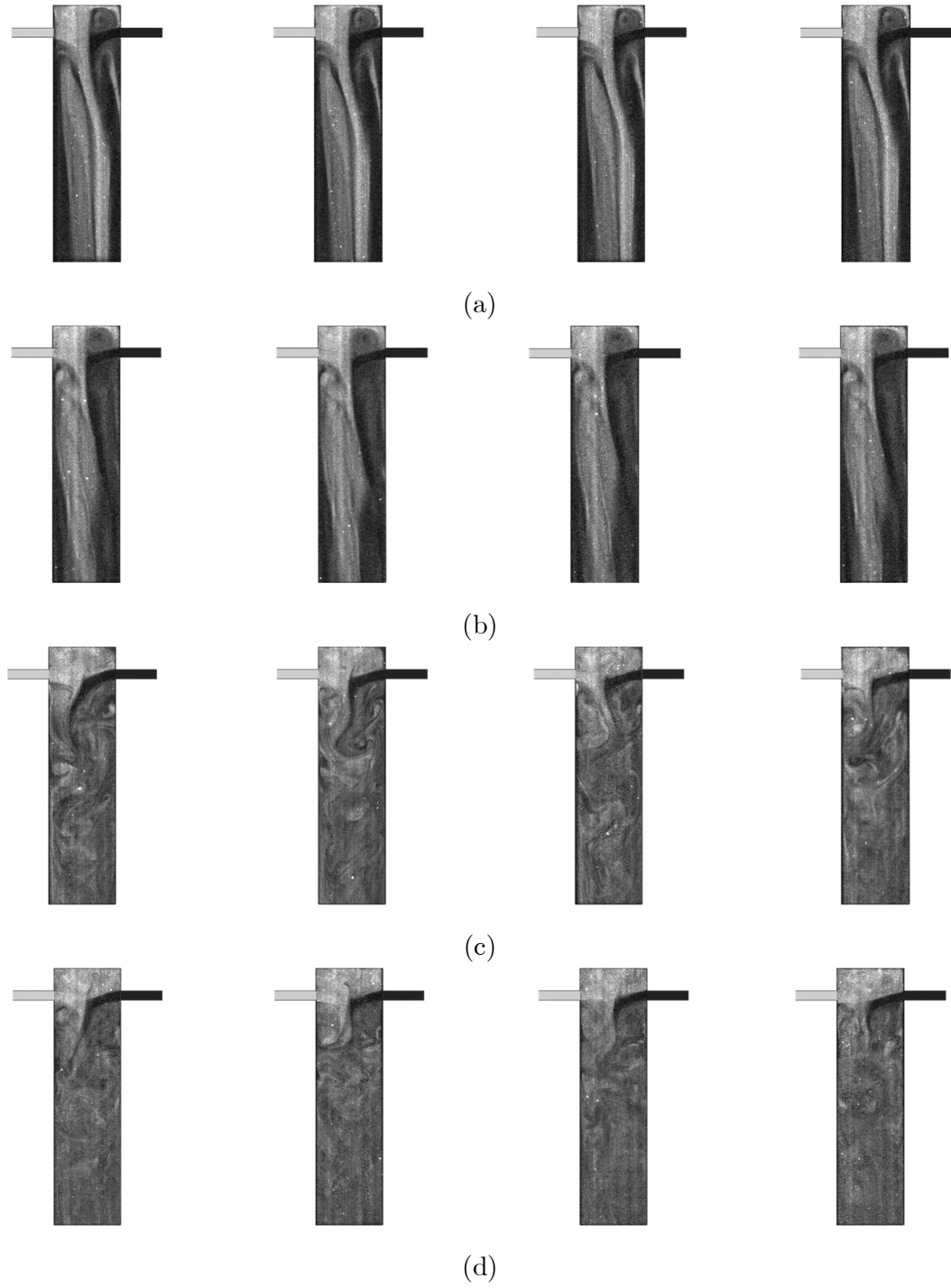


Figure 5.5 Instantaneous 2D concentration fields at the top of the mixing chamber at conditions of Case 0 (fluids with a viscosity ratio 1:1: $\mu_1 = \mu_2 = 1 \text{ mPa} \cdot \text{s}$) using the geometry W6w1e4 at (a) $\text{Re}_{\text{Hjet}} = 90$; (b) $\text{Re}_{\text{Hjet}} = 179$; (c) $\text{Re}_{\text{Hjet}} = 269$ and (d) $\text{Re}_{\text{Hjet}} = 359$.

Geometry W6w1e2

For a geometry W6w1e2, flow images were captured for $75 < \text{Re}_{\text{Hjet}} < 598$. In Figure 5.6a ($\text{Re}_{\text{Hjet}} = 75$), the two streams flow through segregated paths throughout the mixing chamber, i.e. the dyed stream and clear water are injected from the inlet and bend towards the outlet. The interface between phases remains constant with time and coincides to the mixing chamber axis. This configuration is operating at steady-state flow regime. Engulfment and vortex flow regimes are only clearly distinguished in the plane normal to the plane normal to the mixing chamber axis.

For $\text{Re}_{\text{Hjet}} = 224$ (Figure 5.6b), dynamic structures are observed in the mixing chamber, but the sequence of images shows the flow is still steady. Flow apparently broke its symmetry, operating at engulfment flow regime. However, a correct conclusion is only possible from the observation of a central symmetric point from the top view. At $\text{Re}_{\text{Hjet}} = 293$, the flow is characterised by the formation of a vortex street. The same observations are captured at $\text{Re}_{\text{Hjet}} = 598$ (Figure 5.6d), where the flow is termed as self-sustainable chaotic flow regime.

Geometry W2w1e4

Figure 5.7 shows the mixing of similar fluids using W2w1e4 geometry, and the same observations are obtained for $\text{Re}_{\text{Hjet}} = 90$, $\text{Re}_{\text{Hjet}} = 179$, $\text{Re}_{\text{Hjet}} = 269$ and $\text{Re}_{\text{Hjet}} = 359$. The flow is characterised by the steady parallel flow of both stream from the inlet to the outlet, and no dynamic structures are formed at these conditions. These results are in agreement with the literature that says that the shallow geometries are not able to achieve unsteady flow regimes due to the wall effect.

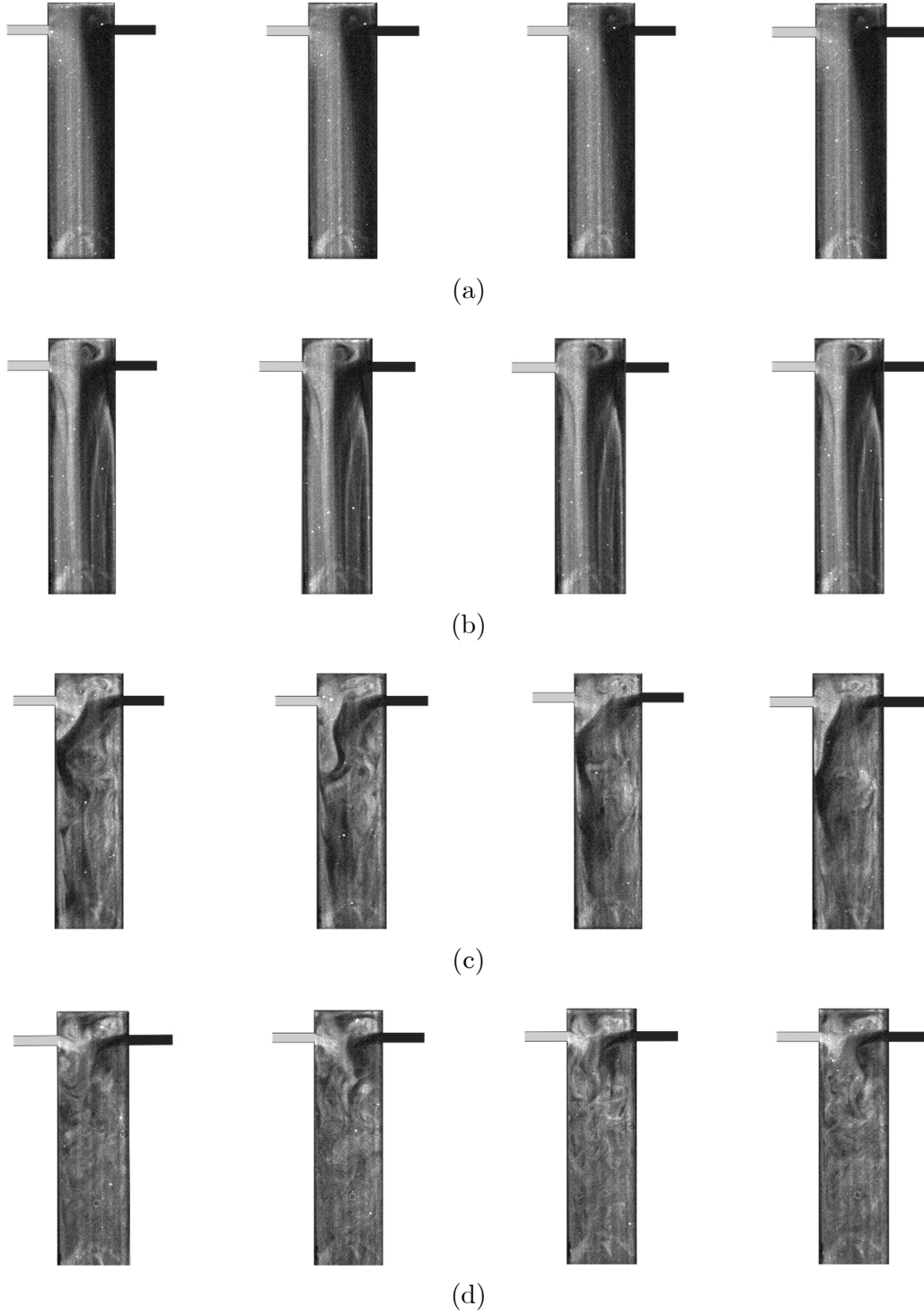


Figure 5.6 Instantaneous 2D concentration fields at the top of the mixing chamber at conditions of Case 0 (fluids with a viscosity ratio 1:1: $\mu_1 = \mu_2 = 1 \text{ mPa} \cdot \text{s}$) using the geometry W6w1e2 at (a)

$\text{Re}_{\text{Hjet}} = 75$; (b) $\text{Re}_{\text{Hjet}} = 224$; (c) $\text{Re}_{\text{Hjet}} = 293$ and (d) $\text{Re}_{\text{Hjet}} = 598$.

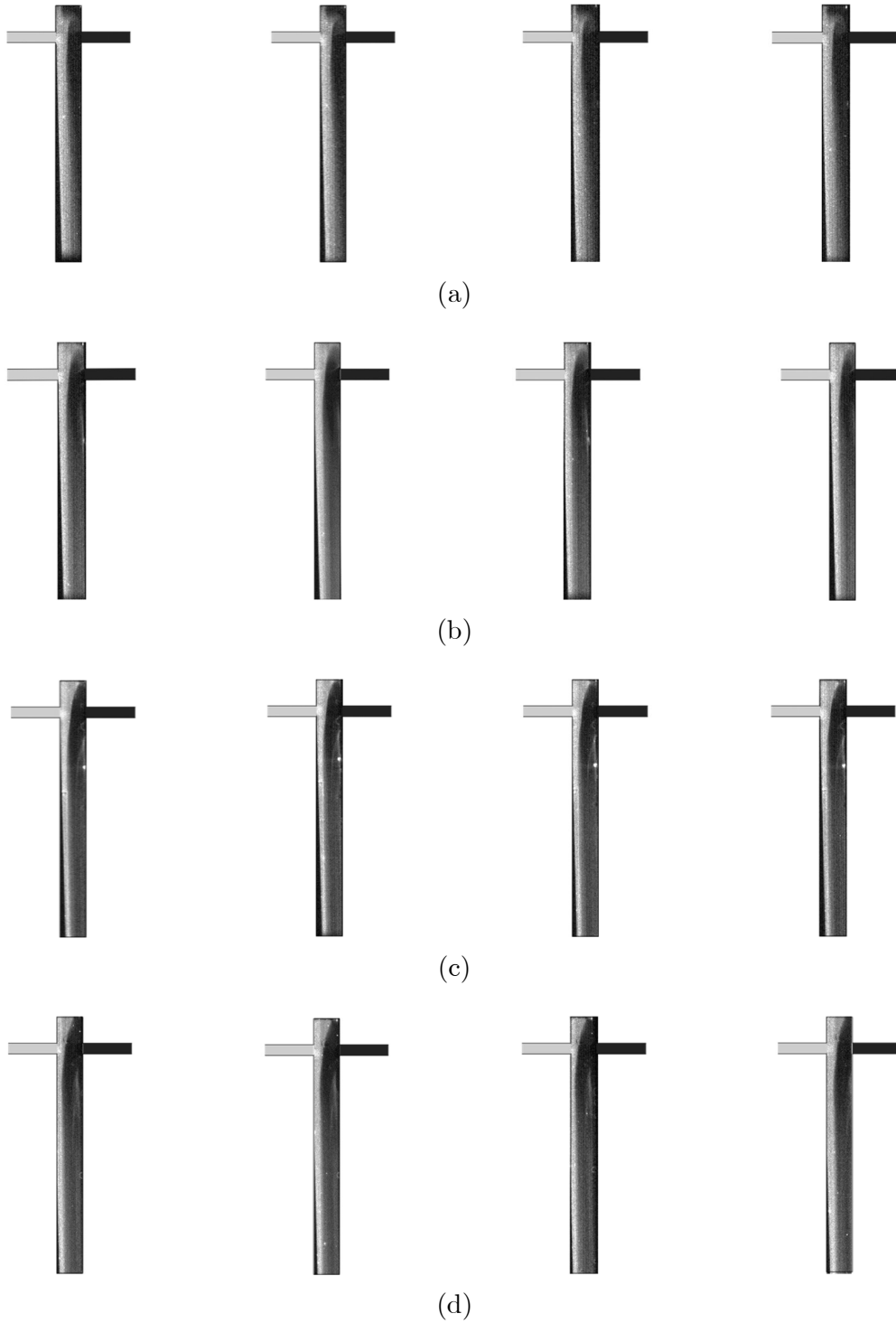


Figure 5.7 Instantaneous 2D concentration fields at the top of the mixing chamber at conditions of Case 0 (fluids with a viscosity ratio 1:1: $\mu_1 = \mu_2 = 1 \text{ mPa} \cdot \text{s}$) using the geometry W2w1e4 at (a)

$\text{Re}_{\text{Hjet}} = 90$; (b) $\text{Re}_{\text{Hjet}} = 179$; (c) $\text{Re}_{\text{Hjet}} = 269$ and (d) $\text{Re}_{\text{Hjet}} = 359$.

In sum, results for mixing of similar fluids with the same conditions of water may be directly compared with results in the literature. Sultan et al. (2012) reported from experimental data the chaotic flow regime and its transition. Geometrical parameters were also considered a fundamental part of the onset of the chaotic flow regime. For W6w1e4 geometry, the flow regime transition occurs at a Re_{Hjet} between 250 and 300, which is mostly in agreement with the results presented in this work, $179 < Re_{Hjet} < 269$.

5.3.2.1.2 Case 1

For tuned fluids with glycerol, the mixing is only tested for two geometries W6w1e4 and W6w1e2. Figure 5.8 and Figure 5.9 shows PLIF images at different Reynolds number using the geometries W6w1e4 and W6w1e2 (Case 1 in Table 5.6). The flow conditions tested in these images are symmetric, and the physical properties at $\theta = 295.15$ K are $\rho = 1051 \text{ kg m}^{-3}$ and $\mu = 1.7 \text{ mPa} \cdot \text{s}$ according to Table 5.6. A glycerol solution dyed with rhodamine 6G is injected from the left side injector, and it is depicted from PLIF images as white fluid. A clear glycerol solution is injected through jet 2 and visualised as a dark fluid.

Geometry W6w1e4

In Figure 5.8, the two fluids are injected at the same flow rate, $Re_{Hjet} = 95$, and the flow field remains mainly steady as observed from the sequence of images. The two liquid streams are continuously injected from both injectors, and no mixing dynamics are identified from PLIF images. The contact point between both streams occurs at the centre of the mixing chamber, whereas the interface is not clearly visualised from these images as well as the symmetry of the flow. Therefore, this geometry is operating at engulfment flow regime.

At $Re_{Hjet} = 161$ (Figure 5.8b), the flow is characterised by the detaching of engulfing vortices that promote the mixing of both streams. A self-sustainable chaotic flow regime

is thus observed from the images sequence, where the mixing is promoted by the convective mixing mechanisms. This means that the transition between the steady flow regime and the chaotic flow regime occurs at $95 < \text{Re}_{\text{Hjet}} < 161$. Further increasing Re (Figure 5.8c and Figure 5.8d) leads to strong interactions between jets, and thinner lamellar structures are observed from PLIF images, which are the result of the decreasing of the mixing scales.

Geometry W6w1e2

For geometry W6w1e2, at $\text{Re}_{\text{Hjet}} = 79$, $\text{Re}_{\text{Hjet}} = 119$, and $\text{Re}_{\text{Hjet}} = 158$ (from Figure 5.9a to Figure 5.9c), the flow field remains segregated. The only interfacial area generated between the two streams is coincident with the chamber axis cutting the chamber in two halves. Mixing between the two streams is promoted by the molecular diffusion through the interface area. At $\text{Re}_{\text{Hjet}} = 395$ (Figure 5.9d), the dark fluid is no longer black and takes a greyish tone. This means that the mixing is enhanced by the formation of vortices inside of each side of the mixing chamber, which is a characteristic feature of the vortex flow regime. Furthermore, molecular diffusion will play an important role in the mixing efficiency. At these flow conditions and for geometry W6w1e2, the transition between the segregated and the chaotic flow regimes is not achieved.

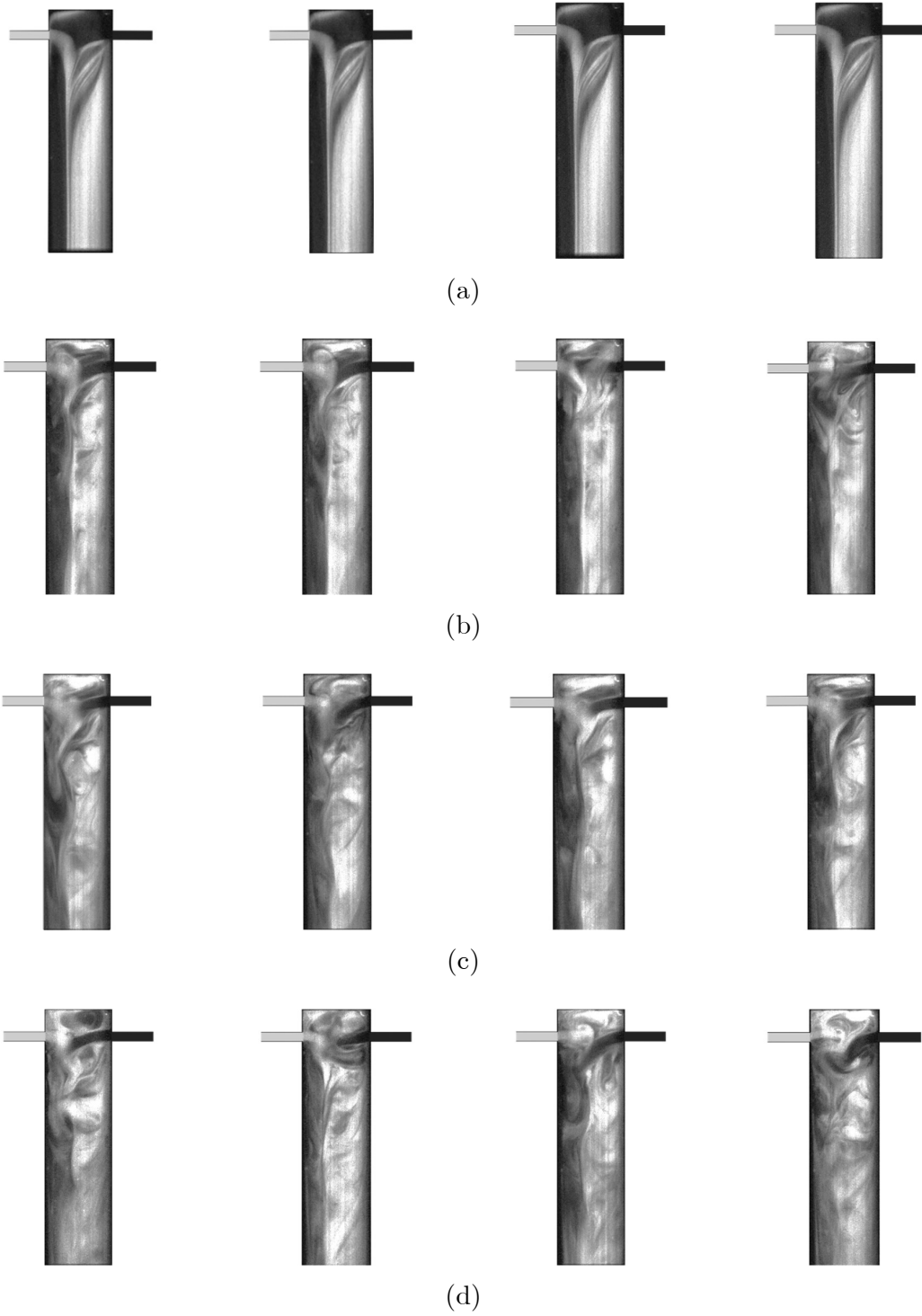


Figure 5.8 Instantaneous 2D concentration fields at the top of the mixing chamber Case 1 (a viscosity ratio 1:1: $\mu_1 = \mu_2 = 1.7 \text{ mPa} \cdot \text{s}$) using the geometry W6w1e4 at (a) $\text{Re}_{\text{Hjet}} = 95$; (b) $\text{Re}_{\text{Hjet}} = 161$; (c) $\text{Re}_{\text{Hjet}} = 190$ and (d) $\text{Re}_{\text{Hjet}} = 237$.

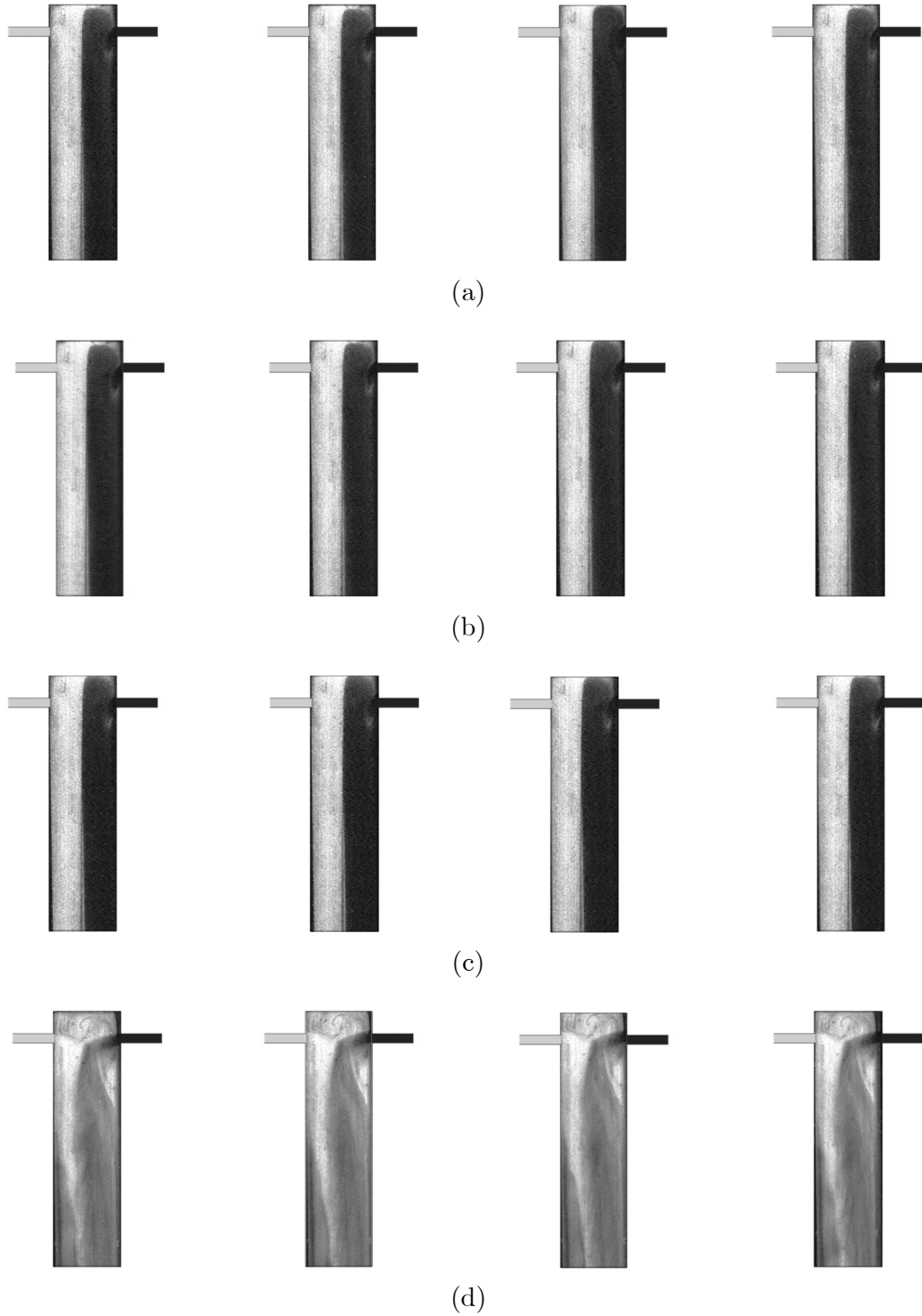


Figure 5.9 Instantaneous 2D concentration fields at the top of the mixing chamber for Case 1 (a viscosity ratio 1:1: $\mu_1 = \mu_2 = 1.7 \text{ mPa} \cdot \text{s}$) using the geometry W6w1e2 at (a) $\text{Re}_{\text{Hjet}} = 79$; (b)

$\text{Re}_{\text{Hjet}} = 119$; (c) $\text{Re}_{\text{Hjet}} = 158$ and (d) $\text{Re}_{\text{Hjet}} = 395$.

5.3.2.1.3 Case 2

A decrease of 20% in viscosity is applied in jet 2 to conclude its impact on the mixing dynamics (Case 2 in Table 5.6). Figure 5.10 to Figure 5.12 show the 2D concentration fields at different Reynolds number using three distinct geometries, W6w1e4, W6w1e2 and W2w1e4. The more viscous fluid (MV fluid) with viscosity $\mu_1 = 1.7 \text{ mPa} \cdot \text{s}$ was dyed with rhodamine, and continuously injected from jet 1. The less viscous fluid (LV fluid) with viscosity $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$ takes a dark colour in PLIF images. Calcium chloride was added to match the refractive indices of LV and MV fluid streams.

Geometry W6w1e4

At $\text{Re}_{\text{Hjet1}} = 50$ and $\text{Re}_{\text{Hjet2}} = 114$ (Figure 5.10a), the flow patterns are characteristic of the steady engulfment flow regime, where structures that engulf fluid from both jet streams are generated. These PLIF images were taken for lower Re in MV fluid stream (jet 1) comparing to conditions at injector 2. In Figure 5.10b, where $\text{Re}_{\text{Hjet1}} = 300$ and $\text{Re}_{\text{Hjet2}} = 343$, the same behaviour of Figure 5.10a is observed. The flow patterns observed are typically generated at engulfment flow regime. Figure 5.10c shows that a self-sustained oscillatory and periodic regime is generated at $\text{Re}_{\text{Hjet1}} = 500$ and $\text{Re}_{\text{Hjet2}} = 514$. This flow is characterised by the formation of detaching engulfing vortices downstream the inlet axis. The respective transition to the chaotic flow regimes occurs at $300 < \text{Re}_{\text{Hjet1}} < 500$ and $343 < \text{Re}_{\text{Hjet1}} < 514$.

Geometry W6w1e2

For W6w1e2 geometry and at the working conditions $\text{Re}_{\text{Hjet1}} = 167$ and $\text{Re}_{\text{Hjet2}} = 190$, the flow is steady, and no mixing dynamics are observed at the plane displayed in Figure 5.11a. The symmetry is not clearly visualised, and thus this geometry should be operating at steady engulfment flow regime. However, a clear conclusion about the flow regime classification should be done from the respective top view. The onset of the

chaotic flow regime occurs at $Re_{Hjet1} = 333$ and $Re_{Hjet2} = 381$ (Figure 5.11b), where it is observed the perturbation of the interface, downstream the impingement point, promoting the mixing of both streams. In Figure 5.11c ($Re_{Hjet1} = 500$ and $Re_{Hjet2} = 476$) and in Figure 5.11d ($Re_{Hjet1} = 667$ and $Re_{Hjet2} = 571$), the mixing dynamics strongly increase, leading to the fast formation of engulfing vortices that detach from the jets impingement point.

Geometry W2w1e4

For $W/w = 2$ and $W/e = 0.5$, Figure 5.12 shows that the two jets are injected in the mixing chamber, and then they bend towards the outlet. For $120 < Re_{Hjet1} < 500$ and $114 < Re_{Hjet2} < 457$, no dynamic structures are captured in PLIF images. The contact point between both streams occurs at the centre of the mixing chamber for all cases. Small shifting of the interface to the right side of the mixing chamber is also captured. The formation of vortices is clearly observed at the top of the mixing chamber, demonstrating that the geometry seems to operate at vortex flow regime. Mixing between flow regimes is promoted by the molecular diffusion, decreasing then the mixing degree.

As a final remark, geometries with $W/w = 2$ and $W/e = 0.5$ are not able to mix dissimilar fluids at these conditions. These experiments also evidence that the effect of W/w and W/e ratios influence the onset of the self-sustainable chaotic flow regimes, in addition to the Reynolds number at injectors. Geometries with $W/w = 6$ and $W/e = 1.5$ or $W/e = 3$ are able to mix two dissimilar liquid streams with viscosity ratio 1:1.2. These observations are in agreement with the results for symmetric flow conditions, presented in this section. For W6w1e4, the onset of the chaotic flow regime occurs for $343 < Re_{Hjet,LV} < 514$ and $300 < Re_{Hjet,MV} < 500$. For W6w1e2, the transition between flow regimes occurs for $190 < Re_{Hjet,LV} < 381$ and $167 < Re_{Hjet,MV} < 333$. These results show that a deviation of 20% in the viscosity ratio promotes an offset of 15%

in the injectors Reynolds number. The lowest Re corresponds to the MV fluid, and so this jet plays a key role in the onset of the self-sustained and periodic flow regime.

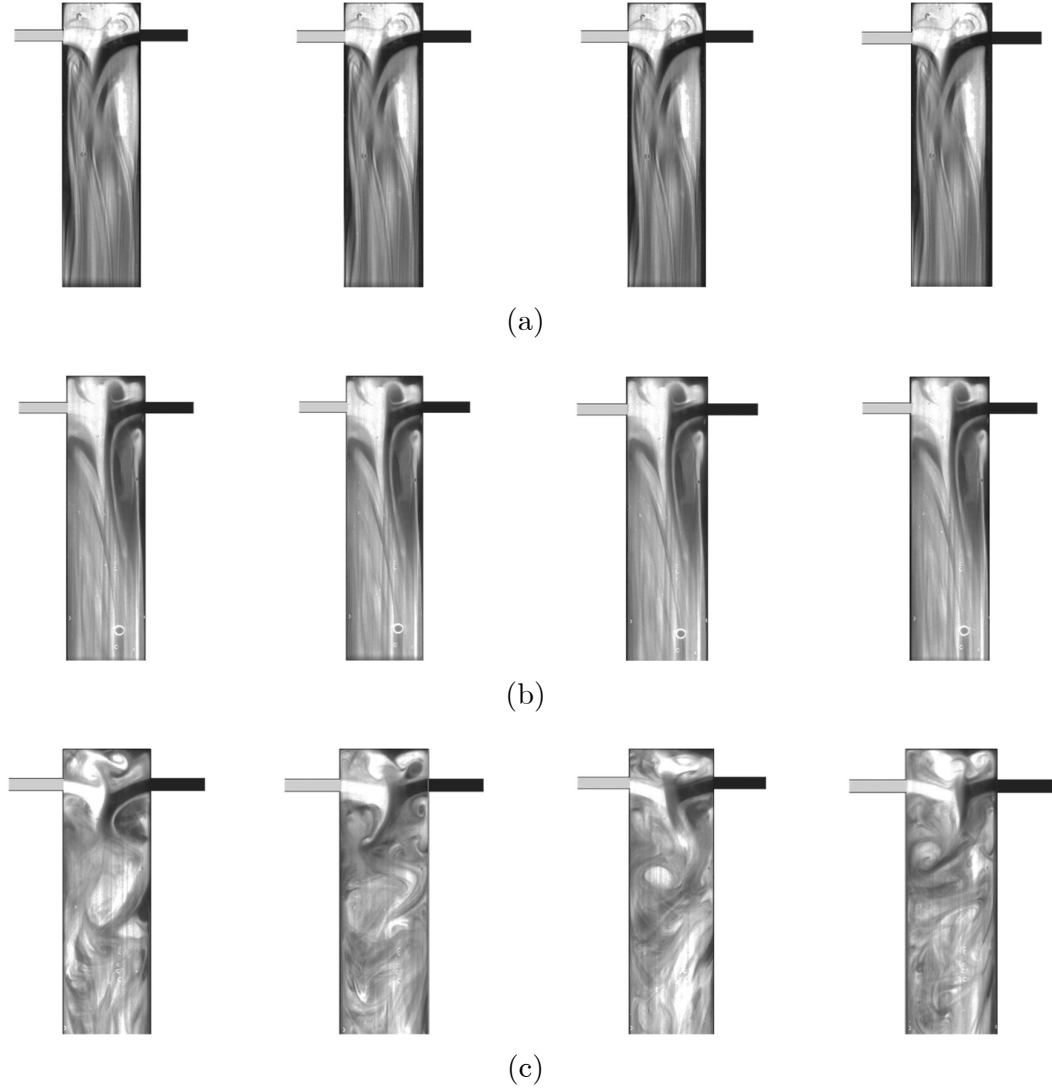


Figure 5.10 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:1.2: $\mu_1 = 1.7 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$, using geometry

W6w1e4 at (a) $Re_{Hjet1} = 50$ and $Re_{Hjet2} = 114$; (b) $Re_{Hjet1} = 300$ and $Re_{Hjet2} = 343$ and (c)

$Re_{Hjet1} = 500$ and $Re_{Hjet2} = 514$.

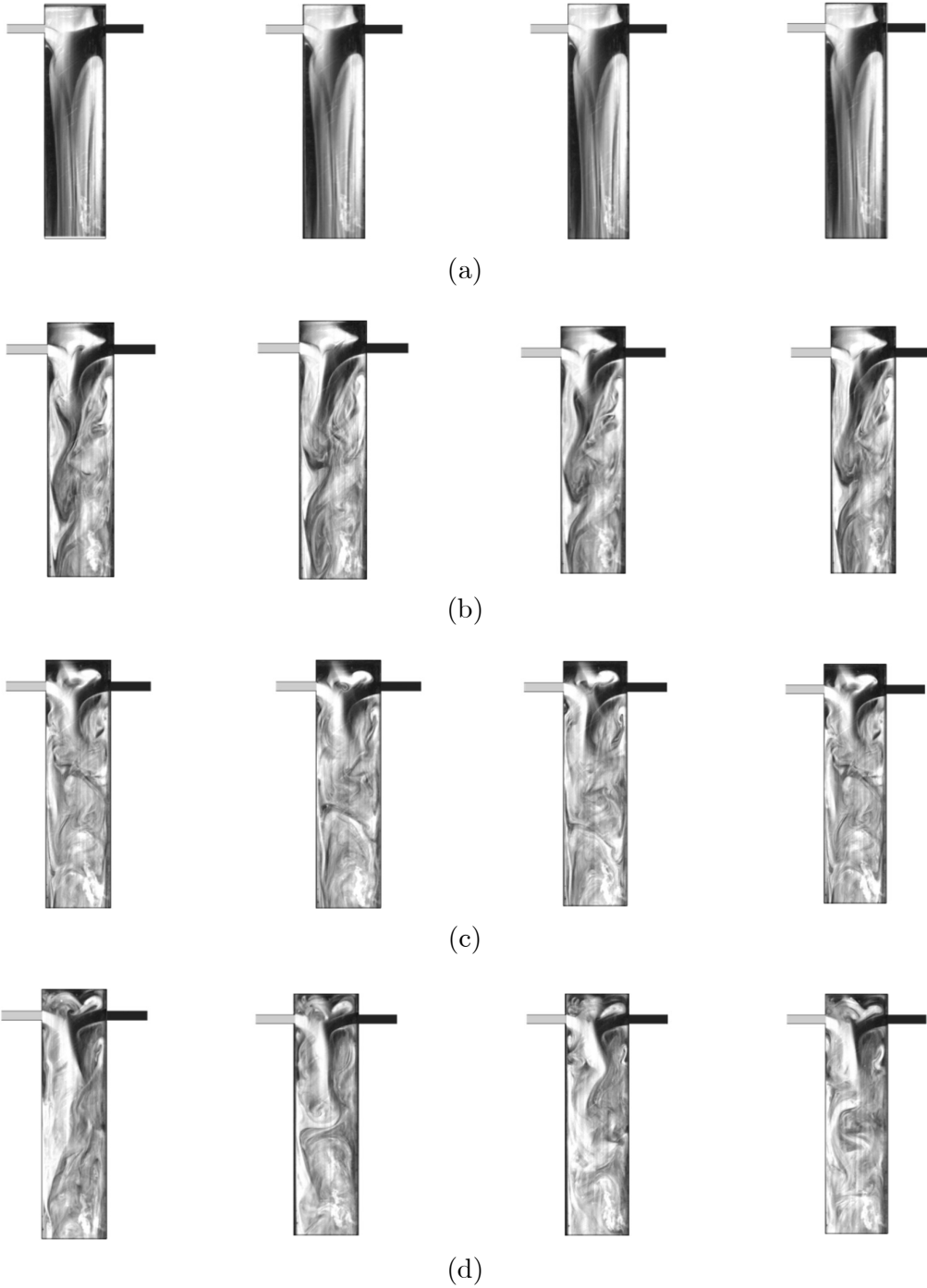


Figure 5.11 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:1.2: $\mu_1 = 1.7 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$, using geometry W6w1e2 at (a) $\text{Re}_{\text{Hjet1}} = 167$ and $\text{Re}_{\text{Hjet2}} = 190$; (b) $\text{Re}_{\text{Hjet1}} = 333$ and $\text{Re}_{\text{Hjet2}} = 381$; (c) $\text{Re}_{\text{Hjet1}} = 500$ and $\text{Re}_{\text{Hjet2}} = 476$ and (d) $\text{Re}_{\text{Hjet1}} = 667$ and $\text{Re}_{\text{Hjet2}} = 571$.

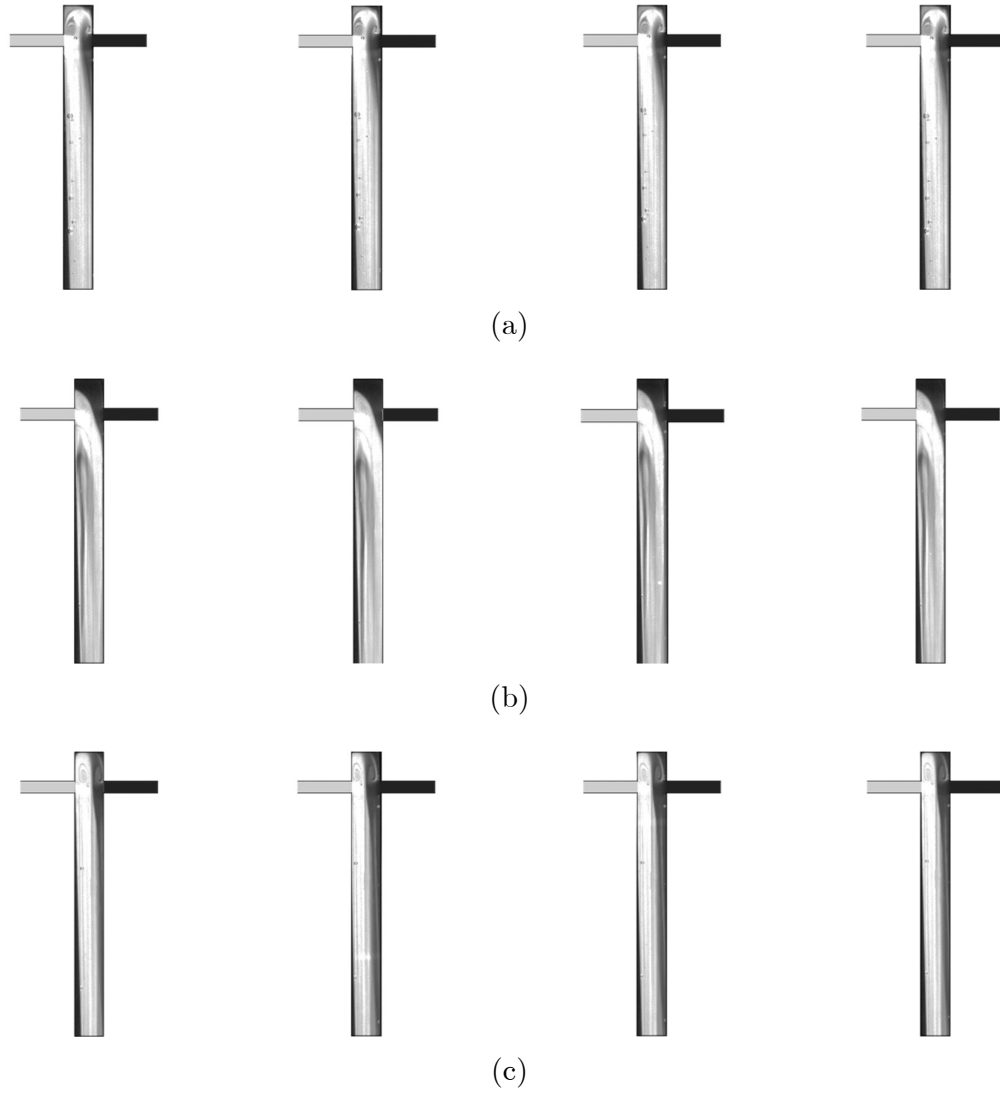


Figure 5.12 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:1.2: $\mu_1 = 1.7 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$, using geometry

W2w1e4 at (a) $\text{Re}_{\text{Hjet1}} = 120$ and $\text{Re}_{\text{Hjet2}} = 114$; (b) $\text{Re}_{\text{Hjet1}} = 400$ and $\text{Re}_{\text{Hjet2}} = 229$ and (c) $\text{Re}_{\text{Hjet1}} = 500$ and $\text{Re}_{\text{Hjet2}} = 457$.

5.3.2.1.4 Case 3

PLIF images were also reported for a viscosity ratio 1.3 (Case 3 in Table 5.6). MV fluid dyed with rhodamine and a viscosity of $\mu_1 = 4.1 \text{ mPa} \cdot \text{s}$ was injected through the left-hand side injector, jet 1, and is captured from PLIF images as a white fluid. LV fluid

with viscosity $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$ is injected through the right-hand side injector, jet 2, and corresponds to the dark fluid in PLIF images. The respective viscosity and density are listed in Table 5.6. Three geometries were used in order to report the effect of W/w and W/e ratios on mixing dynamics: W6w1e4, W6w1e2 and W2w1e4.

Figure 5.13 to Figure 5.15 show a sequence of PLIF images operating at conditions of Case 3 for the three geometries tested.

Geometry W6w1e4

Figure 5.13a shows that the balance between streams occurs at $\text{Re}_{\text{Hjet1}} = 93$ and $\text{Re}_{\text{Hjet2}} = 560$ using the geometry W6w1e4. At these conditions, the mixer seems to operate at steady engulfment flow regime. The symmetry is broken in the mixing chamber, and apparently, vortices are formed in the cross-section, engulfing both streams. At $\text{Re}_{\text{Hjet1}} = 105$ and $\text{Re}_{\text{Hjet2}} = 640$ (Figure 5.13b), PLIF images show the onset of the self-sustainable chaotic flow regime. Both streams start to oscillate at the impingement point position. The result is the formation of coherent vortices structures downstream the impingement point position. The vortices rotation axes are in the normal direction of the mixing chamber axis, contrarily to the ones formed in engulfment flow regime (Figure 5.13a). When Re is increased in both jets, see Figure 5.13c, where $\text{Re}_{\text{Hjet1}} = 136$ and $\text{Re}_{\text{Hjet2}} = 960$, a strong dynamics of mixing of fluid from both jets is promoted by increasing the frequencies of the jets oscillations, which is associated to the vortex shedding.

Geometry W6w1e2

For W6w1e2 geometries, three conditions were tested: $\text{Re}_{\text{Hjet1}} = 151$ and $\text{Re}_{\text{Hjet2}} = 533$, $\text{Re}_{\text{Hjet1}} = 310$ and $\text{Re}_{\text{Hjet2}} = 1068$ and $\text{Re}_{\text{Hjet1}} = 445$ and $\text{Re}_{\text{Hjet2}} = 1600$. In the first case (Figure 5.14a), a pair of vortices are observed at the top of the mixing chamber. From

the visualisation of this plane defined by the injectors and chamber axes, the geometry is operating at steady engulfment flow regime. When Re is increased (Figure 5.14b), the sequence of PLIF images clearly shows that the flow is no longer stable, and perturbations are created at the interface between fluids. In Figure 5.14c, at $Re_{H_{jet1}} = 445$ and $Re_{H_{jet2}} = 1600$ the jets impinge on each other close to the mixing chamber axis, and circular vortices are formed with a rotation axis in the normal direction of the mixing chamber axis. At these conditions, the mixer operates at self-sustainable chaotic flow regime.

Geometry W2w1e4

The last case studied was for a geometry W2w1e4, i.e. for simultaneously the lowest W/w and W/e ratios. Figure 5.15a shows the balance of jets at $Re_{H_{jet1}} = 83$ and $Re_{H_{jet2}} = 400$ from PLIF images. The jets are impinged in the mixing chamber and are then directed towards the outlet. The only interface created between fluids coincides with the mixing chamber axis. From this visualisation plane, the mixer is operating at segregated flow regime. The same observations are reported at $Re_{H_{jet1}} = 245$ and $Re_{H_{jet2}} = 960$, in Figure 5.15b. For this case, the vortex flow regime promotes higher molecular diffusion between jets, as observed from the vanishing of the dark tone and the appearance of the greyish tone. This is the final proof that T-Jets mixers with $W/w = 2$ and $W/e = 0.5$ do not promote a fast and effective mixing of fluids, even when the jets are at equilibrium, which is the necessary condition for the onset of chaotic flow regimes.

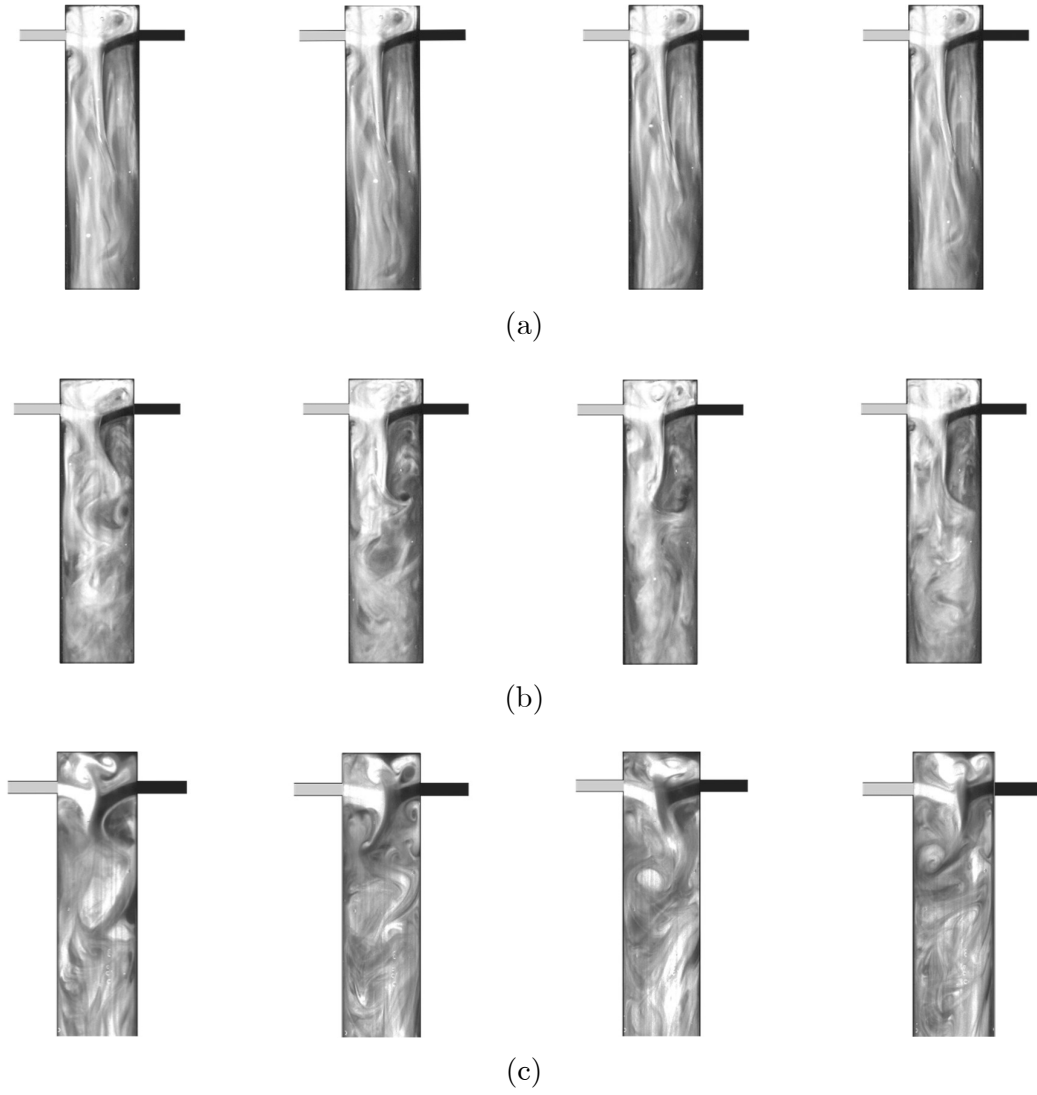


Figure 5.13 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:3: $\mu_1 = 4.1 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$, using geometry

W6w1e4 at (a) $\text{Re}_{\text{Hjet1}} = 93$ and $\text{Re}_{\text{Hjet2}} = 560$; (b) $\text{Re}_{\text{Hjet1}} = 105$ and $\text{Re}_{\text{Hjet2}} = 640$ and (c) $\text{Re}_{\text{Hjet1}} = 136$ and $\text{Re}_{\text{Hjet2}} = 960$.

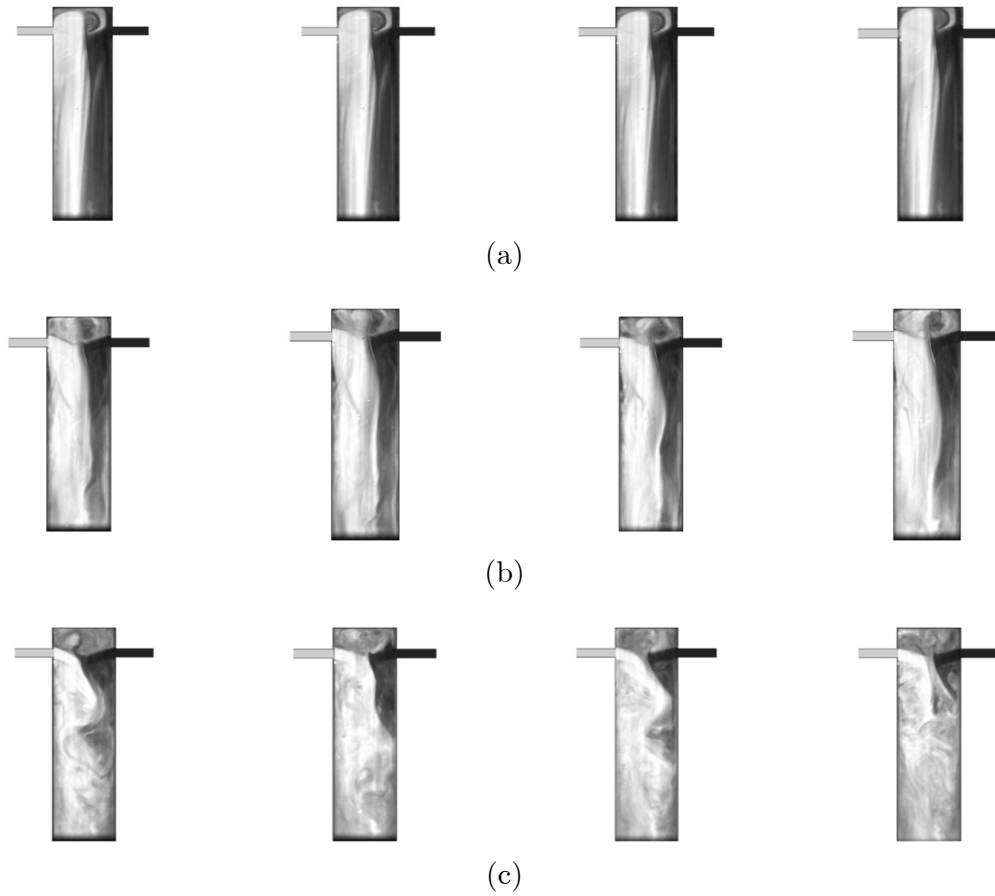


Figure 5.14 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:3: $\mu_1 = 4.1 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$, using geometry W6w1e2 at (a) $\text{Re}_{\text{Hjet1}} = 151$ and $\text{Re}_{\text{Hjet2}} = 533$; (b) $\text{Re}_{\text{Hjet1}} = 310$ and $\text{Re}_{\text{Hjet2}} = 1068$ and (c) $\text{Re}_{\text{Hjet1}} = 445$ and $\text{Re}_{\text{Hjet2}} = 1600$.

Table 5.7 summarises the conditions for the onset of the self-sustainable chaotic flow regime for the previous conditions. PLIF images of mixing of similar fluids show that W/e ratio affects the mixing dynamics. Higher values of Re marking the flow regime transition are typically associated with shallower geometries related to the strong wall effects restraining the vortex formation. This work also shows that the onset of chaotic flow regime does not definitely occur for narrow geometries, as W2w1e4, and so this chamber is not able to efficiently mix similar or dissimilar fluids. In narrow mixing chambers, the jets flowing in the centre of the mixers for a laminar core do not enable

side vortices to form and evolve dynamically. This decrease on the dynamics of vortices will, in turn, hinder the onset of chaotic flow regimes, where instabilities of the jets impingement of point are fed from downstream vortices. The role of downstream vortices on the onset of chaotic flows is well-described in Fonte et al. (2015). For model fluids tuned with glycerol (Case 1), only W6w1e4 geometry is able to promote the fast mixing of liquid streams. W6w1e2 geometry is not able to mix the two liquid streams for the tested Reynolds number range, $80 < Re_{Hjet} < 398$. For mixing of dissimilar fluids (Cases 2 and 3), the transition to the self-sustainable chaotic flow is completely controlled by the lower Re, i.e. by the conditions of the MV fluid (e.g. $Re_{Hjet,MV}$).

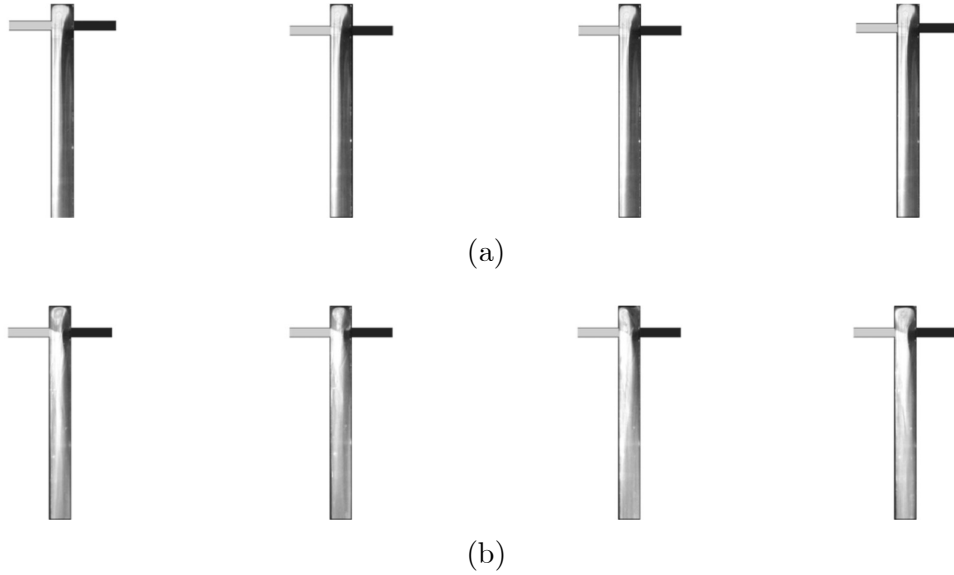


Figure 5.15 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:3: $\mu_1 = 4.1 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$, using geometry W2w1e4 at (a) $Re_{Hjet1} = 83$ and $Re_{Hjet2} = 400$; (b) $Re_{Hjet1} = 245$ and $Re_{Hjet2} = 960$.

The geometries used in this work operate at four distinct flow regime: segregated, vortex, steady engulfment or self-sustainable chaotic flow regime. Other flow regimes were also detected in literature, such as unsteady symmetric flow regimes, unsteady symmetric flow regimes and deflecting oscillations. These regimes were not achieved in this work because the geometrical parameters tested do not enable it.

Table 5.7 Transition to the chaotic flow regimes for different viscosity ratios and geometries.

Case	Viscosity Ratio	Geometry	Transition Re_{Hjet}	Transition Re_{Hjet} (Sultan et al., 2012)
0	1:1	W6w1e4	179-269	262-277
		W6w1e2	224-293	451-475
		W2w1e4	Not detected	Not detected
1	1:1	W6w1e4	95-161	-
		W6w1e2	Not detected	-
		W2w1e4	-	-
2	1:1.2	W6w1e4	$Re_{Hjet,LV} : 343 - 514$ $Re_{Hjet,MV} : 300 - 500$	-
		W6w1e2	$Re_{Hjet,LV} : 190 - 381$ $Re_{Hjet,MV} : 167 - 333$	-
		W2w1e2	Not detected	-
3	1:3	W6w1e4	$Re_{Hjet,LV} : 560 - 640$ $Re_{Hjet,MV} : 93 - 105$	-
		W6w1e2	$Re_{Hjet,LV} : 533 - 1067$ $Re_{Hjet,MV} : 151 - 310$	-
		W2w1e2	Not detected	-

5.3.2.2 Effect of Imbalance of Jets on Mixing

The imbalance of jets was also studied from PLIF images, setting constant the Reynolds number of one of the jets and changing the flow rate at the opposed one. For the specific case of mixing non-identical fluids, the contact point between jets was observed at the mixing chamber, changing the flow rate of the MV fluid stream. The jets impingement point displacement is identified as a function of the hydraulic diameter. The operation at self-sustainable chaotic flow regime was the necessary condition imposed for this study.

Figure 5.16 and Figure 5.17 show PLIF images for Case 0 using two distinct geometries W6w1e4 and W6w1e2. In Figure 5.16, Reynolds number at jet 2 was set to $Re_{Hjet2} = 269$ and Reynolds number at jet 1 was changed to $Re_{Hjet1} = 269$, $Re_{Hjet1} = 314$, $Re_{Hjet1} = 359$, $Re_{Hjet1} = 448$ and $Re_{Hjet1} = 538$. In Figure 5.17, Reynolds number at jet 2 was set at $Re_{Hjet2} = 299$, and Reynolds number at jet 1 was changed for $Re_{Hjet1} = 299$, $Re_{Hjet1} = 598$, $Re_{Hjet1} = 747$ and $Re_{Hjet1} = 896$. The balance conditions for each case were reported for symmetric flow condition, i.e. at $Re_{Hjet1} = Re_{Hjet2} = 269$ and $Re_{Hjet1} = Re_{Hjet2} = 299$. The other flow conditions will enable to visualise the offset of the impingement point in the mixing chamber. MV fluid injected through jet 1 was dyed with rhodamine emitting fluorescence. The dark fluid corresponds to LV fluid and is imaged as a clear fluid.

Figure 5.16a shows the balance of jets when both jets are injected at same flow rate, $Re_{Hjet1} = Re_{Hjet2} = 269$. At these conditions, W6w1e4 geometry operates at self-sustainable chaotic flow regime, as already described in Section 5.3.2.1. Further increasing in Re_{Hjet1} results in the displacement of the impingement point position to the right-hand side of the mixing chamber, as shown in Figure 5.13b to Figure 5.13e. Instabilities are still observed at the contact point between jets, but mixing is no longer promoted by the vortices having a diameter equal to half of the mixing chamber width.

For a W6w1e2 geometry, the balance of jets at $Re_{Hjet1} = Re_{Hjet2} = 299$ promotes the effective mixing between fluids. There is the formation of coherent vortices structures downstream the jets impingement point, originating a vortex street through the entire mixing chamber height (Figure 5.17a). The increase in Re_{Hjet1} results in the offset of the impingement point to the right side of the mixing chamber, and the characteristic dynamic flow is lost (Figure 5.17b). The jets are impinged and bent towards the outlet from the impingement point. Further increasing in Re_{Hjet1} promotes perturbations at the interface evolving to small scale structures (Figure 5.17c). This is the result of the strong energy dissipation at the impingement point due to the fact that the left jet is now above $Re = 500$ and so it starts to form dynamic flow structures without the impinging jets oscillations. Nevertheless, the mixing degree is not so effective as in the well-balanced opposed jets conditions.

The sequence of PLIF images in Figure 5.16 and Figure 5.17 shows that the balance of jets is a critical condition for effective mixing. This is also observed for CIJ mixers, according to the results presented in Chapter 4 of the present thesis.

Experimental studies on the imbalance of model fluids with $\mu_1 = \mu_2 = 1.7 \text{ mPa} \cdot \text{s}$ were only conducted for the geometry W6w1e4. This geometry corresponds to the one able to mix two viscous fluids, as demonstrated in the last section. Figure 5.18 shows a sequence of PLIF images at conditions of Case 1 using the W6w1e4 mixing chamber. Reynolds number at jet 2 was set at $Re_{Hjet2} = 237$, and the flow rate at jet 1 was adjusted according to the following conditions: $Re_{Hjet1} = 47$, $Re_{Hjet1} = 95$, $Re_{Hjet1} = 145$, $Re_{Hjet1} = 190$ and $Re_{Hjet1} = 199$. The white jet corresponds to the liquid stream dyed with rhodamine, which is continuously fed from the left-hand side injector. The dark jet corresponds to the clear fluid and is delivered through the right-hand side injector.

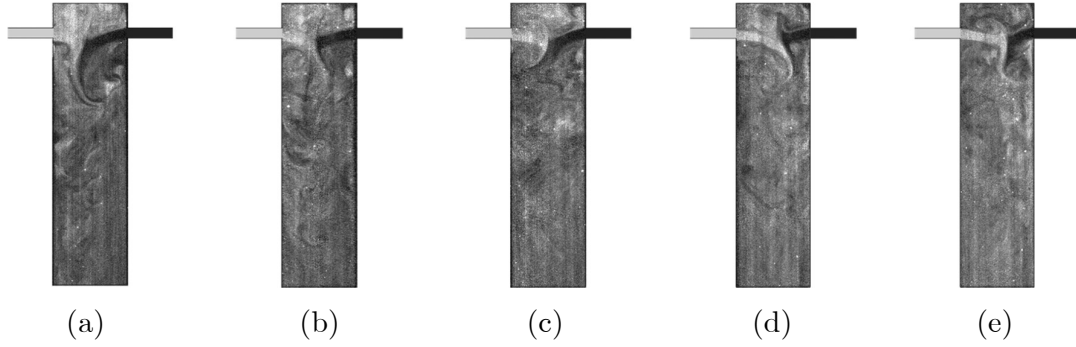


Figure 5.16 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:1: $\mu_1 = \mu_2 = 1 \text{ mPa} \cdot \text{s}$, at $\text{Re}_{\text{Hjet2}} = 269$ for geometry W6w1e4 and (a) $\text{Re}_{\text{Hjet1}} = 269$; (b) $\text{Re}_{\text{Hjet1}} = 314$; (c) $\text{Re}_{\text{Hjet1}} = 359$; (d) $\text{Re}_{\text{Hjet1}} = 448$ and (e) $\text{Re}_{\text{Hjet1}} = 538$.

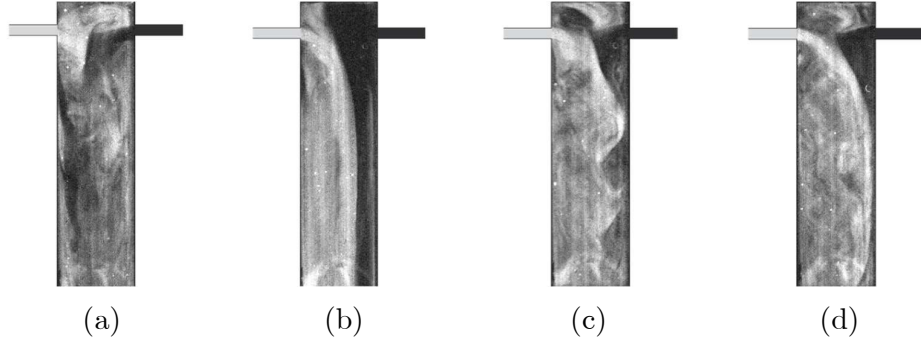


Figure 5.17 Instantaneous 2D concentration fields at the top of the chamber for mixing of two similar fluids with a viscosity ratio 1:1: $\mu_1 = \mu_2 = 1 \text{ mPa} \cdot \text{s}$, at $\text{Re}_{\text{Hjet2}} = 299$ for geometry W6w1e2 and (a) $\text{Re}_{\text{Hjet1}} = 299$; (b) $\text{Re}_{\text{Hjet1}} = 598$; (c) $\text{Re}_{\text{Hjet1}} = 747$ and (d) $\text{Re}_{\text{Hjet1}} = 896$.

At $\text{Re}_{\text{Hjet1}} = 47$ and $\text{Re}_{\text{Hjet2}} = 237$ (Figure 5.18a), the flow rate of jet 2 is much larger than the flow rate of jet 1. Jet 2 impinges directly at the opposed wall (left wall), and afterwards is slightly deflected towards the right mixing chamber sidewall. Then, the flow rate is increased at injector 1 to $\text{Re}_{\text{Hjet1}} = 95$ (Figure 5.17b), compensating the deflection of jet; nevertheless, the jet still flows towards the opposite wall until a point close to injector 1. Further increasing of Re_{Hjet1} to 142 promotes that the contact point is offset to the right-hand side of the mixing chamber, and some dynamic structures are created downstream the impingement point position. At $\text{Re}_{\text{Hjet1}} = 190$ and $\text{Re}_{\text{Hjet2}} = 237$ (Figure 5.17c) and at $\text{Re}_{\text{Hjet1}} = 199$ and $\text{Re}_{\text{Hjet2}} = 237$ (Figure 5.17d) the

impingement point approaches the centre of the chamber, ensuring the formation of vortices with approximately half of the mixing chamber width. At these conditions, the two liquid streams are injected at well-balanced opposed jets conditions.

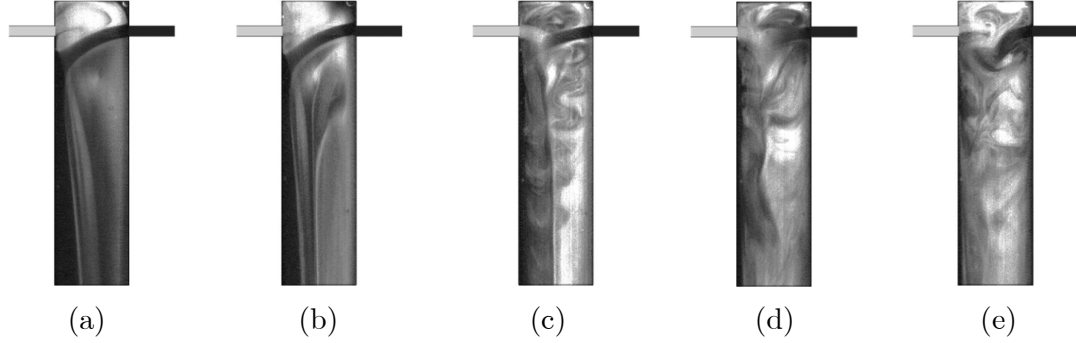


Figure 5.18 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two similar fluids with a viscosity ratio 1:1: $\mu_1 = \mu_2 = 1.7 \text{ mPa} \cdot \text{s}$, at $\text{Re}_{\text{Hjet2}} = 237$ for geometry W6w1e4 and (a) $\text{Re}_{\text{Hjet1}} = 47$; (b) $\text{Re}_{\text{Hjet1}} = 95$; (c) $\text{Re}_{\text{Hjet1}} = 142$; (d) $\text{Re}_{\text{Hjet1}} = 190$ and (e) $\text{Re}_{\text{Hjet1}} = 199$.

PLIF images in Figure 5.19 and Figure 5.20 show that the mixing of two different streams with viscosities $\mu_1 = 1.7 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$ (viscosity ratio 1:1.2) in two distinct configurations, geometry W6e1e4 and W6w1e2. The white jet that corresponds to the MV fluid was dyed with Rhodamine 6G. Both figures show a collection of PLIF images wherein the impact point of jets is shifted from the left to the right side by increasing the flow rate at jet 1 and, setting as constant the flow rate of injector 2.

At $\text{Re}_{\text{Hjet1}} = 50$ and $\text{Re}_{\text{Hjet2}} = 171$ (Figure 5.19a), jet 2 flows towards the opposed wall, i.e. the left sidewall. Setting Re_{Hjet1} to 100 shifts the impingement to the right. However, at these conditions, the flow remains mostly steady. At $\text{Re}_{\text{Hjet1}} = 150$ and $\text{Re}_{\text{Hjet2}} = 171$, the impingement point is slightly offset to the right-hand side of the mixing chamber, and dynamic streams are generated downstream the impingement point. The balance occurs for a Reynolds number range $50 < \text{Re}_{\text{Hjet1}} < 150$, i.e. for lower Reynolds number conditions than for jet 2 (LV fluid). At $\text{Re}_{\text{Hjet1}} = 200$ and $\text{Re}_{\text{Hjet2}} = 171$ (Figure 5.19d), jet 1 flows towards the opposed wall until a position close to the opposed nozzle.

PLIF images in Figure 5.20 show the balance conditions for Case 2 using the geometry W6w1e2. At $Re_{Hjet1} = 167$ and $Re_{Hjet2} = 571$ (Figure 5.20a), the impingement point is still offset to the left, and thus the flow loses the ability to efficiently mix the two fluids. In Figure 5.20b, the impingement point is slightly offset to the left side of the chamber, and a perturbation at the interface occurs downstream the contact point. At $Re_{Hjet1} = 500$ and $Re_{Hjet2} = 571$ (Figure 5.20c), the impact point is almost at the central position of the impingement point, and the balance of jets promotes the formation of vortices. These results clearly show that the effective balance of the two jets and the onset of self-sustainable chaotic flow regime occurs in between the conditions of Figure 5.20b and Figure 5.20c. At $Re_{Hjet1} = 667$ and $Re_{Hjet2} = 571$ (Figure 5.20d), the impingement point position is offset to the right-hand side of the mixing chamber, losing the mixing efficiency achieved in Figure 5.20c, where the jets oscillation occurs immediately downstream the impingement point.

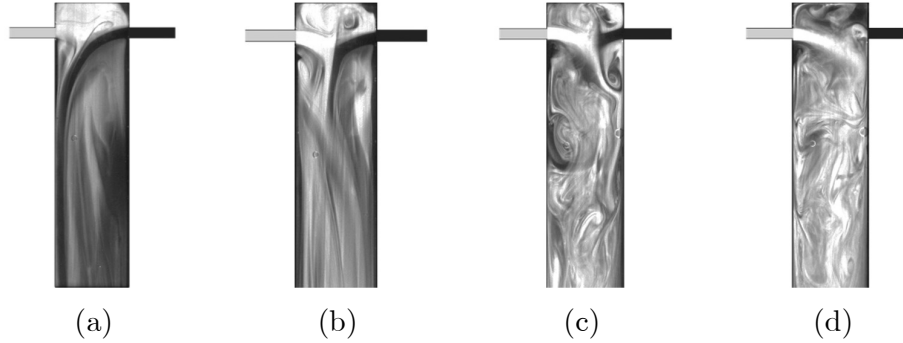


Figure 5.19 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:1.2: $\mu_1 = 1.7 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$, at $Re_{Hjet2} = 171$ for geometry W6w1e4 and (a) $Re_{Hjet1} = 50$; (b) $Re_{Hjet1} = 100$; (c) $Re_{Hjet1} = 150$ and (d) $Re_{Hjet1} = 200$.

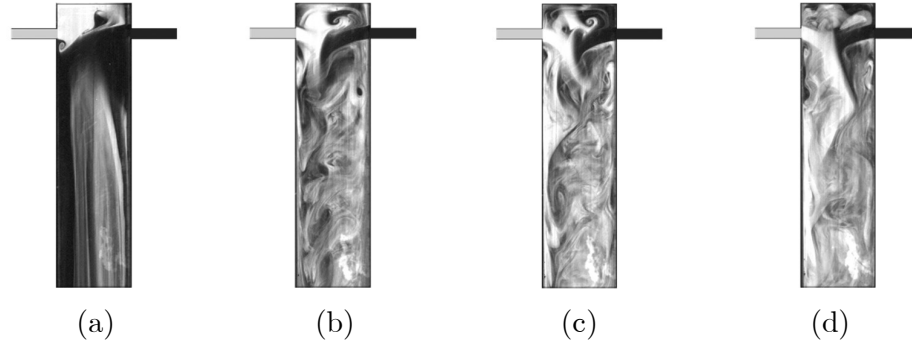


Figure 5.20 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:1.2: $\mu_1 = 1.7 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$, at $\text{Re}_{\text{Hjet2}} = 571$ for geometry W6w1e2 and (a) $\text{Re}_{\text{Hjet1}} = 167$; (b) $\text{Re}_{\text{Hjet1}} = 333$; (c) $\text{Re}_{\text{Hjet1}} = 500$ and (d) $\text{Re}_{\text{Hjet1}} = 667$.

Figure 5.21 and Figure 5.22 shows PLIF images of the displacement of the impingement point for Case 3 (viscosity ratio 1:3) using geometries W6w1e4 and W6w1e2. In Figure 5.21, the LV fluid was set at $\text{Re}_{\text{Hjet2}} = 480$, and for the MV fluid, the flow conditions were changed as follows: $\text{Re}_{\text{Hjet1}} = 74$, $\text{Re}_{\text{Hjet1}} = 89$, $\text{Re}_{\text{Hjet1}} = 97$ and $\text{Re}_{\text{Hjet1}} = 105$. Figure 5.21a shows the flow is almost steady at $\text{Re}_{\text{Hjet1}} = 74$ and $\text{Re}_{\text{Hjet2}} = 480$, and the flow patterns are characteristic of the steady engulfment flow regime. No dynamic structures are observed from the front view plane, and the same behaviour is observed for conditions of Figure 5.21b. The balance of jets is captured in-between conditions of Figure 5.21c and Figure 5.21d. When the jets impingement point is at the centre of the mixing chamber, there is the formation of a vortex street in the entire length of the mixing chamber, enabling the engulfment of both liquid streams. These observations demonstrate that the central impingement point position is achieved for higher Reynolds number at injector from where LV liquid is injected.

For geometry W6w1e2, Figure 5.22 shows that the balance of jets occurs at $\text{Re}_{\text{Hjet1}} = 445$ and $\text{Re}_{\text{Hjet2}} = 1600$. At these conditions, the oscillation of the interface promotes the formation of dynamic structures able to mix two liquid streams. For lower values of Re_{Hjet1} , energy dissipation at the impingement point is not enough to onset the chaotic flow regime, as observed in Figure 5.22a and Figure 5.22b.

The results presented in this section show that the effective mixing at the chaotic flow regime requires the balance of the opposed jets both for mixing of similar and dissimilar fluids. The imbalance of jets may create perturbations at the interface and small scale dynamic scales, but it is not possible to achieve a complete engulfment of both streams in a vortex street that evolves through the mixing chamber.

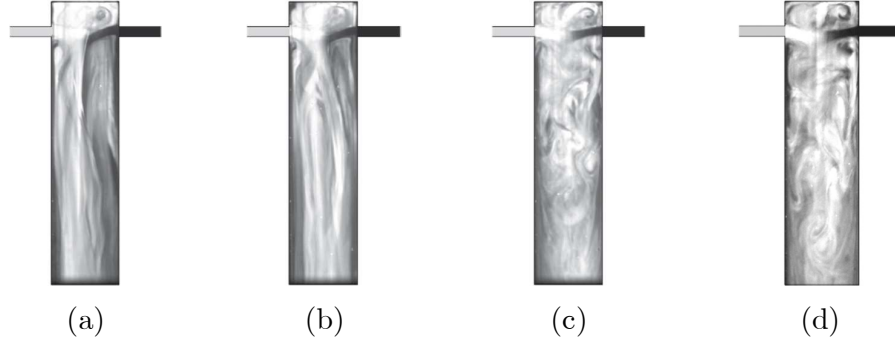


Figure 5.21 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:3: $\mu_1 = 4.1 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$, at $\text{Re}_{\text{Hjet2}} = 480$ for geometry W6w1e4 and (a) $\text{Re}_{\text{Hjet1}} = 74$; (b) $\text{Re}_{\text{Hjet1}} = 89$; (c) $\text{Re}_{\text{Hjet1}} = 97$ and (d) $\text{Re}_{\text{Hjet1}} = 105$.

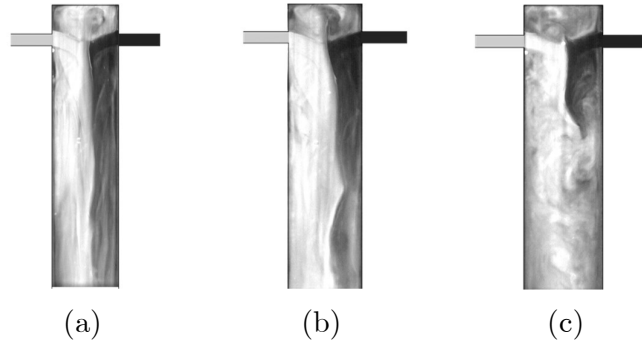


Figure 5.22 Instantaneous 2D concentration fields at the top of the mixing chamber for mixing of two dissimilar fluids with a viscosity ratio 1:3: $\mu_1 = 4.1 \text{ mPa} \cdot \text{s}$ and $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$, at $\text{Re}_{\text{Hjet2}} = 1600$ for geometry W6w1e2 and (a) $\text{Re}_{\text{Hjet1}} = 280$; (b) $\text{Re}_{\text{Hjet1}} = 310$ and (c) $\text{Re}_{\text{Hjet1}} = 445$.

5.4 Part II: 3D CFD Parametric Study and Prediction of the Impingement Point from a Elastic Analogue Model

PLIF images displayed in the last section are useful for the description of the onset of the self-sustainable chaotic flow regime. Experimental results showed two main critical conditions for the self-sustainable chaotic flow: working above the critical Reynolds number and the balance of jets setting the opposed jets impingement point at the mixing chamber central position. Therefore, the description of the offset of the impingement point position as a function of the conditions at injectors would be a quite useful tool to predict a priori the balance of jets at specific working conditions. This is not an easy task due to the complexity to define the impingement point position in T-Jets mixing chamber because it is observed, in most cases, a deflection of at least one of the jets. A method to predict the position of the impingement point is also addressed in this section.

3D CFD simulations are used to predict the impingement point position for different operational conditions. First of all, it is important to validate the experimental results and CFD data directly. After that, the impact of parameters on the impingement point position is tested for different working conditions. The impact of the width ratio, the mixing chamber depth, the inertial forces, the flow rate ratio and the physical properties of streams on the jets' interaction are here addressed from the prediction of the impingement point position in the mixing chamber.

5.4.1 3D CFD Model - Domain, Governing Equations and Discretisation

3D CFD simulations were run using the Finite Volume software package ANSYS/Fluent. The physical domain and the respective dimensions are described in Figure 5.23. The geometry consists of a mixing chamber with 6 mm width, two injectors with 1 mm width and a depth of 4 mm. The length of the mixer is 37.5 mm.

The governing equations that describe the steady laminar flow of jets in the simulation domain are given by the mass and momentum conservation,

$$\nabla \cdot \mathbf{u} = 0 \quad (5.7)$$

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u} \quad (5.8)$$

where $\mathbf{u}$ is the velocity vector, p is the pressure, μ and ρ are the viscosity and density of fluids, respectively. The respective convergence criterion is that the residuals are small than 10^{-6} .

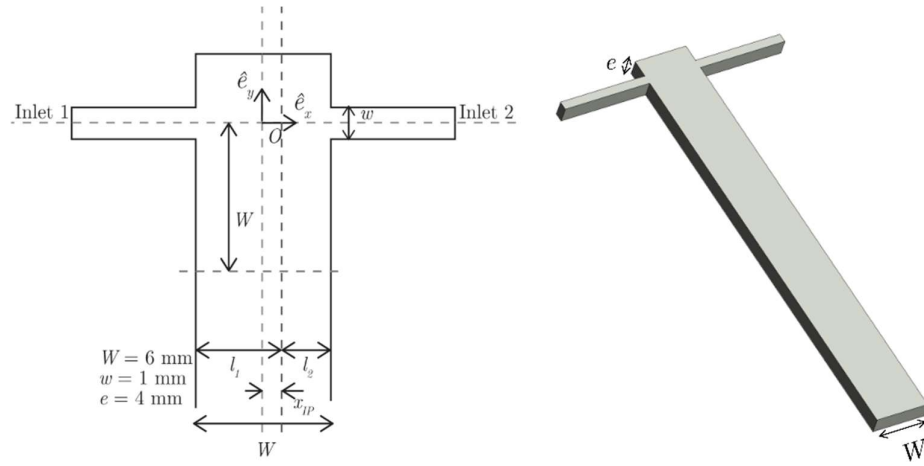


Figure 5.23 Schematic representation of the 3D geometry, 3D domain and the respective dimensions of T-Jets mixer.

Equations (5.7) and (5.8) were solved for the following boundary conditions: a uniform and constant pressure were set at the outlet, and no-slip condition was assumed at the walls. At inlet 1, the velocity is $\mathbf{u} = (v_{inj1}, 0, 0)$, and at inlet 2, the velocity is $\mathbf{u} = (-v_{inj2}, 0, 0)$. The inlet conditions have a great impact on the flow dynamics, and so the injectors have 15 mm long to ensure a fully developed velocity profile at the mixing chamber entrance. The velocities at injectors, v_{inj1} and v_{inj2} , are defined for each working condition and described in the following sections.

The simulation domain was discretized with uniformly sized cubic finite volumes with 0.25 mm of length, that makes a total of 5×10^4 cells.

For flow simulation, a SIMPLE scheme was used as a pressure-velocity coupling, and for spatial discretization, Least Squares Cell based is used as gradient solver. Second Order is set for pressure and Second Order Upwind for momentum.

5.4.2 CFD Results and Validation of Experimental Data

The validation of PLIF data comprises the direct facing with CFD simulation results. The experimental case selected for this study was at working conditions of symmetric physical properties and using the geometry W6w1e4. Reynolds number at injector 2 was set at $Re_2 = 50$, and conditions at injector 1 were changed for $r_s = q_1 / q_2 = \{0.8, 0.9, 1, 1.1, 1.2\}$. The physical properties of fluids set in CFD simulations are the same of experiments, $\rho = 996 \text{ kg m}^{-3}$ and $\mu = 8.89 \times 10^{-4} \text{ Pa} \cdot \text{s}$.

Figure 5.24 shows a PLIF image at $Re_1 = Re_2 = 50$ on the left side and five images on the right side where the streamlines are displayed for $Re_2 = 50$ and $r_s = \{0.8, 0.9, 1, 1.1, 1.2\}$. The streamlines issuing through injector 1 are represented in grey and the opposite injector streamlines in black.

Errors associated with experiments can be estimated from PLIF images and the pathlines. The flow controllers are contributing to a deviation of approximately 10% on the flow rate ratio as shown by the respective streamlines. Therefore, symmetric flow conditions visualized from experimental image corresponds actually to $r_s = 1.1$ obtained from CFD simulations. This is observed from the interface offset to the right side of the mixing chamber. For $r_s = 1$, it would be expected that the two jets deflect from the inlet to the outlet and the interface between the streamlines coincides to the mixing chamber symmetry axis.

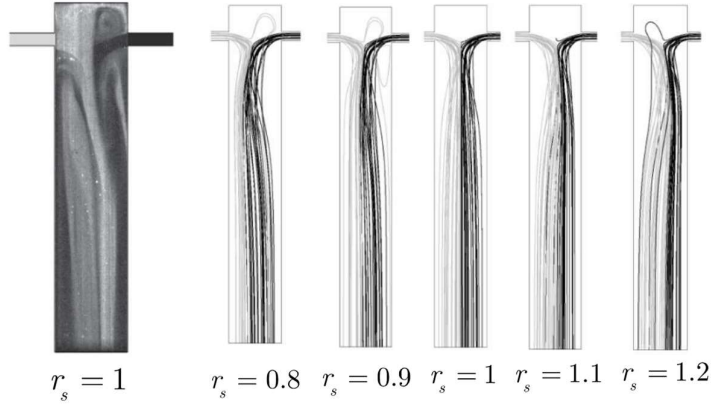


Figure 5.24 PLIF image and streamlines for different flow rate ratios r_s for mixing of two fluids with the same physical properties and $\text{Re}_2 = 50$ using the geometry W6w1e4.

The same comparison was made for $\text{Re}_2 = 80$ using the same geometry and the same flow rate ratios, $r_s = q_1 / q_2 = \{0.8, 0.9, 1, 1.1, 1.2\}$. Figure 5.25 compares the PLIF images and the respective streamlines for different flow rate ratios. This comparison shows again a small error associated with the measurement of the flow rates. In PLIF image, there is an offset of the interface to the right side of the mixing chamber. The comparison between experimental image and streamlines confirms that the experimental condition corresponds to the CFD results for $r_s \approx 1.1$, and thus the flow controller has an associated error of approximately 10%.

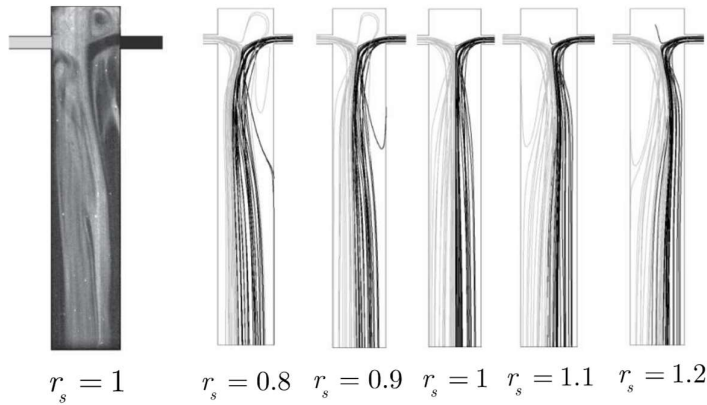


Figure 5.25 PLIF image and streamlines for different flow rate ratios r_s for mixing of two fluids with the same physical properties and $\text{Re}_2 = 80$ using the geometry W6w1e4.

The comparison between the experimental data and CFD results at balancing conditions shows a deviation of approximately 10% in the dark fluid streams. Thus, the prediction of the impingement point position is much more accurate from numerical data than from experimental results because the error associated to the measuring instruments, such as, the flow controller, are eliminated. Therefore, the estimation of the impingement point position from CFD simulations is the method used in this work.

5.4.3 Parametric Study on Jets Interaction

Base CFD Case

In the parametric study, a geometry W6w1e3 is selected as the base geometry. The dimensions of this configuration are 6 mm width of the chamber, 1 mm of injector width and 3 mm depth. The conditions at injector 2 are standardly defined as constant flow conditions, and the flow rate at injector 1 will be changed as defined for each parametric study.

The base simulation case corresponds to the conditions where two fluids with the same physical properties of water, $\rho = 998 \text{ kg m}^{-3}$ and $\mu = 1 \text{ mPa} \cdot \text{s}$, are injected in W6w1e3 geometry. The velocity at the injector 2 was set at $\text{Re}_2 = 50$ and in injector 1, the velocity was defined for a flow rate ratio range $0.1 < r_s < 3$, where $r_s = \rho_1 v_1 w_1 / \rho_2 v_2 w_2$.

This study is divided into three sections that correspond to the three parameters addressed in this work, which are Reynolds number, physical properties and geometrical parameters. Different values of Re_2 are tested for a specific range of flow rate ratio in the first section. In the following section, two dissimilar fluids were injected through the opposed jets to describe the influence of the physical properties on the offset of the impingement point position. In the last section, the geometrical properties were changed to discuss the impact of the width ratio and the mixing chamber depth on the jets interaction.

The objective of this study is the estimation of the offset of the impingement point position at different working conditions and the respective description of the influence of parameters on the balance of jets. The impingement point position was determined using the Eulerian velocity field. A point downstream the injectors axis is considered for the identification of the impingement point. This procedure differs from the one in CIJ mixers, where the analysis was made at the injectors axis because there is a jets deflection to a downstream position before the actual impingement point (Santos et al., 2002). Santos (2003) estimated that the equilibrium between the two opposed jets in a 2D domain occurs at $y \approx W$ and thus, the impingement point can be determined from the maximum velocity v_y at $y = W$, as represented in Figure 5.23.

Figure 5.26 shows the dimensionless impingement point position, $\xi = x_{IP} / (W / 2)$ wherein x_{IP} is the position in the mixing chamber, from CFD results. For $r_s = 1$, the two jets are balanced at the centre of the mixing chamber, $\xi = 0$. Increasing the velocity at inlet 1, $r_s > 1$, the impingement is offset to the right of the mixing chamber, and the results show that the plateau is achieved for $r_s > 1.5$, i.e. the impingement point tends to a constant value. Decreasing the velocity at injector 1, $r_s < 1$, the impingement point position goes to the left side of the mixing chamber. A constant position is also achieved for low r_s , but this value is not symmetric to the one obtained for $r_s > 1$. At $r_s < 1$, the viscous component must have a great contribution to the location of the interface between the two jets. Results in Figure 5.26 show that when viscous forces are clearly dominating, the dynamics of the jets equilibrium is changed. Based on this observation, CFD data for $r_s < 1$ is not used for comparison in the following discussions.

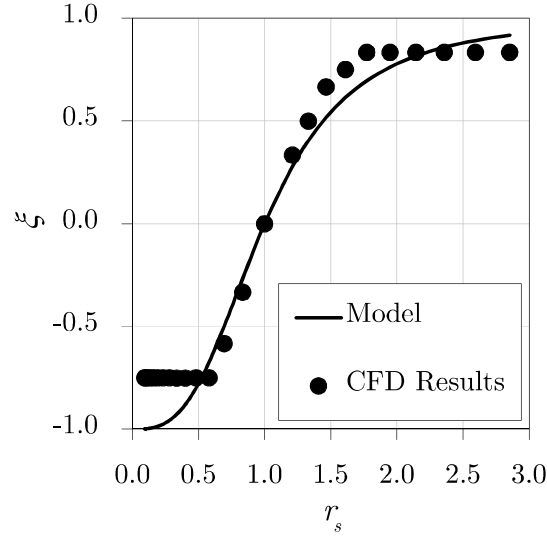


Figure 5.26 Non-dimensionless impingement point position for mixing of two similar at $Re_2 = 50$ determined from CFD results and analogue elastic model for W6w1e3.

Analytical Model Development

A proposal to fundamentally study the mechanisms of the impingement point interaction is based on a mechanistic model that considers that the behaviour of the jets is similar to a system of two strings. The analogy of jets as springs was first proposed by Li et al. (2007) and later by Fonte et al. (2016) to predict the impingement point position in CIJ mixers.

This model considers that the two jets in equilibrium behave as two springs in equilibrium. At the opposed jets balancing condition, one spring is acting a force to the other, given by the Hooke's law $F = kl$, where k is the spring constant and l is the respective deformed length. At the impingement point, the system is in equilibrium, and thus the balance of forces results in $F_{1 \rightarrow 2} / F_{2 \rightarrow 1} = k_2 l_1 / k_1 l_2$, where $F_{1 \rightarrow 2}$ is the force that spring/jet 1 applies to spring/jet 2 and $F_{2 \rightarrow 1}$ is the force that spring/jet 2 applies to spring/jet 1, assuming that jet 1 is on the left side of the mixing chamber and jet 2 is on the right side. Fonte et al. (2016) demonstrated that considering the potential

energy stored in a spring proportional to the kinetic energy rate of the opposed spring forcing the spring to compressed, this assumption results in

$$\frac{\dot{E}_{K1}}{\dot{E}_{K2}} = \frac{l_1}{l_2} \quad (5.9)$$

where the kinetic energy rate, $\dot{E}_K$, is a function of the deformed length from the inlet until the impingement point. The jet's kinetic energy can be estimated at the inlets, neglecting then the evolution of the velocity profile of the jets in the chamber. Thus, considering that both injectors have the same cross area, $A = we$, Equation (5.9) results in

$$\frac{\rho_1 v_1^3}{\rho_2 v_2^3} = \frac{l_1}{l_2} \quad (5.10)$$

The deformed length l is defined according to Figure 5.23. The definition of each jet length from the inlet until the impingement point position, x_{IP} , results in

$$\begin{cases} l_1 = \frac{W}{2} + x_{IP} \\ l_2 = \frac{W}{2} - x_{IP} \end{cases} \quad (5.11)$$

The combination of Equations (5.10) and (5.11) is

$$\xi = \frac{\frac{\rho_1}{\rho_2} \left(\frac{v_1}{v_2} \right)^3 - 1}{\frac{\rho_1}{\rho_2} \left(\frac{v_1}{v_2} \right)^3 + 1} \quad (5.12)$$

Equation (5.12) describes the position of the impingement point in the mixing chamber. For an increase of $v_1 (r_s > 1)$, ξ is offset to the right side of the chamber. Decreasing $v_1 (r_s < 1)$, the impingement point moves to the left. This model only takes into account the density of fluids and the inlet velocities. However, the viscosity of fluids and the

geometrical parameters are not taken into account in this impingement point estimation.

The analogue elastic model (Equation (5.12)) is plotted in Figure 5.26 in order to compare the analytical model and CFD results. A good agreement between this model and numerical data is observed for $0.5 < r_s < 1.5$. However, it cannot describe the plateau at $r_s < 0.5$ and $r_s > 1.5$, that approximately corresponds to the position of the complete deflection of the weakest jet $\xi > 1 - w / (W / 2)$. These results demonstrate the validation of the elastic analogue model in a range $-0.5 < \xi < 0.5$. Outside this range, the jets contacting is constrained by the geometry of the chamber, and the equilibrium based on the strength of the jet is no longer the dominant mechanism.

The agreement between the elastic analogue model and numerical results for other working conditions was also identified. However, this model does not take into account the Reynolds number at each injector, the viscosity of phases and the geometrical parameters.

5.4.3.1 Influence of Reynolds Number in Jets Interaction

Three different working conditions were tested in this section and then compared with the base case. Table 5.8 summarizes the working conditions set for each case, wherein Case 0 is the base case. The velocity at the injector 2 was set at $Re_2 = 50$ for Case 0, $Re_2 = 75$ for Case 1, $Re_2 = 25$ for Case 2 and $Re_2 = 10$ for Case 3. The flow rate ratio, r_s , range was changed, considering 11 random points in a range of flow rate ratio from 1 to 3. The physical properties of fluids correspond to water, $\rho = 998.2 \text{ kg m}^{-3}$ and $\mu = 0.001 \text{ Pa} \cdot \text{s}$.

Figure 5.27 shows the dimensionless position of the impingement point given by $\xi = x_{ip} / (W / 2)$ for Cases 0, 1, 2 and 3. This figure clearly shows that the impingement point position is offset to the right side of the mixing chamber, $\xi > 0$, when the velocity

at injector 1 is larger than the velocity at injector 2 ($r_s > 1$). For all cases, the balance of the opposed jets occurs at the centre of the mixing chamber ($\xi = 0$) for symmetric flow conditions, $r_s = 1$.

Table 5.8 Physical properties for the study of the influence of Reynolds number on the impingement point position in T-Jets mixers.

Case	Re_2	r_s
0	50	$1 < r_s < 3$
1	75	$1 < r_s < 3$
2	25	$1 < r_s < 3$
3	10	$1 < r_s < 3$

Figure 5.27 also shows that the elastic analogue model is able to give a rough estimative of the impingement point positions for Cases 0 ($\text{Re}_2 = 50$), 1 ($\text{Re}_2 = 75$) and 2 ($\text{Re}_2 = 25$). Nonetheless, this model is not able to describe the CFD results of Case 3 ($\text{Re}_2 = 10$), i.e. when the viscous component of flow has a greater contribution to the flow dynamics.

These results are in line with results for lower flow rate ratio, $r_s < 1$, observed for $\text{Re}_2 = 50$ (Figure 5.26) evidencing, once again, that the model does not describe the balance of jets at purely viscous flows. This conclusion permits to make a further adjustment on the validity range of the elastic analogue model, which corresponds to $-0.5 < \xi < 0.5$ and $\text{Re}_2 \geq 25$. This model was not validated at conditions of chaotic flow regime, whereas it is expected that a good prediction is given by Equation (5.12).

It is important to be critical in relation to the method for the determination of the impingement point position. This method considers that the impingement point coincides to the position at $y = W$, where y -velocity is maximum. For lower flow rate ratios, the maximum y -velocity may not coincide with the fluids interface, but it can

be occurring inside one of the fluid streams, i.e. in some cases, for larger viscous forces values, the jets are bent, but the peak velocity may be at the centre of the dominant jet. Nevertheless, CFD results were checked and showed that the impingement point position coincides with the maximum y -velocity at $y = W$ for all working conditions.

Numerical data for Cases 1 ($\text{Re}_2 = 75$) and 2 ($\text{Re}_2 = 25$) also show that a plateau is formed for $r_s > 2$, and the respective constant value is the same for $\text{Re}_2 = 75$, $\text{Re}_2 = 50$ and $\text{Re}_2 = 25$. This value is approximately 0.83, which corresponds to the condition where the fluid flows next to the wall has half of the thickness of the injector width, i.e the position of the interface is at $1 - (w/2)/(W/2)$. This premise will be later validated for geometries with different width ratios.

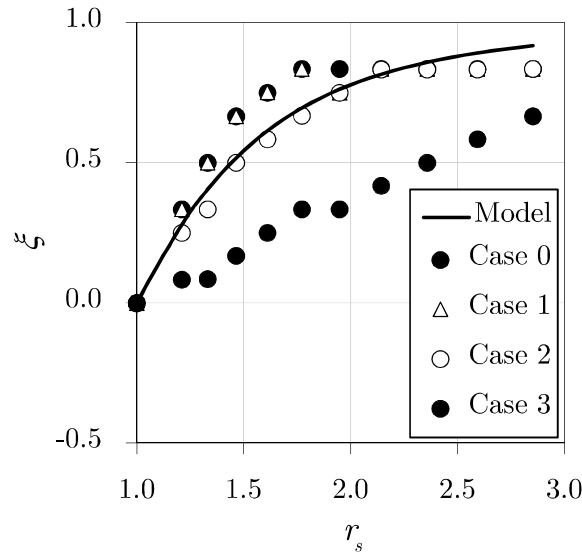


Figure 5.27 Non-dimensional impingement point position for $0.3 < r_s < 3$ for Cases 0 ($\text{Re}_2 = 50$), 1 ($\text{Re}_2 = 75$), 2 ($\text{Re}_2 = 25$) and 3 ($\text{Re}_2 = 10$) and the analogue elastic model.

5.4.4 Influence of Geometrical Parameters on Jets Interaction

The geometrical parameters also have an impact on the mixing dynamics. This was observed from PLIF visualisation presented in the last section and also in the literature (Thomas et al., 2010; Shi et al., 2011; Galletti et al., 2012; Somashekar et al., 2012;

Fani et al., 2013; Orsi et al., 2013a; Orsi et al., 2013b; Zhang et al., 2019). The impact of geometrical parameters on the jets interaction is here studied from CFD simulations. Two sets of experiments were prepared: Case 4 was performed to evaluate the influence of the mixing chamber depth, and Case 5 was simulated to address the impact of w / W ratio. The list of geometrical parameters tested in this work is summarized in Table 5.9. Cases 0 and 4 differ from each other in depth, wherein the depth in Case 4 is half the depth in Case 0. Cases 0 and 5 have different w / W ratios. In Case 5, the mixing chamber width is half than in Case 0, and all other dimensions remain constant. Therefore, geometries in Cases 0, 5 and 6 are named W6w1e3, W6w1e1.5 and W3w1e3. Both working fluids have the same properties of water, $\rho = 998.2 \text{ kg m}^{-3}$ and $\mu_1 = 1 \text{ mPa} \cdot \text{s}$.

The velocity at injector 2 was set at $\text{Re}_2 = 50$, and the conditions at injector 1 were changed considering 11 random points in a range of flow rate ratio from 1 to 3.

Table 5.9 Dimensions of the mixers for the study of the influence of the geometrical parameters on the impingement point position in T-Jets mixers.

Case	Re_1	w [mm]	W/w	e/w
0	50	1	6	3
4	50	1	6	3/2
5	50	1	3	3

Figure 5.28a shows the offset of the dimensionless impingement point position, $\xi = x_{\text{ip}} / (W / 2)$, for geometries W6w1e3 (Case 0) and W6w1e1.5 (Case 4). Results show that, for $1 < r_s < 3$, a slight difference between the results is observed for both geometries. Nevertheless, the values tend to the same value for $r_s > 2$. Both curves have approximately the same shape, that can be roughly described by the analogue

elastic model. These observations show that the mixing chamber depth does not have influence on the impingement point position.

Figure 5.28b shows the offset of ξ for geometries W6w1e3 (Case 0) and W3w1e3 (Case 5). Both plots have the same shape for $1 < r_s < 1.2$, but the curve for geometry W3w1e3 is not described any more by the analogue elastic model for values of flow rate out of this range. This means that the aspect ratio has an important role in the impingement point position, and the model that describes the impingement point position has to take into account this geometrical parameter. The aspect ratio is not considered in Equation (5.12) and so, since this parameter clearly plays a role in the evolution of ξ , further adjustment has to be done to get the complete description of the impingement point position in the mixing chamber.

Figure 5.28b also shows that curves tend to different constant values. For Case 0, $\xi = 0.83$ for $r_s > 2$ and for Case 5, $\xi = 0.67$ for $r_s > 2$. These values validate the premise that for high flow rate ratios, the interface remains constant at $1 - (w/2)/(W/2)$.

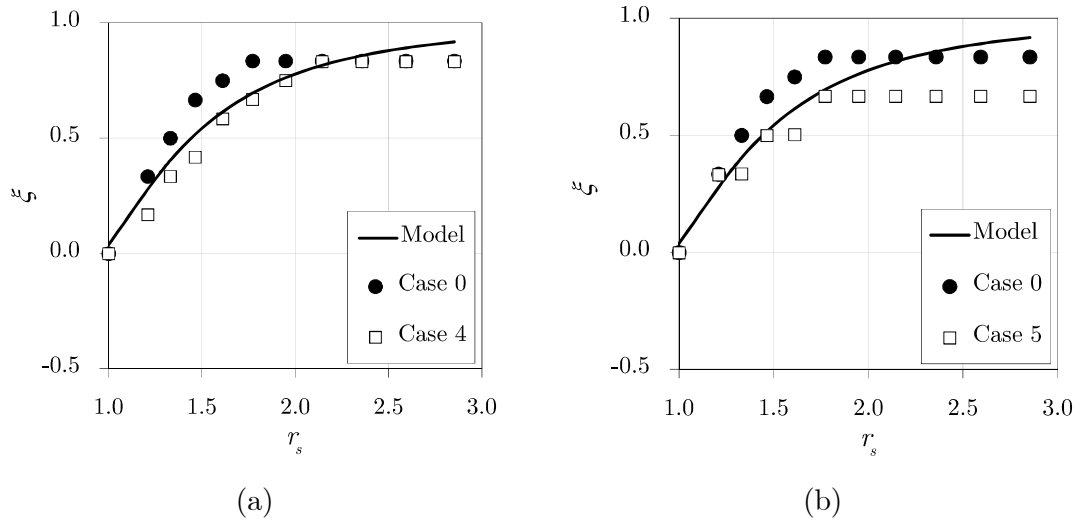


Figure 5.28 Dimensionless impingement point position for $0.3 < r_s < 3$ for (a) Cases 0 and 4 and (b) Cases 0 and 5.

5.4.5 Influence of Physical Properties on Jets Interaction

Results of Case 0 were also faced with two cases wherein the physical properties of fluids were changed. Table 5.10 summarizes the density and the viscosity of phases set for each case. Conditions of Case 6 correspond to real conditions tested in CIJ mixers studies in Chapter 4. On the other hand, conditions of Case 7 correspond to the experimental physical properties of fluids used to capture the PLIF images during the performance of T-Jets experiments. In Case 0, the two liquids have the same physical properties of water. In Case 6, the kinematic viscosity ratio is $\nu_1 / \nu_2 = 2$ and, in Case 7, the kinematic viscosity ratio is $\nu_1 / \nu_2 = 3$.

The less viscous fluid was continuously injected through injector 2, and the Reynolds number was set at $Re_2 = 50$. The more viscous fluid is injected through injector 1, and the Re was adjusted randomly for $0.5 < r_s < 3$.

Table 5.10 Physical properties for the study of the influence of the physical properties on the impingement point position in T-Jets mixers.

Case	Re_2	ν_1 / ν_2	ρ	μ
0	50	1	$\rho_1 = 998 \text{ kg m}^{-3}$ $\rho_2 = 998 \text{ kg m}^{-3}$	$\mu_1 = 1 \text{ mPa} \cdot \text{s}$ $\mu_2 = 1 \text{ mPa} \cdot \text{s}$
6	50	2	$\rho_1 = 1208 \text{ kg m}^{-3}$ $\rho_2 = 1176 \text{ kg m}^{-3}$	$\mu_1 = 40 \text{ mPa} \cdot \text{s}$ $\mu_2 = 20 \text{ mPa} \cdot \text{s}$
7	50	3	$\rho_1 = 1105 \text{ kg m}^{-3}$ $\rho_2 = 1257 \text{ kg m}^{-3}$	$\mu_1 = 4.1 \text{ mPa} \cdot \text{s}$ $\mu_2 = 1.4 \text{ mPa} \cdot \text{s}$

The consideration of two dissimilar fluids requires the simulation of the mass transfer using

$$\rho \left(\frac{\partial C_A}{\partial t} + \mathbf{u} \cdot \nabla C_A \right) = D_m \nabla^2 C_A \quad (5.13)$$

where C is the concentration of species, which can correspond to the liquid injected through injector 1 or 2, and D_m is the diffusivity. $D_m = 10^{-9} \text{ m}^2 \text{ s}^{-1}$ was used in CFD simulations. The mass transfer equation was solved in CFD simulations using *Second-Order Upwind* solver.

The impingement point position determined from CFD results was analysed as a function of Re_1 . This was the same analysis addressed in Chapter 4 for the offset of impingement point in CIJ mixer. Figure 5.29 shows CFD results for Cases 0, 6 and 7 and the respective model for each case. CFD results indicate that the increase of the kinematic viscosity results in a balance of jets at the centre of the mixing chamber for $\text{Re}_1 < \text{Re}_2$, maintaining constant Re_2 . For Case 0 (Figure 5.29a), the balance of jets occurs at the centre of the mixing chamber, $\xi = 0$, for $\text{Re}_1 = \text{Re}_2 = 50$. For Case 6, $\nu_1 / \nu_2 = 2$ (Figure 5.29b), the impingement point is at $\xi = 0$ for $\text{Re}_1 = 27$ and $\text{Re}_2 = 50$. For Case 7, $\nu_1 / \nu_2 = 3$ (Figure 5.29c), the impingement point is at $\xi = 0$ for $\text{Re}_1 = 16$ and $\text{Re}_2 = 50$.

The analogue elastic model in Figure 5.29 shows that the impingement point position in the mixing chamber is completely described for $-0.5 < \xi < 0.5$. For the three cases, CFD results show that the offset of the impingement point position tends to a constant value for the larger flow rate disparity. The analogue elastic model does not accurately predict this plateau because of the weaker jet deflection.

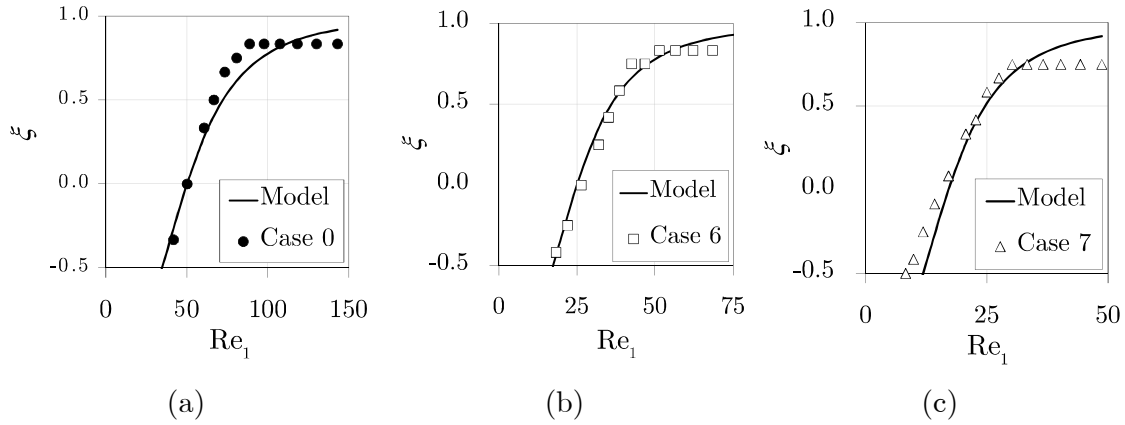


Figure 5.29 Non-dimensional impingement point position for $0.3 < r_s < 3$ for Cases (a) 0 ($\nu_1 / \nu_2 = 1$), (b) 6 ($\nu_1 / \nu_2 = 2$) and (c) 7 ($\nu_1 / \nu_2 = 3$).

In conclusion, an elastic analogue model was demonstrated in this thesis to predict the impingement point position. This model is based on the balance of the kinetic energy of jets and also takes into account the velocity and density of jets. It is considered that the velocity at the nozzle remains constant up to the contact point between jets. The densities of both liquid streams are the only physical properties considered in this model. The validation of this equation was made for a different set of working conditions. Results demonstrate that this model predicts the impingement point position for flows with a strong inertial component, $Re \geq 25$. When one of the streams has $Re \leq 25$, the model is not able to describe the shifting of the impingement point. Furthermore, results show that the elastic analogue model describes the impingement point for $-0.5 < \xi < 0.5$ and for $25 \leq Re \leq 75$ using geometries with any depth and $W/w = 6$. Results also show that w/W ratio has to be considered in a general model. Therefore, further adjustments have to be done in the demonstration of a new model.

For $\xi < -0.5$ and $\xi > 0.5$, CFD results show the impingement point position tend to a plateau not described by this model. For $\xi > 0.5$, the constant value is given by $1 - (w/2)/(W/2)$.

Although this model does not fit the CFD results for $-1 < \xi < 1$, a good estimation for $-0.5 < \xi < 0.5$ is enough for a complete design of the working conditions for the onset of the chaotic flow regime. PLIF images presented in the last section show that the onset of the impingement point occurs for the balance of jets at the centre of the mixing chamber. This observation evidences that the elastic analogue model can be used as a tool for the design of experimental conditions in T-Jets mixers.

5.5 Part III: New Reactive PLIF Method for Characterisation of Mixing Dynamics in T-Jets Mixers

Since the mid-50s, attention has been given to the assessment of the micromixing, leading to the introduction of methods based on chemical reaction selectivity. A reactive PLIF method was introduced in Chapter 3 for flow visualisation in chemical reactors. In this section, the PLIF methods will be tested and optimised for micromixing visualisation studies. The two methods introduced in Chapter 3 consists of an acid-base reaction with fluorescein as the reaction sensitive tracer and the Fenton's reaction, with rhodamine-B as the reaction tracer. The operating conditions determined as suitable for mixing studies were tested in a T-Jets mixer, illuminated in the axial plane with a laser light sheet.

5.5.1 Experimental Setup

The implementation of reactive PLIF (RPLIF) methods was conducted in a T-Jets reactor with a typical geometry shown in Figure 5.1. In this work, only one geometry was tested with a height of $H = 50$ mm, a mixing chamber width of 6 mm, a width of injectors of 1 mm and a depth of 4 mm (W6w1e4 as described in Table 5.5). The selection of this geometry was based on the previous studies, where it is observed that W61e4 geometry is the best combination for the onset of the self-sustainable flow regime.

Two RPLIF methods are tested in this section: an acid/base reaction with a pH tracer, fluorescein, the AB-RPLIF method; and Fenton's reaction with Rhodamine B as a tracer that is oxidized in the reaction region, the oxi-RPLIF method. The test reaction stoichiometry used in both RPLIF methods was previously demonstrated in Section 3.3.3.1., as well as a discussion about the respective performances using Nd:YAG laser. Results presented in Chapter 3 showed that the combination of fluorescein in AB-RPLIF and Nd:YAG laser does not permit the quantification of mixing from a post-processing of PLIF images. Furthermore, studies in Chapter 3 show that it is not possible to work at a linear concentration region with this laser.

Nevertheless, mixing can be characterised from the visualisation of the sequence of images. The optimised working conditions defined in Chapter 3 to conducted AB-RPLIF are $[\text{H}_3\text{PO}_4] = 0.100 \text{ M}$ and $[\text{NaOH}] = 0.165 \text{ M}$. The concentration of fluorescein used in experiments was $C = 20 \text{ mg L}^{-1}$, which generates low values of fluorescence (Figure 3.13). Nonetheless, the performance of this concentration was carried using a Nd:YAG laser.

On the other hand, the oxi-RPLIF method is able to quantify the mixing. The ideal conditions in oxi-RPLIF are 2% H_2O_2 (wt./v) and 0.010 M aqueous solution of Fe^{2+} (as FeSO_4). The RhB concentration was set according to the results in Chapter 3 and the calibration curve for pixel light intensity as a function of dye concentration (Mortensen et al., 2004; Sultan et al., 2012).

The experimental setup used in this experimental study was described in Section 5.3.1. For AB-RPLIF, the acid stream, phosphoric acid (H_3PO_4) and fluorescein, was stored in one of the tanks and the base stream, sodium hydroxide (NaOH) was stored in the other one. Three different flow regimes were tested: $\text{Re} = 50$, $\text{Re} = 150$ and $\text{Re} = 200$ where Re is defined from the width of injectors (Equation (5.1)). The operating conditions were symmetric, i.e. the acid and base liquid streams have the same viscosity, density and flow rate, i.e. $\text{Re}_{\text{acid}} = \text{Re}_{\text{base}}$. Experiments were conducted

injecting the acid fluid stream through the left-side injector, and the base fluid stream through the right-side injector.

For oxi-RPLIF, the iron (Fe^{2+} as FeSO_4) was stored in one of the tanks and the hydroxide peroxide (H_2O_2) was stored in the other one. Both streams were doped with rhodamine B (RhB). Oxi-RPLIF was tested in T-Jets mixers for two different flow regimes: $\text{Re} = 50$ and $\text{Re} = 150$. The operation conditions are symmetric, i.e. solutions delivered from both injectors have the same viscosity, density and flow rate ($\text{Re}_{\text{iron}} = \text{Re}_{\text{H}_2\text{O}_2}$).

The RPLIF methods require the use of a laser sheet that will illuminate the plane within the flow of the acid stream doped with fluorescein (in AB-RPLIF) or the hydrogen peroxide and iron dyed with RhB (in oxi-RPLIF). Fluorescein and RhB will emit fluorescence enabling the visualisation of the reactive regions. The laser sheet was generated in a Nd:YAG laser with an emission peak at 532 nm. The RPLIF images require a light glass filter (545 nm) on the digital camera lens. A schematic representation of PLIF system is in Figure 5.3.

5.5.2 Results and Discussion

5.5.2.1 AB-RPLIF Method

Figure 5.30 shows RPLIF images obtained at the plane defined by the mixing chamber and injector axis, for AB-RPLIF method at $\text{Re}_{\text{acid}} = \text{Re}_{\text{base}} = 50$. At the inlet, the acid fluid stream has $\text{pH} < 2$, and thus the emission intensity of fluorescein was approximately 0, as observed from Figure 3.14. Therefore, the fluid issuing from this jet is capture as dark in PLIF images. PLIF images show that no dynamic structures are formed in the mixing chamber, and thus each fluid stream remains in each side of the mixing chamber. Figure 5.30 also shows the appearance of white flow patterns in the mixing chamber, which results from increasing pH in the acid stream that is associated with an increase of the emission intensity of fluorescein. These visualisations

show that the acid-base reaction of H_3PO_4 and NaOH occurs in the T-Jets mixing chamber, and the flow regime is commonly named by the vortex flow regime (Santos and Sultan, 2013).

These results are in agreement with Bothe (2008) and Hoffman et al. (2006), who reported that, at this flow regime, there is the transport of one fluid from one side to the other due to convective mechanisms. Although these convective mechanisms are not visualised from non-reactive PLIF methods, the appearance of a white colour fluid in AB-RPLIF method enables to conclude that the convective mixing phenomena promote the reaction of H_3PO_4 and NaOH . These convective mechanisms consist of two parallel Dean vortices, particularly visible from the pathlines of segregated regime, which is generally referred in T-jets literature as vortex flow regime, reported Soleymani et al. (2008a, 2008b).

In Figure 5.30, it is also observed the formation of a vortex in each side of the mixing chamber head. Sultan et al. (2012) had already reported the formation of two upper vortices from the intrusion of fluid having different colour in one of the jet streams. These two upper vortices are symmetric and roundish. The residence time in these vortices is generally large, compared with the flow passage time in the mixing chamber, and so there is local accumulation of reaction product in this region.

Once again, the conclusions on the flow regime classification could be clear from the observations of the cross-section of the mixing chamber made from the top of T-jets mixer. It would be expected to visualise a double pair of counter-rotating vortical structures.

Figure 5.31 shows AB-RPLIF images obtained at the plane defined by the mixing chamber and injector axis at $\text{Re}_{\text{acid}} = \text{Re}_{\text{base}} = 125$. The flow is no longer at steady state (segregated or vortex flow). The opposite jets are impinged at the mixing chamber axis and directed towards the outlet, with the formation of vortices on both sides of the jets. These vortices evolve throughout the mixing chamber towards the outlet: vortex

street. The mixing of two streams promotes the acid-base reaction and thus, the pH in the acid stream increases throughout the mixing chamber. This results in the increase of the intensity of emission of fluorescein and the appearance of white colour.

Images in Figure 5.31 also show that a concentration of fluorescein $C = 20 \text{ mg L}^{-1}$ enables to visualise the reactive fronts using a Nd:YAG laser, even emitting a weak fluorescence intensity.

The acid-base reaction is practically instantaneous, and thus the reaction time is very small. This means that there is a general spread of tracer in the reactor, showing product reaction at the contact region of the two streams, which now extends throughout the mixing chamber.

Figure 5.32 shows a sequence of AB-RPLIF images obtained at $\text{Re}_{\text{acid}} = \text{Re}_{\text{base}} = 200$. The overall formation of vortices promotes the interfacial area generation between the two inlet streams resulting in the same observations at $\text{Re} = 125$ in Figure 5.32.

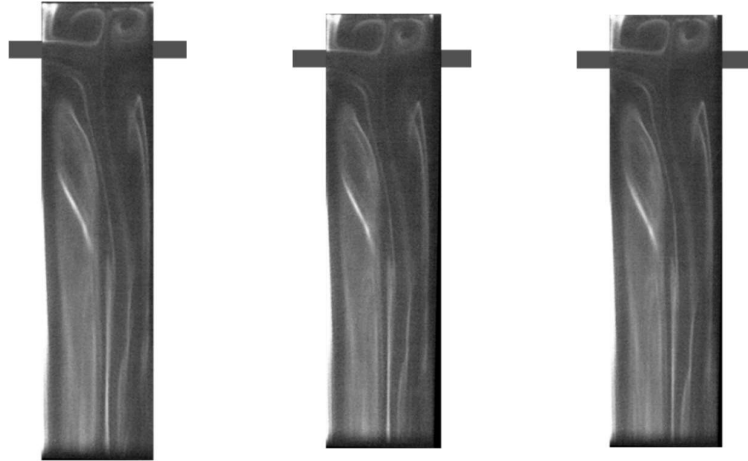


Figure 5.30 PLIF image obtained from AB-RPLIF method at $\text{Re} = 50$.

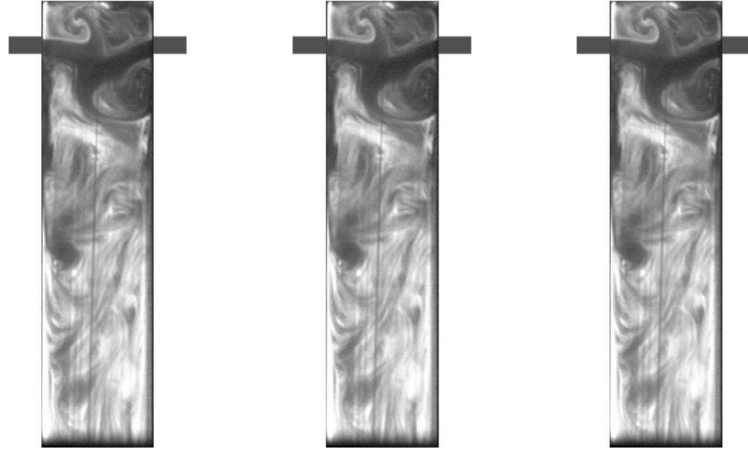


Figure 5.31 PLIF image obtained from AB-RPLIF method for $Re = 125$.

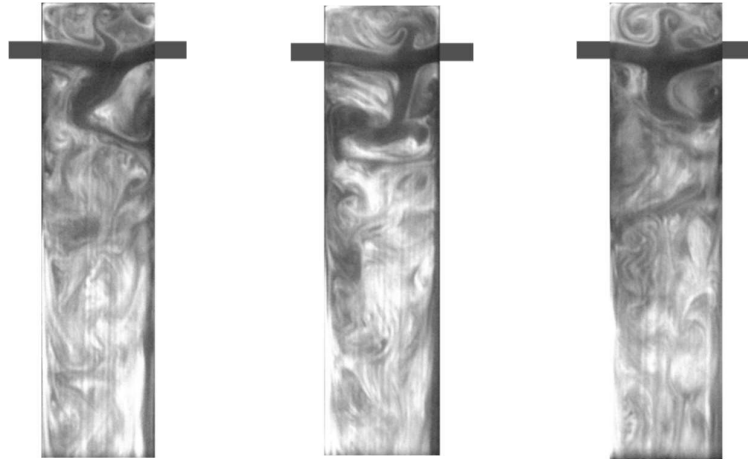


Figure 5.32 PLIF image obtained from AB-RPLIF at $Re = 200$.

AB-RPLIF method enabled the visualisation of the reactive regions in T-Jets mixers at chaotic flow regimes for the first time. The regions where the reaction already took place are marked by a high emission intensity enabling to identify the reactive regions.

5.5.2.2 Oxi-RPLIF Method

Figure 5.33 shows oxi-RPLIF images obtained at the plane defined by the mixing chamber and injector axis at $Re_{\text{iron}} = Re_{\text{H}_2\text{O}_2} = 50$ and at $\theta = 296 \text{ K}$. The two liquid streams injected in the mixing chamber are white because both were dyed with RhB,

which emits fluorescence when illuminated by a laser light sheet. Oxi-RPLIF images show that no dynamic structures are formed in the defined plane at that Re . The disappearance of tracer, associated to changes of liquid streams' colours, from white to black, is shown in Figure 5.33. This is related to the RhB oxidation by hydroxyl radical ($HO\bullet$) (Equation (3.20)).

Figure 5.33 also shows a darker central region on the contact of both reactant streams, where the reaction takes place. This is associated to two Dean vortices formed in each side of the mixing chamber (vortex flow regime), which promotes the reaction between Fe^{2+} and H_2O_2 . These results are in agreement with Bothe (2008), Hoffman et al. (2006) and even with the AB-RPLIF images shown in Figure 5.30.

Figure 5.34 shows oxi-RPLIF images of the plane defined by the mixing chamber and injectors axis at $Re_{iron} = Re_{H_2O_2} = 150$ and at $\theta = 296$ K. At these working conditions, the flow is no longer steady and stratified. Dynamic mixing structures are formed, promoting the engulfment of the two liquid streams. So, at these flow conditions, the disappearance of tracer is more generalised at downstream positions of the mixing chamber. And so, the use of Fenton's reaction as RPLIF method enables to assess chemical reaction rate throughout the reactor. The main mechanism in this method is the saturation of the inlet streams with a tracer and the respective disappearance of the tracer, which can be used as an indicator of the chemical reaction.

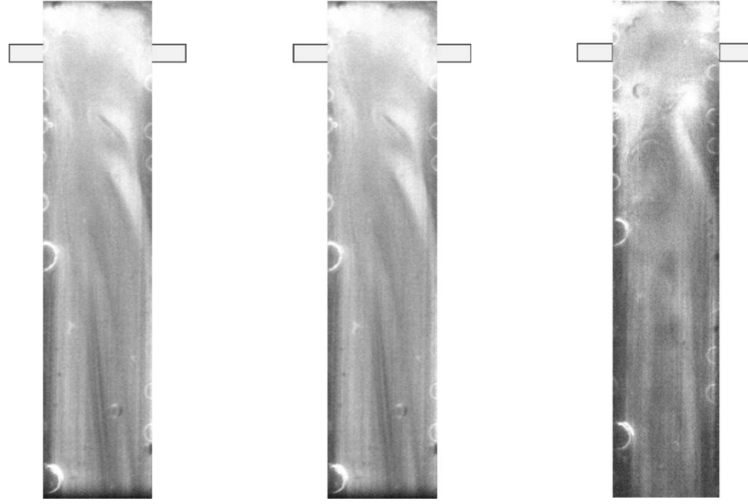


Figure 5.33 PLIF image from oxi-RPLIF method at $Re = 50$.

Figure 5.33 and Figure 5.34 show there is the formation of gas bubbles during the experiments, that makes the visualisation of mixing even more difficult. The formation of oxygen in Fenton's reaction is described by Equation (3.21). This fact does not allow to implement a quantification method for mixing degree, such as the intensity of segregation.

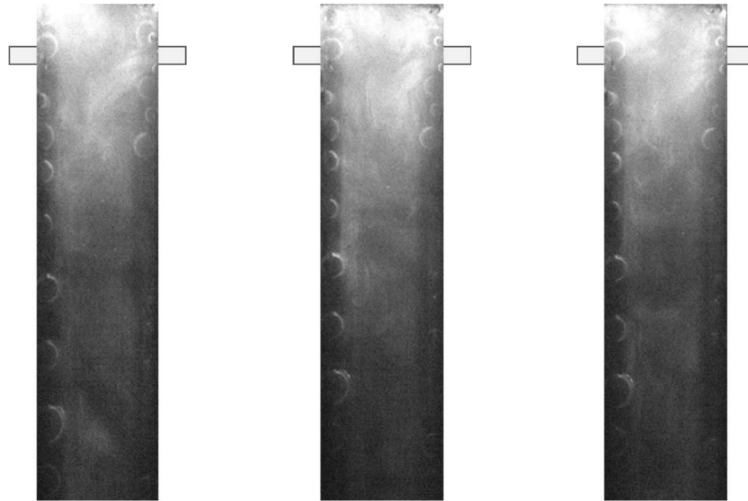


Figure 5.34 PLIF image obtained from oxi-RPLIF method at $Re = 150$.

The production of sludge iron and the degradation of H_2O_2 into O_2 and H_2 could be avoided by lowering the pH of the medium where Fenton's reaction takes place. The experiments carried out at lower pH does not influence the rhodamine performance. However, even at neutral pH, results show that the best performance of RPLIF methods is the one where the intensity of emission is increased, i.e. AB-RPLIF method. The vanishing of the fluorescence does not give a clear visualisation of the chemical reaction and the generation of the interfacial area between the two fluid streams. This feature is particularly useful in chaotic flow regimes where mixing occurs by interfacial area generation (Ottino et al., 1979).

On the other hand, in the oxi-RPLIF method, the streams are initially dyed with a tracer and reaction is assessed from the vanishing of tracer and then the decrease of its emission intensity. So, this method also enables to assess the chemical reaction rate throughout the mixing chamber.

An economic analysis was already done for AB-RPLIF and oxi-RPLIF methods in Chapter 3. This study also demonstrated that AB-RPLIF method is much more profitable than the oxi-RPLIF method, and so the AB-RPLIF method is more promising than oxi-RPLIF method.

5.6 Conclusions

This chapter was divided into three parts: Part I – experimental analysis of the mixing dynamics for different Reynolds number and impact of the imbalance of jets on the onset of the dynamic flow structures; Part II – development of a new model based on the balance of kinetic energy of jets and respective validation from 3D CFD results simulated for different Reynolds number, geometrical parameters and kinematic viscosity ratios; Part III – testing of two new reactive RPLIF methods for the characterization of mixing dynamics in T-Jets mixers.

PLIF visualization of flow dynamics showed that the self-sustainable chaotic flow regime onsets at $179 < \text{Re}_{\text{Hjet}} < 269$ for the injection of two similar fluids with the same properties of water in a W6w1e4 mixing chamber. For W6w1e2 geometry, this transition occurs at $224 < \text{Re}_{\text{Hjet}} < 293$, which corresponds to higher Reynolds number than the previous geometry because shallower geometries have a strong effect of walls restraining the vortex formation. So, the effect of W/e is quite straightforward for the mixing of similar fluids in T-Jets mixers. For narrow geometries, as W2w1e4, the transition to a self-sustainable chaotic flow regime is not observed. Thus, this configuration is not able to efficiently mix two liquid streams. For two similar fluids tuned with glycerol, the transition to the chaotic flow regime occurs at $95 < \text{Re}_{\text{Hjet}} < 161$ for W6w1e4 geometry, and the W6w1e2 geometry cannot mix the two liquid streams in a chaotic flow regime, in a specific range $79 < \text{Re}_{\text{Hjet}} < 395$.

PLIF images were also captured for mixing of dissimilar fluids. The transition to the self-sustainable chaotic flow is completely controlled by the jet with lowest Reynolds number, that is the MV fluid ($\text{Re}_{\text{Hjet,MV}}$). The critical Re number for the geometry W6w1e4 occurs at approximately $\text{Re}_{\text{Hjet,MV}} > 300$ and for the geometry W6w1e2 at $\text{Re}_{\text{Hjet,MV}} > 350$.

The imbalance of jets was also studied from PLIF images by shifting the impingement point position. The effective mixing at chaotic flow regime is only promoted by the balance of jets at the centre of the mixing chamber, even for mixing of similar or dissimilar fluids. The imbalance of jets may create perturbations at the interface and small scale dynamic structures, but it is not possible to achieve a complete engulfment of both streams in the mixing chamber.

An elastic analogue model was demonstrated in this chapter to predict the offset of the impingement point position. This model is developed from an analogy of two impinging jets with a system of two springs. It is based on the balance of the kinetic energy of jets and also takes into account the velocity and density of two liquid streams. This

model considers that the velocity of jets remains constant from the nozzle to the impingement point position. The validation of this equation was made for a different set of working conditions. A validity range for this expression may be described from CFD results: $-0.5 < \xi < 0.5$ and $\text{Re} \geq 25$ for geometries with any depth and $W/w = 6$. This observation shows that the elastic analogue model can be used as a tool for the design of conditions for the balance of jets at the centre of the mixing chamber, which is the effective condition for the onset of the dynamic flow regime.

In the last part of this chapter, two reactive PLIF methods were tested: an acid-base reaction with fluorescein as the reaction sensitive tracer (AB-RPLIF method) and the Fenton's reaction, with rhodamine-B as the reaction tracer (oxi-RPLIF method). The ideal conditions were defined in Chapter 3, and in this chapter, they were implemented in T-Jets mixers. Experiments performed in T-Jets mixers showed that the AB-RPLIF method is the best method for a clear visualisation of mixing dynamics and the interfacial area generation by increasing the emission intensity in the mixing chamber during the reaction course. The other method tested, oxi-RPLIF, also enables the assessment of mixing degree throughout the mixing chamber; the tracer initially added to the pure liquid streams disappears, being associated to a decrease of the emission intensity. However, this method has the disadvantage of the formation of an undesirable iron sludge and more frequent gas bubbles during the experiments. Furthermore, the oxi-RPLIF method is also fivefold more expensive than AB-RPLIF. This work brings a useful contribution to this field of research, by the adaptation and improvement of two test-reactions that could be used as efficient, safe and cost-saving methods for mixing assessment.

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6 Mixing Mechanisms in Split-and-Recombine Mixers

6.1 Introduction and State of the Art

Static mixers are widely used in laboratory and industrial scale applications to mix two or more fluids in a continuous fashion without moving mechanical elements. These mixers are especially suited for applications where flow rates are too small (e.g. microfluidic applications) or viscosity is too large (e.g. polymers, detergents, paints). CIJ and T-Jets mixers are two examples of static mixers.

The use of these mixers in industry only became widespread after the 1970s, but there are patents prior (Sutherland, 1874; Bakker, 1949; Stearns, 1949; Lynn, 1951; Tollar, 1960; Veazey, 1965). The first patent was issued in 1874, and it describes a multilayer reactor without moving parts used to mix air and gaseous fuel (Sutherland, 1874).

Static mixers can have specific geometries that promote secondary and transverse flow, enhancing the mass and heat transfer. Another type of static mixers is the insert-type of multiple stationary parts, called elements. These elements may be blades or conjugated plates that induce changes in the flow. These insets can have channels,

helical elements or obliques blades (Ghanem et al., 2014) to ensure the stretching and engulfment of the incoming fluids promoting distributive mixing.

Mixing in static mixers is completely characterised from the temporal and spatial variations of residence time distribution (Castelain et al., 1997; Aubin et al., 2005; Ghanem et al., 2014) and the striation thickness distribution (Sokolov and Blumen, 1991; Aubin et al., 2005; Ghanem et al., 2014). The design of reactors geometry and the number of static mixing elements are the parameters that most influence the mixing efficiency.

These mixers have been used as an alternative to conventional reactors. The potential advantages of static mixers compared to mechanically agitated vessels are the small space requirements, low equipment cost, better energy efficiency for mixing, no moving parts, narrow span of residence times distribution approaching plug flow, good mixing at low shear rates, flexible production of different products in the same device and self-cleaning (Thakur et al., 2003).

The design of static mixers is tailored for the respective applications. Static mixers have been used for different systems, such as liquid-liquid, gas-liquid and solid-liquid systems with a particular application in chemical, petrochemical, food, pharmaceutical, pulp and paper industries (Thakur et al., 2003). Static mixers are commonly divided into four groups according to their application (Thakur et al., 2003):

- Mixing of miscible fluids working at laminar or turbulent flow regimes;
- Mixing of immiscible fluids with the generation of interfacial area in liquid/liquid, gas/liquid and solid/liquid systems;
- Heat exchange and thermal homogenisation;
- Solids' blending.

Static mixers first applications focus on the mixing of fluids at laminar flow regime conditions. Applications as heat transfer, turbulence and multiphase systems were

introduced later (Thakur et al., 2003). The objective of the first applications was to achieve a good mixing in the cross-section of a circular tube at laminar flow regime. Elements were installed in a static mixer to promote the redistribution of the incoming liquid stream and then the combination into different layers in a sequence. Mixing in these devices does not rely on the onset of inertial mechanisms, like turbulent eddies or chaotic motion, but by the reduction of mixing scales at non-inertial regimes, enhancing the concentration gradients and the molecular diffusion of phases.

Mixing in static mixers can also operate in turbulent flow regime. In these devices, inserts promote turbulence and generate intense radial mixing. Three examples of applications are the mixing of gas at turbulent flow regimes, the blending of polymer melts and aqueous solutions (Ghanem et al., 2014).

In this work, a particular focus is given to single-phase systems in static mixers operating at the Stokes regime.

6.1.1 Fundamentals of Mixing in Static Mixers at Stokes Flow Regimes

Mixing in the laminar flow regime usually occurs for high-viscosity fluids in the food, coatings, cosmetic, polymer, adhesive and detergent industries. At low Reynolds number, the spatial distribution of fluids requires a solution based on the topology of mixing, for instance, in a specific static mixer, the split and recombine (SR) reactors. These reactors are based on the split and recombine principle, which consists in splitting the income fluid into layers and then recombine them in a different sequence. No external agitation is required to ensure the mixing of liquid streams (Gray et al., 1999; Chen and Meiners, 2004; Hirata and Ohkawa, 2016), and the specific geometrical construction of the insert-type configuration promotes the redistribution of fluids.

Mixing in SR mixers working at laminar flow regime can be described by one of the most well-known one-dimensional mathematical transformation, the baker's transformation (Ottino and Wiggins, 2004). Figure 6.1 shows a schematic

representation of baker's transformation. The square A, which consists of two strips (white and black), is split in two rectangles with a length L and a height $L/2$. Then these rectangles are rotated and stretched, resulting in two rectangles with a length $L/2$ and a height L . The fusion of elements forms a new part with 4 strips, which results from the combination of the mechanism of splitting and stretching.

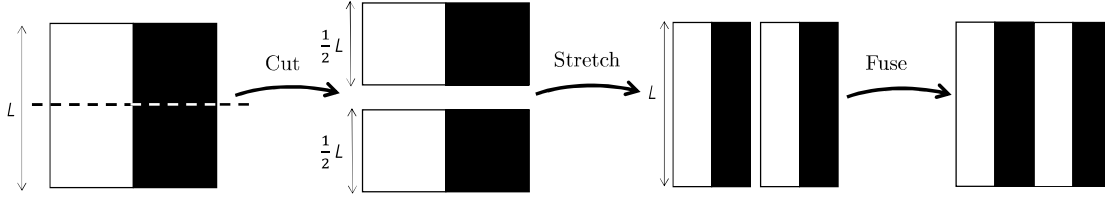


Figure 6.1 The Baker's transformation.

The main contribution of baker's transformation to the mixing efficiency is the increasing of the interfacial area between fluids, enhancing the mixing performance (Ghanem et al., 2014; Hossain and Kim, 2015). The lamellar structure generated from the cutting and re-stacking mechanisms promotes the reduction of diffusion length (Aoki et al., 2011), resulting in the enhanced diffusion through the fluids interface.

The repetition of baker's transformation promotes the creation of a multi-lamination square. Figure 6.2 shows a contour map of a successive implementation of baker's transformation in a system of two strips (Figure 6.2a). This figure shows that the repetition of iterations determines the efficiency of the mixing degree. The result is the formation of 4, 8 and 16 strips, as shown from Figure 6.2b to Figure 6.2d. Considering that the number of transformations is described by n_{me} , the number of strips increases $2^{n_{me}}$ (Wiggins and Ottino, 2004) and so the thickness of each strip is given by $\delta = L / 2^{n_{me}}$ where L is the unit length.

Evolution of interfacial area and the striation thickness decay are commonly used as the metrics to assess the quality of mixing. The interfacial area is promoted by the stretching mechanism and the thinning of striation thickness that accelerates the

interdiffusion at molecular scale. Stretching is related in a fundamental way to the Lyapunov exponent, which is given by

$$\Lambda = \lim_{\substack{n_{me} \rightarrow \infty \\ n_{me}}} \frac{1}{n_{me}} \ln(\lambda(\mathbf{X}, t)) \quad (6.1)$$

where λ is the stretching of a particle in the initial position $\mathbf{X}$ and time t . The stretching factor for baker's transformation is related to the increase of the number of striations, $2^{n_{me}}$, and so $\lambda \approx 2^{n_{me}}$. Therefore, according to Equation (6.1), SR mixer has a characteristic Lyapunov exponent of approximately $\ln(2)$.

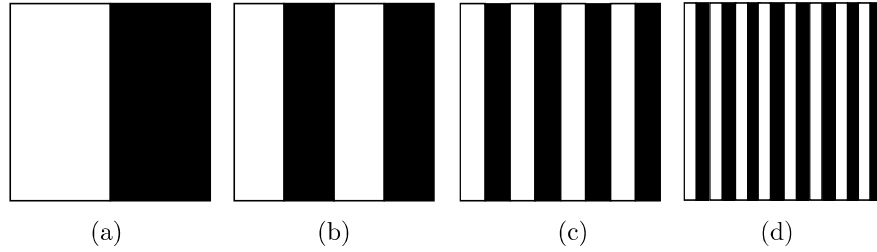


Figure 6.2 Idealised striation thickness (a) at initial state; (b) in the first mixing element; (c) the second mixing element; (d) the third mixing element.

The reproduction of baker's transformation in mixers only occurs for a specific 3D stationary continuous mixer configuration, which is thought to approach the separation/stacking mechanism. Carrière (2007) proposed a geometry that is a network of converging "T"s where two fluids are injected in a mixing chamber. Figure 6.3 shows a schematic representation of this mixer. Each "T" plays an important role in the stretching and re-stacking of the two streams, and thus it corresponds to an element of the static mixer (Ottino, 1989). On the other hand, cutting and splitting take place at the outlet of each mixing element (Carrière, 2007). Carrière (2007) studied the mixing dynamics from CFD simulations in the Stokes regime, intending to mimic the baker's maps. Carrière (2007) also compared the theoretical Lyapunov exponent, $\ln(2)$ with CFD results, demonstrating that the result is $\Lambda = 0.68$, which is close to the value predicted by the baker's transformation, $\ln(2)$.



Figure 6.3 SR mixer proposed by Carrière (2007).

Schönfeld et al. (2004) also validated the SR mixing concept from numerical and experimental results. The mixing performance was investigated in a Reynolds number range from 1 to 100. CFD simulations show that for $Re < 15$, the multi-lamination process has a similar evolution to the idealised theory in Figure 6.2.

Mixing in SR mixers was quantified by Neerinx et al. (2011) from experiments using two coloured epoxies, vitrified and sliced. A specific SR mixer configuration, DentIncx mixer, was used and consisted of a splitting serpentine channel. Results show that the formation of strias in these reactors exactly follows the baker's transformation. Nevertheless, the mapping of the concentration distribution shows a non-uniform striation thickness at the outlet of each element. Other configurations were also studied in Neerinx et al. (2011), and its performance was only compared in terms of pressure consumption and compactness.

Schönfeld et al. (2004) and Nimafar et al. (2012) compared a “T” element and a duct with square cross-section. In these geometries, the ideal striation thickness decay, $\delta = 1/2^{n_{mc}}$, is not attained because a plug flow of viscous fluids is not ensured in the mixing elements. The actual flow velocity profile is set by the no-slip condition at the walls and the viscous stresses.

In the present chapter, a new model for the striation thickness evolution is proposed considering that the two Newtonian fluids will be divided into strips of equal flow rate

for each fluid but maintaining the velocity profile in the channel. This generic model is able to describe the mixing of fluids at unsymmetrical flow conditions, i.e. the two jets have different flow rates. The validation of this model will be made from the comparison with CFD results.

The striation thickness evolution has impact on the mixing degree because the diffusion at molecular scales is controlled by the rate of evolution of the mixing scales and respective rate of interfacial area generation. Thus, the mixing efficiency is strongly dependent on the reduction of scales in SR mixers. The validation and consequent implementation of the striation thickness decay model are quite useful for the design of SR mixers as industrial mixing units.

6.2 Analytical Model Development

The geometry addressed in this work is similar to the one proposed by Carrière (2007), which has been designed to reproduce as closely as possible the mixing properties of a baker's transformation. This geometry consists of a network of converging and diverging “T”s. The number of transformations in this geometry corresponds to the number of mixing elements, i.e. to the number of converging “T”s. It was considered that the first mixing element coincides to the one that transforms two in four strips. Therefore, the number of strias generated in each mixing element is described by $2^{n_{me}+1}$.

As mentioned before, this striation thickness decay law in a real mixer is not feasible due to the impossibility of ensuring a plug flow of viscous fluids in the mixer channels. In practice, SR mixers with rectangular cross-section will develop a velocity profile that can be calculated in its dimensionless form from

$$v(\xi, \psi^*) = \frac{\sum_{i \text{ odd}}^{\infty} \sum_{j \text{ odd}}^{\infty} \frac{\sin(i\pi\xi) \sin(i\pi\psi^*)}{ij(\beta_c^2 i^2 + j^2)}}{\sum_{i \text{ odd}}^{\infty} \sum_{j \text{ odd}}^{\infty} \frac{4}{\pi^2 i^2 j^2 (\beta_c^2 i^2 + j^2)}} \quad (6.2)$$

where $0 \leq \xi \leq 1$ and $0 \leq \psi^* \leq \beta_c$ are the dimensionless spatial coordinates and β_c is the aspect ratio of the channel given by the ratio between height and length of the cross-section channel (Spiga and Morino, 1994). All spatial coordinates have been made dimensionless by a characteristic length L of the channel, and the velocity is divided by its mean value in the cross-section in the channel. This velocity profile will generate after each mixing element a non-homogeneous distribution of striation thicknesses.

The striation evolution after each mixing element can be estimated for steady state flows by performing a mass balance

$$\int_{A_i} \rho v(\xi, \psi^*) dA = \rho Q_i \quad (6.3)$$

that considers that the two fluids will be divided into i striations of equal flow rate for each fluid, Q_i , but accounting for the actual velocity profile in the channel (Equation (4.1)). It was assumed that both fluids have the same physical properties. The position of the striations interface, χ_i , after a transformation n_{me} at a given position ψ^* , in the normal direction of the orientation of strias, can be estimated from

$$\int_{\chi_{i-1}}^{\chi_i} v(\xi, \psi^*) d\xi \Delta\psi^* = \frac{r_s^{a_0}}{2^{n+1}(r_s + 1)} \int_0^1 v(\xi, \psi^*) d\xi \Delta\psi^* \quad (6.4)$$

where $i = 1, 2, \dots, 2^{n_{me}+1}$ according to the baker transformation, where the positions of interfaces for $i=0$ and $i = 2^{n_{me}+1}$ are $\chi_0 = 0$ and $\chi_{2^{n_{me}+1}} = 1$. $\Delta\psi^*$ represents an infinitesimally small spatial coordinate in the ψ^* direction and r_s is the flow rate ratio between the two phases, 1 and 2, given by

$$r_s = \frac{q_1}{q_2} \quad (6.5)$$

The parameter a_0 in Equation (6.4) is

$$a_0 = \begin{cases} 0, & \text{if } i \text{ is even} \\ 1, & \text{if } i \text{ is odd} \end{cases} \quad (6.6)$$

The solution of Equation (6.4) gives the thickness of each stria, which can be calculated by $\delta_i = \chi_i - \chi_{i-1}$ for $i = 1, 2, \dots, 2^{n_{me}+1}$.

A 1D simplification of Equation (6.2) that is a parabolic profile can be considered to predict the velocity profile in ξ direction. A system of two infinite plates was assumed by Bird et al. (1924) to approximately describe the 1D velocity profile in a square duct, which is given by

$$v(\xi) = 6\xi(1 - \xi) \quad (6.7)$$

Equation (6.7) can be used to obtain a simpler and explicit way of calculating the distribution of striation thicknesses. Figure 6.4 shows the comparison between the velocity profile in a square chamber at $\psi^* = 1/2$ and the approximation to a fully parabolic profile. It seems to indicate that this is a sensible step since the profiles are similar. Both profiles in Figure 6.4 have been divided by $\int_0^1 v(\xi) d\xi$ for comparison. This simplification was verified in this work by the use of a spatially resolved computational model of the flow described in Section 0.

The combination of Equations (6.4) and (6.7) results in

$$2\chi_{i-1}^3 - 3\chi_{i-1}^2 - 2\chi_i^3 + 3\chi_i^2 = \frac{r_s^{a_0}}{2^{n_{me}+1}(r_s + 1)} \quad (6.8)$$

that can be further solved to obtain an explicit general solution for the position χ_i of the interface between the two fluids for a given flow rate ratio r_s and after the mixing element n_{me}

$$\chi_i = \cos \left(\frac{1}{3} \cos^{-1} \left(1 + 4\chi_{i-1}^3 - 6\chi_{i-1}^2 - \frac{2^{1-n_{me}} r_s^{a_0}}{r_s + 1} \right) - \frac{2\pi}{3} \right) + \frac{1}{2} \quad (6.9)$$

for $i = 1$ to $2^{n_{me}+1}$ and $\chi_0 = 0$.

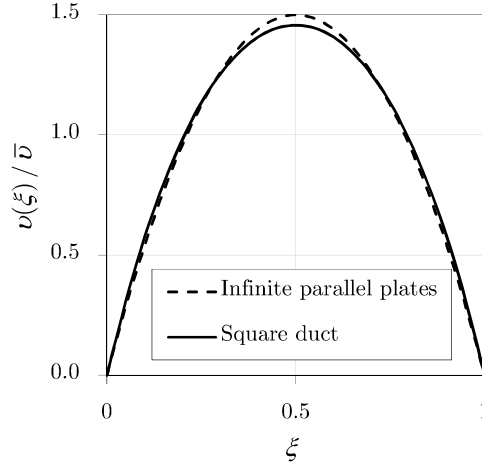


Figure 6.4 Velocity profile in the middle of the square channel and the parabolic approximation.

Figure 6.5 shows the generation of a non-uniform distribution of the striation thickness calculated from Equation (6.9) and the respective velocity profile. The thinnest lamellae are at the centre of the mixing chamber while the thickest lamellae are next to the walls. This observation is in agreement with the shape of the velocity profile in the duct. According to the velocity profile of a square duct and also shown in Figure 6.5, the largest lamellae for each fluid 1 and 2 will be the ones closer to the walls of the mixer. Thus, Equation (6.9) can be further simplified to calculate the thickness decay of the largest strips in the process. Considering that fluid 1 is injected in the left side of the chamber, the decay of the largest lamellae, $\delta_{1,\max} = \chi_1 - \chi_0$, follows

$$\delta_{1,\max}(n_{me}, r_s) = \cos\left(\frac{1}{3}\cos^{-1}\left(1 - \frac{2^{1-n_{me}}r_s}{r_s + 1}\right) - \frac{2\pi}{3}\right) + \frac{1}{2} \quad (6.10)$$

and for fluid 2, the thickness of the largest strip is calculated from

$$\delta_{2,\max}(n_{me}, r_s) = \cos\left(\frac{1}{3}\cos^{-1}\left(1 - \frac{2^{1-n_{me}}}{r_s + 1}\right) - \frac{2\pi}{3}\right) + \frac{1}{2} \quad (6.11)$$

In the particular case of $r_s = 1$, i.e. equal flow rates of both fluids, the largest and smallest strips in the mixer, $\delta_{\max}$ and $\delta_{\min}$, respectively, are given by

$$\delta_{\max}(n_{\text{mc}}) = \cos\left(\frac{1}{3}\cos^{-1}\left(1-2^{-n_{\text{mc}}}\right) - \frac{2\pi}{3}\right) + \frac{1}{2} \quad (6.12)$$

and

$$\delta_{\min}(n_{\text{mc}}) = \cos\left(\frac{1}{3}\cos^{-1}\left(-2^{-n_{\text{mc}}}\right) - \frac{2\pi}{3}\right) \quad (6.13)$$

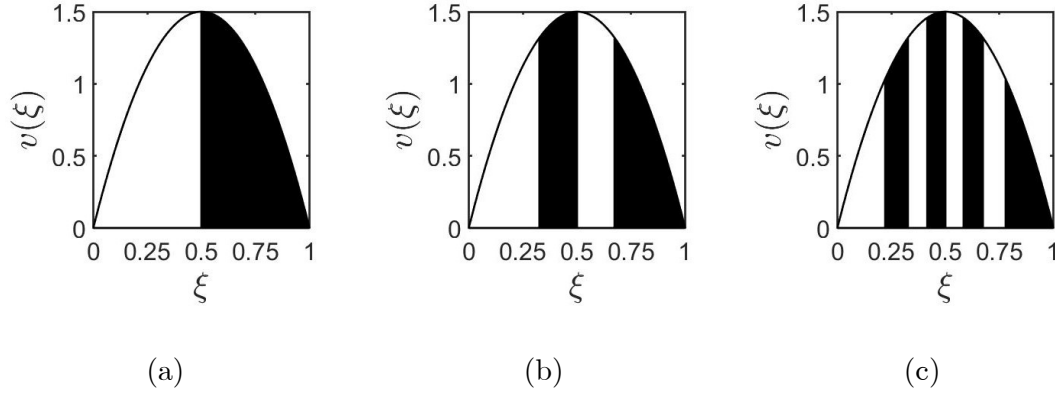


Figure 6.5 Production of unequal thickness strips due to the presence of parabolic-like velocity profiles in the channel of the SR mixer (a) $n_{\text{mc}} = 0$; (b) $n_{\text{mc}} = 1$ and (c) $n_{\text{mc}} = 2$.

6.3 Numerical Simulations of the Flow and Advective Mixing

The physical domain simulated in this work is shown in Figure 6.6 and consists of an SR mixer with two inlets, one outlet and three mixing elements. The cross-section of square duct has dimensions of 2x2 mm. T-mixer has a total length of 32 mm.

The Finite Volume code ANSYS Fluent v18 was used to solve the dimensionless governing equations that describe the steady laminar flow in the SR mixer,

$$\nabla \cdot \mathbf{u} = 0 \quad (6.14)$$

and

$$\frac{1}{\text{Re}} \nabla^2 \mathbf{u} - \nabla p = 0 \quad (6.15)$$

where p is the dimensionless relative pressure and $\mathbf{u}$ is the dimensionless velocity vector field. The simulations were restricted to Stokes regime (i.e. creeping flow conditions), corresponding to a Reynolds number range $\text{Re} \ll 1$. The Volume-of-Fluid (VOF) method was used to track the interface between two different fluids, 1 and 2, entering from each inlet as

$$\mathbf{u} \cdot \nabla \phi_1 = 0 \quad (6.16)$$

where $\phi_1 \in [0,1]$ is the local volume fraction of fluid 1. Surface tension and diffusive transport have been neglected, and both fluids were considered to have the same physical properties, i.e. the same density and viscosity, $\rho = 1145 \text{ kg m}^{-3}$ and $\mu = 1759 \text{ Pa} \cdot \text{s}$.

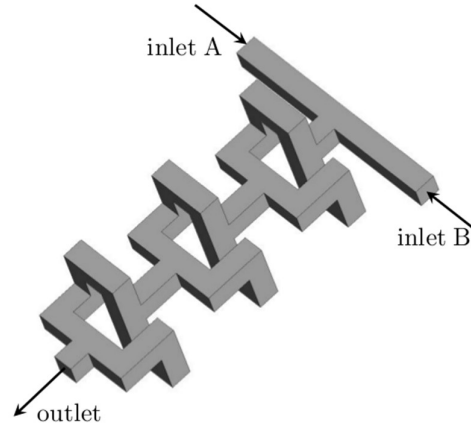


Figure 6.6 Geometrical domain for the CFD simulations.

Uniform discretisation able to completely describe the lamellar structure would result in an expensive computational grid due to the high number of elements. According to the expression that describes the generation of the lamellae, $i = 1, 2, \dots, 2^{n_{\text{me}}+1}$, 16 lamellae are formed at $n_{\text{me}} = 3$. The visualisation of 16 lamellae at the outlet requires the

generation of a mesh with an edge $2 / 16 = 0.125 \text{ mm}$. This simulation would require approximately 6×10^9 elements.

In order to overcome this issue, a dynamic grid-adapting algorithm was used to refine the numerical mesh at each iteration only at the interface between the two fluids. The domain was initially discretised with a structured mesh consisting of finite cubic elements with volume $(L / 20)^3$ able to solve the flow field. The domain was then adapted, at each time step, at the interface of both fluids. Thus, two maximum levels of refinement were used, which corresponds to finite volumes elements with a minimum volume $(L / 80)^3$.

The imposed boundary conditions at the inlets, outlet and the walls were as follows,

$$\begin{aligned}
 \text{Inlet A: } \mathbf{u} \cdot \mathbf{n} &= \frac{r_s}{r_s + 1}, \nabla p \cdot \mathbf{n} = 0, \phi_1 = 0 \\
 \text{Inlet B: } \mathbf{u} \cdot \mathbf{n} &= \frac{1}{r_s + 1}, \nabla p \cdot \mathbf{n} = 0, \phi_1 = 1 \\
 \text{Walls: } \mathbf{u} &= 0, \nabla p \cdot \mathbf{n} = 0, \nabla \phi_1 \cdot \mathbf{n} = 1 \\
 \text{Outlet: } \nabla \mathbf{u} \cdot \mathbf{n} &= \mathbf{0}, p = 0, \nabla \phi_1 \cdot \mathbf{n} = 1
 \end{aligned} \tag{6.17}$$

The simulations of the flow and purely advective mixing were performed for $r_s = \{1, 2, 10\}$ setting the velocity of the left injector at $3.96 \times 10^{-4} \text{ m s}^{-1}$. The Coupled solver was used for solving the flow equations, spatial gradients of pressure were discretised with the PRESTO! scheme and spatial gradients of velocity with the Third Order MUSCL scheme. The simulations were considered converged for residuals smaller than 10^{-8} for all variables.

6.4 Results and Discussion

CFD simulations enable to obtain a realistic distribution of the two liquids inside the SR mixer geometry. Figure 6.7 shows the contour maps of the volume fraction distribution in cross-sections of the mixer placed immediately before the bifurcation that coincides to the outlet of each converging T. Two phases were injected from the opposed jets at three different flow rate conditions, $r_s = \{1, 2, 10\}$. The dark liquid is injected from the left injector, jet 1, and the white phase from the right-hand side injector, jet 2. Position $n_{me} = 0$ corresponds to the chamber where the jets are impinged. $n_{me} > 1$ corresponds to the cross-section right after the converging T of the i -th mixing element and before the diverging T of the $(i + 1)$ -th mixing element.

At $n_{me} = 0$, a structure of two lamellae, one white and one black, are observed independently of the flow rate ratio, $r_s = \{1, 2, 10\}$ (Figure 6.7a to Figure 6.7c). At this mixing element, the thickness of each lamella is the same for $r_s = 1$. However, the dark phase is observed to become thicker for $r_s > 1$, because the flow rate q_1 is larger than q_2 . Then, this structure leaves the first converging T, where it is split, rotated and injected in another converging T. Four lamella are then generated by injection of these streams, as shown in Figure 6.7d to Figure 6.7f. The same procedure is repeated for $n_{me} = 2$ and $n_{me} = 3$.

Figure 6.7 shows that the SR mixer performs a baker's transformation to the flow in the sense that after each mixing element, the number of striations of each fluid follows the sequence $2^{n_{me}+1}$. However, as expected due to the velocity profile in channels, the developed striations do not have the same thickness. For all simulated cases, striations close to the walls remain thicker than the striations at the centre of the chamber. The lamellar structure formation is clearly observed from the contour maps in Figure 6.7, except after the third element for $r_s = 10$ (Figure 6.7). At this condition, the flow rate q_1 is much higher than q_2 , and thus thinner lamellae of white fluid would be formed at the third element of SR mixers. These structures are not clearly observed from the

contour maps because the lamellar thickness is smaller than the size of the smallest possible elements in the grid after adaptation. The insufficient grid refinement results in the break of the lamella, as observed in the contour map of Figure 6.7. This observation shows the difficulty to simulate the mixing of a passive tracer in a SR system even in the Stokes regimes.

Figure 6.8 compares CFD results and the model that describes the position of each lamella interface at each mixing element (Equation (6.9)). These figures show a good agreement between the model and CFD results, thus obtaining a linear relationship between both results. The validation for $r_s = 1$ and $r_s = 2$ was made for $n_{me} = 2$ and $n_{me} = 3$. For $r_s = 10$, the comparison between CFD results and the model is only considered up to the second mixing element because for $n_{me} = 3$, the insufficient grid refinement does not enable an accurate determination of the striation thickness. The good agreement between CFD results and analytical model also proves that the 1D simplification of velocity profile in a square duct is a good approximation of Equation (6.2).

The validation of the position interface by Equation (6.9) enables to predict the maximum and minimum striation thickness decay from Equations (6.12) and (6.13). The rate of the thickness decays of the largest and smallest lamellae for $r_s = 1$ are plotted in Figure 6.9. Figure 6.9 shows that the thickness decay of the maximum mixing scale is described by approximately $2^{-n_{me}/2}$ and for the minimum mixing scale by $2^{-n_{me}}$.

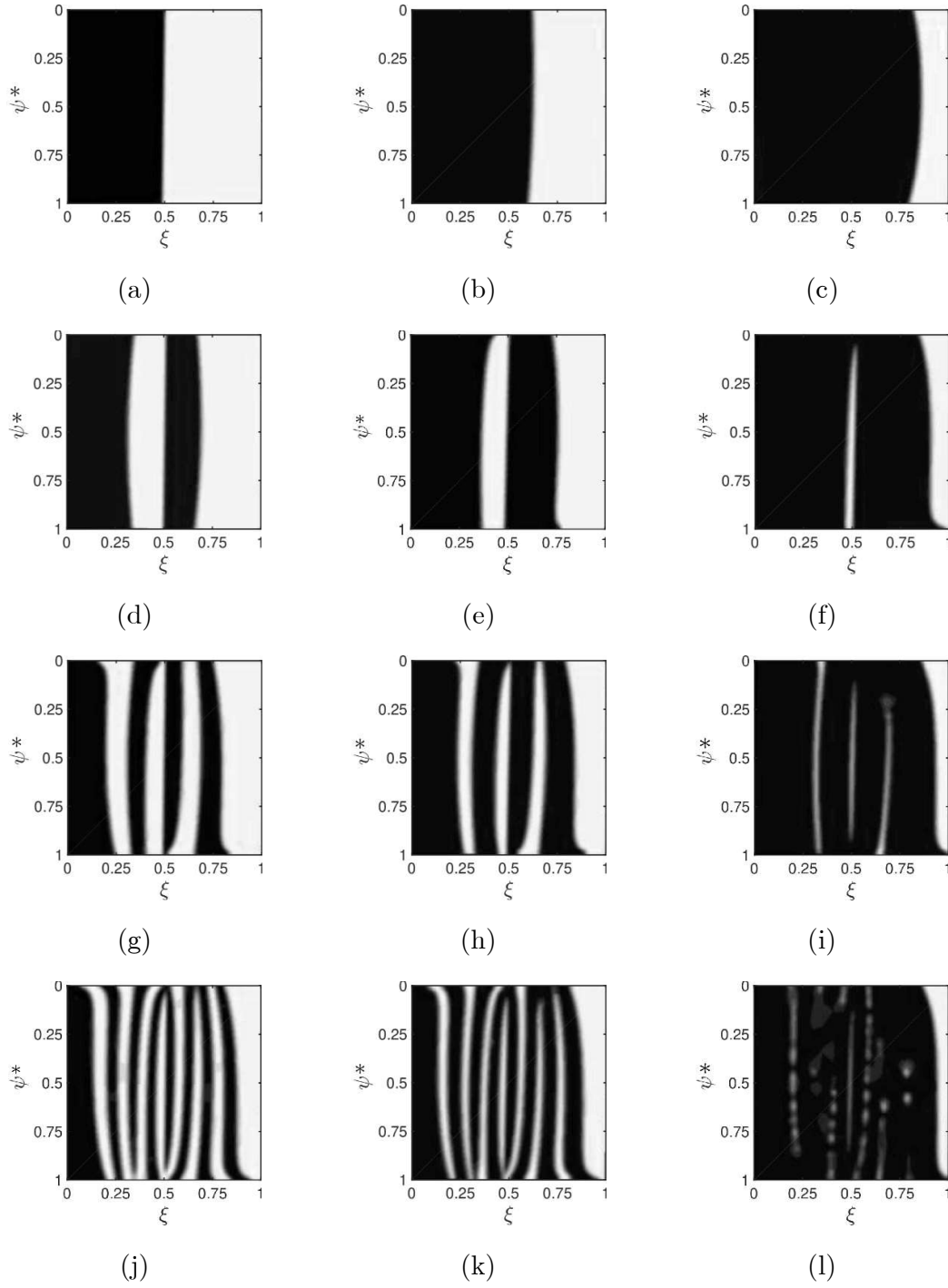


Figure 6.7 Striation Thickness Distribution (a) $r_s = 1, n_{me} = 0$; (b) $r_s = 2, n_{me} = 0$; (c) $r_s = 10, n_{me} = 0$; (d) $r_s = 1, n_{me} = 1$; (e) $r_s = 2, n_{me} = 1$; (f) $r_s = 10, n_{me} = 1$; (g) $r_s = 1, n_{me} = 2$; (h) $r_s = 2, n_{me} = 2$; (i) $r_s = 10, n_{me} = 1$; (j) $r_s = 1, n_{me} = 3$; (k) $r_s = 2, n_{me} = 3$; (l) $r_s = 10, n_{me} = 3$.

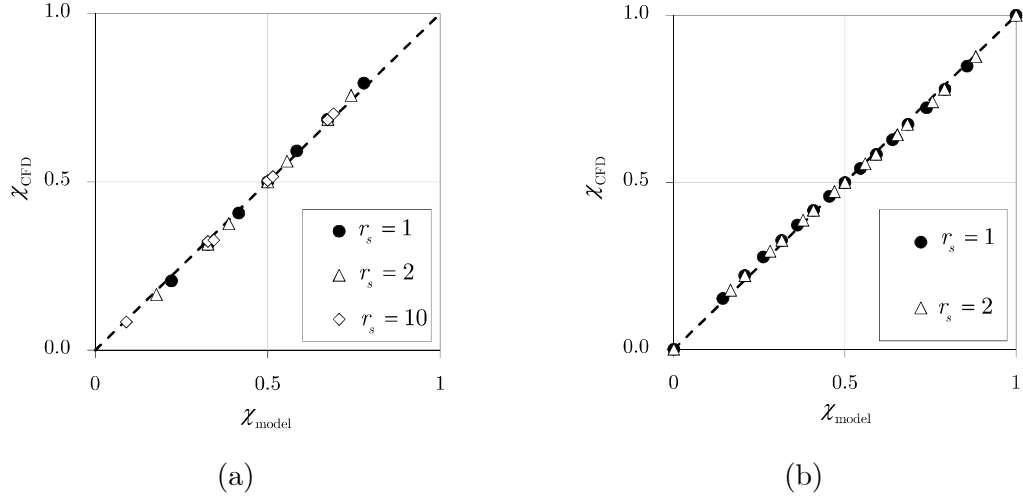


Figure 6.8 Parity plots comparing of the interface positions obtained from the analytical model and from the CFD simulations for different values of r after (a) 2 mixing elements and (b) 3 mixing elements.

The comparison between the idealised model and the expressions for the maximum and minimum lamellae can be made from the determination of Lyapunov exponent. From the mathematical definition, the Lyapunov exponents calculated for the largest and smallest lamellae are respectively,

$$\Lambda_{\max} = \lim_{n_{\text{me}} \rightarrow \infty} \frac{\ln \delta_{\max}^{-1}(n_{\text{me}})}{n_{\text{me}}} = \frac{\ln(2)}{2} \quad (6.18)$$

$$\Lambda_{\min} = \lim_{n_{\text{me}} \rightarrow \infty} \frac{\ln \delta_{\min}^{-1}(n_{\text{me}})}{n_{\text{me}}} = \ln(2)$$

where $\delta_{\max}(t) \sim 2^{-n_{\text{me}}/2}$ and $\delta_{\min}(t) \sim 2^{-n_{\text{me}}}$ according to Figure 6.9. Equation (6.18) shows the mathematical proof that the largest scale in a real SR mixer decays at half the rate of the scales of a baker's transformation, $\Lambda_{\text{theo}} = \ln(2)$. For the smallest lamella, the thickness decays according to baker's transformation. This is preliminary evidence that the necessary length of the mixer will be affected by the fact that the flow has a velocity profile developed by the wall effects.

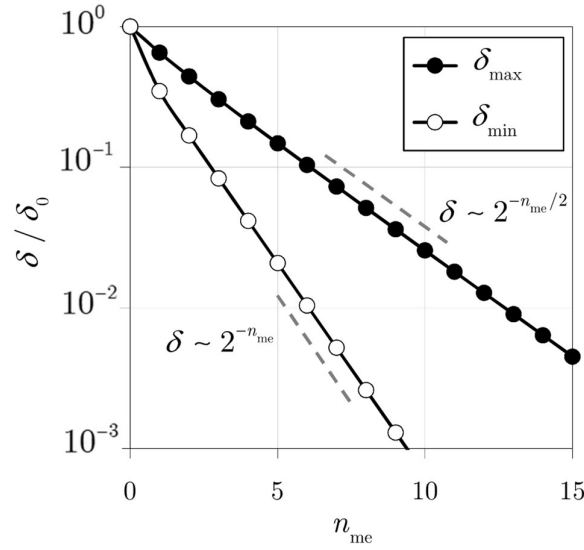


Figure 6.9 Rate of mixing scales decay for $r_s = 1$ calculated for the thickness of the largest and smallest strips.

SR mixers have typically small dimensions, and generally, in these devices, the convection is much faster than the molecular diffusion. The rate of segregation scales decay plays an important role in the complete mixing at the molecular scale. The mixing quality can be calculated from the intensity of segregation at molecular scale, which was defined by Danckwerts (1952) by

$$I_s = \frac{\sigma_c^2}{\bar{C}(1-\bar{C})} \quad (6.19)$$

where $\sigma_{c_1}^2$ is the variance of the concentration of species 1, $\bar{C}_1$ and $\bar{C}_2$ is the mean concentration of phases 1 and 2.

The quality of mixing should be analysed from the intensity of segregation determined from the worst scenario, i.e. for the mixing of two largest strips. For these conditions, the description of concentration over space and time can be determined from the lamellar model described by Ottino et al. (1979). In this model, the coordinate system is set up at the interface of the two lamellae and the conservation equation is given by

$$\frac{\partial C}{\partial \Gamma^*} = \frac{\partial^2 C}{\partial \xi^{*2}} \quad (6.20)$$

where ξ^* is nondimensional space scale based on the instantaneous value of the striation thickness, $\xi^* = x / s(t)$, and Γ^* is the warped time given by

$$\Gamma^* = \frac{1}{t_D} \int_0^t \eta(t')^2 dt' \quad (6.21)$$

where $\eta'(t)$ is given by $\eta(t') = s_0 / s(t')$ and $t_D = s_0^2 / D_m$ is the characteristic diffusion time for an initial striation scale, wherein the molecular diffusivity, D_m .

The time t' in Equation (6.21) can be written as a function of the number of elements,

$$t' = n_{me} \frac{V_{element}}{Q} \quad (6.22)$$

where $V_{element}$ is the volume of each mixing element, $V_{element} = N_e L^3$, wherein N_e is the geometrical parameter, and Q is the volumetric flow rate given by $Q = L^2 u$. Equation (6.22) can be replaced in Equation (6.21) and

$$\Gamma^* = \frac{2N_e}{Pe} \int_0^{n_{me}} \delta(n'_{me})^{-2} dn'_{me} \quad (6.23)$$

Equation (6.23) considers that Pe is the Peclet number is given by $Pe = s_0 \nu / D_m$ and $\eta(n_{me}) = \delta^{-1}(n_{me})$ for two large lamellae. Note that, for the sake of simplicity, it has been considered that the variable n_{me} is continuous.

Equation (6.20) describes the changes of species concentration in the normal direction of the interface when a lamellar structure is formed by the impingement of the reactants in SR mixer. Considering that two fluids are injected through two opposed jets, the initial condition of Equation (6.20) is given by

$$\Gamma^* = 0 : C = H(\zeta), \forall \zeta \in \left[-\frac{1}{2}, \frac{1}{2}\right] \quad (6.24)$$

where $H(\zeta)$ is a Heaviside function, which coincides with the mixing chamber axis. The boundary conditions correspond to the gradient of concentrations at the boundaries of a single stria, $\zeta = -0.5$ and $\zeta = 0.5$, which is equal to 0,

$$\Gamma^* > 0 : \frac{\partial C}{\partial \zeta} = 0 \text{ for } \zeta = \pm \frac{1}{2} \quad (6.25)$$

The PDE equation in Equation (6.20) has the following analytical solution

$$C(\zeta, \Gamma^*) = \frac{1}{2} \left(1 + 4 \sum_{i \text{ odd}} \frac{1}{i\pi} \sin(i\pi\zeta) \exp(-(i\pi)^2 \Gamma^*) \right) \quad (6.26)$$

Equation (6.26) describes the evolution of the diffusive front thickness in a mixing element for a nondimensional space scale and warped time. This expression can be used to calculate the intensity of segregation (Equation (6.19)),

$$I_s(\Gamma^*) = \frac{\int_{-1/2}^{1/2} (C(\zeta, \Gamma^*) - \bar{C}(\Gamma^*))^2 d\zeta}{\bar{C}(\Gamma^*)(1 - \bar{C}(\Gamma^*))} \quad (6.27)$$

where $\sigma_{C_1}^2 = \int_{-1/2}^{1/2} (C(\zeta, \Gamma^*) - \bar{C}(\Gamma^*))^2 d\zeta$ and $\bar{C}(\Gamma^*)$ can be calculated from

$$\bar{C}(\Gamma^*) = \int_{-1/2}^{1/2} C(\zeta, \Gamma^*) d\zeta \quad (6.28)$$

The intensity of segregation can take values from 0 to 1. For $I_s = 0$, it means that the system is completely homogenised, $C(\Gamma^*) = \bar{C}(\Gamma^*)$, and for $I_s = 1$, fluids are completely segregated.

Figure 6.10a shows the evolution of the intensity of segregation as a function of $\Gamma^* / 2$. It was considered the worst scenario for the determination of the intensity of

segregation, i.e. $\delta(n_{me}) = \delta_{\max}(n_{me})$ in Equation (6.12). As the warped time increases ($0 < \Gamma^* / 2 < 1$), I_s decreases sharply in an exponential decay. This evidences once again that the striation thickness decay contributes to the reduction of the concentration gradients, enhancing the molecular diffusion.

Figure 6.10b shows the evolution of $\ln(\Gamma^* \text{Pe} / (2N_e))$ as a function of the number of elements n_{me} . Peclet number used in this work is the typical value for liquids, $\text{Pe} = 1 \times 10^9$ and the number of cubic elements considered was $N_e = 22$. According to Equation (6.27), the term $\Gamma^* \text{Pe} / (2N_e)$ is determined from $\int_0^{n_{me}} \delta(n'_{me})^{-2} dn'_{me}$. This integral can be determined taking into account the theoretical expression $\delta_{\text{theo}}(n_{me}) = 2^{-(n_{me}+1)}$ or the model for the thickness of the maximum mixing scale described in Equation (6.12). The analysis of these two curves shows the differences between δ_{theo} and $\delta_{\max}$. A complete description of the striation thickness decay in SR mixers is crucial for a good estimation of the mixing quality.

The impact of striation thickness decay in diffusion may be identified from these results. In real SR mixer, the thickness of the largest lamellae fully controls the efficiency of mixing at molecular scales. These scales are thicker than the idealised ones, and so the design of mixers must be adapted in order to achieve the same mixing degree. Figure 6.10a and Figure 6.10b give useful tools for the prediction of the reactor length required to achieve the complete mixing. For $I_s = 10^{-3}$ that corresponds to 99% of the mixing efficiency, the mixer length must have, at least, 11 elements for a SR mixer, whose mixing mechanisms are based on the idealised baker's transformation. However, the same intensity of segregation is achieved in real SR mixers with 20 elements. This evidences that the length of a real SR mixer has to be twice the length of the idealised reactor.

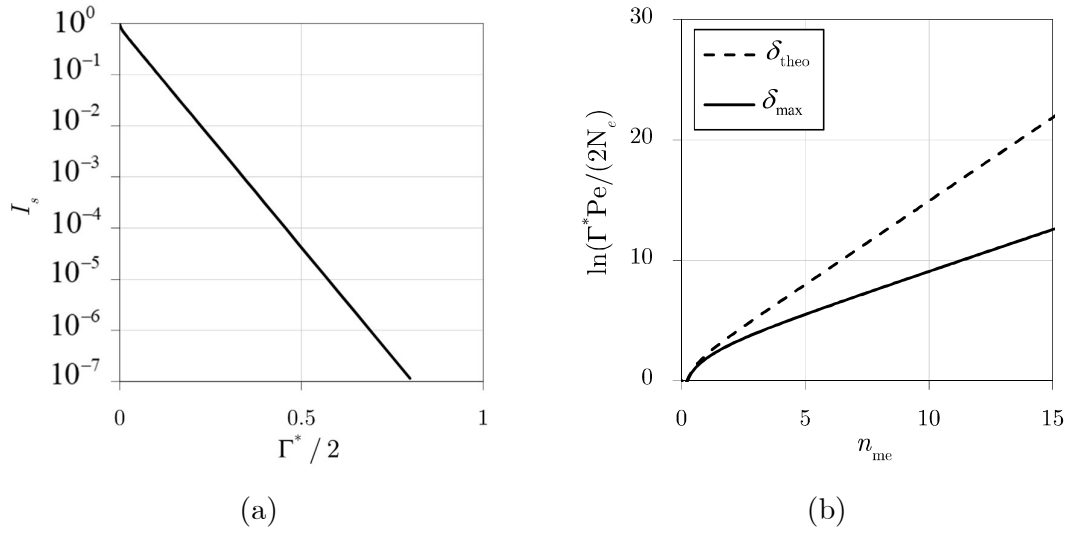


Figure 6.10 (a) Intensity of segregation as a function of a warped time Γ^* and (b) $\ln(\Gamma^*Pe/N)$ is a function of a number of elements n_{me} .

In sum, the validation of the decay of the largest lamellae from CFD simulations enables to use this model as a design tool in SR mixers. The number of elements required to achieve the same mixing degree in ideal and real SR mixers can be determined from the description of the maximum mixing scales decay in the Stokes regime.

6.5 Conclusions

Mixing highly viscous liquids in non-inertial flows is not an easy task due to the absence of turbulent eddies or chaotic dynamic flow structures that promote efficient mixing. The alternative studied here is mixing in Split-and-Recombine mixers, which ensure the generation of multiple fluid lamellae even at vanishingly low Reynolds numbers. CFD simulations results show that the thickness of fluid striations, developed in a split-and-recombine mixers, are not uniform in the Stokes regime. An analytical expression, which describes the thickness distribution of scales for any flow rate ratio, is proposed and validated. The impact of assuming an idealised striation thickness decay on the complete mixing at the molecular scale of the full domain was addressed.

Results show that the molecular diffusion is controlled by the striation thickness decay and so a full description of the evolution of mixing scales in Split-and-Recombine mixer approaches the real mixing mechanisms.

Micromixing in this system is achieved by the laminar stretching and folding, associated to the striation thickness decay down to molecular diffusion scales. Thus, the distribution of the thicknesses of the minimum and maximum mixing scales enables to define a range for the concentration gradients. Nevertheless, the estimation of the thickness decay for the largest lamellae are the ones that control the mixing degree at molecular scales. In the present chapter, the maximum thickness is mostly described by approximately $2^{-n_{me}/2}$. This tendency has never been demonstrated in the literature, but it explains the experimental results obtained in Neerinx et al. (2011), and CFD simulations proposed by Carrière (2007).

The non-homogeneous distribution of striation thicknesses in split-and-recombine mixers due to wall effects implies that the design of mixing devices must be made taking into account the striation thickness distribution of the largest strip. This means that the device must be designed with a longer height to achieve the same mixing degree in those devices based on an ideal baker's transformation.

These results give an explicit and straight forward design expression to calculate the maximum and minimum striation thickness of each phase, that will be the limiting step in mixing operation in this type of mixers. This design methodology is more industrially relevant than the tools already presented in the literature, i.e. the average Lyapunov exponent. The working mixing conditions set in this chapter are $Re \ll 1$. However, if the mixing device would be operating at laminar inertial flow regimes rather than in the Stokes regime, the number of elements would be non-practical because, as demonstrated from the previous chapters, the striation thickness decay would be even faster. Therefore, the definition of the number of elements is crucial for the successful implementation of split-and-recombine mixers in the industry.

6.6 References

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7 Final Remarks

A summary of the main conclusions of this thesis is presented in this chapter. The foremost results, regarding the mixing mechanisms in 2D mixing devices, are summarised in Section 7.1. Section 7.2 provides a list of suggestions for future work.

7.1 Conclusions

The main goals of this work are the description of the mixing mechanisms in 2D reactors and the characterisation of the flow conditions for effective mixing. Four mixing devices are addressed in the present thesis: rotational devices, Confined Impinging Jets (CIJ), T-Jets and Split-and-Recombine (SR) mixers. The range of the studied flow regimes is between Stokes and laminar regimes. A new methodology for product development is also presented in this work, contributing to high throughput material development.

This thesis was written based on the following four issues: How can the industrial processes be scale-down to closely replicate plant mixing conditions in the lab, simplifying the formulation process?; How to mix efficiently two different liquid

streams? Are opposed jets static mixers, without obstacles, able to efficiently mix dissimilar fluids?; How to design opposed jets static mixers in order to reduce the scale-up and formulation costs?

An introduction to mixing, 2D reactors and the impact of mixing problems in the industry are presented in Chapter 1. It is followed by the relevance of this work, the objectives and the layout of this thesis.

A new rotational device with similar geometries to plate-plate and cone-plate rheometers is introduced in Chapter 2 to describe the mixing scales formed in pilot machines or even in industrial devices. The evolution of the interfacial area and striation thickness was estimated from Computational Fluid Dynamics (CFD) simulations. This methodology was implemented in an industrial case study: the production of polyurethanes in RIM machines (Chapter 4).

This thesis also presents a description of the flow dynamics in CIJ (Chapter 4) and T-Jets mixers (Chapter 5) for asymmetric flow conditions, i.e. for fluids with dissimilar physical properties, flow rate ratios, and inlets with different diameters. The flow was studied numerically from CFD tools and experimentally from Planar Induced Laser (PLIF). These experiments involved the mixing of fluids with different optical properties. In this sense, a method to match the refractive index is also described in Chapter 3.

The conditions for effective mixing are studied from experimental and numerical studies to define tools to design the opposed jets mixers. Mechanistic models to estimate the impingement point position are also described in Chapter 4 for CIJ mixers and in Chapter 5 for T-Jets mixers.

The main achievements of this thesis can be grouped in the following categories: mixing mechanisms in inertial and non-inertial flow regimes in 2D reactors (Section 7.1.1), topology of mixing in chemical reactors (Section 7.1.2), fully modelling and simulation

to assess micromixing in opposed jets mixers (Section 7.1.3), mixing of dissimilar fluids in opposed jets mixers (Section 7.1.4), design of processes in static mixers (Section 7.1.5) and methods of flow visualisation in transparent reactors (Section 7.1.6).

7.1.1 Mixing Mechanisms in Inertial and Non-Inertial Flows in 2D Reactors

This work has demonstrated 2D mixing mechanisms, based on the striation thinning of fluid lamellae for both Stokes flow regimes in rotational plate-plate devices and in split-and-recombine mixers, and for chaotic flow regimes in opposed jets mixers. Conclusions on mixing mechanisms can be summarised for each mixing technology, rotational devices, CIJ, T-Jets and SR mixers.

In rotational devices, as in rheometric geometries, fluids are deformed by shearing, and a pure shear flow is generated, creating adjacent layers of fluid which slide over each other with different speeds. This flow promotes the creation of the interfacial area and then the formation of a lamellar structure, as described by the framework of chaotic mixing (Ottino et al., 1979). The two mixing mechanisms involved in the pure shear flows are the stretching of the interface and the stratification of phases giving rise to a lamellar structure.

In CIJ mixers, the efficient mixing of the two fluids being impinged in the chamber only occurs due to the onset of the self-sustainable chaotic flow regime. This flow regime is characterised by the oscillation of the jets impingement point position, the intense dissipation of energy at the contact region of jets, and the formation of a vortex street downstream the injector axis. These dynamic structures play an important role in the stretching of the interfacial area between the fluids, promoting the striation thinning. On the other hand, the folding of the lamellar structures made by the vortices ensures the formation of a lamellar structure.

In T-Jets mixers, the efficiency of mixing depends on the geometrical parameters and Reynolds number at injectors. For geometries with headspace of $h = 2$ mm, the self-

sustainable chaotic flow regime can be achieved for particular flow conditions and reactor designs: (for symmetric flow conditions), a ratio between chamber and injectors widths of $W / w = 6$ and a ratio between width and depth of the chamber of $W / e \leq 2$. This chaotic flow regime is also characterised by the formation of a vortex street downstream the injector axis, and thus the mixing mechanisms involved are stretching and folding. For T-Jets configuration without headspace, the mixing efficiency is improved by the engulfment flow regime and turbulent flow regime.

Mixing in split-and-recombine mixers occurs in creeping flows. The mixing mechanisms in these devices consist of the distribution of fluids in the radial and tangential directions. In this sense, the liquid stream is divided, then rotated and finally recombined, achieving the stretching and folding described by the baker's transformation. This mixing principles ensure the growth of the interfacial area, promoting the increase in the concentration gradients and enhancing the molecular diffusion between phases. The wall effects in split-and-recombine mixers promote the development of a velocity profile and the formation of a non-homogenous baker's transformation in terms of the striation thickness. This work presents a prediction of the largest striation thickness, which is placed next to the walls according to the velocity profile. The evolution of the maximum striation thickness plays an important role in the mixing degree, in the sense that it controls the molecular diffusion in a single-phase system.

These conclusions evidence that good levels of mixing can be achieved at lower Reynolds number ($Re < 500$). The operation at the most efficient mixing conditions depends on the geometrical parameters of reactors, which have to be tailored according to the industrial application. Mixing in rotational devices, CIJ mixers, T-Jets mixers and Split-and-Recombine mixers were also studied for asymmetric flow conditions, i.e. for different physical properties or different flow rate ratios at inlets.

7.1.2 Topology of Mixing in Chemical Reactors

Topology of mixing, i.e. the initial position of a reactant in relation to the other, was explored in this thesis using well-defined flows as those occurring in rheometric devices. These devices typically operate in transitional regimes, which are generally non-isotropic flows. As this flow has a predominant direction for shearing, the initial topology plays a major role in the evolution of the mixing scales.

Two topologies were addressed: when both fluids are initially side-by-side and when the two phases were set over each other parallel to the rotating top plate. For the first topology, the induced shear stretches out the interface between fluids creating striation thinning laminae. In the second condition, the mixing scales and the interface of both phases are kept without changes.

Different topologies of the fluid interface are associated to different flow regimes. An analogy between the topology set in the plate-plate geometry and CIJ mixers flow regimes can be done: when the two fluids are initially placed side-by-side in the rotational devices, this corresponds to chaotic flow regimes, where there is the formation of vortices that reduce the scales of the lamella of fluids; when the fluids are initially placed one on top of the other, it corresponds to the segregated flow regime where the interface between two phases is preserved without any change. Although the segregated flow regime has vortices engulfing fluids, these vortices are placed in opposite sides of the mixing chamber failing in this way to engulf fluid from both jets.

The flow in plate-plate and cone-plate enable to set quite homogeneous mixing scales throughout the flow domain. This is particularly useful to generate chemical data for reactor design or product development. Therefore, the rotation devices are proposed as a methodology of high-throughput material development for 2D reactors. The implementation of rotational devices in the production of polyurethanes in RIM machines was demonstrated in Chapter 4.

7.1.3 Fully Resolved Modelling and Simulation Tools to Assess Micromixing in Opposed Jets Mixers

In the 1970s, the issue of micromixing modelling was tackled from phenomenological models with several environments reach in different reactants or products, which were connected by transfer functions related to mixing rate: IEM, 3E and 4E (Costa and Trevissoi, 1972; Ritchie and Tobgy, 1979; Mehta and Tarbell, 1983; Dutta and Tarbell, 1989). Some mechanistic model address the rate of transfer of chemical species from turbulence intensity, namely engulfment, deformation and diffusion model, and the E-model (Baldyga and Bourne, 1984,1989). A particular mechanistic model, the lamellar mixing model was introduced in 1979 and developed by Ottino during the 1980s, and incorporated the description of chaotic mixing mechanisms in a 1D model (Ranz, 1979; Ottino, 1982). The Lamellar Micromixing (LM) model uses the transport equation with diffusion coupled to a space that warps the concentration gradients by the effect of the shear field, which causes the striation thinning of two reactant strias.

This thesis presents an analysis of the lamellar microstructure generated by impinging jets flows, with application to RIM machines, from a LM model. This model was solved using striation thickness data from the models proposed by Lee et al. (1980) and Baldyga and Bourne (1983) and compared with the experimental data from Nunes et al. (2012).

Results from LM model show that the striation thickness function proposed by Lee et al. (1980) gives the best estimation of the striation thickness evolution for a range of Reynolds number $200 < Re < 600$. The description of the micromixing from LM model and the respective validation clearly show that this model could be used as a simulation tool in chemical reactors.

7.1.4 Mixing of Dissimilar Fluids in Opposed Jets Mixers

Opposed jets mixers, such as CIJ and T-Jets mixers, are commonly applied in plants involving the mixing of two dissimilar fluids, i.e fluids with different densities and viscosities. Experimental and numerical studies presented in this thesis show that CIJ and T-Jets mixers are able to mix dissimilar fluids under self-sustainable chaotic flow regime.

The necessary conditions for effective mixing are the balance of jets, and the conditions of the most viscous liquid stream must be above the critical Reynolds number. For typical CIJ mixers with the diameter of the injectors ~ 1 mm and the for the mixing chamber ~ 10 mm, the critical Reynolds number of the more viscous liquid stream is above 150 for a viscosity ratio from 2 to 9. The viscosity ratio plays a critical role in the onset of chaotic flow regimes with dissimilar fluids in CIJ mixers. The balance of the momentum of the opposed jets is set by the jet velocity profile evolution, which in turn is influenced by the viscosity.

It was also made a clear proof that for T-Jets mixers, the conditions for effective mixing are mainly affected by the geometrical parameters. The jets in T-jets are bent before the contacting point, and thus the mechanisms for mixing of dissimilar fluids are different. From the evidence gathered in this work, the ratio of the physical properties of dissimilar fluids also affects the operation parameters for the onset of chaotic flow regimes.

7.1.5 Design of Processes in Static Mixers

Experimental and numerical data of flow dynamics in CIJ and T-Jets mixers indicate that mixing relies on the balance of jets at the centre of the mixing chamber. The prediction of the impingement point was described from mechanistic models.

In CIJ mixers, three models were considered for the description of the contact point of both phases: the elastic analogue model, kinetic energy model and momentum model. The elastic analogue model only predicts the mixing of similar fluids. The momentum model is able to estimate the contact point for symmetric conditions and for mixing of fluids with different viscosities (validity range from 2 to 9) and similar densities (density ratio of approximately 1). The kinetic energy model is the one with a broader validity range because it predicts both the mixing of similar fluids as dissimilar fluids with viscosity and density ratios above the unity. This means that the equilibrium of the kinetic energy totally describes the balance of two opposed jets at the impingement point. The results show that the kinetic energy model can be used as a design tool for experiments with CIJ mixers and for the design of industrial CIJ reactors.

In T-Jets mixers, an elastic analogue model was demonstrated as the best prediction of the offset of the impingement point position in the mixing chamber. This model is demonstrated from an analogy of two impinging jets with a system of two springs. It is based on the balance of the kinetic energy of jets and also takes into account the velocity and density of two liquid streams. This model considers that the velocity of jets remains constant from the nozzle to the impingement point position. A validity range for this model may be described from CFD results: $-0.5 < \xi^* < 0.5$ and $\text{Re} \geq 25$ for geometries with any depth and $W/w = 6$. This observation shows that the elastic analogue model can be used as a design tool for the balanced conditions of jets at the centre of the T-Jets mixing chamber, which is the effective condition for the onset of the dynamic flow regime.

Slit-and-recombine mixers typically operate in the Stokes flow regimes, and the distribution of striation thickness relies on the developed velocity profile. The non-homogeneous distribution of mixing scales due to wall effects implies that the design of mixing devices must consider the striation thickness distribution, particularly the stria having the largest thickness. This means that the device must be designed with a longer length to achieve the same mixing degree, in comparison to the devices based

on the ideal baker's transformation. These results give an explicit and straight forward design expression to calculate the maximum and minimum striation thickness of each phase, that will be the limiting step in mixing operation in this type of mixers.

7.1.6 Methods of Flow Visualisation in Transparent Reactors

Since the mid-50s, attention has been given to micromixing assessment by the scientific community with the introduction of methods based on chemical reaction selectivity. Two methods were addressed in this work for flow visualisation: PLIF using non-reactive fluids and reactive-PLIF where a test reaction is involved.

PLIF experiments were conducted to track the fluid streams dying one of the streams with a marker that emits fluorescence with a laser. For experimental studies on mixing of dissimilar fluids in CIJ and T-Jets mixers, the optical properties of liquids are distinct and a methodology to match the refractive index of both liquids is drafted in Chapter 3. A salt, calcium chloride, is used to match the refractive index of two dissimilar fluids, guaranteeing the success of the PLIF technique.

Reactive PLIF methods for micromixing visualisation studies were also tested and optimised from an acid-base reaction with fluorescein and the Fenton's reaction, with rhodamine-B as the reaction tracer. Both test-reactions were studied in a stopped-flow equipment to define suitable operational conditions, namely the chemical composition of the inflow streams, the concentration of reagents and fluorophore, and suitable excitation light wavelength. The experimental conditions determined as suitable for mixing studies were tested in a T-jets mixer in Chapter 5. This mixer was illuminated in the axial plane with a laser light sheet. The mixing dynamics and the reaction course were clearly visualised from the acid-base reactive PLIF images. Fenton reactive PLIF method showed the overall distribution of mixing and reaction regions.

This work brings a useful contribution to this field of research, by the adaptation and improvement of two test-reactions that could be used as efficient, safe and cost-saving methods for micromixing assessment.

7.2 Future Work

This thesis presents an extensive study on the mixing mechanisms in rheometric flows, CIJ, T-Jets and SR mixers. Further studies are suggested, concerning work that was not possible to execute in the time frame of this thesis:

- A deeper insight into the mixing in cone-plate rheometer for similar and dissimilar fluids could be aimed from 3D CFD simulations. The validation of these numerical results should be made from the comparison with 2D results in Chapter 2.
- Kinetic studies with plate-plate or cone-plate geometries could be explored. These studies could involve CFD simulation and experiments. A polymerisation could be selected as the test reaction. These results would also be useful for the validation of mixing scales at lab-scale (rotational devices) and in pilot machines (e.g. CIJ mixers);
- The best balance between emulsifier dosages and the time of stability in CIJ mixers could be tested for different emulsifiers. This will contribute to further validation of production of oil/water emulsions in CIJ mixers. The performance of experiments with less amount of emulsifiers is advantageous for production purpose;
- The lamellar micromixing (LM) model could be implemented in T-Jets mixers. For this, the striation thickness evolution should be estimated from CFD simulations and then used in LM model;
- Flow visualisations of mixing of dissimilar fluids from reactive LIF methods using an acid-base test reaction. For this, the liquid streams have to be tuned

in terms of viscosity, with for instance glycerol, in order to guarantee the viscosities are the desired ones;

- Further development or validation of the model that estimates the impingement point position in T-Jets mixers could be done for a large validity range.

7.3 References

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