NETMIX® Static Mixer
Modelling, CFD Simulation and Experimental Characterisation

Ph.D. Dissertation in Chemical Engineering by

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To my parents
I'm not confused. I'm just well mixed.

Robert Frost (1874-1963)
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Abstract

The present work concerns the development of a new static mixing device, the NETMIX® static mixer, including its modelling, CFD, Computational Fluid Dynamics, simulation and experimental characterisation.

A mixing and chemical reaction model, the NETMIX® model, using a combined network model and network-of-zones model formulation, is first introduced as a macromixing and micromixing and chemical reaction model. The NETMIX® model allows the calculation of the yields and selectivities of different reaction schemes on different network structures, and therefore can be used to design network structure based static mixers.

The commercial CFD code FLUENT™ 6.1 is used to simulate the flow field in a network structure such as the NETMIX® model, in the range of Reynolds numbers $Re = 50$ to $Re = 700$. From the CFD simulations, the existence of two flow field regimes is observed. The Reynolds number marking the flow regime transition is denoted as the critical Reynolds number. The studied network structure presents, above a certain Reynolds number, strong flow field dynamics that promotes mixing with high energetic efficiency.

A NETMIX® pilot unit was designed and built. The core of the unit is a network structure based on the NETMIX® model, the NETMIX® static mixer. Pressure drop experiments and imaging experiments are presented for the NETMIX® static mixer between $Re = 25$ and $Re = 700$. CFD simulations are validated through comparison of the computed pressure drop with the NETMIX® static mixer experimental pressure drop. A consecutive competitive reaction system is used as test reaction to study the mixing efficiency of the NETMIX® static mixer in the range of Reynolds numbers $Re = 50$ to $Re = 700$.

From the imaging experiments and the chemical reaction experiments, the NETMIX® model is ultimately validated as a macromixing and micromixing and chemical reaction descriptive model for the NETMIX® static mixer, under the appropriate conditions.
Resumo

O presente trabalho consiste no desenvolvimento de um novo dispositivo de mistura estática, o misturador estático NETMIX®, incluindo a sua modelização, simulação em CFD, Computational Fluid Dynamics, e caracterização experimental.

Um modelo de mistura e reacção química, o modelo NETMIX®, usando uma formulação combinada do modelo de rede e do modelo de rede-de-zonas, é primeiramente introduzido como um modelo de macromistura e de micromistura e reacção química. O modelo NETMIX® permite o cálculo das conversões e selectividades de diferentes esquemas reacionais em diferentes estruturas de rede, podendo assim ser usado no projecto de misturadores estáticos baseados em estruturas de rede.

O código comercial de CFD FLUENT™ 6.1 é usado para simular o escoamento numa estrutura de rede como o modelo NETMIX®, na gama de números de Reynolds de $Re = 50$ a $Re = 700$. As simulações de CFD mostram a existência de dois regimes de escoamento. O número de Reynolds que marca a transição entre os regimes de escoamento é denominado $número de Reynolds crítico$. A estrutura de rede estudada apresenta, acima de um determinado número de Reynolds, uma forte dinâmica do campo de escoamento que promove a mistura com uma elevada eficiência energética.

Uma unidade piloto NETMIX® foi projectada e construída. O núcleo desta unidade é uma estrutura de rede baseada no modelo NETMIX®, o misturador estático NETMIX®. São apresentadas experiências de perda de pressão e experiências de visualização para o misturador estático NETMIX®, na gama de números de Reynolds de $Re = 25$ a $Re = 700$. As simulações de CFD são validadas por comparação entre a perda de pressão calculada e a perda de pressão experimental do misturador estático NETMIX®. Um sistema de reacções consecutivas competitivas é usado como reacção teste para o estudo da eficiência de mistura do misturador estático NETMIX®, na gama de números de Reynolds de $Re = 50$ a $Re = 700$.

Das experiências de visualização e das experiências de reacção química, o modelo NETMIX® é finalmente validado como um modelo descritivo da micromistura e da macromistura e reacção química para o misturador estático NETMIX®, nas condições apropriadas.
Résumé

Ce travail concerne le développement d'un nouveau dispositif de mélange statique, le mélangeur statique NETMIX®, comprenant sa modélisation, simulation de CFD, *Computational Fluid Dynamics*, et caractérisation expérimentale.

Un modèle de mélange et de réaction chimique, le modèle NETMIX®, utilisant une formulation combinée de *modèle de réseau* et de *modèle de réseau-de-zones*, est d'abord présenté comme un modèle de macromélange et de micromélange et réaction chimique. Le modèle de NETMIX® tient compte du calcul des conversions et des sélectivités de différents schémas de réaction sur différentes structures de réseau, et peut donc être utilisé pour concevoir les mélangeurs statiques basés sur structure de réseau.

Le logiciel commercial de CFD FLUENT™ 6.1 est utilisé pour simuler le champ d'écoulement dans une structure de réseau telle que le modèle de NETMIX®, dans la gamme du nombre de Reynolds de $Re = 50$ à $Re = 700$. Les simulations de CFD montrent l'existence de deux régimes de champ d'écoulement. Le nombre de Reynolds marquant la transition entre les régimes d'écoulement est noté *nombre de Reynolds critique*. La structure de réseau étudiée présente, au-dessus d'un certain nombre de Reynolds, une forte dynamique de champ d'écoulement qui favorise le mélange avec une efficacité énergétique élevée.

Une unité pilote NETMIX® a été conçue et construite. Le noyau de l'unité est une structure de réseau basée sur le modèle NETMIX®, le mélangeur statique NETMIX®. Des expériences de chute de pression et des expériences de visualisation sont présentées pour le mélangeur statique NETMIX®, dans la gamme du nombre de Reynolds de $Re = 25$ à $Re = 700$. Des simulations de CFD sont validées par la comparaison de la chute de pression calculée avec la chute de pression expérimentale du mélangeur statique NETMIX®. Un système de réaction consécutif compétitif est employé comme réaction d'essai pour étudier l'efficacité de mélange du mélangeur statique NETMIX®, dans la gamme du nombre de Reynolds de $Re = 50$ à $Re = 700$.

Des expériences de visualisation et des expériences de réaction chimique, le modèle NETMIX® est finalement validé comme un modèle descriptif de macromélange et de micromélange et réaction chimique pour le mélangeur statique NETMIX®, dans les conditions appropriées.
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...
Roman Letters

\(a\) maximum amplitude of perturbation
\(A\) area, \([m^2]\)
\(\bar{A}\) surface area vector, \([m^2]\)
\(A\) incidence matrix
\(A_{friction}\) specific friction area, \([m^{-1}]\)
\(A_{impeller}\) projected area of the impeller, \([m^2]\)
\(A_{wall}\) total friction area, \([m^2]\)
\(b_{inlet}\) inlet boundary
\(b_{outlet}\) outlet boundary
\(C\) concentration, \([mol/m^3]\)
\(C_D\) drag coefficient
\(d\) channel diameter / width, \([m]\)
\(D\) chamber diameter / width, \([m]\)
\(\varphi\) diffusion coefficient, \([m^2/s]\)
\(d_H\) hydraulic diameter, \([m]\)
\(D^L\) utmost left chamber diameter, \([m]\)
\(D^R\) utmost right chamber diameter, \([m]\)
\(Da\) Damköhler number
\(E\) total absorbance
\(E(t)\) residence time distribution function
\(E(\Theta)\) dimensionless residence time distribution function
\(Eu\) Euler number
\(f\) frequency / oscillation frequency, \([Hz]\)
\(F_D\) drag force, \([N]\)
\(f_{friction}\) friction factor
\[ f_{\text{induced}} \] induced oscillation frequency, [Hz]

\[ f_{\text{observed}} \] observed oscillation frequency, [Hz]

\[ Fr \] Froude number

\[ g \] hydraulic conductance, \([m^3 \text{ Pa}^{-1} \text{s}^{-1}]\)

\[ \dot{g} \] gravity acceleration, \([m/s^2]\)

\[ \dot{G} \] power spectrum

\[ G \] channels conductance matrix, \([m^3 \text{ Pa}^{-1} \text{s}^{-1}]\)

\[ h \] calotte height, [m]

\[ H(t) \] Heaviside function

\[ l \] ionic strength, \([\text{mol/m}^3]\)

\[ I \] identity matrix

\[ I_{\text{flow}} \] incidence of the flow

\[ k \] reaction rate constant

\[ \ell \] linearized coefficient

\[ L_x \] network length in the \(x\)-axis, [m]

\[ L_y \] network length in the \(y\)-axis, [m]

\[ L^h \] distance between the centres of horizontally interconnected chambers, [m]

\[ l^h \] length of the horizontal channel, [m]

\[ L^o \] distance between the centres of obliquely interconnected chambers, [m]

\[ l^o \] length of the oblique channel, [m]

\[ m \] quantity of \(B\) present in \(R\) and \(S\)

\[ n_{\text{calottes}} \] number of calottes

\[ n_{\text{chambers}} \] number of chambers

\[ n_{\text{channels}} \] number of channels

\[ n_{\text{faces}} \] number of faces

\[ n_{\text{outlet}} \] number of outlet boundaries

\[ N_p \] power number

\[ n_{\text{rollers}} \] number of rollers
\( n_{\text{samples}} \) \hspace{1cm} \text{total number of time instants}

\( n_s \) \hspace{1cm} \text{number of rows}

\( n_y \) \hspace{1cm} \text{number of columns}

\( n_{\text{zones}} \) \hspace{1cm} \text{number of injection zones}

\( n^h_{\text{channels}} \) \hspace{1cm} \text{number of horizontal channels}

\( n^o_{\text{channels}} \) \hspace{1cm} \text{number of oblique channels}

\( p \) \hspace{1cm} \text{pressure, \([\text{Pa}]\)}

\( \mathbf{p} \) \hspace{1cm} \text{chambers pressure vector, \([\text{Pa}]\)}

\( \mathbf{P} \) \hspace{1cm} \text{power, \([\text{W}]\)}

\( P_0 \) \hspace{1cm} \text{discharging pressure, \([\text{Pa}]\)}

\( P_1 \) \hspace{1cm} \text{feeding pressure, \([\text{Pa}]\)}

\( \mathbf{P}_{\text{mixing}} \) \hspace{1cm} \text{power consumption in mixing, \([\text{W}]\)}

\( P_w \) \hspace{1cm} \text{length of wetted perimeter, \([\text{m}]\)}

\( p^* \) \hspace{1cm} \text{source pressure, \([\text{Pa}]\)}

\( p(t) \) \hspace{1cm} \text{perturbation time function}

\( \text{pdf}(x) \) \hspace{1cm} \text{probability density function of } x

\( q \) \hspace{1cm} \text{flowrate, \([\text{m}^3/\text{s}]\)}

\( \mathbf{q} \) \hspace{1cm} \text{channels flowrate vector, \([\text{m}^3/\text{s}]\)}

\( q_T \) \hspace{1cm} \text{total flow rate, \([\text{m}^3/\text{s}]\)}

\( \mathbf{q}^* \) \hspace{1cm} \text{flow source vector, \([\text{m}^3/\text{s}]\)}

\( r \) \hspace{1cm} \text{rate of reaction, \([\text{mol m}^3 \text{s}^{-1}]\)}

\( R \) \hspace{1cm} \text{hydraulic resistance, \([\text{Pa s/m}^3]\)}

\( \mathcal{R} \) \hspace{1cm} \text{computed residue}

\( R_y(x) \) \hspace{1cm} \text{cross-correlation function of } x

\( \text{Re} \) \hspace{1cm} \text{Reynolds number}

\( s \) \hspace{1cm} \text{skewness}

\( S \) \hspace{1cm} \text{source term}

\( \text{speed} \) \hspace{1cm} \text{speed, \([\text{min}^{-1}]\)}
$St$ Strouhal number

$St_{chamber\ 3D}$ Strouhal number based on the total chamber volume

$St_{effective\ 3D}$ Strouhal number based on the volume of the chamber

$t$ time, $[s]$

$T$ temperature, $[^\circ C]$

$t_p$ perturbation time interval, $[s]$

$\cdot period$ period, $[s]$

$T_T$ total time of a time series, $[s]$

$U$ approach velocity of the fluid relative to the impeller blade, $[\text{m/s}]$

$v$ variance

$V$ volume, $[\text{m}^3]$

$V_{chamber}$ volume of the chamber, $[\text{m}^3]$

$V_{channel}$ volume of the channel, $[\text{m}^3]$

$V_{channels}$ channels volume, $[\text{m}^3]$

$V_{effective}$ chamber effective mixing volume, $[\text{m}^3]$

$V_{flow}$ geometric volume for flow, $[\text{m}^3]$

$V_{NETMIX}$ volume of the NETMIX® static mixer, $[\text{m}^3]$

$V_{network}$ network volume, $[\text{m}^3]$

$x$ space coordinate

$X$ yield / selectivity

$\tilde{X}$ Fourier Transform / Discrete Fourier Transform

$y$ space coordinate

$Y$ admittance matrix, $[\text{m}^3\ \text{Pa}^{-1}\ \text{s}^{-1}]$

$z$ space coordinate

$Z$ $Z$ factor
Greek Letters

$\alpha$ segregation parameter

$\gamma$ under-relaxation factor

$\Gamma(k,x)$ incomplete gamma function

$\delta$ optical path length, [nm]

$\Delta p$ pressure drop, [Pa]

$\Delta \mathbf{p}$ channels pressure vector

$\Delta p_{\text{correlated}}$ CFD correlated pressure drop, [Pa]

$\Delta p_{\text{NETMIX}}$ pressure drop across the NETMIX$^\text{®}$ static mixer, [Pa]

$\Delta p_{\text{static mixer}}$ pressure drop across the static mixer, [Pa]

$\Delta p_{\text{steady state}}$ CFD steady state simulations pressure drop, [Pa]

$\Delta p_{\text{transient}}$ CFD transient simulations pressure drop, [Pa]

$\Delta p_{\text{turbulent}}$ turbulent pressure drop, [Pa]

$\Delta \mathbf{p}^s$ pressure source vector, [Pa]

$\Delta t$ time step, [s]

$\varepsilon$ extinction coefficient, [m$^2$/mol]

$\varepsilon'$ static mixer porosity

$\varepsilon_{\text{turbulent}}$ rate of dissipation of turbulent kinetic energy, [m$^2$/s$^3$]

$\zeta$ scalar quantity

$\eta_k$ Kolmogorov scale of length, [m]

$\Theta$ dimensionless residence time

$\Theta_m$ dimensionless mean residence time

$\lambda$ wavelength, [nm]

$\mu$ viscosity, [Pa s]

$\nu$ kinematic viscosity, [m$^2$/s]

$\xi$ lag between two time records, [s]

$\rho$ density, [kg/m$^3$]

$\sigma$ turbulence intensity, [m/s]
\( \sigma_D \)  
chambers diameter standard deviation, [m]

\( \sigma_d \)  
channels diameter standard deviation, [m]

\( \tau \)  
mean residence time, [s]

\( \tau \)  
stress tensor, [Pa]

\( \tau_{cell} \)  
mean residence time in an elementary cell, [s]

\( \tau_{chamber} \)  
mean residence time in a chamber, [s]

\( \tau_K \)  
Kolmogorov scale of time, [s]

\( \nu \)  
velocity, [m/s]

\( \vec{\nu} \)  
velocity field, [m/s]

\( \phi \)  
angle

\( \phi' \)  
angle

\( \psi \)  
stream function, [m²/s]

\( \omega \)  
vorticity, [s⁻¹]
Indices

* dimensionless variable

2D for the two-dimensional geometry

3D for the three-dimensional geometry

A chemical species $A$

B chemical species $B$

centre refers to the coordinate of the channel centre

CSTR for the CSTR

empty tube refers to the empty tube

eq corrected parameter for the 2D geometry

f refers to the cell face

final refers to the final reaction concentration

i index or counter

in refers to the inlet channels

initial refers to the initial reaction concentration

j index or counter

k index or counter

l index or counter

m index or counter

max maximum value for a variable

min minimum value for a variable

model refers to the NETMIX® model

n denotes component in the normal flow direction

nb refers to the neighbouring cell centre

NETMIX refers to the NETMIX® static mixer

old old value for a variable

oR chemical species $oR$

$J$ refers to cell $J$ centre
PFR for the PFR

$pR$ chemical species $pR$

$R$ chemical species $R$

$S$ chemical species $S$

$x$ denotes component in the $x$ direction

$y$ denotes component in the $y$ direction
### Abbreviations

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>2D</td>
<td>Two-Dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-Dimensional</td>
</tr>
<tr>
<td>AMG</td>
<td>Algebraic Multigrid Method</td>
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<tr>
<td>BDF</td>
<td>Backward Differentiation Formulas</td>
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<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
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<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
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<tr>
<td>CNC</td>
<td>Computer Numerical Controlled</td>
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<tr>
<td>COV</td>
<td>Coefficient of Variation</td>
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<td>CSTR</td>
<td>Continuous Stirred Tank Reactor</td>
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<tr>
<td>CT</td>
<td>Concentration-Time</td>
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<tr>
<td>DFT</td>
<td>Discrete Fourier Transform</td>
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<tr>
<td>DNS</td>
<td>Direct Numeric Simulation</td>
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<td>FAS</td>
<td>Full Approximation Storage</td>
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<td>FFT</td>
<td>Fast Fourier Transform</td>
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<td>FRW</td>
<td>Flow Rate Weighting</td>
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<td>HC</td>
<td>Horizontal Channels</td>
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<td>LDA</td>
<td>Laser Doppler Anemometry</td>
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<td>LIF</td>
<td>Laser Induced Fluorescence</td>
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<td>LSF</td>
<td>Least Squares Fit</td>
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<td>NPBC</td>
<td>Non-Periodic Boundary Conditions</td>
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<td>OC</td>
<td>Oblique Channels</td>
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<td>ODE</td>
<td>Ordinary Differential Equations</td>
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<tr>
<td>PBC</td>
<td>Periodic Boundary Conditions</td>
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<tr>
<td>PDF</td>
<td>Probability Density Function</td>
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<tr>
<td>PISO</td>
<td>Pressure-Implicit with Splitting of Operators</td>
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<td>PFR</td>
<td>Plug-Flow Reactor</td>
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<td>RTD</td>
<td>Residence Time Distribution</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>SIMPLE</td>
<td>Semi-Implicit Method for Pressure-Linked Equations</td>
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<tr>
<td>SIMPLEX</td>
<td>SIMPLE-Consistent</td>
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<tr>
<td>TISM</td>
<td>Tanks-in-Series Model</td>
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1. INTRODUCTION

1.1 Motivation and Relevance

Mixing is an essential component of nearly all industrial processes, ranging from simple mixing of fluids of differing composition or temperature to complex chemical reactions for which the reaction yield and selectivity are highly dependent on the mixing performance. The selectivity is a key aspect of any reactive process since it is known that the profitability of a process can vary with changes as low as 1% of its selectivity (Ottino, 1994).

Before proceeding, it is important to clarify a number of concepts that are used throughout this work. Under the broad term mixing, different processes and several mechanisms are comprised. According to Nienow et al. (1997), mixing processes can be classified regarding the phases between which transfer of matter occurs:

- liquid-liquid miscible mixing: all phases are miscible liquids;
- liquid-liquid immiscible mixing: all phases are liquids unable to mix, such as oil and water, and the purpose of mixing is just to increase the interfacial area between the phases so that mass transfer is enhanced;
- gas-liquid mixing: consists of the dispersion of gas bubbles within a liquid medium in order to create an interface between the two phases so mass transfer is enhanced;
- solid-liquid mixing: generally in this mixing process the purpose is to keep solid particles suspended in the liquid phase in the course of the chemical reaction;

- solid-solid mixing: all phases are solids, generally granulated, with purpose of mixing different powders yielding a powder of uniform composition.

This list is not complete but just an illustration of the variety of situations to which the term mixing can be applied. In the present work mixing studies are focused on single-phase liquid mixing, a process divided in two main stages: convective mixing and diffusive mixing (Bourne, 1997). Convective mixing comprises the spread of material throughout the reactor by action of large scale eddies, a process called macromixing due to its scale. Convective mixing also includes the homogenisation of the material on a microscopic scale by action of the smaller scale eddies and diffusion, a process called micromixing.

Another important concept for the classification of mixing is the reactor hydrodynamic regime. The hydrodynamic regime is associated to the Reynolds number, Re, a dimensionless number defined as the ratio between the inertial and the viscous forces. Laminar regime occurs at low Reynolds numbers where the flow patterns scale is generally large without small scale eddies. The convective mixing mechanisms at laminar regimes spread the species throughout the reactor and the fluid is deformed into laminas of decreasing thickness (Edwards, 1997). Diffusive mixing under the laminar regime is only significant when the lamina thickness is reduced to a sufficiently low level. Mixing under a turbulent regime is called turbulent mixing and comprises the following mixing mechanisms: spread of the material throughout the reactor by the formation of large eddies and its homogenization by the small scales eddies up to a level where transport can occur by diffusion.

Examples of industrial processes, where the chemical reaction rate is controlled by mixing, include polymerisation, precipitation, combustion and neutralization (Villermaux and Falk, 1996; Zalc and Muzzio, 1999). Mixing plays a critical role in the initiator consumption and final product properties in many polymerisation processes (Kolodziej et al., 1980; Lee et al., 1980; Chella and Ottino, 1983; Chella and Ottino, 1984; Mehta and Tarbell, 1987; Kusch et al., 1989). Similarly, the degree of mixing strongly influences precipitation processes, where the shape and size distribution of relatively insoluble precipitate particles can be significantly altered by changing the local mixing environment near the feed port (MacMullin and Weber Jr., 1935; McCabe and Stevens, 1951; Smythe, 1967; Garside, 1985). Mixing is also recognised as a key factor in the overall
performance of a combustor, both in terms of fuel efficiency and pollutants formation (Bilger, 1976; Pratt, 1976; Spalding, 1976; El-Hamdi et al., 1993). Substantial mixing effects have further been noted in many neutralization reactions (Lamberto et al., 1996).

Improper mixing can result in non-reproducible processing and lowered product quality, with the associated need for more complex downstream purification processes and increased waste disposal costs. Hence, mixing is not only of economic importance but also an environment related issue.

Over the past years, static mixer technology has matured into an integral and essential unit operation used in most areas of chemical engineering such as homogenisation, liquid-liquid dispersion, heat and mass transfer and chemical reaction. Static mixers present at the same time an alternative and a complement to the traditional agitated systems. Further, many batch processes can be converted to continuous processes via a static mixer, by taking advantage of the small size, intense mixing and enhanced mass and heat transfer capabilities of such units.

Although static mixers are well established in numerous process industries, research and development of new static mixers has been lately reduced. The published works on static mixers are essentially focused on commercially available static mixers, as can be seen in Chapter 2, where the literature on this area is reviewed.

Thus the design of new static mixers and the development of mathematically well defined and simple models capable of describing their mixing performances is of great importance and is the purpose of this thesis.

1.2 Thesis Objectives and Layout

The general objective of this work is the development of a new static mixing device, the NETMIX® static mixer, including its modelling, CFD simulation and experimental characterisation. Furthermore, the present work shows the role that CFD can play in the design stage of process equipment, enabling a more fundamental understanding of the mixing process and reducing development costs.

The layout of the present work is divided as follows.

In Chapter 2 the state-of-the-art on static mixers is presented. A description of most commercially significant static mixers is given, followed by an overview on the range of
applications found in literature for static mixers. In addition, a review on published CFD simulation and experimental work on static mixers is given.

In Chapter 3 the NETMIX® model is introduced as a general mixing and chemical reaction model based on a network structure of chambers and channels. Such model is capable of coupling macromixing and micromixing and of predicting the steady-state yield and selectivity for different types of reaction schemes, namely: first-order reaction, second-order reaction, and consecutive competitive second-order reactions.

In Chapter 4, the flow field and viability of mixing in a network structure of chambers and channels, such as the NETMIX® model, are studied by means of the CFD simulation. CFD simulations for a 2D model are performed in the range of Reynolds numbers $Re = 50$ to $Re = 700$. The flow field variables velocity and pressure are directly obtained from the CFD simulations. Derived flow field variables are computed for a greater insight into the flow field structures and dynamics, namely: vorticity and streamlines; mixing intensity; power energy spectra; and cross-correlations function.

Chapter 5 starts by presenting detailed information concerning the experimental setup and the NETMIX® static mixer. Experimental results for the NETMIX® static mixer are further included as reported next:

- To study the pressure drop across the NETMIX® static mixer, pressure drop experiments were carried out in the range of Reynolds numbers $Re = 25$ to $Re = 700$ and results compared with simulations obtained both with the NETMIX® model (Chapter 3) and the 2D CFD model (Chapter 4).

- Tracer flow visualisation experiments are shown for Reynolds numbers ranging from $Re = 25$ to $Re = 700$. From the imaging of the dynamic flow field instantaneous patterns at different $Re$, further insight is gained into the Reynolds number influence on the flow field structures and dynamic behaviour of the NETMIX® static mixer. Imaging experiments provide a first validation of the NETMIX® model as a macromixing model for the NETMIX® static mixer and further validation data for the CFD simulations.

- The mixing efficiency of the NETMIX® static mixer is studied using a consecutive competitive reaction system as test reaction. Imaging and mixing-reactions
experiments are compared with the computed results from the NETMIX® model in order to ultimately validate the NETMIX® model as a macromixing and micromixing and chemical reaction descriptive model for the NETMIX® static mixer.

Finally, the general conclusions drawn from this work and some suggestions for future simulation and experimental work are presented in the Chapter 6.
2. STATIC MIXERS: STATE-OF-THE-ART

2.1 Introduction

Motionless or static mixers have become standard equipment in the process industries since the 1970s, for the mixing of liquids, especially for highly viscous materials, and to contact different phases to enhance heat and mass transfer (Szalai and Muzzio, 2003). Producing dispersions in two-phase and multiphase systems (e.g. emulsions, suspensions, foams) is also the common aim of using motionless mixers (Gyenis, 2002; Thakur et al., 2003). Static mixers are employed in a wide range of industries (pharmaceutical, petrochemical, food, cosmetics and biotechnology) (Zalc et al., 2002). Recent studies and applications further gave evidence to the behaviour, capabilities and applications of static mixers in bulk solids treatments (Gyenis, 2002).

Static mixers are used inline in an once-through process or in a recycle loop where they supplement or even replace a conventional stirrer. In many continuous processes, static mixers are undeniably an attractive alternative to conventional agitation. Static mixers eliminate the need for mechanical stirrers and therefore have a number of benefits: small space requirement; low equipment cost; no power requirement except pumping; the flow of materials through them may be induced by gravity, pressure difference or by using the existing potential or kinetic energy; easy and quick installation; low set-up and operating costs; self-cleaning; reduced maintenance requirements (Gough and Rogers, 1987;
Baker, 1991; Martin and Galey, 1994; Graefelman and Meagher, 1995; Gyenis, 2002; van Wageningen et al., 2004).

The standard design of a static mixer is a series of identical, flow-modifying motionless inserts, called elements, built into a tubular housing. These motionless inserts use the pressure difference or the kinetic and potential energy of the processed materials, causing splitting, shifting, shearing, rotating, accelerating, decelerating and recombining of materials.

There are at the present approximately 2 000 US patents and more than 8 000 published articles that describe static mixers and their applications (Thakur et al., 2003). More than two hundred commercial models are currently available (Kandhai et al., 1999). Commercial motionless mixers are available from a number of manufacturers and in different types, shapes and geometries. The materials of construction available for static mixers are broad, including most materials that can be formed or welded (Baker, 1991). Static mixers can therefore be selected to meet process requirements and the features of the processed materials.

This chapter is organised as follows. In Section 2.2 the most commonly used commercial static mixers are described and compared. In Section 2.3 several applications of static mixers are referenced. In Section 2.4 works concerning the CFD simulation of static mixers are reported. Section 2.5 presents a review on the published experimental work on static mixers. The final conclusions of this chapter are presented in Section 2.6.

Static micromixers are not reviewed in this work. A comprehensive review on static micromixers and their mixing principles can be found in Hessel et al. (2005).

2.2 Commercial Designs

Numerous designs of static mixers are available commercially. The most widely known and various industrial applications static mixers are:

- the SMX®, SMXL®, SMRX® and SMV® static mixers (Sulzer Chemtech, Ltd.);
- the LPD® static mixer (Ross Engineering, Inc.);
- the KM® also known as Kenics® static mixer (Chemineer, Inc.);
- the ISG® static mixer (Ross Engineering, Inc.).
Other commercial static mixer geometries include:

- the SMF® and SMI® static mixers (Sulzer Chemtech, Ltd.);
- the KVM®, KHT®, SMF® and Kfbe® static mixers (Koch-Glitsch, LP);
- the Cleveland® static mixer (Cleveland Eastern Mixers, Inc.);
- the Inliner® static mixer (Lightnin, Inc.);
- the KMA®, KMS® and HEV® static mixers (Chemineer, Inc.);
- the Komax® static mixer (Komax Systems, Inc.);
- the Oxynator® (Air Liquide, S.A.).

Classification schemes have been proposed to explain the behaviour differences between the several static mixers based on the geometry of the mixing elements (Baker, 1991; Myers et al., 1997). Commercial static mixers can be divided into five main families: open designs with helices (e.g. Kenics® static mixer); open design with plates (e.g. LPD®, Komax®, Inliner® and HEV® static mixers); corrugated plates (e.g. SMV® static mixer); multilayer designs (e.g. SMX®, SMXL® and SMRX® static mixers); and closed designs with channels (e.g. ISG® static mixer).

- The SMX® (see Figure 2.1), SMXL® and SMRX® static mixers are lamellar mixers, composed of narrow strips or lamellas placed side by side within a tubular housing. The strips constitute a 3D series of X forms, declining alternately from axial direction by positive and negative angles, crossing the planes of each other. During flow, the material is split into several streams or layers corresponding to the number of strips, shifted to opposite directions relative to each other. Each SMX®, SMXL® and SMRX® static mixers element mixes principally in the two dimensions along the plane of the X forms. Therefore, each element is rotated by 90° with respect to the previous element to ensure 3D mixing. The SMX®, SMXL® and SMRX® static mixers are characterised by excellent transversal mixing and a high dispersing effect.
• The SMV® static mixer (see Figure 2.2) consists of mixing elements arranged in a tubular housing. Each mixing element has several corrugated plates, which form partial channels open on one side. The SMV® static mixer geometry causes the material to be continuously divided and deflected in different directions creating strong cross flows with inherent good transversal mixing.

• The LPD® static mixer (see Figure 2.3) consists of a series of distorted semi-elliptical plates positioned in an oblique manner in a tubular housing. During flow, the material is split and diverted repeatedly in different directions along the cross-section of the tube. Since the flow at a given tubular section is divided into two streams only, shear and material exchange takes place essentially between the two half-tube cross-sections, thus the mixing effect along a given length is weaker than in the SMX® static mixer. Naturally, the pressure drop in the LPD® static mixer is also lower.
• The KM® usually referred as Kenics® static mixer (see Figure 2.4), consists of a long tubular housing containing helical elements twisted by 180° in an alternating sequence, perpendicular to flow direction. The outlet edge of a given element and the inlet edge of the next one are perpendicular to each other. The alternating helical elements continually divide, stretch and reorient the flow, enhancing mixing. Because of the smooth bending surfaces of the helices, the pressure drop along the Kenics® static mixer is very low. The Kenics® static mixer appears to have received most attention on published experimental investigations, possibly due to its large North American popularity (Jaffer and Wood, 1998) and simple geometry.

![Figure 2.4 The Kenics® static mixer.](image)

• The FixMix® static mixer is very similar to the KM® static mixer, with the essential difference that the individual elements are distorted relative to the tube axis and become gradually narrower along their length. These features provide intensive cross-flow between the neighbouring channels, resulting in improved mixing efficiency, lower pressure drop and more uniform radial and tangential velocity fields.

• The ISG® static mixer (see Figure 2.5) consists of several mixing elements inserted into a tubular housing. Each element has four channels designed at oblique angles to the axial direction to redirect the flow of material as it passes through the element. This results in the material flow moving from the outside to the centre and with a 90° turn of the material between successive elements. The ISG® static mixer is characterised by extraordinary radial mixing.
Numerical simulations for six static mixer types indicate the superior overall performance of the SMX\textsuperscript{\textregistered} static mixer compared to the Kenics\textsuperscript{\textregistered}, the Inliner\textsuperscript{\textregistered}, the LPD\textsuperscript{\textregistered} and the ISG\textsuperscript{\textregistered} static mixers (Rauleine et al., 1998) and the greater efficiency of the SMX\textsuperscript{\textregistered} static mixer as compared to the Kenics\textsuperscript{\textregistered} static mixer (Rauleine et al., 2000). However, the proper selection of a static mixer for a specific operation is not an easy task. General guidelines for choosing a particular type of static mixers can be retained (Cybulski and Werner, 1986; Gynies, 2002; Thakur et al., 2003), but there are exceptions to the following generalisations:

- Static mixers with plates and large sections available for flow (e.g. LPD\textsuperscript{\textregistered} and Komax\textsuperscript{\textregistered} static mixers) are suitable for simple turbulent flow applications such as mixing, heat transfer and thermal homogenisation.

- Static mixers with helical elements (e.g. Kenics\textsuperscript{\textregistered} and FixMix\textsuperscript{\textregistered} static mixers) are optimal for laminar flow, inline mixing and thermal homogenisation.

- Static mixers with multilayer design (e.g. SMX\textsuperscript{\textregistered}, SMXL\textsuperscript{\textregistered} and ISG\textsuperscript{\textregistered} static mixers) are adequate for highly viscous fluids in the laminar regime and also for liquid-liquid, liquid-solid and gas-liquid systems when the continuous phase is viscous or viscoelastic.

2.3 Applications

Static mixers were initially developed for mixing of fluids in laminar flow. Applications to heat transfer, turbulence and multiphase systems appeared later (Thakur et al., 2003). Static mixers are now widely applied and easy to use (Pahl and Muschelknautz, 1982) as a way of improving fluid-dynamic behaviour, enhancing efficiency, attaining concentration and
temperature homogeneity, lowering energy costs, and so on (Cavatorta et al., 1999). Static mixers are also used as reactors, particularly for polymerisations.

This section aims to portray a global picture of the applications of static mixers. Static mixers applications can be classified in three groups, depending on the materials involved: fluid-fluid systems; fluid-solid systems; and solid-solid systems.

In Section 2.3.1 and Section 2.3.2 are reviewed the applications of static mixers for fluid-fluid and fluid-solid systems, respectively. Several short reviews on this subject can be found (Middleman, 1977; Pahl and Muschelknautz, 1982; Baker, 1991). More complete reviews can be found in Gavrilescu and Tudose (1995), Gyenis (2002) and Thakur et al. (2003).

Solid-solid systems applications are not of fundamental interest to this study and consequently are not analysed here. Comprehensive reviews on this particular subject can be found in Chen et al. (1972) and Gyenis (2002).

### 2.3.1 Fluid-Fluid Systems

In the last years, numerous publications have dealt with the applications of static mixers to liquid-liquid, gas-liquid and gas-gas systems, including mixing of miscible fluids in single phase, dispersion of immiscible fluids, enhancement of mass transfer coefficient between phases, enhancement of heat transfer and blending of polymer melts.

The simplest use of a static mixer is mixing of fluids to eliminate the concentration gradients that would occur in an empty tubular housing, since despite the high diffusivities of gases, additional mixing is sometimes required for a mixture to achieve homogeneity. When conditions of good intimate contact between a gas and a liquid are required, static mixers appear to be an interesting alternative to achieve high gas transfer efficiency (Munter, 2004). Static mixers are reported to be more efficient than other contacting devices, such as spray nozzles, venturi scrubbers and randomly packed columns (Thakur et al., 2003). A few relevant references are reviewed next.

- Dechlorination of effluents is often required prior to discharge because free chlorine can react with organic material in a river or lake to form carcinogenic trihalomethane compounds. Although chlorine dissolution is an easy task, static mixers are used to ensure uniform mixing of the dechlorinating solution into the effluent (Baker, 1991).
• Baker (1991) reports the use of static mixers in chemical processes that require adequate pre-reactor gas feed mixing to operate efficiently. The use of static mixers is expressly proposed to prevent the rapid platinum catalyst degradation in the production of nitric acid from ammonia oxidation with air.

• Disinfection process in water treatment plants requires both dissolution and mixing of ozone, introduced as gas. Ozone is used in water treatment as a biocide, as an oxidant and as a pre-treatment reagent in order to improve the performance of the downstream coagulation/flocculation/settling and filtration processes. Static mixers offer an alternative method for improving the efficiency of the dissolution of ozone gas into the main stream and for optimizing its use (Martin et al., 1992).

• Martin and Galey (1994) presented pilot plant studies in water treatment plants composed of a static mixer for the transfer of ozone from gas to liquid, linked to an air lift to separate gas from liquid, providing ozonated water. Such process enabled to control the concentration-time (CT) values, i.e., the product of the residual disinfectant concentration and the effective contact time.

• Braun et al. (1998) carried out experiments in a premix combustion test rig at moderate pressure, revealing the key role of fuel-air mixture as determinant parameter for the amount of nitric oxides emissions. Results indicate the potential use of static mixers to reduce nitric oxides emissions in premixed combustors and fuel staged combustors.

• The standard for sampling effluent air from nuclear industry stacks and ducts places limits on the non-uniformity of velocity and pollutant profiles at the sampling location. McFarland et al. (1999) studied the suitability of air sampling locations downstream of static mixers. Static mixers were shown to greatly enhance the mixing process, reducing non-uniformity of both velocity and tracer gas concentration profiles downstream the static mixer.

• Mysore et al. (2004) evaluated the potential benefits of using a static mixer for ozone dissolution in drinking water treatment through comprehensive pilot-scale and full-scale studies under a variety of operating conditions and source waters. The results from pilot-scale studies showed that higher ozone residuals were obtained in a short interval of time at the outlet of the static mixer due to intense mixing and ozone
transfer through the static mixer elements. Enhanced microbial inactivation was also observed due to the higher CT values reached along the static mixer unit.

Other application of static mixers is pH control in water treatment plants. Works in this area include:

- Williams et al. (1990) who first used static mixers for pH neutralization in a wastewater treatment process.

- Lee and Choi (2000) later reported static mixers as useful tools for adaptive control of chemical addition for pH neutralization in water treatment plants.

Recent advances have revealed the potential use of static mixers in countermeasure processes to global climate change:

- Tajima et al. (2004) proposed and validated at a laboratory-scale simulation a new method for releasing anthropogenic liquid carbon dioxide into the ocean. In this method, the liquefied carbon dioxide is transported through a pipeline to a submerged static mixer, were it is mixed with seawater and released into the ocean at intermediate depths.

Static mixers have also been incorporated in bubble columns as a way of improving fluid-dynamic behaviour and increase mass transfer. In other column operations, as for instance reactive distillation, oxidising of organic products or bioreactors in bubble columns, static mixers are now used in order to create a large interface for mass transfer. Some examples are included in the following group of works:

- Fan et al. (1975) determined the mass-transfer coefficient and pressure-drop data of a two-phase oxygen-water system in a bubble column packed with static mixers and compared them with data from an unpacked column. Static mixers were shown to be effective in aeration or oxygenation systems. The mass-transfer coefficient was found to be almost double in the bubble column packed with the static mixers, while the pressure drop only slightly increased.

- Chisti et al. (1990) investigated the effect of static mixers on the overall gas-liquid volumetric mass transfer coefficient in an external-loop airlift bioreactor. Under identical conditions, the inclusion of static mixers improved 30% to 500% the mass
transfer coefficient and increased gas hold-up and gas-liquid interfacial area in the studied bioreactor.

- Gaspillo and Goto (1991) and Goto and Gaspillo (1992) reported measurements of gas-liquid and liquid-solid mass transfer rates in two bubble columns with and without static mixers. The static mixers were found to be effective in increasing rates of mass transfer when a single nozzle was used as the gas distributor.

- Rusnac et al. (1992) achieved continuous hydrogenation of industrially refined soybean oil with nickel catalyst was in a slurry column equipped with static mixers.

- Demmink et al. (1994) performed the oxidative absorption of hydrogen sulfide into a solution of the ferric chelate of nitrilotriacetic acid, in a cocurrent down flow column packed with static mixers.

Applications of static mixers in heat exchange operations have also been used to improve heat transfer coefficients and to mitigate recurring problems as fouling, crystallisation, polymerisation or biological growth at the wall.

- Gough and Rogers (1987) have shown that by using static mixers, boundary-layer fluid is continuously displaced from the tube surface and remixed with the bulk fluid, creating uniform temperature and velocity distributions, achieving high heat transfer rates, and inhibiting fouling in heat exchangers. Industrial results for coal-tar-oil-residues heaters revealed sharp reductions in the cleaning operation intervals from 8 weeks, for trial exchanger with no static mixers, to more than 4 years, for new exchangers designed with static mixers.

Static mixers have further been used for several years as cocurrent extractors in the oil and gas industry (Baker, 1991). Applications included amine washing, caustic washing, water washing of organics and extraction of hydrogen sulfide from liquefied petroleum gas by treatment with diethanolamine. Static mixers are also used to enhance cocurrent extractions with supercritical carbon dioxide and countercurrent liquid-liquid extractions.

- Merchuk et al. (1980) experimentally investigated the use of different static mixers in countercurrent liquid-liquid extraction of copper by LIX 64N, reporting static mixers to be a good choice in comparison with stirred vessels.
• Jancic et al. (1983) tested the performance of static mixers as packing in several countercurrent liquid-liquid extractions with four test systems: kerosene-water, butanol-succinic acid-water, toluene-acetone-water and carbon tetrachloride-propionic acid-water.

• Pietsch and Egers (1999) used static mixers for the regeneration of caffeine-loaded carbon dioxide at various conditions using water. Water is sprayed into the carbon dioxide flow and the resulting two-phase flow passes through a static mixer to intensify phase contact and prevent coalescence of the water phase. An efficiency of 80% to 90% in comparison with the theoretical maximum based on ternary equilibrium data from the literature was obtained.

• Catchpole et al. (2000) proposed the use of static mixers as an alternative to packed columns to carry out the fractionation of shark liver oil and olive oil deodorizer distillate using supercritical carbon dioxide. Both lipid mixtures contain squalene, which is the desired end product. The mass transfer performance of the static mixer for the recovery of squalene was experimentally found to be similar to that of the pilot-scale packed column.

Static mixers find a variety of applications in polymer processing. Many polymerisations are moderately or highly exothermic and static mixers are beneficial to improve heat transfer, but also to reduce composition differences from polymer blending and colouring. Static mixers are well suited for reaction injection moulding processes where their role is to quickly blend the reactive components before mould injection.

• Schott et al. (1975) determined the pressure drop and heat transfer data for polyethylene, polypropylene, polystyrene and ABS during flow through a pipe containing a static mixer and open pipe, concluding that the static mixer reduced the temperature gradients in the molten polymer.

• Craig (1987) analysed the performance of a large-diameter conventional static mixer used as a continuous reactor for styrene polymerization. Static mixers with internal heat-transfer surface were recommended to avoid adiabatic polymerization and the associated danger of runaway reactions.

• Tien at al. (1985) and Tien et al. (1990) describe the thermal bulk polymerization of styrene conducted in pilot plants of different sizes, each pilot plant consisting of a
tubular recycle reactor connected in series with a tubular reactor, both completely filled with static mixers.

- Yoon and Choi (1996) also studied radical solution polymerization of styrene using a binary mixture of symmetrical bifunctional initiators in a filled tubular reactor packed with static mixers. Static mixers induced intensive radial mixing in the reactor conducting to a near plug flow pattern with low axial dispersion effect.

- Jurkowski and Olkhov (1997) blended immiscible polymers such as low-density polyethylene and polyamide 6 using a laboratory equipment based on a modified Brabender plastograph, by attaching a static mixer to the extruder of the plastograph. It was found that the use of a static mixer significantly improved the homogeneity of blends of thermodynamically immiscible polymers.

- Fourcade et al. (2001a) and Hoefsloot et al. (2001) experimentally treated controlled polypropylene degradation by peroxides in static mixers.

- Sulzer Chemtech, Ltd. (2005) recently published information about what is believed to be the first static mixer ever developed for PVC. The static mixer is reported to improve thermal mixing and melt homogenizing, minimise flow lines, and improve colour distribution.

Static mixers are also used to intensify transfer processes in applications for biotechnology and pharmaceutics industries (Gavrilrescu and Tudose, 1995), although published works are very scarce.

- Metzendorf et al. (1985) investigated a new reactor design, fluidized bed reactors equipped with static mixers, for lactose hydrolysis in whole whey or partially deproteinized whey. Fluidized bed reactors equipped with static mixers exhibited an outstanding hydrodynamic stability together with an increase of the operating range in terms of flow rate by a factor of four compared to the classical fluidized bed.

- Junker et al. (1994) investigated the production of attenuated hepatitis A virus antigen from anchorage-dependent MRC-5 cells in a titanium static mixer reactor.

- Gavrilrescu et al. (1995) used static mixers to overcome the effects of high viscosities in the biosynthesis of cephalosporin C in a pilot-plant external-loop airlift bioreactor. Gavrilrescu et al. (1997) performed experimental investigation results for liquid
circulation superficial velocity and gas hold-up behaviours in an external-loop airlift bioreactor, with corrugated plates static mixers and under forced-loop operation mode. The use of static mixers resulted in significant gas hold-up increased and homogeneous bubble distribution over the bioreactor cross-section.

- Grafelman and Meagher (1995) achieved starch gelatinization and liquefaction using single-screw extrusion and a post-extrusion static-mixer reactor as alternative to conventional jet cookers. The static mixer reactor tube improved mixing of the gelatinized slurry and increased residence times, resulting in increased starch degradation and reduced viscosity. Comparison of costs further indicated extrusion as a cost-effective alternative to conventional technology.

- Subramanian and Hanna (1996) and Cha and Hanna (2002) added a static mixer to the die end of a laboratorial extruder as postextruder reactor modifications. The extrusion process of mixtures of starch, ethylene glycol, and concentrated sulfuric acid was greatly improved by the use of static mixers.

- Chamayou et al. (1996) refers the use of a continuous pilot plant loop-reactor packed with static mixers for the synthesis of amiodarone, a widely used anti-arrhythmic drug produced by a liquid-liquid-solid reaction.

- Maa and Hsu (1997) incorporated a protein drug in microspheres made of a hydrophobic polymer via double liquid-liquid emulsification and via dispersing a powdered protein in a polymer solution followed by liquid-liquid emulsification. In both emulsification processes, the operating step that produced the microspheres was conducted in a static mixer.

- Ugwu et al. (2002) have shown the feasibility of improving mass transfer characteristics of inclined tubular photobioreactors by installing static mixers. The volumetric oxygen transfer coefficient, gas hold-up and biomass productivities of the photobioreactor with internal static mixers were significantly higher than those of the photobioreactor without static mixers.

- Hirech et al. (2003) performed a two-step microencapsulation process, with the first step corresponding to the formation of an oil/water dispersion in a static mixer and the second step to the microencapsulation by interfacial polymerisation in a stirred tank reactor.
Among other applications enhanced by static mixers are those for continuous emulsification (Wieringa and Kieft, 1996; Thakur et al., 2003). Emulsions are important when processing explosives (Teipel, 1992) and many food products and cosmetics (Chen, 1973).

- Belyaeva et al. (2004) described a new approach in the formulation of hydrogel beads by emulsification/thermal gelation with a sunflower oil at ambient temperature as the continuous phase using a static mixer technology.

Finally, applications of static mixers in food processing are also reported in the literature:

- Cybulski and Werner (1986) referred the use of static mixers to mix acids, juices, oils, beverages, milk drinks and sauces.

- Baker (1991) reported the possible application of static mixers in heat exchangers to cool melted chocolate prior to coating on ice cream and candy.

- Lammers and Beenackers (1994) developed a continuous reactor for the chemical derivation of aqueous hydroxypropyl starch solutions for the food and pulp and paper industries, based on static mixers.

- Thakur et al. (2003) pointed out the use of static mixers for heating and cooling of sugar solutions.

2.3.2 Fluid-Solid Systems

Static mixers are not restricted to fluid-fluid systems and have also found numerous applications in fluid-solid, both liquid-solid and gas-solid, systems. Examples include separation of particles from gases, wet mixing of ceramic powders or drying. In spite of this, published literature on this field is scarce.

- Static mixers play a positive role in sludge conditioning in wastewater treatment. Adding chemicals such as polymer, alum, lime or ferric chloride improves sludge dewatering process. The conditioning agent must be evenly dispersed in the sludge suspension, yet shear must be minimised to avoid breaking the coagulated solids. Static mixers are shown to increase the solids contents of the dewatered sludge and to reduce additive requirements (Baker, 1991).
Jean et al. (1987) studied the application of static mixers in the continuous production of narrow-sized titanium dioxide particles. The results are comparable to those obtained using a batch technique. Narrower particle-size distributions of titania powders were produced with greater flow rates giving greater superficial velocities and shorter residence times.

Metzendorf et al. (1991) investigated experimentally the effect of static mixers on expansion and dispersion of liquids in a liquid-solid fluidized bed reactor. Authors observed that the use of static mixers in fluidized bed reactors results in high hydrodynamic stability accompanied by an increase in the operating range in terms of flow rate.

Heat treatment is frequently carried out in rotary heater or kiln, as used in cement industries and, in smaller dimensions, in food processing. Static mixers mounted inside a rotating unit can enhance the heat transfer between particles and streaming gas or between particles and heated surface (Gyenis, 2002).

Applications to ultrafiltration (Derradji et al., 2000), ultrafloculation and turbulent microflotation (Rulyov, 1999) show that the use of static mixers leads to manifest process improvements.

Darko et al. (2004) evaluated the influence of static turbulence promoter on permeate flux during skim milk cross-flow microfiltration and the potential application of this arrangement for an industrial development. The insertion of the static mixer caused improvement of permeate flux of more than 700% at the same feed flow rate, and additionally reduced the energy consumption for more than 80%.

Static mixers are also applicable for the separation of particles from gases. The dust and volatile solids content of hot industrial gases often causes difficulties in pipeline orientation due to deposition.

Ujhidy et al. (2001) described a new gas purification method and equipment, based on experimental work, using a static mixer.

Application of static mixers for the production of powder coatings using a high-pressure spray process appears as an alternative to the conventional extrusion technique to produce coatings with improved properties. The components of a powder coating mixture are melted in
separated tanks and are dosed to a static mixer by means of high-pressure pumps. In the static mixer the melts are homogenized and simultaneously compressed carbon dioxide is dissolved (Weidner et al., 2001).

Finally, Khinast et al. (2003) suggest the wall-coated tubular reactor inserted with static mixers as a new tool for reaction engineering, e.g., to replace catalyst-pellet-filled tubes in multi-tubular reactors to suppress hot-spot formation. These authors demonstrated through carbon monoxide oxidation that radial mass transfer is significantly enhanced using static mixers. Experiments were conducted at various flow rates, carbon monoxide concentrations and temperatures, with higher yields than the obtained for an empty tube under limited mass-transfer conditions.

2.4 CFD Simulations

Numerical simulation is nowadays a valuable tool for research in static mixers since experiments can hardly provide precise and versatile means of local measurements with such complex geometries as the ones provided by static mixers (Fradette et al., 1998). CFD simulations allow further insight into the hydrodynamics of static mixers at the design stage, since all the hydrodynamic variables are known at every instant and every point of the physical domain, ultimately reducing development costs.

Published works on the computational analysis of fluid flow and mixing process in static mixers use the decoupled CFD-mixing approach (Heniche et al., 2005). This approach is divided into two steps. The first step, related to CFD, consists in solving the Navier-Stokes equations to determine the flow velocity and pressure. The second step, related to quantifying mixing performance, uses tools from theories in the field of chaotic systems.

For chaotic systems, it is observed that the equations governing the hydrodynamics, i.e., the continuity and Navier-Stokes equations, present different solutions for very similar initial conditions, and this characteristic is a signature and a major criterion to classify a system as chaotic. In spite of the fact that most time dependent flows are in general chaotic, the term chaotic flow has been generally used to address those dynamic flows below the turbulent regime. The key contribution of chaos theory is thus providing tools to infer the inner workings of systems that on the first step of the decoupled CFD-mixing approach appear inaccessible (Doherty and Ottino, 1988).
For the study of mixing using CFD simulations, different tools arising from the development of the lamellar model (Ottino et al., 1979; Ranz, 1979) and from chaos theory (Doherty and Ottino, 1988) have been used, namely:

- particle tracking (Mickaily-Huber et al., 1996; Avalosse and Crochet, 1997; Hobbs and Muzzio, 1997; Hobbs and Muzzio, 1998; Byrde and Sawley, 1999b; Byrde and Sawley, 1999a; Visser et al., 1999; Fourcade et al., 2001b; Zalc et al., 2002; Szalai and Muzzio, 2003; Heniche et al., 2005);

- stretching of fluid elements (Khakhar and Ottino, 1987; Hobbs and Muzzio, 1998; Heniche et al., 2005);

- striation thickness (Hobbs and Muzzio, 1998; Fourcade et al., 2001b);

- shear rate field (Fradette et al., 1998; Rauline et al., 2000; Heniche et al., 2005);

- Lyapunov exponents (Hobbs and Muzzio, 1997; Rauline et al., 2000; Heniche et al., 2005);

- Poincaré maps (Khakhar and Ottino, 1987; Ling and Zhang, 1995; Mickaily-Huber et al., 1996; Hobbs and Muzzio, 1997; Visser et al., 1999; Heniche et al., 2005).

Most relevant works for CFD simulation of flow and mixing applied to static mixers are pointed out next.

- Arimond and Erwin (1985a) and Arimond and Erwin (1985b) were among the first to study mixing properties of the Kenics® static mixer by CFD techniques. The mixing of two similar fluids that differed only in colour (black and white) was simulated. Results were found to be in good agreement with a comparable experiment.

- Dackson and Nauman (1987), Khakhar et al. (1987), Ling (1993) and Bakker and LaRoche (1993) made computational investigations of a Kenics® static mixer and obtained analytical solutions for the decoupled fully developed axial and cross-sectional flow, neglecting element-to-element transitions effects.

- Lang et al. (1995) have numerically simulated the fluid flow in a SMV® static mixer to analyse and gain further insight into the character of the mixing process. Simulation
results were compared with experimental data to check the ability of the CFD simulation as a tool for the design and development process of static mixers.

- Ling and Zhang (1995) analysed mixing in a Kenics® static mixer for various combinations of twist angle per element and aspect ratio of a mixing element from CFD simulations. An optimal design of the static mixer element is suggested, which enables producing high mixing efficiency with minimum pressure drop. Good agreement between simulation of some mixing processes and existing experiments is reported.

- Mickaily-Huber et al. (1996) focused the numerical simulations on the flow characteristics and mixing induced by a SMRX® static mixer. It was found that the pressure drop increases linearly with the velocity and with the strips crossing angle. Analysis of pressure drop results, particle tracking and intensity of segregation further suggested that and SMRX® static mixer with the strips forming a 90° crossing angle provides maximum mixing efficiency.

- Avalosse and Crochet (1997) performed 3D CFD flow calculations in a Kenics® static mixer. To assess the accuracy of the calculations, photographs of cross-sections in an experimental Kenics® static mixer device were compared with computed concentration maps.

- Hobbs and Muzzio (1997) and Hobbs and Muzzio (1998) investigated numerically a Kenics® static mixer 3D static mixer to characterise mixing. Particle tracking simulations were used to compute residence time distributions, striation evaluation and variation coefficient as a function of the number of mixer elements. Simulation results were compared with experimental data from the literature indicating that the simulation technique used accurately represented the physical system.

- Hobbs et al. (1998) obtained the fully 3D velocity field for a Kenics® static mixer under laminar flow conditions using a commercial CFD software. In order to assess the validity of the simulation results, a comparison between the simulated pressure field and available correlations for pressure drop was made. Cross-sectional profiles of the magnitude of the rate-of-strain tensor, elongation velocity and shear velocity were calculated from the CFD simulation results for the velocity field.

- Rauline et al. (1998) compared the performance of six static mixer (Kenics®, Inliner®,
LPD®, Cleveland®, SMX® and ISG® static mixers) using 3D CFD simulations in laminar creeping flow regime. Computed pressure drops were found in overall good agreement with experimental data. Based on the extensional efficiency, stretching, mean shear rate and intensity of segregation, the Kenics®, Inliner®, LPD® and Cleveland® static mixers are reported as very similar. Both the SMX® and the ISG® static mixers are considered efficient, but the pressure drop for the ISG® static mixer is reported as excessively high.

- Fradette et al. (1998) performed CFD simulations aiming to understand the flow pattern of both Newtonian and non-Newtonian fluids through a SMX® static mixer. Pressure drop from the simulations and experimental measurements was compared and presented good agreement, showing that CFD simulations can properly represent the complex velocity field generated by the static mixer. Simulations further provided otherwise inaccessible information used to trace back the energy levels at various points of the SMX® static mixer.

- Visser et al. (1999) applied CFD to calculate flow velocities, pressure drops, residence time distributions and heat transfer in a 3D model of a SMX® static mixer for both Newtonian and non-Newtonian fluids. The energy equation was uncoupled from the Navier-Stokes equations by applying a temperature independent viscosity. After obtaining the velocity fields, the temperature fields were calculated straightforwardly. Calculated variables were reported in good agreement with experimental values from literature.

- Byrde and Sawley (1999a) and Byrde and Sawley (1999b) computed the flow field in a Kenics® static mixer with a CFD code. The effect of the mixing elements twist angle on the effectiveness of mixing was evaluated employing a Lagrangian approach involving particle tracking. The flow computation was performed using a conventional Eulerian approach to solve the Reynolds-averaged Navier-Stockes equations.

- Rauline et al. (2000) compared the performance of the Kenics® and the SMX® static mixers in laminar creeping flow regime using 3D CFD simulations. Several criteria were chosen as the basis for the performance evaluation: pressure drop; mixer length; Lyapunov exponent; mean shear rate; and intensity of segregation. The SMX® mixer was found more efficient than the Kenics® mixer to achieve a difficult mixing task or when installation space is restricted.
• Fourcade et al. (2001b) performed CFD calculations on both Kenics® and SMX® static mixers. The velocity field was computed using a commercial CFD code and the shape of the developing striations is inferred using a particle tracking procedure to the CFD flow field obtained. A good agreement between numerical and measured pressure drops was obtained validating the CFD modelling. Laser Induced Fluorescence (LIF) was used to further validate the CFD computations. Good agreement was found between model results and LIF measurements, when visually compared the striation distribution patterns.

• Jones et al. (2002) used a CFD model to predict the turbulent flow in a Kenics® static mixer. The mean velocity contours, cross-flow velocity vectors and longitudinal velocity contours are presented to illustrate the complex mixing patterns that drive the mixing process in the Kenics® static mixer. In the absence of experimental measurements for turbulent flows in a Kenics® static mixer, the model was validated against experimental data of the turbulent flow in a pipe bend, showing excellent agreement.

• Zalc et al. (2002) assessed flow and mixing in a SMX® static mixer at low and moderate Reynolds numbers using a CFD solver which solves the fully-coupled mass and momentum equations. Mixing performance is evaluated by using Lagrangian particle tracking methods to examine the evolution of mixing patterns of two streams with similar physical properties and flow rates. Simulated pressure drop was found to closely agree with experimental data from literature. Excellent agreement was obtained between computed and experimental mixing rates.

• Szalai and Muzzio (2003) established a detailed analysis of flow and mixing in the Kenics® static mixer using CFD. The effects of nine variations in geometry (including the standard design) and six flow conditions were considered. Mixing intensity was found not to depend monotonically on geometry and flow rate, highlighting the value of effective CFD simulations rather than correlation-based methods.

• van Wageningen et al. (2004) investigated the flow in the Kenics® static mixer using two different CFD methods. The CFD results were validated by experiments Laser Doppler Anemometry (LDA). For both methods, the simulated velocity profiles and power spectra are reported in good agreement with the LDA data. The pressure drop calculations were also found in good agreement with correlations and experimental
data in the literature.

- Heniche et al. (2005) used 3D high-resolution CFD simulations to compare the mixing performance of the KM® and SMX® static mixers. Several criteria were retained to compare both static mixers: pressure drop; stream function; mean share rate; stretching efficiency; Lyapunov exponent; intensity of segregation; stretching of trajectories; and residence time. Analysis of flow pattern and mixing parameters showed that the KM® static mixer provides a higher mixing rate than the SMX® static mixer at the expense of a slightly higher pressure drop.

### 2.5 Experimental Studies

One of the main characteristics of static mixers is the combination of low pressure drop and efficient mixing (Heniche et al., 2005). Pressure drop is an important parameter common to all applications of static mixers since it governs the mixing energy costs. Works reporting pressure drop data across static mixers are referenced in Section 2.5.1.

Pressure drop is not a measure of mixing. However, evaluation of mixing is crucial for the design of a static mixer and for the assessment of process enhancements introduced by its presence. A common method for the quantification of mixing is the measurement of the product distribution of test reactions. Section 2.5.2.1 presents a short discussion on reaction schemes of interest. A comprehensive review on mixing and selectivity of chemical reactions can be found in Bourne (2003). Published works on micromixing studies in static mixers using test reactions are presented in Section 2.5.2.2.

Micromixing studies lack the insight into the mixing mechanisms of the static mixers. Experimental works using LIF as a tool for studying mixing in static mixers are reviewed in Section 2.5.3. In Section 2.5.4 are reported the works using LDA for locally resolved measurements of the velocity in static mixers.

#### 2.5.1 Pressure Drop

Pressure drop measurements in static mixers are necessary for the establishment of mixing energy consumption as well as for objective comparisons of the performance of different static mixers. Further, experimental results for pressure drop are commonly used for the validation of CFD simulations.
A common approach when considering the pressure drop across static mixers is to report the dimensionless ratio between the pressure drop across the static mixer and the pressure drop on an empty tube of equal length and diameter. This ratio, denoted as the \( Z \) factor, is given by

\[
Z = \frac{\Delta p_{\text{static mixer}}}{\Delta p_{\text{empty tube}}}
\]

(2.1)

where \( \Delta p_{\text{static mixer}} \) is the pressure drop across the static mixer and \( \Delta p_{\text{empty tube}} \) is the pressure drop in an empty tube of equal length. \( Z \) factor values are directly related to the increase in energy costs when static mixers are installed in a continuous-flow process.

Published works providing correlations of the \( Z \) factor for several commercial designs of static mixers are next reviewed.

- For the SMX\textsuperscript{®} static mixer, most \( Z \) factor values available in the literature apply only to cases in which the Reynolds number is \( Re \leq 10 \). Pahl and Muschelknautz (1982) reported \( Z \) factor values ranging from \( Z = 10 \) to \( Z = 60 \), whereas Alloca (1982) reported that \( Z = 38.7 \) for slow flows. Cybulski and Werner (1986) indicated \( Z \) factor values between \( Z = 10 \) and \( Z = 100 \) and Streiff et al. (1999) reported \( Z = 37.5 \).

- For the SMV\textsuperscript{®} static mixer, Cybulski and Werner (1986) found values of the \( Z \) factor in laminar flow between \( Z = 60 \) and \( Z = 300 \), and Streiff et al. (1999) estimated the \( Z \) factor to be between \( Z = 100 \) and \( Z = 200 \).

- Literature studies for the KM\textsuperscript{®} static mixer are widely available. Grace (1971) found the \( Z \) factor to be a function of the Reynolds number in the KM\textsuperscript{®} static mixer as

\[
Z = 3.24\left(1.5 + 0.21\sqrt{Re}\right)
\]

(2.2)

Bor (1971), Chen (1973) and Pahl and Muschelknautz (1982) have also estimated \( Z \) factor values in the range \( Z = 5 \) and \( Z = 8 \) for the KM\textsuperscript{®} static mixer in laminar regime.

Wilkinson and Cliff (1977) have correlated the \( Z \) factor for the KM\textsuperscript{®} static mixer with the Reynolds number as

\[
Z = 7.19 + \frac{Re}{32}
\]

(2.3)
A summary of several correlations of the $Z$ factor for KM® static mixers is also available in Heywood et al. (1984).


$$Z = a' + b' \text{Re}^{m'}$$  \hspace{1cm} (2.4)

where $a'$, $b'$ and $m'$ are reported parameters.

- The LPD®, Inliner® and ISG® static mixers have been less studied. Heywood et al. (1984) reported $Z$ factor values of approximately $Z = 6$ for the LPD® static mixer and $Z = 284$ for the ISG® static mixer elements. Pahl and Muschelknautz (1982) reported $Z$ factor values of $Z = 9$ for the Inliner® static mixer and $Z$ values in the range of $Z = 250$ to $Z = 300$ for the ISG® static mixer elements.

2.5.2 Micromixing Studies

Measurement of mixing is crucial for reactor design and for the assessment of any changes on a reactor. *Test reactions* whose *product distribution* is a signature of mixing quality have been known and developed for more than 40 years. Test reactions are used to generate experimental data and to assess the validity of models for product distribution of fast mixing-sensitive reactions and the suitability of various reactors for carrying out such reactions. In Section 2.5.2.1, a short review on test reactions is done. Works using the product distribution of test reactions for the quantification of micromixing in static mixers are reviewed in Section 2.5.2.2.

2.5.2.1 Test Reactions

One of the first problems in the study of mixing was its quantification. Danckwerts (1952) introduced a couple of concepts related to mixing efficiency: the *scale of segregation* and the *intensity of segregation*. The scale of segregation gives a measure of the mixing texture, quantifies the fluid’s homogeneity or graininess, and the intensity of segregation gives a measure of the deviation from the mean of the concentration of a chemical species in the clumps of fluid. The value of intensity of segregation varies from zero in the case of complete
homogenisation at the molecular level, that is complete micromixing, to one in the case of complete segregation.

Danckwerts (1952) and Danckwerts (1958) suggested the use of a second order chemical reaction to quantify the intensity of segregation. Zwietering (1959) have shown that mixing has an important effect on chemical reaction. Toor (1962), Keeler et al. (1965), Vassillatos and Toor (1965), Kattan and Adler (1967) and Weinstein and Adler (1967) among others, later published experimental and theoretical work in this area with a primary focus on the study of micromixing.

Weinstein and Adler (1967) experimentally studied the influence of mixing in continuous chemical reactors, using single first-order and second-order reactions, consecutive second-order reactions and consecutive competitive second-order reactions, concluding that although single reactions are strongly dependent on macromixing they are almost insensitive to micromixing, whereas simultaneous reactions are both macromixing and micromixing sensitive. Although segregation could retard single reactions, this is easily compensated by expanding the reactor size. For consecutive reactions different product distribution occurs depending on mixing, and this cannot be compensated by increasing the reactor volume (Bourne, 1983).

Other experimental studies on the chemical and physical aspects of mixing-sensitive reactions in stirred tank reactors and tubular reactors have been published (e.g. Rice et al., 1964; Mao and Toor, 1971; Klein et al., 1980; Bourne et al., 1981b; Li and Toor, 1986).

Fast multiple reactions were found to offer the best way to investigate mixing. For slow reactions, the mixing has no effect on the final product. Fast reactions, however, can be influenced by both the micromixing and macromixing.

Four different reaction schemes have been broadly used to assess mixing with chemical reactions:

- The first reaction scheme uses consecutive competitive second-order reactions, and may be written as

  \[ A + B \xrightarrow{k_1} R \]  
  \[ R + B \xrightarrow{k_2} S \]  

  (very fast)  
  (fast)  

\[
\text{(2.5)}
\]
The product distribution is denoted by $X_S$, which is the selectivity in $S$,

$$X_S = \frac{2C_S}{C_R + 2C_S} \quad (2.6)$$

where $C_R$ and $C_S$ are the product concentrations after reaction.

The minimum selectivity in $S$ for these reactions is obtained when the contact of $A$ and $B$ at the molecular level scale is done before significant reaction occurs. However, if micromixing is slower, there is a boundary between $A$ and $B$ and the formed product $R$ quickly reacts with high concentration of $B$ to form product $S$, causing the selectivity in $S$ to tend to unity (Bourne, 1982).

Several studies on specific reactions of this type have been suggested in literature, including:

- $L$-tyrosine and iodine (Paul and Treybal, 1971);

- $p$-cresol and iodine (Truong and Methot, 1976);

- glycol diacetate and hidrozone ion (Truong and Methot, 1976);

- 1,3,5-trimthoxybenzene and bromium (Bourne and Kozicki, 1977);

- resorcinol and bromium (Bourne et al., 1977b);

- $m$-xylene and $p$-xylene, mesitylene, prehnitene and nitronium ion (Truong and Methot, 1976);

- 1-naphtol-6-sulfonic acid and phenylidazonium ion (Bourne et al., 1977a);

- 1-naphtol and diazotised sulphanilic acid (Bourne et al., 1981b).

This last reaction is the most well known and has received the most attention in both theoretical and experimental works.
• A second reaction scheme was proposed by Bourne et al. (1992a), the azo couplings between 1-naphthol and 2-naphthol with diazotised sulphanilic acid, described as

\[
\begin{align*}
A + B & \rightarrow R \quad (\text{very fast}) \\
R + B & \rightarrow S \quad (\text{fast}) \\
AA + B & \rightarrow Q \quad (\text{fast})
\end{align*}
\]  

By including reactant AA, this reaction scheme is much faster than the scheme where only reactant A is included (Bourne, 2003), presenting higher mixing sensibility. The product distribution is represented by the selectivity in S, \( X_S \), in the form

\[
X_S = \frac{2C_S}{C_R + 2C_S + C_Q}
\]  

where \( C_R, C_S \) and \( C_Q \) are the product concentrations after reaction.

• The third reaction scheme uses parallel competitive second-order reactions, which can also be subjected to mixing effects, as shown by Baldyga and Bourne (1990), Paul et al. (1992) and Wang and Mann (1992). Many variations are proposed, but the basic reaction scheme is as follows

\[
\begin{align*}
A + B & \rightarrow R \quad (\text{very fast}) \\
C + B & \rightarrow S \quad (\text{fast})
\end{align*}
\]  

The product distribution is given by the selectivity in S, \( X_S \), defined as

\[
X_S = \frac{C_S}{C_R + C_S}
\]  

where \( C_R \) and \( C_S \) are the product concentrations after reaction.

If micromixing is instantaneous, reactant \( B \) is completely consumed in the first reaction, which is much faster than the second reaction and thus only minimum quantities of \( S \) are formed. Conversely, if micromixing is slow, reactant \( B \) is consumed in the ratio of concentrations of \( A \) and \( C \) present in the medium (Villermaux et al., 1994).
Experimentally the following reaction schemes have been used:

- precipitation of ferric hydroxide and alkaline hydrolysis of monochloroacetate ester (Baldyga and Bourne, 1990);

- neutralisation of monochloroacetic acid and alkaline hydrolysis of monochloroacetate ester (Bourne and Yu, 1994);

- neutralisation of boric acid and iodate-iodide reaction (Villermaux et al., 1994; Fournier et al., 1996; Guichardon and Falk, 2000);

- precipitation of cupric hydroxide and alkaline hydrolysis of monochloroacetate ester (Brucato et al., 2000);

- precipitation of cupric hydroxide and alkaline hydrolysis of \( \gamma \)-butyrolactone (Zhao et al., 2002).

- The fourth reaction scheme used in mixing studies consists of triplet consecutive competitive second-order reactions (Bourne and Yu, 1994; El-Hamouz and Mann, 1998)

\[
\begin{align*}
A + B & \rightarrow R \quad \text{(very fast)} \\
R + B & \rightarrow S \quad \text{(fast)} \\
S + B & \rightarrow T \quad \text{(fast)}
\end{align*}
\]

(2.11)

The product distribution is expressed by the selectivity in \( S \), \( X_s \),

\[
X_s = \frac{2C_s}{C_R + 2C_s + 3C_T}
\]

(2.12)

where \( C_R \), \( C_s \) and \( C_T \) are the product concentrations after reaction (El-Hamouz and Mann, 1998).

Such reaction scheme presents, in contrast with the consecutive competitive second-order reaction scheme, an additional degree of freedom in the reaction selectivity, giving rise to three products \( R \), \( S \) and \( T \). The formation of product \( R \) is improved yield perfect mixing conditions, while product \( T \) is always favoured by segregation. The selectivity in \( S \) is favoured for initial conditions of complete
segregation for A and B whereby the reaction proceeds by micromixing (El-Hamouz and Mann, 1998).

2.5.2.2 Product Distribution from Test Reactions

Static mixers develop high rates of energy dissipation and have short residence times, which are useful characteristics for reactions needing fast mixing to obtain high selectivity (Bourne et al., 1992b). However, hardly any published literature exists on experimental studies of micromixing in static mixers:

- Meyer et al. (1988) assessed micromixing in a static mixer and in an empty tube using a modification of the precipitation of barium sulphate (Pohorecki and Baladyga, 1988) by characterising the product distribution of barium sulphate EDTA complex in alkaline medium under the influence of an acid. Experiments were carried out in the range of Reynolds numbers $0.4 < Re < 300$ by varying the fluid viscosity and the flow rate.

- Bourne and Maire (1991) determined the mixing intensity of three static mixers, differing mainly in the width of their channels, by applying the engulfment model (Baladyga and Bourne, 1989a; Baladyga and Bourne, 1989b) to the measured product distribution of fast consecutive competitive azo coupling between 1-naphthol and diazotized sulphanilic acid (Bourne et al., 1981b).

- Bourne et al. (1992b) and Baladyga et al. (1997) further extended the study of Bourne and Maire (1991) and applied azo couplings between 1-naphthol and 2-naphthol with diazotised sulphanilic acid to the SMX® and SMXL® static mixers. Comparable results with the studies of Bourne and Maire (1991) were reported. The more open structure of the SMXL® static mixer was found more attractive for fast reactions where high selectivity calls for rapid mixing.

- Fang and Lee (2001) quantitatively measured the micromixing efficiency of the Kenics® static mixer at Reynolds number ranging from $Re = 66$ to $Re = 1066$ on the basis of the reaction scheme proposed by Villermaux et al. (1994), Fournier et al. (1996) and Guichardon and Falk (2000). The static mixer was found to enhance micromixing efficiency in the range of Reynolds numbers studied in comparison with that in an empty tube. Results further revealed that the Kenics® static mixer could yield better degree of micromixing than a CSTR.
2.5.3 Visualisation with LIF

Imaging of the flow field always allows a greater insight into the development of flow and mixing. LIF (Laser Induced Fluorescence) allows the imaging of flow patterns at a given plane by lighting it with a laser sheet. Structures revealed with this technique can be readily compared with patterns identified by particle tracking in computational flow fields. In addition, the intensity of emitted light can be correlated to the dye concentration in each region of the static mixer to quantify mixing (e.g. Arcoumanis et al., 1990; Unger and Muzzio, 1999). Only a few works can be found in the literature, as it is presented next.

- Jaffer and Wood (1998) studied the laminar flow field in Plexiglas® Kenics® static mixers using LIF and digital image analysis. Information about striation widths in an assembly of number average striation thickness, variance of striation widths and interfacial area was obtained to quantify mixing in elements of length to diameter ratios of 0.8, 1.0 and 1.5.

- Karoui et al. (1998) applied LIF to measure local concentrations at the outlet of different configurations of SMV® static mixers placed in a tube. Results show that the number of elements, their position and the ratio between the velocities of the two compounds on the mixing have influence on the quality of mixing.

- Fourcade et al. (2001b) conducted LIF experiments for Kenics® and SMX® static mixers, using dye rhodamine WT as tracer. Measured striations were compared with calculated striations to validate CFD modelling. A Spectra-Physics® 5W (Ar+) laser was employed as the light source. LIF images were captured downstream the static mixers.

- Ventresca et al. (2002) investigated the mixing efficiency of the SMX® static mixer as a function of the viscosity ratio and Reynolds number of two miscible liquid streams using LIF and image analysis. Two aqueous solutions of carboxymethylcellulose were separately injected in the static mixer, one of them containing a small amount of rhodamine 6G, homogenously mixed with it. Transverse cross-sections were illuminated with frequency-doubled Nd:YAG 532 nm laser light and the resulting fluorescence was captured with a 1024(H)×1024(V) pixels CCD camera (Kodak® ES 1.0). LIF images were acquired at two different positions: as close as
possible to the static mixer exit and at two diameters downstream from the static mixer. The mixing quality downstream the static mixers was evaluated using the coefficient of variation (COV) values.

- Wadley and Dawson (2005) studied the performance of the Kenics®, HEV®, and SMV® static mixers, using a LIF technique. A rhodamine WT solution was injected upstream of the static mixers and a laser sheet was shone through a transparent pipe section downstream from the static mixers. Sequences of 150 images of the dye fluorescing in the laser light were captured with a 640 (H) × 480 (V) pixels CCD camera (Pulnix® TM6701AN) at 25 frames over a 6 s time period. Time-averaged COV values were used to quantify mixing quality downstream the static mixers. Results were compared with the correlations for the mixture quality supplied by Sulzer Chemtech, Ltd. and Chemineer, Inc.

2.5.4 LDA Measurements

LIF measurements allow the understanding of mixing mechanisms but they lack the quantification of hydrodynamic variables. LDA is a non-invasive technique used to measure velocity components at single locations. Experimental studies of flow fields in static mixers using LDA (Laser Doppler Anemometry) are following listed.

- Barrué et al. (2001) measured velocities and root mean square velocities in the Oxyantor® gas-gas static mixer and the KMA® and SMI® static mixers using LDA. LDA requires particles that can scatter the incident light. The injected gas flow was seeded with paraffin oil droplets having a mean diameter of 3.5 μm. For the Oxyantor® static mixer, LDA measurements were carried out on three half axes located at 10 mm, 20 mm and 500 mm downstream the static mixer. For the KMA® and SMI® static mixers, the flow was only characterised at the outlet of the static mixers at a distance downstream of 500 mm. LDA measurements inside the KMA® and SMI® static mixers were not possible since their stainless walls do not permit laser penetration.

- van Wageningen et al. (2004) made LDA experiments in a Kenics® static mixer at Reynolds number ranging from $Re = 20$ to $Re = 500$ for the characterisation of the dynamic behaviour of the flow. The measurement section was made optically
accessible by a Plexiglas® tube and was surrounded by a square box with glass windows in it to reduce refraction. A dual-beam 4W (Ar+) laser was used and the light transmitted by a 2D probe in back-scatter mode allowing simultaneous measurements of both axial and tangential velocity components. The velocity components were measured by detecting the back-scattered light of glass hollow spheres (neutrally buoyant and with a diameter in the order of 10 µm) added to the flow.

2.6 Conclusions

Static mixers have offered new solutions to a variety of mixing problems. A wide range of applications is claimed by the manufacturers and this seems to be confirmed by the large number of published literature on this subject. Traditional mixing applications such as pre-reactor mixing and water treatment can be accomplished more easily. Static mixers used as cocurrent contactors can streamline absorption and extraction. Viscous mixing operations can be improved with static mixers, particularly plug flow reactions and heat transfer enhancement applications. Static mixers further offer strong potential in the area of reaction technology.

Commercially available static mixers have been produced based on the principle of manipulating flow fields by a series of cleverly designed metal baffles. These baffles consist of twists of metal, corrugated plates, parallel bars or small diameter channels. However, from the chemical engineering point of view the existing literature on static mixers is very poor. The only quantitative calculations that can be performed relate to pressure drop and energy requirements. There seems to be no prompt way of estimating the mixture quality for most static mixers and it follows that quantitative comparisons of the various available commercial designs is still somehow difficult.

Computational fluid dynamics has become an essential tool in the analysis of static mixer performance, since experiments cannot provide the precise local measurements needed to understand the effects of complex designs.

Although static mixer technology is continually evolving, there is still substantial room for improvements both in the mixing characterisation and in the physical designs, making it possible to achieve a range of new applications beyond those traditionally associated with static mixers.
3. NETMIX® MODEL

3.1 Introduction

The importance of mixing can hardly be exaggerated. Mixing is at the heart of many operations in the chemical, petrochemical and pharmaceutical process industries and is often accompanied by chemical reactions whose outcome depends strongly upon the efficiency of the mixing process (Villermaux and Falk, 1996; Zalc and Muzzio, 1999). Therefore, a computationally efficient mathematical model capable of predicting mixing and chemical reaction is clearly desirable for the design of process equipment such as static mixers (Mehta and Tarbell, 1983).

The purpose of the present work is the development of a mixing and chemical reaction model, the NETMIX® (Network Mixing) model, using a combined network model and networks-of-zones model formulation, capable of coupling macromixing and micromixing and of calculating the yield and selectivity for various types of reaction schemes, namely: first-order reaction, second-order reaction and consecutive competitive second-order reactions.

Network models have been widely adopted as a basis for describing the void structure and transport properties of porous media for over 40 years. A network model is intuitively desirable, since it avoids a detailed geometric description of the void space in favour of an idealised description.
The concept that fluid paths in a porous medium may split and, later on, join other paths, has prompted most authors to think of a network model of pore space in which the branches represent the pore throats or the narrow channels that connect the nodes that represent the pore bodies. Many authors ignore nodes and assign them no volume, although there have been several papers in which this assumption has been relaxed (Ioannidis and Chatzis, 1993; Thauvin and Mohanty, 1998; Wang et al., 1999), and currently it is even considered that most of the void space of a porous medium is associated not with the network branches but with the nodes (Berkowitz and Ewing, 1998).

One of the earliest attempts of using network models to model flow through a porous medium was the work of Fatt (1956). Network models were later used to predict the macroscopic transport and capillary equilibrium properties of porous media, for example: simulation of mercury intrusion porosimetry curves of sandstones (e.g. Chatzis and Dullien, 1977; Conner et al., 1983; Lapidus et al., 1985; Tsakiroglou and Payatakes, 1990; Mata et al., 2001); prediction of air-mercury and oil-water drainage capillary curves (e.g. Chatzis and Dullien, 1985; Diaz et al., 1987) and relative permeability curves of sandstones (e.g. Kantzas and Chatzis, 1988); and study of two-phase flow immiscible displacement at finite capillary numbers (e.g. Koplik and Lasseter, 1985; Dias and Payatakes, 1986; Lenormand et al., 1988; Blunt and King, 1990; Constantinides and Payatakes, 1996). Saffman (1959) and Avilés and LeVan (1991) among others, have also considered network models to describe flow with dispersion in porous media in the absence of adsorption. Meyers and Liapis (1998) and Liapis et al. (1999), for example, used network models to describe quantitatively the mass transfer and sorption mechanisms occurring in porous adsorbent particles and monoliths packed columns.

Research on mixing in stirred vessel reactors conducted to the development of the networks-of-zones model, based on a network of perfectly mixed interconnected zones. Its application includes: description of mixing in fixed beds of spheres (e.g. Deans and Lapidus, 1960) and fixed bed reactors (e.g. Schnitzlein and Hofmann, 1987); tracer dispersion and mixing in stirred reactors (e.g. Khang and Levenspiel, 1976; Mann and Knysh, 1984); and gas dispersion in stirred gas-liquid reactors (e.g. Mann, 1986). Recent works have further adopted the networks-of-zones model as a basis to study gas-liquid bioreactors (e.g. Zahradník et al., 2001) and multiple-impeller operation (e.g. Brucato et al., 1991) and to predict the semi-batch selectivity in products for multiple reactions (e.g. Wang and Mann, 1992; Rahimi and Mann, 2001).
This chapter is organised as follows. The description of the model used to generate the network structure and to simulate the flow field is given in Section 3.2. In Section 3.3 are detailed the governing equations used for micromixing and chemical reaction modelling. Simulation results are shown and discussed in Section 3.4, and concluding remarks are presented in Section 3.5.

3.2 Macromixing Modelling

In the NETMIX® model a network structure determines the overall flow patterns and thus the distribution of residence times, i.e., macromixing. In this section the network structure is described as well as the methodology for determining the hydrodynamics inside the generated network.

3.2.1 Network Structure

The NETMIX® model consists of a network structure that combines in an organised manner two different types of elements – chambers and channels. The 2D arrangement of the basic elements that constitute the network is presented in Section 3.2.1.1, and its design parameters computation is assessed in Section 3.2.1.2. The 2D network spatial arrangement is subjected to some physical restrictions that are described in Section 3.2.1.3. Finally, Section 3.2.1.4 includes a brief description of the network construction numerical implementation.

3.2.1.1 Construction of the Network

The network is generated by repetition of a unit cell, composed of one chamber and three channels, as shown in Figure 3.1. The direction of the flow is assumed to be in the x-axis. According to the set coordinate system, the channels normal to the x-axis are denoted horizontal channels (HC), while the remaining channels, forming an angle $\phi$ with the x-axis, are denoted oblique channels (OC). Each chamber is modelled as a sphere with diameter $D_j$ and each channel is modelled as a cylinder with diameter $d_i$ and length $l_i$. 
Unit cells are repeated and connected through both the horizontal and the oblique channels by fixing the distance between the centres of obliquely interconnected chambers, $L'$, as shown in Figure 3.2.

The network size is specified by the number of unit cells in the $x$ and $y$ directions, i.e. the number of rows and number of columns, $n_x$ and $n_y$, respectively. Adding exit channels to the last row of chambers completes the two-dimensional network generation (see Figure 3.2).

Figure 3.3 shows various representations of a $n_x = 5$ by $n_y = 4$ network. The model includes the possibility of generating networks with horizontal channels, Figure 3.3a and Figure 3.3b, and without horizontal channels, Figure 3.3c and Figure 3.3d. It is also possible to simulate two different types of boundary conditions: periodic boundary conditions (PBC) to simulate a fraction of an infinitely large network, shown in Figure 3.3a and Figure 3.3c, where the boundary channels are considered directly connected to the respective chambers on the network opposite side; and non-periodic boundary conditions (NPBC), simulating a finite
network, shown in Figure 3.3b and Figure 3.3d, and obtained by removing the boundary channels on both sides of the network.

![Diagram of network types](image)

*Figure 3.3 Network types: (a) PBC with HC; (b) NPBC with HC; (c) PBC without HC; (d) NPBC without HC. Examples for $n_x = 5$ and $n_y = 4$."

The model further includes the possibility of generating *regular networks* where both the channel and chamber diameters are constant, or *random sized networks*, where both the channel and chamber diameters vary randomly (see Figure 3.4). The average values for the channels and chambers diameters are represented as $d$ and $D$, respectively.

![Diagram of NPBC networks](image)

*Figure 3.4 NPBC without HC network: (a) regular; (b) random sized. Examples for $n_x = 5$ and $n_y = 4$."

With respect to the network structure the model furthermore includes the additional possibility of removing chambers and or channels in a random or specified manner and thus encompassing the adjustment to different specific situations.

3.2.1.2 Network Parameterisation

The first step in the network parameterisation is the computation of the total number of chambers. Given the number of rows, \( n_x \), and the number of columns, \( n_y \), the number of chambers is given by

\[
n_{\text{chambers}} = n_x n_y \tag{3.1}
\]

regardless of the network type selected, considering no chambers are removed.

The number of HC, \( n_{\text{channels}}^h \), and the number of OC, \( n_{\text{channels}}^o \), depend on the type of network selected, and can be calculated according to Table 3.1, considering no channels are removed.

<table>
<thead>
<tr>
<th>Table 3.1</th>
<th>Number of network channels.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Network Type</td>
<td>( n_{\text{channels}}^h )</td>
</tr>
<tr>
<td>PBC with HC</td>
<td>( n_x n_y )</td>
</tr>
<tr>
<td>PBC without HC</td>
<td>0</td>
</tr>
<tr>
<td>NPBC with HC</td>
<td>( n_x(n_y - 1) )</td>
</tr>
<tr>
<td>NPBC without HC</td>
<td>0</td>
</tr>
</tbody>
</table>

The total number of channels is then given by

\[
n_{\text{channels}} = n_{\text{channels}}^h + n_{\text{channels}}^o \tag{3.2}
\]

The connection of a channel, with diameter \( d_i \), to a chamber, with diameter \( D_j \), results in the formation of a calotte, as shown in Figure 3.5, with height

\[
h_y = \frac{D_j}{2} \left[ 1 - \sqrt{1 - \left( \frac{d_i}{D_j} \right)^2} \right] \tag{3.3}
\]
The number of calottes, $n_{\text{calottes}}$, in a network with $n_x$ rows and $n_y$ columns can be determined as listed in Table 3.2, considering no chamber and or channels are removed.

**Table 3.2  Number of network calottes.**

<table>
<thead>
<tr>
<th>Network Type</th>
<th>$n_{\text{calottes}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBC with HC</td>
<td>$6n_xn_y - 2n_x + 1$</td>
</tr>
<tr>
<td>PBC without HC</td>
<td>$4n_xn_y - n_x + 1$</td>
</tr>
<tr>
<td>NPBC with HC</td>
<td>$6n_xn_y - 4n_x$</td>
</tr>
<tr>
<td>NPBC without HC</td>
<td>$4n_xn_y - 2n_x$</td>
</tr>
</tbody>
</table>

As each calotte is shared by the channel and the chamber connected to it, in order to avoid the double quantification when determining the chambers and channels volumes, the calottes must be considered associated to a single type of element. In the present work, the calottes were considered an integrant part of the channels.

It is now possible to determine the channels lengths as follows. Since the distance between the centres of two obliquely neighbouring chambers is imposed constant and equal to $L'$, the length of the oblique channel $i$, $l'_i$, connecting chamber $j_i$ to chamber $j_z$, is given by

$$l'_i = L' - \frac{1}{2}(D_{j_i} + D_{j_z}) + (h_{j_i} + h_{j_z})$$  \hspace{1cm} (3.4)$$

where $D_{j_i}$ and $D_{j_z}$ are the chamber $j_i$ and chamber $j_z$ diameters, respectively, and $h_{j_i}$ and $h_{j_z}$ are the calottes heights resulting from the connections with channel $i$, determined by Equation 3.3.
Similarly, the length of the horizontal channel \( i \), \( l_i^h \), connecting two horizontally contiguous chambers \( j_i \) and \( j_2 \), is given by

\[
l_i^h = L^h - \frac{1}{2} \left( D_{j_i} + D_{j_2} \right) + \left( h_{j_i} + h_{j_2} \right)
\]  \( \text{(3.5)} \)

where \( L^h \) is the horizontal distance between both chambers centres

\[
L^h = 2L^v \sin \phi
\]  \( \text{(3.6)} \)

To complete the network geometric parameterisation process, it is at last required to determine the channels and chambers volumes. The volume of channel \( i \) is given by

\[
V_{\text{channel},i} = \frac{\pi}{4} d_i^2 l_i
\]  \( \text{(3.7)} \)

where \( d_i \) and \( l_i \) are its diameter and length, respectively. By considering that calottes are part of the channels, the volume of chamber \( j \) becomes

\[
V_{\text{chamber},j} = \frac{\pi}{6} D_{j}^3 - \frac{\pi}{3} \sum_k \left[ (h_{j,k})^2 (1.5 D_j + h_{j,k}) \right]
\]  \( \text{(3.8)} \)

where \( k \) is the number of channels connected to the chamber, and the \( h_{j,k} \) are the respective calottes associated to each channel \( i_k \).

From the parameters above described, the network volume, \( V_{\text{network}} \), may be calculated as

\[
V_{\text{network}} = \sum_{n_{\text{channels}}} V_{\text{chamber},j} + \sum_{n_{\text{channels}}} V_{\text{channel},i}
\]  \( \text{(3.9)} \)

The network length in the \( x \)-axis is obtained from geometrical considerations

\[
L_x = (n_x + 1)L^v \cos \phi
\]  \( \text{(3.10)} \)

and the network length in the \( y \)-axis is given accordingly to the network boundary conditions

\[
L_y = \begin{cases} (n_y + 0.5)L^h & \text{(PBC)} \\ (n_y - 0.5)L^h + 0.5 \left( D_{\text{max}}^{l_j} + D_{\text{max}}^{k_j} \right) & \text{(NPBC)} \end{cases}
\]  \( \text{(3.11)} \)

where \( D_{\text{max}}^{l_j} \) and \( D_{\text{max}}^{k_j} \) are the maximum diameters of the utmost left and utmost right chambers in the network, respectively.
3.2.1.3 Physical Restrictions

As in most geometric models, the NETMIX® model has inevitably associated restrictions in the values of its input parameters.

Physical Restrictions for Regular Networks

The spatial homogeneity of the regular networks allows the definition of general limiting values and limiting relationships, which require initial one-time validation, between the input geometric parameters $\phi$, $d$, $D$ and $L'$ (see Figure 3.1).

From the definition of $L'$, the distance between the centres of obliquely interconnected chambers, and imposing that the chambers do not intersect each other, a limiting relationship between $L'$ and $D$ results as

$$\frac{L'}{D} \geq 1 \quad (3.12)$$

An additional restriction imposes that the chamber diameter must be larger than the diameter of the channels connected to it, that is

$$\frac{d}{D} \leq 1 \quad (3.13)$$

However, this condition alone does not prevent channels to intersect at the chamber inlet, and thus a more restrictive relationship must be established between the values of $d$ and $D$. For a given angle $\phi$, the upper limiting relation between $d$ and $D$ depends on the existence or not of horizontal channels. For regular networks without HC, the limiting relationship is given by

$$\frac{d}{D} \leq \min\{\sin \phi, \cos \phi\} \quad (3.14)$$

while for the case of regular networks with HC, a more limiting relationship is obtained

$$\frac{d}{D} \leq \min\{\sin \phi, \sqrt{2(1 - \sin \phi)}\} \quad (3.15)$$

So far, the angle $\phi$ was considered as an independent input parameter, resulting in restrictive relationships between the remaining input parameters $d$, $D$ and $L'$. However $\phi$ is not totally
independent, that is it cannot take any given value due to the presence and geometry of the chambers.

Given \( d, D \) and \( L' \), the limiting values of \( \phi \) depend on the network type selected, i.e., on the existence or not of horizontal channels. For regular networks without HC it is further possible to distinguish two limit cases, as shown in Figure 3.6.

The values of \( \phi \) are upper limited by

\[
\phi_{\text{max}} = \frac{\pi}{2} - \arcsin \left( \frac{D}{2L'} \right) \tag{3.16}
\]

corresponding to the case where two vertically contiguous chambers contact (see Figure 3.6a), and lower limited by

\[
\phi_{\text{min}} = \arcsin \left( \frac{D}{2L'} \right) \tag{3.17}
\]

corresponding to the case where two horizontally contiguous chambers contact (see Figure 3.6b).

\[\text{(a)} \quad \text{(b)}\]

*Figure 3.6* Limiting values of angle \( \phi \) for networks without HC: (a) \( \phi_{\text{max}} \); (b) \( \phi_{\text{min}} \).

Examples for the NPBC regular network shown in Figure 3.3d.

Similarly, for regular networks with horizontal channels is possible to distinguish two limit cases, as shown in Figure 3.7. The values of \( \phi \) are here upper limited by

\[
\phi_{\text{max}} = \frac{\pi}{2} - \arcsin \left( \frac{D + d}{2L'} \right) \tag{3.18}
\]

corresponding to the case where chambers contact the horizontal channels, as shown in
Figure 3.7a, and lower limited by Equation 3.17, corresponding to the case to the case where two horizontally contiguous chambers contact, as shown Figure 3.7b.

\[ \text{Figure 3.7} \quad \text{Limiting values of angle } \phi \text{ for networks with HC: (a) } \phi_{\text{max}}, \text{ (b) } \phi_{\text{min}}. \text{ Examples for the NPBC regular network shown in Figure 3.3b.} \]

Physical Restrictions for Random Sized Networks

Contrary to regular networks, in random sized networks the limiting values and limiting relationships between the geometric parameters \( \phi \), \( d_i \), \( D_j \) and \( L^o \) are not global and must be locally verified for all network elements.

The first limiting relationship in the generation of random sized networks comes now from the condition that the diameter of any channel \( i \) must be smaller than the diameters of both chambers, \( j_i \) and \( j_2 \), connected to it, that is

\[
\frac{d_i}{\min\{D_{j_i}, D_{j_2}\}} \leq 1
\]  

(3.19)

Further, from the definition of \( L^o \), the distance between the centres of obliquely interconnected chambers \( j_i \) and \( j_2 \), and imposing that chambers do not intersect each other, a limiting relationship between \( L^o \), \( D_{j_i} \) and \( D_{j_2} \) results as

\[
\frac{2L^o}{D_{j_i} + D_{j_2}} \geq 1
\]  

(3.20)

Depending on the network type, i.e., the existence or not of horizontal channels, two types of elementary cells must be considered, as shown in Figure 3.8.
Figure 3.8 Elementary cells: (a) network with HC; (b) network without HC.

Similarly to the regular networks, the restriction that any chamber diameter must be larger than the diameter of the channels connected to it, is here applied as

\[
\frac{d_j}{D_j} \leq 1
\]  

(3.21)

However, now the restriction that channels cannot intersect at the chamber inlet assumes a rather more complex mathematical formulation. Given the angle \( \phi \), it is possible to define the limiting relationships between the diameter of a chamber \( j \) and the diameters of the channels to it connected, as expressed in Table 3.3.

**Table 3.3** Limiting relationships for nonintersecting of channels.

<table>
<thead>
<tr>
<th>Network Type</th>
<th>Channels</th>
<th>Limiting Relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without HC</td>
<td>( i_1 ) and ( i_2 )</td>
<td>( \sum_k \arcsin \left( \frac{d_k}{D_j} \right) \geq 2\phi )</td>
</tr>
<tr>
<td></td>
<td>( i_3 ) and ( i_4 )</td>
<td>( \sum_k \arcsin \left( \frac{d_k}{D_j} \right) \geq \pi - 2\phi )</td>
</tr>
<tr>
<td></td>
<td>( i_1 ) and ( i_4 )</td>
<td>( \sum_k \arcsin \left( \frac{d_k}{D_j} \right) \geq \pi - 2\phi )</td>
</tr>
<tr>
<td></td>
<td>( i_2 ) and ( i_3 )</td>
<td>( \sum_k \arcsin \left( \frac{d_k}{D_j} \right) \geq 2\phi )</td>
</tr>
<tr>
<td>With HC</td>
<td>( i_1 ) and ( i_6 )</td>
<td>( \sum_k \arcsin \left( \frac{d_k}{D_j} \right) \geq \frac{\pi}{2} - \phi )</td>
</tr>
<tr>
<td></td>
<td>( i_4 ) and ( i_6 )</td>
<td>( \sum_k \arcsin \left( \frac{d_k}{D_j} \right) \geq \frac{\pi}{2} - \phi )</td>
</tr>
<tr>
<td></td>
<td>( i_2 ) and ( i_5 )</td>
<td>( \sum_k \arcsin \left( \frac{d_k}{D_j} \right) \geq \frac{\pi}{2} - \phi )</td>
</tr>
<tr>
<td></td>
<td>( i_3 ) and ( i_4 )</td>
<td>( \sum_k \arcsin \left( \frac{d_k}{D_j} \right) \geq \frac{\pi}{2} - \phi )</td>
</tr>
</tbody>
</table>
So far, the angle $\phi$ was considered as an independent input parameter.

However, and contrary to regular networks, in the case of random sized networks, given $d$, $D$ and $L^o$, it is only possible to set the limiting values of $\phi$, i.e., its upper and lower limits, $\phi_{\text{max}}$ and $\phi_{\text{min}}$, once the network has been generated, i.e., once all values of $d_i$ and $D_j$ have been attributed.

For random networks without HC, the angle $\phi$ is upper limited by

$$\phi_{\text{max}} = \frac{\pi}{2} - \max \left\{ \arcsin \left( \frac{D_{j_i} + D_{j_m}}{4L^o} \right) \right\}$$ (3.22)

corresponding to the case where any two vertically contiguous chambers $j_i$ and $j_m$ first contact, and lower limited by

$$\phi_{\text{min}} = \max \left\{ \arcsin \left( \frac{D_{j_i} + D_{j_m}}{4L^o} \right) \right\}$$ (3.23)

corresponding to the case where any two horizontally contiguous chambers $j_i$ and $j_m$ first contact.

For random networks with HC, the value of $\phi$ is upper limited by

$$\phi_{\text{max}} = \frac{\pi}{2} - \arcsin \left( \frac{D_{j_i} + d_i}{2L^o} \right)$$ (3.24)

corresponding to the case where, since chambers $j$ and $j_i$ are connected through oblique channels $i_j$ (see Figure 3.8a), chamber $j_i$ contacts the horizontal channel $i_j$ from chamber $j$. Equation 3.23 provides the lower limit for $\phi$.

3.2.1.4 Numerical Implementation

In this section the network structure construction process, implemented in a software package written in Fortran 90 and compiled with Absoft™ Pro Fortran for Mac™ OS X v8.0, is briefly described.

For the network structure to be macroscopically defined, the parameters $n_x$ and $n_y$, the dimension $L^o$ and the angle $\phi$ must be pre-defined. The local structure is then assessed by
selecting the type of boundary conditions (PBC or NPBC) and the presence or not of HC, and setting the average dimensions of the two types of elements and the respective size distributions (regular or random sized).

Regular networks are generated by assigning to all channels and chamber the diameters \( d \) and \( D \), respectively, after all restrictive relations for regular networks are verified.

Random sized networks are generated by randomly assigning the channels and chambers diameters, \( d_i \) and \( D_j \), respectively. In the absence of specific data, an appropriate mathematical expression for the chambers and channels diameter distributions must be assumed (see for example, Diaz et al., 1987; Constantinides and Payatakes, 1989; Petropoulos et al., 1989; Hampton et al., 1993; Ioannidis and Chatzis, 1993; Sahimi, 1993; Suchomel et al., 1998). In this work, the following chambers and channels size distributions were implemented due to their versatility and mathematical simplicity:

- **Normal (Gaussian) distribution** (computed from routine G05DDF from NAG™) with probability density function (PDF) given by

  \[
  f(d_i) = \frac{1}{\sigma_d \sqrt{2\pi}} e^{-\frac{(d_i - d)^2}{2\sigma_d^2}}
  \]

  \[
  f(D_j) = \frac{1}{\sigma_D \sqrt{2\pi}} e^{-\frac{(D_j - D)^2}{2\sigma_D^2}}
  \]

- **Uniform (rectangular) distribution** (computed from routine G05DAF from NAG™) with PDF expressed by

  \[
  f(d_i) = \begin{cases} 
  \frac{1}{2\sigma_d} & d - \sigma_d \leq d_i \leq d + \sigma_d \\
  0 & \text{otherwise}
  \end{cases}
  \]

  \[
  f(D_j) = \begin{cases} 
  \frac{1}{2\sigma_D} & D - \sigma_D \leq D_j \leq D + \sigma_D \\
  0 & \text{otherwise}
  \end{cases}
  \]

  where \( d \) and \( D \) are the distribution means and \( \sigma_d \) and \( \sigma_D \) the respective standard deviations.

The restrictive relationships, expressed in Section 3.2.1.3, are queried at the end of the network construction process to determine the acceptance (or not) of a particular network structure.
3.2.2 Hydrodynamics

In this section the hydrodynamic model used to simulate the flow within the network structure described in Section 3.2 is presented.

3.2.2.1 Solution of the Flow in the Network

The hydrodynamic model purpose is the simulation of single-phase flow in laminar regime in order to obtain the pressure field and the flow map inside a network. The following assumptions were considered:

- incompressible, isothermal, and steady state flow;
- perfectly mixed chambers, with no flow resistance;
- piston flow in the channels;
- negligible gravitational effects;
- negligible pressure drop resulting from the sudden contraction and expansion of flow area in the channels and chambers intersections.

Further, it is assumed that the \( n \) network inlet chambers are connected through the inlet channels to a reservoir of fluid at pressure \( P_1 \), whereas the \( n \) network outlet chambers are connected through the outlet channels to a sink of pressure \( P_0 \) (for simplicity \( P_0 = 0 \)). The imposed pressure difference is then

\[
\Delta p = P_1 - P_0
\]  
(3.29)

The hydrodynamics is here simulated using an analogy to a pure resistive electrical circuit, where the flow rate trough the channels, \( q_i \), and the pressure inside the chambers, \( p_j \), correspond to the current across the resistances \( i \) and to the voltage in the nodes \( j \), respectively (Dias and Payatakes, 1986). Figure 3.9a shows a schematic representation of the electrical analogue of the PBC without HC regular network of Figure 3.3c.
The mass conservation equation for the network chamber $j$ is

$$\sum_k q_{ik} = 0$$  \hspace{1cm} (3.30)

where $q_{ik}$ are the flow rates in channels $i$, connected to the chamber $j$.

From Ohm’s law, the pressure drop across a channel $i$ is

$$\Delta p_i = p_{jn} - p_{jm} = R_i q_i$$  \hspace{1cm} (3.31)

where $R_i$ is the hydraulic resistance associated with channel $i$, $q_i$ is the flow rate through channel $i$, and $p_{jn}$ and $p_{jm}$ are the pressures in chamber $j_n$ and chamber $j_m$, respectively, as shown in Figure 3.9b.

Since pressure drop calculations take only into account the frictional effects on the channel walls, the hydraulic resistance may be expressed in terms of the Darcy friction factor, $f_{friction}$, as

$$R_i = f_{friction} \left( \frac{8 \rho l_i q_i}{\pi^2 d_i^5} \right)$$  \hspace{1cm} (3.32)

where $\rho$ is the fluid density and $l_i$ and $d_i$ are the length and diameter of channel $i$, respectively.
For laminar regime, the friction factor $f_i$ is given by (see for example, Shames, 1992)

$$f_i = \frac{64}{Re_i} \quad (3.33)$$

where $Re_i$ is the channel Reynolds number, defined as

$$Re_i = \frac{\rho d v_i}{\mu} \quad (3.34)$$

where $\mu$ is the fluid viscosity.

3.2.2.2 Mathematical Formulation

In order to obtain the pressure field, given by $p_j$, and the flow map, given by $q_i$, inside a network, the mass conservation equation (see Equation 3.30) and the momentum equation (see Equation 3.31) must be written for all chambers and channels, respectively, and simultaneously solved.

The conservation of energy and conservation of charge when applied to electrical circuits are known as Kirchoff’s Laws, that can be applied to the network electrical circuit analogue to set the system of equations as described next (see for example, Desoer and Kuh, 1969).

Kirchoff’s Current Law states that the algebraic sum of the currents flowing through a junction is zero, and can be mathematically expressed as

$$Aq = 0 \quad (3.35)$$

where $q$ is the vector containing the $n_{channels}$ values of $q_i$ and $A$ is the reduced incidence matrix with dimensions $n_{chambers} \times n_{channels}$, having a maximum number of six non-zero entries per row. The element $a_{mk}$ is set to: −1 if the fluid in channel $i_k$ flows towards the chamber $j_m$; 1 if the fluid in channel $i_k$ flows outwards the chamber $j_m$; and 0 if the channel $i_k$ and the chamber $j_m$ are not connected.

Kirchoff’s Voltage Law states that the algebraic sum of the potential differences in a circuit loop must be zero, and can be mathematically traduced as

$$\Delta p = A^T p \quad (3.36)$$
where $\Delta \mathbf{p}$ is the channels pressure vector, having $n_{\text{channels}}$ elements, and defined such that $\Delta p_i$ is the pressure drop across channel $i$, $\mathbf{p}$ is the chambers pressure vector, with $n_{\text{chambers}}$ elements, and defined such that $p_j$ is the pressure in chamber $j$, and $\mathbf{A}^\top$ is the transposed matrix of the reduced incidence matrix $\mathbf{A}$.

Based on the Kirchoff’s Laws and standard resistive network analysis principles, the pressure field is obtained as the solution of the linear equation system

$$ \mathbf{Yp} = \mathbf{q}^s $$

(3.37)

where $\mathbf{Y}$ is the admittance matrix and $\mathbf{q}^s$ is the flow source vector. The admittance matrix $\mathbf{Y}$, with dimensions $n_{\text{chambers}} \times n_{\text{chambers}}$, is defined as

$$ \mathbf{Y} = \mathbf{AGA}^\top $$

(3.38)

where: the element $y_{jm}$, denoted as the self-admittance of chamber $j_m$, is the sum of the conductances of all channels $i$ connected to the chamber $j_m$; and the element $y_{m} = y_{jm}$, denoted as the mutual admittance between chamber $j_m$ and chamber $j_i$, is set to the negative of the conductance of channel $i$ connecting chamber $j_m$ and chamber $j_i$, or to 0 if the chamber $j_m$ and chamber $j_i$ are not directly connected. The flow source vector $\mathbf{q}^s$, with $n_{\text{chambers}}$, is given by

$$ \mathbf{q}^s = \mathbf{AGp}^s $$

(3.39)

The channels conductance matrix, $\mathbf{G}$, is a diagonal matrix with dimensions $n_{\text{channels}} \times n_{\text{channels}}$, where each element, $g_{kk}$, corresponds to the hydraulic conductance of channel $i_k$

$$ g_{kk} = \frac{1}{R_i} $$

(3.40)

The channels pressure source vector, $\Delta \mathbf{p}^s$ with $n_{\text{channels}}$ elements, is defined such that $p_i^s$ is the source pressure in channel $i$, and is set to: $P_t$ if the channel is connected to the reservoir of fluid at pressure $P_t$; and 0 for the remaining channels.

Once $\mathbf{p}$ is obtained from solving Equation 3.37, $\mathbf{q}$ is readily determined from

$$ \mathbf{q} = \mathbf{G(\Delta p - \Delta p^s)} $$

(3.41)

where $\Delta \mathbf{p}$ is calculated from Equation 3.36.
3.2.2.3 Numerical Implementation

The above mathematical formulation for hydrodynamics description was implemented in a software package written in Fortran 90 and compiled with Absoft™ Pro Fortran for Mac™ OS X v8.0.

Imposing a given pressure difference, $\Delta p$, between the inlet and outlet channels of a particular network structure, with structure as described in Section 3.2.1, the pressure field is obtained as the solution of the linear equation system defined by Equation 3.37, once the admittance matrix $Y$ and the flow source vector $q^i$ are defined (see Section 3.2.2.2).

The admittance matrix $Y$ is a sparse symmetric positive definite matrix, having a maximum number of seven non-zero entries per row, thus the NAG™ routine F04MCF for linear systems with symmetric positive definite variable bandwidth coefficient matrixes was used to compute the approximate chambers pressure vector $p$ solution. The use of the NAG™ routine F04MCF to solve the linear equation system $Yp = q^i$ follows a call of NAG™ routine F01MCF to determine the $LDL^T$ factorisation of the matrix $Y$.

Given the pressure vector $p$, the distribution of flow rates inside the network, $q_i$, is immediately assessed by Equation 3.41, and can later be used namely for the calculation of the RTD function.

3.2.3 Residence Time Distribution Function

The concept of using the distribution of residence times in the analysis of chemical reactors performance was apparently first proposed by MacMullin and Weber Jr. (1935). However, the concept was not used extensively until the early 1950s, when Danckwerts (1953), in a now famous paper, introduced an organizational structure to this subject. This main concept may be summarized as: molecules passing through continuous-flow systems (paper main title) possess distributions of residence times (paper subtitle).

From a global point of view, an important insight on the network hydrodynamics may be gained by analysing the Residence Time Distribution (RTD) function, $E(i)$, sometimes called exit-age distribution function (see for example, Fogler, 1992). In the present work, the RTD concerns the age distribution of the fluid elements that are in the effluent stream and is a characteristic of the mixing occurring within the network (macromixing), neglecting however
detailed information on different mixing levels (micromixing). Even though not all RTDs are unique to a particular network, and markedly different network geometries can display similar RTDs, the RTD exhibited by a network is an important informative characterisation of the network.

For regular networks with PBC an analytical expression for the network RTD can be derived and is shown in Section 3.2.3.1. A new parameter, related to the geometry and the mixing assumptions in each type of network elements, the segregation parameter, is introduced in Section 3.2.3.2.

3.2.3.1 Regular Networks with PBC

For the particular case of regular networks with PBC, it is possible to obtain an analytic solution for the dimensionless RTD function, as described next.

Assuming the hydrodynamic behaviour of the chambers and the channels as described in Section 3.2.2.1 and that the volumetric flow rate in the network, \( q_r \), is constant and equally divided between all the inlet channels, the hydrodynamics of a regular network with PBC is analogue to an alternate sequence of \( n_x \) piston flow channels and perfectly mixed chambers finishing with one piston flow channel at the exit. Figure 3.10 shows this hydrodynamics analogy for the particular case of a \( n_x = 5 \) by \( n_y = 4 \) network.

![Diagram](image)

**Figure 3.10** Hydrodynamics analogy: (a) network with PBC without HC; (b) equivalent sequence of piston flow channels and perfectly mixed chambers.

Defining the dimensionless residence time, \( \Theta \), as

\[
\Theta = \frac{t}{\tau}
\]  

(3.42)
where $\tau$ is the mean residence time,

$$\tau = \frac{V_{\text{network}}}{q_T}$$  \hspace{1cm} (3.43)

the dimensionless RTD function, $E(\Theta)$, becomes \cite{laranjeira2001}

$$E(\Theta) = \frac{n_s}{(1-\alpha)(n_s-1)!} \left( \frac{n_s(\Theta - \alpha)}{1-\alpha} \right)^{n_s-1} e^{-\frac{n_s(\Theta - \alpha)}{1-\alpha}} H(\Theta - \alpha)$$  \hspace{1cm} (3.44)

$$\alpha = \frac{V_{\text{channels}}}{V_{\text{network}}}$$  \hspace{1cm} (3.45)

where $n_s$ is the number of network rows, $V_{\text{channels}}$ is the channels volume

$$V_{\text{channels}} = \sum_{n_{\text{channels}}=1}^{n_{\text{channels}}} V_{\text{channel}_i}$$  \hspace{1cm} (3.46)

and $H(t)$ is the Heaviside function

$$H(t) = \begin{cases} 0 & \text{if } t < 0 \\ 1 & \text{if } t \geq 0 \end{cases}$$  \hspace{1cm} (3.47)

Hence, for the particular case of regular networks with PBC, the network RTD function may be directly estimated using the network geometric parameters, see Section 3.2.1.2, and the volumetric flow rate.

Contrarily to regular networks with PBC, for other network types analytic solutions for the RTD functions are not directly obtained. Yet, for the case of regular networks with NPBC, Equation 3.44 is an increasingly good approximation of the exact RTD function for higher $n_s$ values.

### 3.2.3.2 Segregation Parameter

In the NETMIX® model, mixing between different streams only occurs in the chambers, restricting the total volume for actual mixing to the volume of the chambers. The ratio
between the channels volume and the network volume, $\alpha$, defined by Equation 3.45, is therefore a key parameter related to mixing, defined as the segregation parameter.

From Equation 3.44, it follows that, as far as regular networks with PBC are considered, macromixing in the NETMIX® model is entirely governed by $n_s$ and $\alpha$.

Later in Section 3.4 these two parameters are also shown to be related to micromixing.

### 3.3 Micromixing and Chemical Reaction Modelling

The distribution of flow rates inside a given structure determines the macromixing patterns (Villermaux and Falk, 1996). On the other hand, micromixing is coupled to the hydrodynamics.

In the NETMIX® model, modelling of micromixing uses a networks-of-zones model formulation based on the mixing behaviour of two different ideal continuous-flow reactors, each associated to one type of network elements:

- channels behave as plug-flow reactors (PFR), zones of total segregation;
- chambers behave as perfectly mixed continuous stirred tank reactors (CSTR), zones of complete micromixing.

For constant volumetric flow rate, $q$, the conservation equations for a CSTR and a PFR are respectively (see for example, Fogler, 1992)

\[ qC_A^{\text{inlet}} - qC_A = -r_A V_{\text{CSTR}} \]  \hspace{1cm} (3.48)

and

\[ q \frac{dC_A}{dV_{\text{PFR}}} = r_A \]  \hspace{1cm} (3.49)

where $-r_A$ is the rate of consumption of reactant $A$, $C_A^{\text{inlet}}$ and $C_A$ are the inlet and the outlet concentrations of reactant $A$ and $V_{\text{CSTR}}$ and $V_{\text{PFR}}$ are the CSTR and the PFR volumes.

Combining the network flow field results with the above conservation equations, a chemical reaction model, coupling macromixing and micromixing can be implemented. The following reaction schemes have been studied:
• first-order reaction (see Section 3.3.1);

\[ A \rightarrow R \quad (3.50) \]

\[ \dot{\kappa}_1 \]

• second-order reaction (see Section 3.3.2);

\[ A + B \rightarrow R \quad (3.51) \]

\[ \dot{\kappa}_2 \]

• consecutive competitive second-order reactions (see Section 3.3.3);

\[ A + B \rightarrow R \quad (3.52) \]

\[ \dot{\kappa}_1 \]

\[ R + B \rightarrow S \]

where \( k_1 \) and \( k_2 \) are the reaction rate constants.

3.3.1 First-Order Reaction

For the first-order reaction in Equation 3.50, the rate law is

\[ -r_A = k_1 C_A \quad (3.53) \]

where \( k_1 \) is the reaction rate constant. Substituting in Equation 3.48 and Equation 3.49 results in

\[ C_A - \frac{q C_A^{\text{inter}} - k_1 V_{\text{CSTR}} C_A}{q} = 0 \quad (3.54) \]

and

\[ C_A = e^{-\frac{V_{\text{FR}}}{q} C_A^{\text{inter}}} \quad (3.55) \]

Consider now a network branch, as shown in Figure 3.11a, and the schematic representation of its analogue cascade of continuous-flow reactors, shown in Figure 3.11b, assuming the fluid in channel \( i \) flows towards chamber \( j_n \).
Using Equation 3.54, the concentration of reactant $A$ in chamber $j_n$, $C_{A,j_n}$, can be obtained by

$$C_{A,j_n} = \frac{\sum \left[ \left( 1 - I_{\text{flow},ij_n} \right) q_i C_{A},i \right]}{\sum \left( I_{\text{flow},ij_n} q_i \right)} - k_i V_{j_n} C_{A,j_n} = 0$$  \hspace{1cm} (3.56)$$

where $q_i$ is the flow rate in channel $i$, $V_{j_n}$ is the volume of chamber $j_n$, $I_{\text{flow},ij_n}$ denotes the flow sense, and is set to: 0 if the stream in channel $i$ is an inlet stream to the chamber $j_n$; and 1 otherwise. $C_{A,j_n}$ is the concentration at the outlet of channel $i$, entering chamber $j_n$, and is given by (see Equation 3.55)

$$C_{A,j_n} = e^{-k_i \frac{V_{j_n}}{q_i}} C_{A,i}$$  \hspace{1cm} (3.57)$$

where $C_{A,j_n}$ is the concentration in chamber $j_m$ and $V_i$ is the volume of channel $i$.

Thus, combining Equation 3.56 and Equation 3.57, results in a linear system of $n_{\text{chambers}}$ equations to be solved for the concentration of reactant $A$ in each network chamber, given the input parameters (see Section 3.3.4.1).
### 3.3.2 Second-Order Reaction

For the second-order reaction in Equation 3.51, the rate law is given by

$$-r_A = k_2 C_A C_B$$  \hspace{1cm} (3.58)

where $k_2$ is reaction rate constant, and the conservation equations for a CSTR and a PFR become now, in that order, as follows

$$C_A - \frac{q C_A^{\text{inlet}} - k_2 V_{\text{CSTR}} C_A C_B}{q} = 0$$  \hspace{1cm} (3.59)

$$C_B - C_A - (C_B^{\text{inlet}} - C_A^{\text{inlet}}) = 0$$  \hspace{1cm} (3.60)

and

$$q \frac{dC_A}{dV_{\text{PFR}}} + k_2 C_A C_B = 0$$  \hspace{1cm} (3.61)

$$C_B = C_B^{\text{inlet}} - (C_A^{\text{inlet}} - C_A)$$  \hspace{1cm} (3.62)

where $C_A^{\text{inlet}}$, $C_A$, and $C_B^{\text{inlet}}$ and $C_B$ are the inlet and the outlet concentrations of reactants $A$ and $B$, respectively.

As in Section 3.3.1, using Equation 3.59 and Equation 3.60, the concentration of reactants $A$ and $B$ in chamber $j_n$, $C_{A_{j_n}}$ and $C_{B_{j_n}}$, respectively, can be obtained by

$$C_{A_{j_n}} = \sum_j \left( (1 - I_{\text{flow}_{j_n}}) q_i C_{A_{j_n}}^{i} - k_2 V_{j_n} C_{A_{j_n}}^{i} C_{B_{j_n}}^{i} \right) = 0$$  \hspace{1cm} (3.63)

$$C_{B_{j_n}} - C_{A_{j_n}} = \sum_i \left( (1 - I_{\text{flow}_{j_n}}) q_i^{i} C_{B_{j_n}}^{i} - \sum_j \left( (1 - I_{\text{flow}_{j_n}}) q_i^{i} C_{A_{j_n}}^{i} \right) \right) = 0$$  \hspace{1cm} (3.64)

where $q_i$ is the flow rate in channel $i$, $V_{j_n}$ is the volume of chamber $j_n$, $I_{\text{flow}_{j_n}}$ denotes the incidence of the flow, and $C_{A_{j_n}}^{i}$ and $C_{B_{j_n}}^{i}$ are the concentrations at the outlet of channel $i$, entering chamber $j_n$. 
From Equation 3.62, $C_{A,j_n}^i$ and $C_{B,j_n}^i$ are related to the concentrations in chamber $j_n$, $C_{A,j_n}$ and $C_{B,j_n}$, as

$$C_{B,j_n}^i = C_{B,j_n} - \left( C_{A,j_n} - C_{A,j_n}^i \right)$$

(3.65)

where $C_{A,j_n}^i$, given by Equation 3.61, depends on whether $C_{A,j_n} = C_{B,j_n}$

$$C_{A,j_n}^i = \frac{C_{A,j_n}}{1 - k_2 \frac{V}{q_i} C_{A,j_n}}$$

(3.66)

or $C_{A,j_n} = C_{B,j_n}$

$$C_{A,j_n}^i = \frac{C_{A,j_n} \left( C_{B,j_n} - C_{A,j_n} \right) e^{-k_2 \frac{V}{q_i} (C_{B,j_n} - C_{A,j_n})}}{1 - k_2 \frac{V}{q_i} e^{-k_2 \frac{V}{q_i} (C_{B,j_n} - C_{A,j_n})}}$$

(3.67)

Combining Equation 3.63 to Equation 3.67 results in a nonlinear system of $2n_{chambers}$ equations (Equation 3.63 and Equations 3.64 written for all network chambers) to be solved for the concentrations of reactants $A$ and $B$, given the input parameters (see Section 3.3.4.2).

### 3.3.3 Consecutive Competitive Second-Order Reactions

In the case of the consecutive competitive second-order reactions in Equation 3.51, the rate laws, for the first and second reaction, are

$$-r_A = k_1 C_A C_R$$

(3.68)

$$r_B = k_2 C_B C_R$$

(3.69)

where $k_1$ and $k_2$ are the corresponding reaction rate constants.

As before, the conservation equations for a CSTR and a PFR may be written as

$$C_A - \frac{q C_{A,inlet}}{q} - k_1 V_{CSTR} C_A C_B = 0$$

(3.70)
\[ C_B - \frac{q C_{B_{inlet}}^{inlet}}{q} - k_1 V_{CSTR} C_A C_B - k_2 V_{CSTR} C_B C_R = 0 \]  
(3.71)

\[ C_R - \frac{q C_{R_{inlet}}^{inlet}}{q} + k_1 V C_A C_B - k_2 V C_B C_R = 0 \]  
(3.72)

and

\[ q \frac{dC_A}{dV_{PFR}} + k_1 C_A C_B = 0 \]  
(3.73)

\[ q \frac{dC_B}{dV_{PFR}} + k_1 C_A C_B + k_2 C_B C_R = 0 \]  
(3.74)

\[ q \frac{dC_R}{dV_{PFR}} - k_1 C_A C_B + k_2 C_B C_R = 0 \]  
(3.75)

respectively, where \( C_{A_{inlet}} \) and \( C_A \), \( C_{B_{inlet}} \), and \( C_B \) and \( C_{R_{inlet}} \) and \( C_R \) are the inlet and the outlet concentrations of reactants \( A \) and \( B \) and of intermediate product \( R \), respectively.

Referring to the network branch analogy with a cascade of continuous-flow reactors, introduced in Figure 3.11, the concentrations of reactants \( A \) and \( B \), \( C_{A_{j_n}} \) and \( C_{B_{j_n}} \), and of intermediate product \( R \) in chamber \( j_n \), \( C_{R_{j_n}} \), can be computed, see Equation 3.73 and Equation 3.75, from

\[ C_{A_{j_n}} = \frac{\sum_i \left[ (1 - I_{flow_{j_n}}) q_i C_{A_{j_n}}^i \right] - k_1 V_{j_n} C_{A_{j_n}} C_{B_{j_n}}}{\sum_i I_{flow_{j_n}} q_i} = 0 \]  
(3.76)

\[ C_{B_{j_n}} = \frac{\sum_i \left[ (1 - I_{flow_{j_n}}) q_i C_{B_{j_n}}^i \right] - k_1 V_{j_n} C_{A_{j_n}} C_{B_{j_n}} - k_2 V_{j_n} C_{B_{j_n}} C_{R_{j_n}}}{\sum_i I_{flow_{j_n}} q_i} = 0 \]  
(3.77)

\[ C_{R_{j_n}} = \frac{\sum_i \left[ (1 - I_{flow_{j_n}}) q_i C_{R_{j_n}}^i \right] + k_1 V_{j_n} C_{A_{j_n}} C_{B_{j_n}} - k_2 V_{j_n} C_{B_{j_n}} C_{R_{j_n}}}{\sum_i I_{flow_{j_n}} q_i} = 0 \]  
(3.78)
where \( q_i \) is the flow rate in channel \( i \), \( V_{j_n} \) is the volume of chamber \( j_n \), \( I_{\text{flow},j_n} \) denotes the incidence of the flow, and \( C_{A,j_n}^i \), \( C_{B,j_n}^i \) and \( C_{R,j_n}^i \) are the concentrations at the outlet of channel \( i \), entering chamber \( j_n \).

Since here the molar conservation equations for the network channel \( i \), do not present an analytic solution, \( C_{A,j_n}^i \), \( C_{B,j_n}^i \) and \( C_{A,j_n}^i \) are obtained by solving for \( V = V_i \) the set of first-order nonlinear ODEs (Ordinary Differential Equations)

\[
q_i \frac{dC_A}{dV} + k_i C_A C_B = 0
\]  
(3.79)

\[
q_i \frac{dC_B}{dV} + k_1 C_A C_B + k_2 C_R C_R = 0
\]  
(3.80)

\[
q_i \frac{dC_R}{dV} - k_1 C_A C_B + k_2 C_B C_R = 0
\]  
(3.81)

with boundary conditions \( C_A(0) = C_{B,j_n}^i \), \( C_B(0) = C_{B,j_n}^i \) and \( C_R(0) = C_{R,j_n}^i \), where \( C_{A,j_n}^i \), \( C_{B,j_n}^i \) and \( C_{R,j_n}^i \) are the concentrations in chamber \( j_n \).

Writing Equation 3.76 to Equation 3.78 for all network chambers results in a nonlinear system of \( 3n_{\text{chambers}} \) equations, to be solved for the concentrations of reactants \( A \), \( B \) and \( R \) in each network chamber, given the input parameters (see Section 3.3.4.3).

### 3.3.4 Numerical Implementation

The chemical reaction model was implemented in a software package written in Fortran 90 and compiled with Absoft™ Pro Fortran for Mac™ OS X v8.0.

Using the data obtained from the network construction and hydrodynamics modelling software packages, the chemical reaction software package employs different numerical methods to progress towards a solution, according to the selected reaction scheme, as described next.

#### 3.3.4.1 First-Order Reaction

In the case of a first-order reaction (see Equation 3.50), for a given constant volumetric flow rate, \( q \), the required input parameters to define the problem are solely the reaction rate
constant, $k_i$, and the feeding concentration distribution of reactant A, i.e., the concentration of reactant A at each inlet channel.

The resulting $n_{\text{chambers}}$ linear equation system (see Section 3.3.1) may be formulated as a band system of linear equations, and solved using the NAG™ routine F07BEF, preceded by a call of NAG™ routine F07BDF to compute the LU factorization of the coefficient matrix.

### 3.3.4.2 Second-Order Reaction

In the case of a second-order reaction (see Equation 3.51) additional degrees of freedom are introduced. Besides the volumetric flow rate, $q$, the reaction rate constant, $k_2$, and the feeding concentration distributions of both A and B, it is further required to set independently the inlet channels associated to each reactant, i.e., the reactants injection schemes, in order to define the problem.

The resulting $2n_{\text{chambers}}$ linear equation system (see Section 3.3.2) is solved using the IMSL™ routine DNEQNF. The routine DNEQNF, based on the MINPACK subroutine HYBRD1, uses a modified Powell hybrid algorithm. This algorithm is a variation of Newton’s method, and uses a finite-difference approximation to the Jacobian, taking precautions to avoid large step sizes or increasing residuals (for further description, see More et al., 1980).

The stopping criterion for the solution to be accepted was set for a relative error between two successive approximations less than $10^{-6}$.

### 3.3.4.3 Consecutive Competitive Second-Order Reactions

For consecutive competitive second-order reactions (see Equation 3.52), the required input parameters are the same as for a second-order reaction, apart from the two reaction rate constants, $k_1$ and $k_2$, now required to define the problem.

The $3n_{\text{chambers}}$ nonlinear equation system (see Section 3.3.3), was solved using the IMSL™ routine DNEQNF, and a stopping criterion of $10^{-6}$. The system of first-order nonlinear ODEs is solved for the network channel using the IMSL™ routine DIVPAG. This routine solves an initial-value problem for ordinary differential equations using the Gear’s backward differentiation formulas, BDF, method (Gear, 1971), appropriate for solving stiff ODEs problems.
3.4 Simulations

The NETMIX® model is capable of describing various mixing states, by considering the appropriate network input parameters and network type. However, the purpose of this section is not to present a parametric investigation of the effect of the model parameters on the model predictions, but to show that the model is capable of coupling micromixing with macromixing and simultaneously retaining the distinction between both. And therefore, all simulations were performed for regular networks with PBC and without HC, referred from this point on as regular networks.

This section is structured as follows. First, macromixing inside the network is assessed from purely theoretical analysis. Among the countless number of RTDs that can be obtained for different networks, some are shown and discussed in Section 3.4.1. In Section 3.4.2, micromixing is assessed from chemical reaction simulations for different network geometries, reaction schemes and reactants injection schemes.

3.4.1 Macromixing

Macromixing is determined from the hydrodynamics on chemical reactors and is commonly assessed from the RTD. For regular networks, the theoretical RTD function was obtained in Section 3.2.3. It was shown that the RTD directly depends on two parameters: number of rows, \( n_s \), and segregation parameter, \( \alpha \). The effect of each parameter is separately evaluated next.

Plots of the RTD functions for regular networks with \( n_s = 10 \) and \( n_s = 50 \), respectively, and segregation parameter values ranging from \( \alpha = 0.010 \) to \( \alpha = 0.750 \), are shown in Figure 3.12 and Figure 3.13. For a given number of rows, the behaviour of the system approaches that of the PFR as the segregation parameter tends to one. Such result is easily understood recalling that as the chambers volume is reduced, the network structure tends to a battery of plug-flow reactors in series, equivalent to a single plug-flow reactor with the same mean residence time.

Figure 3.14 and Figure 3.15 show plots of the RTD functions for regular networks for \( \alpha = 0.100 \) and \( \alpha = 0.500 \), respectively, and number of rows ranging from \( n_s = 5 \) to \( n_s = 100 \). For a given segregation parameter, as the number of rows increases the closer the system behaves as a PFR, as expected from the network structure similitude with the tanks-in-series model (TISM) (see for example, Fogler, 1992).

Simulations have further shown to exist no significant changes on the \( E(\Theta) \) for values of \( \alpha \) lower than 0.010.
Figure 3.12  RTDs for regular networks with $n_x = 10$ and various $\alpha$.

Figure 3.13  RTDs for regular networks with $n_x = 50$ and various $\alpha$. 
Figure 3.14  RTDs for regular networks with $\alpha = 0.100$ and various $n_z$.

Figure 3.15  RTDs for regular networks with $\alpha = 0.500$ and various $n_z$. 

It is apparent from Figure 3.12 to Figure 3.15 that similar RTDs can be obtained for different pairs of parameters $n_e$ and $\alpha$, which corresponding to different network geometries.

A common method of characterizing the RTD in flow systems is by using their moments (see for example, Coker, 2001). It is thus common to compare RTDs using their moments instead of comparing their entire distributions (see for example, Wen and Fan, 1975). For this purpose, the first three moments will be used. These are known as the mean, variance and skewness and are usually sufficient for a reasonable characterisation of a RTD, despite rigorously all moments need to be compared.

The first moment is the dimensionless mean residence time, defined as

$$\Theta_m = \int_0^\infty E(\Theta) \, d\Theta$$  \hspace{1cm} (3.82)

The second centred moment is taken about the mean and is denoted as the variance

$$\nu^2 = \int_0^\infty (1 - \Theta)^2 E(\Theta) \, d\Theta$$  \hspace{1cm} (3.83)

The magnitude of the variance represents the square of the distribution spread and the greater the value of this moment, the greater the spread of the RTD.

The third centred moment is also taken about the mean and is related to the RTD skewness

$$s^3 = \frac{1}{\nu^{3/2}} \int_0^\infty \left(1 - \frac{1}{\Theta}\right)^3 E(\Theta) \, d\Theta$$  \hspace{1cm} (3.84)

The magnitude of this moment measures the extent to which the distribution is skewed in one direction or another in reference to the mean.

For regular networks analytical solutions for $\Theta_m$ and $\nu^2$ were obtained. Using Equation 3.44 and Equation 3.82 the dimensionless mean residence time simply becomes (Laranjeira et al., 2001)

$$\Theta_m = 1$$  \hspace{1cm} (3.85)
Substituting Equation 3.44 into Equation 3.83, it can be shown that the variance is given by

$$v^2 = \left( \frac{1 - V_{\text{channels}}}{V_{\text{network}}} \right)^2 = \frac{(1 - \alpha)^2}{n_x}$$

(3.86)

However, no analytical solution for $s^3$ was possible to obtain and a numerical quadrature has been used for numerically approximating the integral in Equation 3.84.

From the calculation of the RTD moments it is possible to design regular networks having different design parameters $n_x$ and $\alpha$, but matching RTDs, i.e., similar macromixing. For example, given a pair of parameter $n_x$ and $\alpha$, a new value of the segregation parameter, $\alpha$, can be determined from Equation 3.86, by changing the number of rows in the network, $n_x$, so that macromixing, or at least the first and second moments of both RTDs, is maintained. Conversely, if the segregation parameter is changed, Equation 3.86 directly sets the new number of rows in the network.

Table 3.4 gives the number of rows, the segregation parameter and the first three RTD moments for various regular networks. All regular networks have equal first and second moments.

<table>
<thead>
<tr>
<th></th>
<th>$n_x$</th>
<th>$\alpha$</th>
<th>$\Theta_m$</th>
<th>$v^2$</th>
<th>$s^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Network 1</td>
<td>20</td>
<td>0.010</td>
<td>1</td>
<td>$4.900 \times 10^{-2}$</td>
<td>$4.85 \times 10^{-3}$</td>
</tr>
<tr>
<td>Network 2</td>
<td>2</td>
<td>0.687</td>
<td>1</td>
<td>$4.901 \times 10^{-2}$</td>
<td>$1.53 \times 10^{-2}$</td>
</tr>
<tr>
<td>Network 3</td>
<td>5</td>
<td>0.505</td>
<td>1</td>
<td>$4.900 \times 10^{-2}$</td>
<td>$9.703 \times 10^{-3}$</td>
</tr>
<tr>
<td>Network 4</td>
<td>10</td>
<td>0.300</td>
<td>1</td>
<td>$4.900 \times 10^{-2}$</td>
<td>$6.861 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

RTD functions of the networks listed in Table 3.4 are plotted from Figure 3.16 to Figure 3.18. These figures show that the equality of the two first moments is not a sufficient condition to ensure that the RTD functions are similar.

More, the direct comparison between the third moments of different RTDs is shown to be an erratic method. Although this parameter measures the distribution skewness and tends to similar values for similar RTDs, it is not easy to quantify how similar they really are only based on these values, without the recourse to the evaluation and visual observation of actual curves.
Figure 3.16  RTDs for network 1 and network 2.

Figure 3.17  RTDs for network 1 and network 3.
Figure 3.18 RTDs for network 1 and network 4.

Given the difficulties of direct comparison of the first three moments of different RTDs for macromixing similitude evaluation, two new methodologies are here proposed and described next.

The first methodology is based on the deterministic role of macromixing in the yield of first-order reactions (see Equation 3.50), regardless of micromixing. For a first-order reaction, the extent of micromixing does not affect the rate of change of yield and so the RTD is sufficient to calculate the yield in any type of reactor. In this way, two different regular networks may be assumed to have similar macromixing if both RTD functions have equal two first moments and both networks lead to equal yields for a first-order reaction under the same reaction conditions.

The RTD function is next used to calculate the first-order reaction yield in regular networks with PBC and without HC, considering a constant feeding concentration distribution of reactant A, i.e., the concentration of reactant A at each inlet channel is equal. Using the segregation model (Danckwerts, 1953), the mean reaction yield, $X_A$, is given by

$$X_A = \int_0^\infty X_A(t) E(t) dt \quad (3.87)$$
where the batch reactor equation for \( X(t) \) is

\[
X_A(t) = 1 - e^{-k_A t}
\]  

(3.88)

Substituting in Equation 3.87 for the RTD function for a regular network with PBC and without HC (Equation 3.44), and making use of tables of integrals (Erdélyi et al., 1954; Abramowitz and Stegun, 1972), it can be shown that

\[
X_A = 1 - \left[ \frac{e^{-\alpha Da}}{\left( \frac{1 - \alpha}{n_x} \right)^{n_x} \Gamma(n_x, -\alpha Da)} \right] + \frac{(-1)^{n_x-1} e^{-\alpha Da}}{\left( \frac{1 - \alpha}{n_x} \right)^{n_x+1} \Gamma(n_x, -\alpha Da)}
\]  

(3.89)

where \( \Gamma(k, x) \) is the incomplete gamma function and \( Da \) is the Damköhler number, defined as

\[
Da = k_x \tau
\]  

(3.90)

Considering the series expansion of the gamma function (Nielsen, 1906)

\[
\Gamma(n_x, -\alpha Da) = (n_x - 1)! \left[ 1 - e^{\alpha Da} \left( \sum_{m=0}^{n_x-1} \frac{(-\alpha Da)^m}{m!} \right) \right]
\]  

(3.91)

and the expansion in Maclaurin series of the exponential function

\[
e^{-\alpha Da} = \sum_{m=0}^{\infty} \frac{(-\alpha Da)^m}{m!}
\]  

(3.92)

it is demonstrated that for large \( n_x \) values, the mean yield simply reduces to

\[
X_A = 1 - \frac{e^{-\alpha Da}}{Da \left( \frac{1 - \alpha}{n_x} \right)^{n_x} \left( \frac{1 - \alpha}{n_x} \right) + 1}
\]  

(3.93)

Yield calculations using Equation 3.93 are presented in Table 3.5 for the various regular networks listed in Table 3.4 and \( Da = 1 \).
Table 3.5  
First-order reaction yield for $Da = 1$ in various regular networks.

<table>
<thead>
<tr>
<th>Network</th>
<th>$X_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>62.33%</td>
</tr>
<tr>
<td>2</td>
<td>62.39%</td>
</tr>
<tr>
<td>3</td>
<td>62.36%</td>
</tr>
<tr>
<td>4</td>
<td>62.34%</td>
</tr>
</tbody>
</table>

Despite the different degrees of resemblance between RTD functions, similar first-order reaction yields were obtained for all 4 networks. Again, as occurred with the third RTD moments calculation, the yield results do not allow to quantify how similar the RTDs really are.

The second methodology is only based on the inspection of the RTDs resemblance. Assuming that both the first and second moments of two RTD functions are equal, an heuristic evaluation criteria may be obtained by overlapping both curves and determining the area of the non-intersecting regions (dashed regions in Figure 3.16 to Figure 3.18) as

$$
\frac{|E_i - E_j|}{E_i} = \int_0^n \frac{|E_i(\Theta) - E_j(\Theta)|}{E_i(\Theta)} d\Theta
$$

(3.94)

Table 3.6 compares the relative differences between the area of the RTD functions of the various networks listed in Table 3.4 and the area of the RTD function of network 1.

Table 3.6  
Relative differences between the area of the RTD functions of various networks and the area of the RTD function of network 1.

| Network | $\frac{|E_i - E_j|}{E_i}$ |
|---------|--------------------------|
| 1       | 0.00%                    |
| 2       | 30.2%                    |
| 3       | 12.5%                    |
| 4       | 4.98%                    |

Contrarily to the previous methodology, the heuristic evaluation criteria in Equation 3.94 shows responsiveness and correlation with the degree of resemblance between the different
RTDs. Thus it seems acceptable to assume that two networks with \( \frac{|E_i - E_j|}{E_i} \leq 5\% \) have similar RTDs, that is, similar macromixing behaviour, although they may present different micromixing behaviour. The validity of this assumption is shown in next section.

### 3.4.2 Micromixing and Chemical Reaction

Micromixing is here directly assessed from chemical reaction simulations with a twofold importance: first with the purpose of validating the NETMIX® model numerical implementation, the NETMIX® model computations, using first-order and second-order reactions, are compared in Section 3.4.2.1 and Section 3.4.2.2, respectively, with case studies for which chemical reaction results are known from previous relevant works; second the validated NETMIX® model is used to study the effect of the network input parameters on the reaction selectivity of consecutive-competitive second-order reactions.

#### 3.4.2.1 First-Order Reaction

For a first-order reaction, micromixing has no effect on the reactor performance. Therefore, the yield is predicted exactly by the segregation model and knowledge of the degree of micromixing is not required. This well known result is next used to query the numerical implementation.

Two particular regular networks based on network 1 and network 4 were constructed with the required input parameters given in Table 3.7. These parameters were obtained imposing that the network volumes do not differ more 0.5%.

<table>
<thead>
<tr>
<th>Table 3.7</th>
<th>Input parameters for network 1 and network 4.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Network 1</td>
</tr>
<tr>
<td>( n_x )</td>
<td>20</td>
</tr>
<tr>
<td>( n_y )</td>
<td>16</td>
</tr>
<tr>
<td>( d \text{[mm]} )</td>
<td>1.500</td>
</tr>
<tr>
<td>( D \text{[mm]} )</td>
<td>9.064</td>
</tr>
<tr>
<td>( L^0 \text{[mm]} )</td>
<td>10.00</td>
</tr>
<tr>
<td>( \phi )</td>
<td>45°</td>
</tr>
<tr>
<td>( V_{\text{net}} \text{[cm}^3\text{]} )</td>
<td>126.0</td>
</tr>
</tbody>
</table>
For a first-order reaction, the mean reaction yield is defined as

$$X_A = \frac{C_A^{\text{final}} - C_A^{\text{initial}}}{C_A^{\text{initial}}}$$  \hspace{1cm} (3.95)

where $C_A^{\text{final}}$ is the mean network outlet concentration of reactant $A$.

Table 3.8 compares the computed mean reaction yield by the NETMIX® model with the predicted data from the segregation model for network 1 and network 4, using a first-order reaction with reaction rate constant $k_i = 1.0 \text{ s}^{-1}$.

For the sake of comparison with the segregation model, a constant feed concentration distribution of reactant $A$ was used. Both simulations were performed for $Da = 1$ and with an initial concentration of reactant $A$ of $C_A^{\text{initial}} = 1.0 \text{ mol m}^{-3}$.

Table 3.8  \hspace{1cm} Mean reaction yields for the NETMIX® model and the segregation model for network 1 and network 4.

<table>
<thead>
<tr>
<th></th>
<th>NETMIX® model</th>
<th>Segregation model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Network 1</td>
<td>$X_A = 62.33%$</td>
<td>$X_A = 62.33%$</td>
</tr>
<tr>
<td>Network 4</td>
<td>$X_A = 62.34%$</td>
<td>$X_A = 62.34%$</td>
</tr>
</tbody>
</table>

As expected, the segregation model exactly describes the behaviour of the regular networks for a first-order reaction. Further, as network 1 and network 4 have similar macromixing, see Section 3.4.1, equal yields were computed for a first-order reaction under the same reaction condition, thus validating the NETMIX® model simulations.

3.4.2.2 Second-Order Reaction

For a first-order reaction (or a series of first-order reactions), micromixing has no effect on the reactor performance, and the segregation model exactly predicts the yield. Micromixing, if reactants are considered initially pre-mixed, decreases the yield for reaction orders greater than 1 and increases for orders less than 1 (see for example, Coker, 2001). This assertion is next compared with the simulations using the NETMIX® model.
Using a second-order reaction scheme (see Equation 3.51) the mean reaction yields for network 1 and network 4 were computed, considering equimolar initial concentrations of reactants \( A \) and \( B \) and a reaction rate constant of \( k_2 = 1.0 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \). For a second-order reaction, the Damköhler number is defined as

\[
Da = k_2 \tau \, C_{A}^{\text{initial}}
\]  
(3.96)

For comparison purposes both simulations were performed for \( Da = 1 \) with an initial concentration of reactant \( A \) of \( C_{A}^{\text{initial}} = 1.0 \text{ mol m}^{-3} \) and \textit{pre-mixed injection scheme}, with reactants \( A \) and \( B \) injected in every other feeding channels, maximising the reactants feed distribution.

The mean reaction yields computed for network 1 and network 4 were 49.16\% and 48.46\%, respectively.

Even though the difference in the yields is small for the parameter values selected, the point to be emphasised is that there is a difference. Since micromixing decreases the yield for reaction orders greater than one, it can be directly inferred from these simulations that network 4 possesses a higher degree of micromixing, i.e., a higher \textit{effectiveness of mixing}, than network 1.

This result constitutes evidence that the number of rows and the segregation parameter are not just macromixing parameters, but also micromixing parameters. Network 4 has a segregation parameter 30 times higher than network 1 (see Table 3.7), which contributes to a lower effectiveness of mixing, i.e., higher mean reaction yield. On the other hand, network 4 has half the number of rows of network 1, contributing decisively in the opposite way, that is, to a higher effectiveness of mixing of network 4 and thus to a lower mean reaction yield. The overall degree of micromixing results thus from the simultaneous contribution of the number of rows and the segregation parameter. Both parameters work in the same manner, increasing micromixing as their values are decreased.

Furthermore, the accordance of simulation results with theory highlights the good numerical implementation of the NETMIX® model.
In the previous simulations, no relevance was given to the reactants injection scheme. Since mixing is akin to the spatial re-arrangement of entities, different reactants injection schemes were here used, corresponding each to a different initial state of effectiveness of mixing.

Danckwerts (1952) has demonstrated, for second-order reactions, that if the purpose of mixing two reactants \( A \) and \( B \) is to enable them to react with one another, the highest rate of reaction is achieved when the inverse of the effectiveness of mixing is zero, i.e., for the maximum mixedness condition. The agreement of the NETMIX® model with this relevant result is next presented.

Using a second-order reaction, the mean reaction yield in network 1 was computed for different reactants injection schemes, corresponding each to a different degree of mixing in the reactants feed distribution, \textit{segregated injection schemes}. The reaction rate constant is \( k_2 = 1.0 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \). All simulations were performed for \( Da = 1 \), considering equimolar initial concentrations of reactants \( A \) and \( B \) and with an initial concentration of reactant \( A \) of \( C_A^{\text{initial}} = 1.0 \text{ mol m}^{-3} \).

Two cases, denoted as case 1 and case 2, were analysed:

- In case 1, the network inlet chambers are divided in a given even \textit{number of injection zones}, \( n_{\text{zones}} \), and reactants \( A \) and \( B \) are injected at the inlet channels of every other injection zone (see Figure 3.19). Each injection zone is constituted by an equal number of inlet chambers and the number of injection zones where reactant \( B \) is injected is referred as \textit{number of reactant B injection zones}, \( n_{\text{zonesB}} \).

- In case 2, reactant \( B \) is injected through the inlet channels of one or more separate reactant \( B \) injection zones, equally spaced, and reactant \( A \) is injected on the remaining injection zones. Each reactant \( B \) injection zone is now constituted by a maximum of one or two inlet chambers (see Figure 3.20). For each reactants injection scheme, the reactants concentrations, \( C_A^{\text{inlet}} \) and \( C_B^{\text{inlet}} \), are adjusted to ensure the same mean initial concentrations of reactants \( A \) and \( B \).
Figure 3.19 Segregated injection schemes for case 1.
Figure 3.20  Segregated injection schemes for case 2.
In Table 3.9 are listed the inlet concentrations of reactants $A$ and $B$, according the segregated injection schemes. A column with the number of injection zones, $n_{\text{zones}}$, and a column with the number reactant $B$ injection zones, $n_{\text{zones}B}$, are introduced to assist the reader.

<table>
<thead>
<tr>
<th>Case 1a</th>
<th>$C_A^{\text{in}}$ [mol m$^{-3}$]</th>
<th>$C_B^{\text{in}}$ [mol m$^{-3}$]</th>
<th>$n_{\text{zones}}$</th>
<th>$n_{\text{zones}B}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.000</td>
<td>2.000</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Case 1b</td>
<td>2.000</td>
<td>2.000</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Case 1c</td>
<td>2.000</td>
<td>2.000</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Case 1d</td>
<td>2.000</td>
<td>2.000</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>Case 2a</td>
<td>1.143</td>
<td>8.000</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Case 2b</td>
<td>1.333</td>
<td>4.000</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Case 2c</td>
<td>1.333</td>
<td>4.000</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>Case 2d</td>
<td>1.600</td>
<td>2.667</td>
<td>11</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 3.21 to Figure 3.28 show the computed concentration field maps of reactant $B$ and product $R$ in network 1 for $Da = 1$ and the segregated injection schemes of case 1 and case 2.
Figure 3.21  Concentration field maps of reactant B and product R in network 1 for Da = 1 and case 1a.

Figure 3.22  Concentration field maps of reactant B and product R in network 1 for Da = 1 and case 1b.
Figure 3.23  Concentration field maps of reactant B and product R in network 1 for $Da = 1$ and case 1c.

Figure 3.24  Concentration field maps of reactant B and product R in network 1 for $Da = 1$ and case 1d.
Figure 3.25  Concentration field maps of reactant B and product R in network 1 for $Da = 1$ and case 2a.

Figure 3.26  Concentration field maps of reactant B and product R in network 1 for $Da = 1$ and case 2b.
Figure 3.27  Concentration field maps of reactant B and product R in network 1 for Da = 1 and case 2c.

Figure 3.28  Concentration field maps of reactant B and product R in network 1 for Da = 1 and case 2d.
The effect of the number of reactant $B$ injection zones on the mean reaction yield, $X_A$, is shown, for both cases at $Da = 1$, in Figure 3.29. The dashed curves in Figure 3.29 represent the CSTR and the PFR limits using the pre-mixed injection scheme. As expected, the mean reaction yield increases with the increase in the number of reactant $B$ injection zones increases, i.e., as the initial state of effectiveness of mixing in the reactants is increased.

![Figure 3.29: Plot of the mean reaction yield versus the number of injection zones for case 1 and case 2 at $Da = 1$.](image)

From Figure 3.29 it is also clear that, for low number of reactant $B$ injection zones, case 2 presents a more effective behaviour in terms of mean reaction yield, however for a number of reactant $B$ injection zones higher than two, case 1 becomes more efficient.

These results are explained by noticing that although for a given number of reactant $B$ injection zones, $n_{zones B}$, there are, in both cases, $2n_{zones B}$ contact fronts between $A$ and $B$, the reactants concentration level on these contact fronts is different in each case.

It could be anticipated that case 2 would always lead to higher mean reaction yields, due to higher reaction rate on its contact fronts. Yet this is only true for low numbers of reactant $B$ injection zones. For a number of injection zones, $n_{zones B} \geq 3$, case 1 promotes better mixing between reactants, resulting in higher mean reaction yields. Both cases tend to the maximum limiting yield of 49.2%, which occurs for the premixed injection scheme, bellow the mean reaction yield for a CSTR or a PFR, 61.8% and 50.0%, respectively.
Figure 3.29 provides evidence that the reactants injection scheme strongly affects the mean reaction yield, and therefore it becomes a model parameter for micromixing.

Three parameters have been clearly identified to be related with micromixing: the number of rows, the segregation parameter and the reactants injection scheme. The effect of all three parameters on micromixing is further explored in Section 3.4.2.3.

3.4.2.3 Consecutive Competitive Second-Order Reactions

Section 3.4.2.1 and Section 3.4.2.2 treated first-order and second-order reactions, respectively. In this section, studies are extended to include consecutive competitive second-order reactions.

Multiple reactions offer a way to evaluate the predictions of models which aim to describe interactions between mixing and chemical reaction (see for example, Baldyga and Bourne, 1999). Next, the effect of the previously identified micromixing parameters is further observed using a consecutive competitive second-order reaction scheme, described by Equation 3.52. In this reaction the selectivity in either product, \( R \) or \( S \) can be used to express the product distribution. In this work, the resulting product distribution is expressed by the fraction of \( B \) present in \( S \), that is the selectivity in \( S \), defined as (Bourne et al., 1981b)

\[
X_S = \frac{2C_S^{\text{final}}}{C_R^{\text{final}} + 2C_S^{\text{final}}} 
\]  
(3.97)

where \( C_R^{\text{final}} \) and \( C_S^{\text{final}} \) is the mean network outlet concentration of products \( R \) and \( S \), respectively.

Figure 3.30 and Figure 3.31 show the selectivity in \( S \) as a function of the Damköhler number for the various regular networks given in Table 3.10. All simulations results were obtained for \( k_1 = 12500 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \) and \( k_2 = 1000 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \), using the pre-mixed injection scheme, with reactants \( A \) and \( B \) injected in every other feeding channels, and considering equimolar initial concentrations of reactants \( A \) and \( B \), with an initial concentration of reactant \( A \) of \( C_A^{\text{initial}} = 1.0 \text{ mol m}^3 \). The Damköhler number is here defined as

\[
Da = k_1 \tau C_R^{\text{initial}} 
\]  
(3.98)
Since equimolar initial concentrations of reactants $A$ and $B$ are used, $B$ becomes the limiting reactant, and thus the product distribution provides an assessment for micromixing. The dashed curves in these figures represent the limits for the CSTR and the PFR, obtained by classical kinetic methods (see for example, Levenspiel, 1972).

Table 3.10  Number of rows, number of columns and segregation parameter of various regular networks.

<table>
<thead>
<tr>
<th>Network</th>
<th>$n_x$</th>
<th>$n_y$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>10</td>
<td>32</td>
<td>0.015</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>32</td>
<td>0.377</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>32</td>
<td>0.755</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>32</td>
<td>0.014</td>
</tr>
<tr>
<td>9</td>
<td>100</td>
<td>32</td>
<td>0.357</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>32</td>
<td>0.739</td>
</tr>
</tbody>
</table>

Figure 3.30 and Figure 3.31 clearly show that the segregation parameter has a strong impact on $X_x$, although the selectivity in $S$ is always contained between the CSTR and the PFR limits. More, an increase in the segregation parameter results, independently of the number of rows considered, in an approach of the selectivity in $S$ curve to the one from the PFR. This approach to the PFR limit occurs more markedly in the lower range of Damköhler numbers, showing that for higher $Da$ values increasingly smaller parts of the network are effectively used for reaction, up to the limit where reaction occurs only in the network inlet chambers, and thus all curves tend to overlap with the CSTR limit.

More, when comparing Figure 3.30 with Figure 3.31 for the same Damköhler number and roughly same segregation parameter, different selectivities in $S$ are observed.

These observations constitute further and final evidence of the impact of the number of rows and the segregation parameter on both macromixing and micromixing. However, contrary to Section 3.4.2.2, direct inferring of the effect of number of rows and the segregation parameter on micromixing is not possible since macromixing conditions were not kept constant between the various simulated networks.
Figure 3.30  Selectivity in $S$ versus $Da$ for network 5, network 6 and network 7, using the pre-mixed injection scheme.

Figure 3.31  Selectivity in $S$ versus $Da$ for network 8, network 9 and network 10, using the pre-mixed injection scheme.

Although from the above results and the results in Section 3.4.2.2, it can be concluded that the CSTR limit cannot be reached using the pre-mixed injection scheme, this may not be said for other injection schemes, as shown next.
The segregated injection schemes, as shown in Figure 3.32, were simulated in network 5 and network 8. All simulations were performed for $k_1 = 12,500 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_2 = 1000 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$, considering equimolar initial concentrations of reactants $A$ and $B$, with an initial concentration of reactant $A$ of $C_A^{\text{initial}} = 1.0 \text{ mol m}^{-3}$.

Figure 3.32 Segregated injection schemes for network 5 and network 8.
The curves of the selectivity in S against the Damköhler number are shown in Figure 3.33 and Figure 3.34. The dashed curves in Figure 3.33 and Figure 3.34 represent the CSTR and the PFR limits, whereas the full dots curve represents $X_s$ for the corresponding network using the pre-mixed injection scheme.

![Graph showing selectivity $X_s$ versus Da for network 5, using segregated injection schemes.](image)

**Figure 3.33** Selectivity in S versus Da for network 5, using segregated injection schemes.

![Graph showing selectivity $X_s$ versus Da for network 8, using segregated injection schemes.](image)

**Figure 3.34** Selectivity in S versus Da for network 8, using segregated injection schemes.

Figure 3.33 and Figure 3.34 show that the use of segregated injection schemes, in general
leads to higher $X_S$ than the pre-mixed injection scheme and the CSTR limit. More, the increase in the number of reactant $B$ injection zones results in a decrease in the selectivity in $S$, for the same Damköhler number. In Figure 3.35 and Figure 3.36 the change of $X_S$ with $n_{zones B}$ is presented, for the particular case of network 5 at $Da = 1$ and $Da = 10$, respectively. The dashed curves in Figure 3.35 and Figure 3.36 represent the CSTR and the PFR limits using the pre-mixed injection scheme.

**Figure 3.35** Plot of $X_S$ versus $n_{zones B}$ for network 5 at $Da = 1$.

**Figure 3.36** Plot of $X_S$ versus $n_{zones B}$ for network 5 at $Da = 10$. 
These simulation results are in agreement with the well-known observation that the selectivity in $S$ is, for similar consecutive competitive second-order reactions, reduced by promoting good mixing between reactants $A$ and $B$ before significant reaction occurs (see for example, Bourne, 1982), i.e., by increasing the initial state of effectiveness of mixing of the reactants.

For further insight into the use of segregated injections schemes, Figure 3.37 to Figure 3.39 show the computed concentration field maps of reactant $A$ and products $R$ and $S$ in network 5 for $Da = 1$ and $n_{zones_B}$ variable.

The fact that reactants $A$ and $B$ are separately injected strongly affects products $R$ and $S$ distribution. Product $R$ is mainly formed on the contact fronts between reactants $A$ and $B$, with almost complete consumption of $A$. Conversely, product $S$ is mainly formed between contact fronts were unreacted $B$ promotes the consumption of $R$ into $S$, which origins the darker red colour. The increase in the number of reactant $B$ injection zones flattens the reactants concentration gradients, which causes reducing the excess of $B$ present after consumption of $A$ and preventing the formation of product $S$, thus the fading of the dark red colour between contact fronts, as can be seen from Figure 3.38 to Figure 3.39.

The NETMIX® model is shown to describe with qualitative consistency the impact of the number of rows, segregation parameter and reactants injection scheme, as micromixing parameters, on the product distribution for consecutive competitive second-order reactions.
Figure 3.37  Concentration field maps of reactant A and products R and S in network S for Da=1 and n_{zones B} = 1.
Figure 3.38  Concentration field maps of reactant A and products R and S in network S for $Da=1$ and $n_{zones R} = 3$. 
Figure 3.39  Concentration field maps of reactant A and products R and S in network 5 for $Da = 1$ and $n_{zones} = 5$. 
3.5 Conclusions

Based on a network structure of unit cells, a new model for mixing has been developed. The unit cell of the NETMIX® model consists of one chamber and three channels, modelled as a perfectly mixed continuous stirred tank reactor and plug-flow reactors, respectively.

Describing one conceivable way of coupling macromixing and micromixing in a continuous flow system, the NETMIX® model given in the present work proves to be a practical simulation instrument, capable of straightforwardly be adjusted to specific situations. Being a simple model, mathematically well defined, it can serve as a basis for a diversity of calculations, and especially it gives a plausible description of chemical reaction under distinct macromixing and or micromixing states.

The model presents the possibility of generating networks with or without horizontal channels, networks with channels and or chambers diameters regular or varying randomly, and networks with different boundary conditions. Further, the model includes the additional possibility of removing from the network structure channels and or chambers in a random or specified manner, thus adjusting to particular situations. However, in the simulations reported here only regular networks with periodic boundary conditions and without horizontal channels were used.

Analysis of simulated RTDs lead to the development of a simple methodology to design regular networks having different design parameters but similar macromixing. The parameters identified to affect macromixing are: the number of rows and the segregation parameter.

Chemical reaction simulations were performed for three reaction schemes – first-order reaction, second-order reaction and consecutive competitive second-order reactions – with the purpose of validating the model numerical implementation and studying the yield and selectivity dependency on micromixing.

For first-order reaction, the well-known result that the output is independent of the micromixing was proved.

Simulations for second-order reaction showed yield dependency on micromixing for network structures with indistinguishable yields for the first-order reaction, allowing to identified as micromixing parameters the number of rows and the segregation parameter. Second-order reaction simulations further revealed the reactants injection scheme to be the
third micromixing related parameter. Simulations showed good agreement with case studies for which chemical reaction results are known from previous works.

Simulations for consecutive competitive second-order reactions showed strong product distribution dependency on the identified micromixing parameters. Under certain reactants injection schemes, the NETMIX® model is capable of simulating large deviations from the selectivity predicted by the classical kinetic methods. More, published experimental results agree with the trends shown from the NETMIX® model.

Thus, the present model allows for a systematic investigation of macromixing and micromixing outcomes for different reaction schemes on different network structures, so that qualitative results obtained a priori can be used to design network structure based static mixers with improved effects on both the yield and selectivity of reaction.

Specific comparison of computed with experimental results will be included in Chapter 5, essential to compare the performance of the NETMIX® model with wide-ranging experiments. In Chapter 5, the NETMIX® model will be applied to consecutive competitive second-order reactions, used as test reaction for micromixing, in a model structure based on the NETMIX® model, the NETMIX® static mixer, for which reliable experimental data for the flow field and chemical reaction is determined.

Before this task is undertaken, a CFD analysis on flow field dynamics in a regular network of chambers and channels without horizontal channels such as the NETMIX® model, is carried out in Chapter 4 to assess mixing inside that structure.
4. CFD SIMULATION

4.1 Introduction

The purpose of this chapter is to study the flow field in a regular network of chambers and channels such as the NETMIX® model, by means of CFD simulation, aiming to check the viability of mixing in that structure. Furthermore, this study inspects the deviations of the actual flow field in the chambers relative to the perfect mixing assumption established in the Chapter 3.

The flow field is simulated with a 2D model described in Section 4.2, using the commercial CFD code FLUENT™ 6.1, from Fluent Inc.. Section 4.3 includes a short review of the FLUENT™ numerical solver for modelling fluid flow. In Section 4.4 the flow field simulations are presented and analysed. In view of the simulation results a hypothesis regarding the flow dynamics dependency on geometry is established in Section 4.5. In Section 4.6 the hydrodynamics space and time scales are calculated, showing that present simulations account even for the smallest involved scales. The conclusions from this chapter are presented in Section 4.7.
4.2 Model Description

The model geometry used for the CFD simulations is described in Section 4.2.1, the general governing equations for incompressible viscous flow field, in Section 4.2.2, and the set of boundary and initial conditions for both steady state simulations and transient simulations, in Section 4.2.3 and Section 4.2.4, respectively.

4.2.1 Geometry

The 2D model consists of a single axial cut passing through the centre of a regular network of chambers and channels. Figure 4.1 shows the geometry of the network composed of 22 chambers connected by channels used in the CFD simulations.

![Diagram of the 2D model](image)

*Figure 4.1 Schematic drawing of the 2D model used in the CFD simulations.*

Comparing with the regular networks in previous chapter, one boundary chamber at every odd-numbered row and respective channels were removed to obtain a symmetric geometry.
The fluid enters the network through the eight network inlet channels, segments $b_i^{\text{inlet}}$ to $b_i^{\text{inlet}}$, and exits through the eight network outlet channels, segments $b_i^{\text{outlet}}$ to $b_i^{\text{outlet}}$. The remaining segments and curves represent the network walls, both the channels and chamber walls.

In Chapter 3 the symbols $D$ and $d$ were used to represent the chambers and the channels diameters, respectively. These same symbols are used in the 2D geometry for the chambers diameter and channels width, respectively, since these dimensions, although not strictly the same, intend to represent the 3D structure of the network.

### 4.2.2 Governing Equations

The flow field simulation is achieved by numerical integration of the equations that govern the hydrodynamics, i.e., the continuity and Navier-Stokes equations. For incompressible flow, the equation for conservation of mass, or *continuity equation*, assumes the form

$$\nabla \cdot (\rho \vec{v}) = 0$$  \hspace{1cm} (4.1)

where $\vec{v}$ is the velocity field. The conservation of momentum for Newtonian fluids is described by the *Navier-Stokes equation*

$$\rho \frac{D\vec{u}}{Dt} = -\nabla p + \mu \nabla^2 \vec{v} + \rho \vec{g}$$  \hspace{1cm} (4.2)

where $\rho$ and $\mu$ are the fluid density and molecular viscosity, respectively, $t$ is the time, $p$ is the static pressure and $\vec{g}$ is the local gravity force per unit mass.

### 4.2.3 Boundary Conditions for Steady State Simulations

Boundary conditions specify the flow variables on the *boundaries* of the physical model. They are, therefore, a critical component of the FLUENT™ simulations and it is important that they are specified appropriately. The model boundary conditions at the network walls, network inlet channels and network outlet channels are presented in this section.

#### 4.2.3.1 Network Walls

The no slip condition is assumed at the network walls, meaning that the $x$ and $y$ velocity components, $v_x$ and $v_y$, respectively, are equal to the wall velocity in each direction. For this
problem this condition is translated by setting both velocity components to zero at the walls, i.e., \( v_x = 0 \) and \( v_y = 0 \).

4.2.3.2 Network Inlet Channels

The fluid enters the network inlet channels from a direction parallel to the channel walls, i.e., at the entrance of each channel \( v_x = 0 \) or \( v_y = 0 \), depending on if the channel is parallel to the \( y \)-axis or \( x \)-axis, respectively (see Figure 4.1). Furthermore, the value of the velocity at all inlet channels, \( u_m \), is imposed to be the same, and at the inlet channels entrance the flow profile is assumed parabolic with \( v_x = 0 \) and \( v_y = 0 \) at the walls.

The space-averaged velocity at the network inlet channels, \( u_m \), is, by definition, the average flow rate per unit area, which for the case of the 2D inlet channels parallel to the \( x \)-axis is given by

\[
    u_m = \frac{1}{d} \int_0^d v_x \, dy
\]

and for the case of the 2D inlet channels parallel to the \( y \)-axis, \( u_m \) is given by

\[
    u_m = \frac{1}{d} \int_0^d v_y \, dx
\]

Therefore, the velocity profile of the inlet channels parallel to the \( x \)-axis is obtained as

\[
    v_x = 1.5 u_m \left\{ 1 - \left( \frac{y - y_{centre}}{\frac{d}{2}} \right)^2 \right\}
\]

where \( y_{centre} \) is the \( y \) coordinate of the channel centre, relatively to the coordinate system origin. For the case of the inlet channels parallel to the \( y \)-axis the velocity profile is

\[
    v_y = 1.5 u_m \left\{ 1 - \left( \frac{x - x_{centre}}{\frac{d}{2}} \right)^2 \right\}
\]
where \(x_{\text{centre}}\) is the \(x\) coordinate of the channel centre, relatively to the coordinate system origin.

### 4.2.3.3 Network Outlet

At exit of each of the network outlet channel, the *outflow* boundary condition is used. For FLUENT™ these boundary conditions are described as:

- a zero normal diffusion flux for all flow field variables;
- an overall mass balance distribution.

The zero diffusion flux condition means that the conditions of the outflow plane are extrapolated from within the domain and have no impact on the upstream flow. The outflow velocity and pressure are imposed by FLUENT™ in a way that is consistent with a fully-developed flow assumption. The outflow boundary condition is verified in fully-developed flows where the normal diffusion flux for all flow variables in the exit plane is null, and it can also be used with confidence if the assumption of a zero diffusion flux at the exit is expected to have no substantial impact on the flow solution, as is the case of the present simulation.

Coupled with the use of multiple outflow boundaries in FLUENT™ is the *Flow Rate Weighting* (FRW) that is required to be set at each boundary. The Flow Rate Weighting at boundary \(b_{i \text{outlet}}\), \(\text{FRW}_i\), is a weighting factor defined as

\[
\text{percentage flow through boundary } b_{i \text{outlet}} = \frac{\text{FRW}_i}{\sum_{j=1}^{n_{\text{outlet}}} \text{FRW}_j}
\]  

(4.7)

where \(n_{\text{outlet}}\) is the total number of outlet boundaries. For every outlet boundaries \(\text{FRW}\) is set to 1, meaning that the flow is equally divided among all channels. This assumption is based on the fact that all outlet channels present the same flow resistance and pressure and thus there is no preferential exit path.

### 4.2.4 Initial Conditions for Transient Simulations

The initial conditions and the imposed perturbation for the transient simulations are presented in this section.
4.2.4.1 Initial Conditions

The simulations of the 2D flow field are first made at steady state. An iterative convergence process is used to obtain the steady state solution, by setting the time dependent terms to zero in the governing equations (Equation 4.2), and considering a zero initial guess for all variables in the physical domain.

For a given set of operational conditions, the 2D flow field for $t = 0$ is equal to the respective steady state solution and the transient simulation is obtained by imposing a perturbation to the system, as described next.

4.2.4.2 Imposed Perturbation

For the case of transient simulations the fluid velocity in channel $b^\text{inter}_i$ is perturbed during a short time interval to rupture the steady state. The velocity is varied with time according to

$$v_j(t,x) = v_j(x)p(t)$$  \hspace{1cm} (4.8)

where $v_j(x)$ describes the steady state velocity profile and $p(t)$ is the perturbation time function affecting the profile. A smooth time function with a continuous first order derivative is used, avoiding in this way to induce any discontinuity in the flow field, given by

$$p(t) = 1 + \frac{a}{2}(1 - H(t - t_p))\left[1 - \cos\left(\frac{2\pi t}{t_p}\right)\right]$$  \hspace{1cm} (4.9)

where $a$ is the maximum amplitude of the perturbation and $t_p$ is the time interval over which the system is submitted to this perturbation. In all presented simulations, $t_p$ was set equal to a tenth of the elementary cell mean residence time, $\tau_{cell}$, as defined in Chapter 3.

Figure 4.2 shows the perturbation function $p(t)$ represented over one elementary cell mean residence time. In the present simulations, the amplitude $a$ was set to 1 and no other external perturbation is imposed to the system after the perturbation time $t_p = 0.1\tau_{cell}$. The fluid velocity achieves the maximum value of $2.0v_j$ for time $t = 0.05\tau_{cell}$. 
4.3 Numerical Solution

FLUENT™ provides comprehensive modelling capabilities for a wide range of incompressible and compressible, laminar and turbulent fluid flow problems. The analysis can be steady state or transient. In Section 4.3.1, the available methods for the numerical solution of the governing equations are described and in Section 4.3.2 a more detailed insight into the numerical scheme used by FLUENT™ is presented.

4.3.1 Overview of Numerical Schemes

FLUENT™ permits to solve the differential governing equations for the conservation of mass and momentum using either of two different numerical methods:

- the segregated solver, used in the present work, where the governing equations are solved sequentially (i.e., segregated from one another);
- the coupled solver where the governing equations are solved simultaneously (i.e., coupled together).

Both schemes use a control-volume-technique consisting of:

- partition of the physical domain into discrete control volumes, using a computational grid. The physical domain used in the simulations is shown in Figure 4.1. Figure 4.3 shows, for an elementary cell, the numerical grid used for domain partition. To build the geometry and generate the computational grid or mesh, the integrated geometry pre-processor for CFD analysis, GAMBIT™, was used. The unstructured
face mesh in Figure 4.3, consisting of quadrilateral mesh elements, was created applying the GAMBIT™ Quad-Pave meshing scheme;

- integration of the governing equations on each control volume, constructing algebraic equations for the discrete dependent variables;

- linearization of the discretized governing equations, resulting in a linear system of equations for the dependent variables;

- solution of the linear equation system.

Even though both methods use a similar discretization process, succinctly described next, the approach used for linearization and solution of the discrete equations is distinct. A brief description on the accessible linearization methods in FLUENT™ is also presented.

![Numerical grid, mesh, inside an elementary cell.](image)

Figure 4.3 Numerical grid, mesh, inside an elementary cell.

4.3.1.1 Discretization

The equations that govern the motion of fluids are partial differential equations. These equations cannot be directly computed to produce an analytical solution, therefore, the partial differential equations have to be transformed into a numerical analogue given by the
numerical discretization. From the three major numerical discretization techniques – the finite differences method, the finite elements method and the finite volumes method – FLUENT™ uses the third.

To better understand this discretization method consider the steady state conservation equation for transport of a scalar quantity \( \zeta \) written in integral form for a control volume \( V \)

\[
\oint \rho \zeta \vec{v} \cdot d\vec{A} = \oint \partial_t \zeta \vec{V} \cdot d\vec{A} + \oint s_{\zeta} dV
\]  

(4.10)

where \( \rho \) is the density, \( \vec{v} \) the velocity vector, \( \vec{A} \) the surface area vector, \( \partial_t \zeta \) the diffusion coefficient, \( \nabla \zeta \) the gradient of \( \zeta \) and \( s_{\zeta} \) the source of \( \zeta \) per unit volume. Equation 4.10 is applied to each cell, and its discretization on a given cell yields

\[
\sum_{f}^n \rho_f \vec{v}_f \cdot \vec{A}_f = \sum_{f}^n \partial_t \zeta \nabla \zeta \cdot \vec{A}_f + s_{\zeta} V
\]  

(4.11)

where \( n_{faces} \) is the number of faces encircling the cell, \( \zeta_f \) is the value of \( \zeta \) convecting trough face \( f \), \( \rho_f \vec{v}_f \cdot \vec{A}_f \) is the mass flux trough the face, \( \vec{A}_f \) is the area of the face, \( \nabla \zeta \) is the magnitude of \( \nabla \zeta \) normal to the face and \( V \) is the cell volume.

By default, the discrete values of \( \zeta \) are stored by FLUENT™ at the cells centres, yet, the values of \( \zeta \) at the faces, \( \zeta_f \), are required for Equation 4.11. Therefore \( \zeta_f \) have to be interpolated from the cell centre values using an upwind scheme. FLUENT™ allows the selection of the desired discretization scheme for the convection terms of each governing equation. Several upwind schemes are available, namely: first-order upwind; second-order upwind; power law; and QUICK. Details about these schemes may be found in the software theory manual (FLUENT 6.1 User’s Guide, 2003). In this work the first-order upwind was used.

4.3.1.2 Temporal Discretization

For transient simulations, the governing equations are discretized in both space and time. The spatial discretization for the time-dependent equations is similar to the steady state case; still, the temporal discretization involves the integration over a time step \( \Delta t \) of every term in the differential equations.
When the segregated solver is used, the integration of the transient terms is evaluated by means of an *implicit time integration* method, as described next.

A generic expression for the time evolution of a variable $\zeta$ is given by

$$
\frac{\delta \zeta}{\delta t} = T(\zeta)
$$

(4.12)

where the function $T(\zeta)$ incorporates any spatial discretization. If the time derivative is discretized using backward differences, the first-order accurate temporal discretization is given by

$$
\frac{\xi^{n+1} - \xi^n}{\Delta t} = T(\xi)
$$

(4.13)

and the second-order discretization, used in the present work, is given by

$$
\frac{3\xi^{n+1} - 4\xi^n + \xi^{n-1}}{2\Delta t} = T(\xi)
$$

(4.14)

where $n + 1$ is the value at next time level $t + \Delta t$, $n$ is the value at the current time level $t$ and $n - 1$ is the value at the previous time level $t - \Delta t$ of the scalar quantity $\xi$. Once the time derivative has been discretized, $T(\xi)$ is evaluated at the future time level

$$
\frac{\xi^{n+1} - \xi^n}{\Delta t} = T(\xi^{n+1})
$$

(4.15)

This is referred to as implicit integration since $\xi^{n+1}$ in a given cell is related to $\xi^{n+1}$ in neighboring cells through $T(\xi^{n+1})$. The implicit Equation 4.15 is solved iteratively by initializing $\xi^{i}$ to $\xi^{n}$ until $\xi^{i}$ stops changing. At that point $\xi^{n+1}$ is set to $\xi^{i}$. The advantage of the fully implicit scheme is that it is unconditionally stable with respect to time step size (FLUENT 6.1 User’s Guide, 2003).

A second method, referred to as the *explicit time integration* method, is available only when the coupled solver is used. Details for the explicit integration, although not relevant for present work, can be found in the software theory manual (FLUENT 6.1 User’s Guide, 2003).
4.3.1.3 Linearization

Once discretized, the non-linear governing equations of continuity and momentum must be linearized to produce a linear system of equations for the dependent variables in every computational cell, that once solved will result in an updated flow field solution. For example, recalling Equation 4.11, a linearized form of the discretized scalar transport equation on a given cell \( J \) can be written as

\[
\tau_j \zeta = \sum_{nb} \tau_{nb} \zeta_{nb} + S_j
\]

(4.16)

where \( \zeta_{nb} \) is the value of \( \zeta \) in the neighbouring cells, \( \tau_j \) and \( \tau_{nb} \) are the linearized coefficients for \( \zeta \) and \( \zeta_{nb} \), and \( S_j \) is the source term. Similar equations can be written for each cell in the grid.

The manner in which the governing equations are linearized in FLUENT™ may take an implicit or explicit form with respect to the dependent variable, or set of variables, of interest, as follows:

- In the segregated solver with implicit linearization, the unknown value of a given variable in each cell is computed using a relation that includes existing and unknown variables from the adjacent cells, resulting in a system of linear equations with one equation per cell. The subsequent system of linear equations is solved using a point implicit linear equation solver (Gauss-Seidel) in conjunction with an **algebraic multigrid method** (AMG). Then for the next variable all cells are once more considered at the same time, and a new system of linear equations is produced and solved. This procedure is repeated for all field variables. In this way, all variables are determined, one variable at a time for all cells.

- In the coupled solver with implicit linearization, for every cell, each governing equation is linearized in an implicit form with respect to all dependent variables in the set of governing equations, resulting in a system of linear equations with \( N \) equations per cell, where \( N \) is the number of coupled governing equations. The unknown value of a given variable in each cell is computed using a relation that includes existing and unknown variables from the adjacent cells. The subsequent system of linear equations, with \( N \) equations for each cell, is solved as described above, but now all variables are determined in all cells at the same time.
In the coupled solver with *explicit linearization*, each governing equation is linearized in an explicit form with respect to all dependent variables in the set of governing equations, resulting again in a system of linear equations with $N$ equations per cell. This system of equations is explicit in the unknown dependent variables, and the unknown value of a given variable in each cell is computed using a relation that includes only existing values. For this reason the solution is obtained using a multi-stage solver (Runge-Kutta). For this explicit approach, a *full approximation storage* (FAS) multigrid scheme can be employed to accelerate the multi-stage solver convergence. In this case all variables are determined one cell at a time.

In the present work all steady state and transient simulations were done using the segregated solver with implicit linearization.

### 4.3.2 The Segregated Solver

Following the overview of numerical schemes used in FLUENT™ in this section are presented of the particularities related with the discretization of the governing equations and their solving procedure by means of the segregated solver.

#### 4.3.2.1 Discretization of the Governing Equations

Writing the continuity equation in integral form as

$$ \oint \rho \bar{v} \cdot d\bar{A} = 0 $$

(4.17)

the discrete equation is easily obtained after integration over the control volume

$$ \sum_{f}^{n_{vol}} \rho v_n A_f = 0 $$

(4.18)

where $v_n$ is the magnitude of the velocity normal to face $f$, $\rho v_n A_f$ is the mass flux through face $f$ and $A_f$ is the face area.

The discretization scheme described in the previous Section 4.3.1.1 for a scalar transport equation is similarly applied here to discretize the momentum equations. For example, considering the momentum equation written in integral form
\[ \oint \rho \vec{v} \cdot d\vec{A} = -\oint p \mathbf{I} \cdot d\vec{A} + \oint \vec{\tau} \cdot d\vec{A} \]  \hspace{1cm} (4.19)

where \( \mathbf{I} \) is the identity matrix, the discretized \( x \)-momentum equation assumes the following structure

\[ t_f v_x = \sum_{nb} t_{nb} v_x + \sum p_f \vec{A} \cdot \hat{x} \]  \hspace{1cm} (4.20)

where \( t_f \) is the centre coefficient, \( t_{nb} \) are the influence coefficients from the neighbour cells, \( p_f \) is the pressure field and \( \vec{A} \cdot \hat{x} \) is the surface area projection over the \( x \)-axis.

4.3.2.2 Pressure Interpolation Scheme and Pressure-Velocity Coupling

If the pressure field and face mass fluxes were known, Equation 4.20 could be easily solved to yield the velocity field. The pressure field and mass fluxes are obtained as a part of the solution, and, as mentioned in Section 4.3.1.1, their discrete values are stored by FLUENT\textsuperscript{TM} at every cell centre. However, Equation 4.20 requires the value of pressure at the face between cells, and therefore an interpolation scheme is required to compute the face values of pressure using the cell values.

Several pressure interpolation schemes are available in FLUENT\textsuperscript{TM}: the standard scheme; the second-order scheme; the body-force-weighted scheme; and PRESTO! (Pressure Staggering Option). In the simulations presented here, the standard scheme, which interpolates the pressure values at the faces using momentum equation coefficients, was used (Nurick, 1976). Since a smooth pressure variation between cell centres is expected, as a consequence of the employment of a highly packed mesh in the domain, the use of this interpolation scheme is adequate to resolve the pressure field.

As outlined in Section 4.3, the segregated solver solves the momentum and continuity equations sequentially. Yet, and since pressure does not appear explicitly in Equation 4.18 for incompressible flows, the continuity equation is used as an equation for pressure. In order to derive an equation for pressure from the discrete continuity equation, FLUENT\textsuperscript{TM} provides the option to choose among three pressure-velocity coupling algorithms, that are all part of the SIMPLE (Semi-Implicit Method for Pressure-Linked Equations) family of algorithms: SIMPLE; SIMPLEC (SIMPLE-Consistent) and PISO (Pressure-Implicit with Splitting of Operators).
In the steady state simulations, the pressure-velocity coupling algorithm was set to its default option, the SIMPLE algorithm, given that both SIMPLE and SIMPLEC have similar convergence rates, except for complicated flows involving turbulence and or additional physical models, which is not the case.

In the transient simulations the SIMPLE algorithm was also used. Although the PISO algorithm is highly recommended for transient flows when small time steps are required, as in the present simulations, it results in increased computational expense.

Further details about the pressure interpolation schemes and pressure-velocity coupling algorithms may be found in the FLUENT 6.1 User’s Guide (2003).

4.3.2.3 Under-Relaxation Parameters

Due to the non-linearity of the equation set solved by FLUENT™, it is necessary to control the change of the computed variables produced during each iteration. To this purpose, the segregated solver uses under-relaxation. In a simple form, under-relaxation means that the new value of a variable $\xi_j$ within a cell $J$ depends upon the old value, $\xi_{j,\text{old}}$, according to:

$$
\xi_j = \xi_{j,\text{old}} + \gamma \Delta \xi_j
$$

(4.21)

where $\Delta \xi_j$ is the computed change in $\xi_j$ and $\gamma$ is the under-relaxation factor.

In all simulations the under-relaxation factors for all variables were set to FLUENT™ default values: 0.3 for pressure; 1 for density; 1 for body forces; and 0.7 for momentum.

4.3.2.4 Convergence Criteria

Convergence during the solution process is checked by FLUENT™ by dynamically monitoring of residuals for each defined variable. The solution stops automatically when convergence criteria are simultaneously met for all variables.

Consider the discretized conservation equation, without source terms, for a generic variable $\xi$ at a cell $J$

$$
\xi_j = \sum_{nb} t_{nb} \xi_{nb}
$$

(4.22)
where \( t_j \) is the centre coefficient, \( t_{nb} \) are the influence coefficients from the adjacent cells. In the segregated solver, the computed residual \( R_{\xi} \) is the imbalance, summed over all the computational cells in Equation 4.18. This is referred as the \textit{unscaled residual} and may be written as

\[
R_{\xi} = \sum_j \left| \sum_{nb} t_{nb} \xi_{nb} - t_j \xi_j \right| \tag{4.23}
\]

In general, it is difficult to judge the convergence by examining the residuals defined in Equation 4.23, since no scaling is employed. FLUENT\textsuperscript{TM} scales the residual using a scaling factor representative of the flow rate of \( \xi \) through the domain. The \textit{scaled residual} is defined as

\[
R_{\xi} = \frac{\sum_j \left| \sum_{nb} t_{nb} \xi_{nb} - t_j \xi_j \right|}{\sum_j |t_j \xi_j|} \tag{4.24}
\]

The scaled residual is a more appropriate indicator of convergence for most problems (FLUENT 6.1 User’s Guide, 2003).

In all simulations the residuals were set to \( 10^{-3} \) for the continuity and both the momentum equations, which is equivalent to a momentum and total mass conservation of 0.10% relatively to the system inlet.

4.4 Simulations

From the CFD simulations, the basic flow field variables, that is the velocity components in both \( x \) and \( y \) directions, \( v_x \) and \( v_y \), and the pressure, \( p \), are directly obtained for each discretized cell in the physical domain. Other physical quantities related to these three variables are then computed for a greater insight into the flow field structures and dynamics, namely: \textit{vorticity} and \textit{streamlines}; \textit{mixing intensity}; \textit{power spectra}; and \textit{cross-correlation function}.

Steady state simulations and transient simulations were performed for Reynolds numbers \( Re = 50, 75, 100, 150, 200, 300, 500 \) and \( 700 \), using FLUENT\textsuperscript{TM} in a dedicated 3.00 GHz Intel\textsuperscript{R} Pentium\textsuperscript{R} IV with 2 048 MB RAM.
The dimensions of the model are the following: chambers diameter, \( D = 7.0 \) mm, channels width, \( d = 1.5 \) mm, and distance between the centres of obliquely interconnected chambers, \( L^o = 10.0 \) mm.

For all simulated Reynolds numbers, a numerical grid with 436,007 elements was used. From the hydrodynamic scales analysis later shown in Section 4.6, this grid density has been proven to be sufficient for the all simulations.

The Reynolds number is defined at the inlet channels as

\[
Re = \frac{\rho v_{in} d}{\mu}
\]  

(4.25)

where \( \rho \) is the fluid density, \( v_{in} \) is the velocity at the inlet channels, \( d \) is the channels width and \( \mu \) is the fluid viscosity. The values of \( v_{in} \) and the 2D network mean residence times, \( \tau \), for each \( Re \) are listed in Table 4.1 for liquid water at 20°C.

<table>
<thead>
<tr>
<th>( Re )</th>
<th>( v_{in} [\text{ms}^{-1}] )</th>
<th>( \tau [\text{s}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>3.36×10^-2</td>
<td>2.562</td>
</tr>
<tr>
<td>75</td>
<td>5.03×10^-2</td>
<td>1.708</td>
</tr>
<tr>
<td>100</td>
<td>6.71×10^-2</td>
<td>1.281</td>
</tr>
<tr>
<td>150</td>
<td>1.01×10^-2</td>
<td>0.854</td>
</tr>
<tr>
<td>200</td>
<td>1.34×10^-2</td>
<td>0.641</td>
</tr>
<tr>
<td>300</td>
<td>2.01×10^-2</td>
<td>0.427</td>
</tr>
<tr>
<td>500</td>
<td>3.36×10^-2</td>
<td>0.256</td>
</tr>
<tr>
<td>700</td>
<td>4.70×10^-2</td>
<td>0.183</td>
</tr>
</tbody>
</table>

Table 4.1 Values of \( v_{in} \) and \( \tau \) for the 2D model using liquid water at 20°C.

Transient simulations were performed up to a final time of ten network mean residence times, using a fixed integration time step, corresponding to one tenth of the time interval over which the system is perturbed (see Section 4.2.4.2), i.e.,

\[
\Delta t = \frac{1}{10} t_p = \frac{1}{100} \tau_{cell}
\]  

(4.26)
In Section 4.4.1 and 4.4.2, respectively, the steady state simulations and transient simulations results are presented and analysed. Particular attention is given to chamber 1 and chamber 2, shown in Figure 4.1. The relative positions of chamber 1 and chamber 2 in the simulated geometry were chosen so that they are both at an equal maximum distance from the network limits, with the least influence of the boundary conditions over the recorded data.

4.4.1 Steady State Simulations

CFD simulations of the 2D flow field were first performed at steady state for Reynolds numbers between $Re = 50$ and $Re = 700$. A symmetric solution was always obtained.

Flow field maps are presented with the purpose of quickly and qualitatively evaluate the flow field at steady state. Aiming to enhance the flow field visualisation, vorticity and streamlines are computed for each of the simulated Reynolds number.

Vorticity, $\omega$, is a measure of the rotation of a fluid element as it moves in the flow field, and is defined as the curl of the velocity vector

$$\omega = \frac{\partial v_y}{\partial x} - \frac{\partial v_x}{\partial y}$$

(4.27)

In dimensionless form it may be expressed as

$$\omega^* = \frac{d}{v_{in}} \left( \frac{\partial v_y^*}{\partial x} - \frac{\partial v_x^*}{\partial y} \right) = \frac{\partial v_y^*}{\partial x} - \frac{\partial v_x^*}{\partial y}$$

(4.28)

where $\omega^*$ is the dimensionless vorticity and $v_x^*$ and $v_y^*$ are the dimensionless velocity components.

A streamline is a continuous line on which the tangent at any point is parallel to the velocity vector at that point. Streamlines computation is based on the stream function, $\psi$, since they correspond to the locus of points with a constant value of the stream function at time $t$. Therefore, in steady flow, lines of constant $\psi$ will form a fixed array of lines, while, in unsteady flow, the array will continuously evolve.

In steady flow solutions, the streamlines define the flow paths, since by definition there can be no fluid flow in the normal direction to a streamline, while in unsteady flow solutions, and
for each time instant, the streamlines represent the flow paths that would occur if no further flow field time evolution is assumed.

The stream function is related with the velocity field according to

\[ d\psi = \frac{\partial\psi}{\partial x} dx + \frac{\partial\psi}{\partial y} dy \]  \hspace{1cm} (4.29)

To avoid duplication of figures, since the steady state solution is used as the initial state for the transient simulations, the velocity magnitude, vorticity and streamline maps for the steady state simulations, at Reynolds numbers in the range \(50 \leq Re \leq 700\), are presented in Figure 4.4 to Figure 4.19 at time instant \(t/\tau = 0.0\). For each value of \(Re\), a set of two figures is presented:

- the entire physical domain flow field is shown from the velocity magnitude maps;
- the streamline and vorticity maps are presented for chamber 1 and chamber 2.

4.4.2 Transient Simulations

For each simulated Reynolds number, the transient simulation is done using as an initial condition the steady state solution and imposing a perturbation to the system, as described in Section 4.2.4.2.

In addition to the general description of the flow field structures from the flow field maps shown in Section 4.4.2.1 and with the purpose of further insight into its dynamics, the normal velocity time histories for two probe points, the centres of chamber 1 and chamber 2, are presented in Section 4.4.2.2. Although velocity history plots provide comprehensive description of the system dynamics, information not observed directly from the time histories is gained by further presenting other related quantities such as: the mixing intensity in Section 4.4.2.3; the power spectra in Section 4.4.2.4; and the velocity cross-correlograms in Section 4.4.2.5. In Section 4.4.2.6 pressure drop calculation results are presented.

4.4.2.1 Flow Field Maps

As previously referred, flow field visualization provides a quick and qualitative assessment of the flow field. Further, flow visualization has the advantage of describing the entire flow field, unlike velocity probes that provide only local information. For unsteady flows in
particular, flow visualization renders details of the flow field far more quickly than a compilation of point-by-point measurements. The most effective scheme is to use flow visualization to describe the general characteristics of the flow field, and then to use selected point measurements to provide detail.

Figure 4.4 to Figure 4.19 present velocity magnitude, vorticity and streamline maps at several time instants, for Reynolds numbers in the range $50 \leq Re \leq 700$. For each value of $Re$, a set of two figures is presented:

- the entire physical domain flow field is shown from the velocity magnitude maps at time instants $t/\tau = 0.0$ and $t/\tau = 10.0$;

- a dynamic sequence of the flow field evolution, from streamline and vorticity maps, is presented at time instants $t/\tau = 0.0, 0.5, 1.0, 2.5, 5.0$ and $10.0$ for chamber 1 and chamber 2.

A first overview of all maps shows clearly the existence of two flow field regimes in the range of $Re$ studied. In maps up to $Re = 100$ (see Figure 4.4 to Figure 4.7), there is no sustainable evolution of the flow field, while for Reynolds numbers in the range $100 \leq Re \leq 700$ (see Figure 4.9 to Figure 4.19) the flow field tends to a fully developed self-sustained oscillatory state. The value of Reynolds number marking the onset of self-sustainable oscillatory states, $Re = 100$, is denoted as the critical Reynolds number.

For $Re$ lower than the critical Reynolds number, $Re = 50$ (Figure 4.4 and Figure 4.5) and $Re = 75$ (Figure 4.6 and Figure 4.7), a final steady state flow regime is always identified. In this flow regime, once a perturbation occurs, the system passes trough a transient period, but it always evolves towards the initial steady state, i.e., the steady state solution.

Above the critical Reynolds number, the flow field shifts, almost instantaneously after the perturbation, to a self-sustainable oscillatory regime, and all maps show a strong time dependency.

For the steady state regime, vorticity and streamlines maps show the presence of two types of flow structures: jets and vortices. In detail it is observed the existence of: two jets impinging approximately in the chamber centre, each one trapping a vortex with its adjacent wall; two vortices trapped between the inlet jets and the upper wall of the chamber; and two other vortices trapped between the jets outlet and the lower chamber wall.
For Reynolds numbers in the range $100 \leq Re \leq 700$, and even thought a flow regime transition occurs, the same flow structures are observed, but now the vortices continuously modify their locations, shapes and sizes with time, interacting \textit{ad infinitum} with the jets.

The self-sustainability of the system dynamics for $Re \geq 100$, comes from the interaction of two opposed well balanced forces, i.e., the two jets. Remarkably, in different geometries with impinging jets, such as confined impinging jets mixers (Lee et al., 1980; Tucker and Suh, 1980; Kusch et al., 1989; Harris et al., 1992; Unger and Muzzio, 1999; Santos et al., 2002), the critical Reynolds number, marking the transition from steady to transient flow regimes, closely matches the value observed for this system.

In the range of Reynolds numbers with self-sustainable oscillatory regimes here studied, the interaction between the different flow structures is shown to increase continuously. From the dynamic sequence maps shown in Figure 4.15, Figure 4.17, and Figure 4.19, for $Re = 300, 500$ and $700$, it can be seen that vortices are intensely deformed, occasionally occurring the coalescence of the upper and lower vortices, and jets are further disturbed in their paths changing the location of the interface between them with time. This is the most likely cause for the increasing randomness in the jets oscillation, as it will be later shown in the power spectra analysis in Section 4.4.2.4.

Besides the flow field observations inside the chambers, the spatial evolution of the flow may be also depicted from the single chambers flow field maps. Below the critical Reynolds number, maps in Figure 4.4 to Figure 4.7 show an identical flow field in both chambers. For Reynolds numbers $Re = 100, 150$ and $200$, the flow field maintains its resemblance, showing however some minor loss of synchronization between chambers. Above $Re = 200$, the flow field inside the chambers presents a growing loss of similitude.

Further insight can be obtained from the velocity magnitude maps, of which dynamic visualization movies were made for all Reynolds numbers. From the movies, the overall flow field dynamics is clearly observed, highlighting most of the above described flow behaviour. However, these results are not here presented, due to the obvious limitations of a written publication.
Figure 4.4  Network velocity magnitude map for $Re = 50$ at $t/\tau = 0.0$ and $t/\tau = 10.0$. 
Figure 4.5  Vorticity and streamline maps for chamber 1 and chamber 2 for Re = 50 at several time instants.
Figure 4.6  Network velocity magnitude map for $Re = 75$ at $t/\tau = 0.0$ and $t/\tau = 10.0$. 
Figure 4.7  Vorticity and streamline maps for chamber 1 and chamber 2 for $Re = 75$ at several time instants.
Figure 4.8  Network velocity magnitude map for $Re = 100$ at $t/\tau = 0.0$ and $t/\tau = 10.0$. 
Figure 4.9  Vorticity and streamline maps for chamber 1 and chamber 2 for $Re = 100$ at several time instants.
Figure 4.10  Network velocity magnitude map for $Re = 150$ at $t/\tau = 0.0$ and $t/\tau = 10.0$. 
Figure 4.11 Vorticity and streamline maps for chamber 1 and chamber 2 for $Re = 150$ at several time instants.
Figure 4.12  Network velocity magnitude map for $Re = 200$ at $t/\tau = 0.0$ and $t/\tau = 10.0$. 
Figure 4.13  Vorticity and streamline maps for chamber 1 and chamber 2 for $Re = 200$ at several time instants.
Figure 4.14  Network velocity magnitude map for $Re = 300$ at $t/\tau = 0.0$ and $t/\tau = 10.0$. 
Figure 4.15  Vorticity and streamline maps for chamber 1 and chamber 2 for $Re = 300$ at several time instants.
Figure 4.16  Network velocity magnitude map for $Re = 500$ at $t/\tau = 0.0$ and $t/\tau = 10.0$. 
Figure 4.17  Vorticity and streamline maps for chamber 1 and chamber 2 for \( Re = 500 \) at several time instants.
Figure 4.18  Network velocity magnitude map for $Re = 700$ at $t/\tau = 0.0$ and $t/\tau = 10.0$. 
Figure 4.19  Vorticity and streamline maps for chamber 1 and chamber 2 for Re = 700 at several time instants.
4.4.2.2 Velocity Time Histories

The dynamic behaviour of the flow field can be depicted from the time histories of the velocity components at different locations.

As a result of the elementary cells geometry, the chamber inlet streams are forced to impinge in the chamber centre at a 90° angle, and then shift their paths to a 45° angle towards the main flow direction (see Figure 4.20). Therefore, and since this last flow direction is not aligned with either of the Cartesian axis, a calculation is required to obtain the velocity component collinear with the main flow fluctuations, referred as the normal velocity, \( v_n \).

The analysis of the mixing dynamics inside the chambers is tackled by studying the time dependence of the normal velocity at a single point located in the chamber centre.

![Figure 4.20](image)

*Figure 4.20  Transformation of Cartesian coordinates into natural flow field coordinates.*

The dimensionless normal velocity, \( v_n^* \), is therefore calculated as

\[
v_n^* = (v_x^* - v_y^*) \cos \phi'
\]

where \( \phi \) is the angle formed between the \( x \)-axis and the normal flow direction, and \( v_x^* \) and \( v_y^* \) are the dimensionless velocity components in both \( x \) and \( y \) directions, defined as

\[
v_x^* = \frac{v_x}{v_{in}}
\]

\[
v_y^* = \frac{v_y}{v_{in}}
\]
where $v_{in}$ is the velocity at the network inlet channels, which for the present case of incompressible flow and regular network is equal to the space-averaged velocity at every channels.

In Figure 4.21 the time histories of two typical velocity components $v_x^*$ and $v_y^*$ are shown, and Figure 4.22 presents the derived normal velocity from these velocity plots.

![Figure 4.21 Typical $v_x^*$ and $v_y^*$ time histories.](image)

![Figure 4.22 $v_n^*$ time history from the $v_x^*$ and $v_y^*$ time histories shown in Figure 4.21.](image)

Figure 4.23 and Figure 4.24 show the normal component of the velocity time series, $v_n^*$, at the two different probe positions, chamber 1 and chamber 2 centres, from the CFD simulations for $Re = 50, 75, 100, 150, 200, 300, 500$ and $700$, and up to a final time of $10\tau$. 
Figure 4.23 shows a remarkably similar behaviour of $v_n^*$ for both chambers location, at each Reynolds number, but the system evolution is clearly dependent on the simulated flow conditions, i.e., on the Reynolds number.

For $Re < 100$, the imposed initial perturbation (see Section 4.2.4.2) results in an overall instability of the system, with consequent effects over the flow field dynamics, as can be seen from the oscillations of the normal velocity component. Yet, the normal velocity oscillations are quickly damped and the system evolves to the steady state from which initially departed (see Figure 4.23).

For $Re \geq 100$, the system is no longer capable of achieving a steady state flow regime, but instead evolves to states with fully self-sustained oscillatory behaviour (see Figure 4.23 and Figure 4.24). Again this is the critical Reynolds number, or the Reynolds number value above which the system achieves fully developed oscillatory self-sustainability.

From Figure 4.23 and Figure 4.24 it can also be depicted that $v_n^*$ shows increasing amplitude as the Reynolds number increases. This amplitude increase is clearly seen in Figure 4.23 from $Re = 100$ to $Re = 150$, while for Reynolds numbers ranging from $Re = 200$ to $Re = 700$ (Figure 4.24) such increase is no longer visually perceptive. This last issue will be further addressed and discussed in the spectral analysis studies in Section 4.4.2.4.

Above the critical Reynolds number, a *warm-up time*, for the system to evolve from the initial steady state to states with fully developed oscillatory states, is observed, and is most probably associated with the time necessary for the growth of the instabilities. This warm-up time takes up to $2.5\tau$ for $Re = 100$, decreasing for higher Reynolds numbers. Although such high warm-up time is only verified for the critical Reynolds number, in the flow field analysis presented here, the first $2.5\tau$ of both time series were not included in the calculations for all Reynolds numbers.
Figure 4.23  Time histories of $v_n^*$ at the chamber 1 and chamber 2 centres for Reynolds numbers ranging from $Re = 50$ to $Re = 150$. 
Figure 4.24  Time histories of $\psi_n$ at chamber 1 and chamber 2 centres for Reynolds numbers ranging from $Re = 200$ to $Re = 700$. 
4.4.2.3 Mixing Intensity

The mixing intensity is here estimated from the standard deviation of the flow field velocity fluctuations. The dimensionless mixing intensity, $\sigma_n^*$, was computed for the normal component of the velocity, as

$$\sigma_n^* = \frac{1}{n_{\text{samples}}} \sqrt{\sum_{i=1}^{n_{\text{samples}}} \left( v_n^*(i) - \langle v_n^* \rangle \right)^2}$$

(4.33)

where $n_{\text{samples}}$ is the total number of time instants considered, $v_n^*(i)$ is the dimensionless normal velocity component at a time instant $i$, and $\langle v_n^* \rangle$ is the average value of $v_n^*(i)$, calculated as

$$\langle v_n^* \rangle = \frac{1}{n_{\text{samples}}} \sum_{i=1}^{n_{\text{samples}}} v_n^*(i)$$

(4.34)

The dimensionless mixing intensity is a measure of the fluctuations in the normal velocity component and since it is normalized by the velocity at the inlet channels allows a direct comparison of the mixing dynamics between the different values of $Re$. Higher values of the mixing intensity from higher velocity fluctuations are directly associated with mixing mechanisms, given that these fluctuations promote the mixing of fluid with its surroundings.

The transient flow field simulations were done up to $10\tau$, however, as referred in the previous section and in view of the fact that the first $2.5\tau$ of the $v_n^*$ time series were removed, the analysed time series have only a total time of $7.5\tau$.

In Figure 5.16 the dimensionless mixing intensity, $\sigma_n^*$, calculated from Equation 4.33 is presented for Reynolds numbers in the range $100 \leq Re \leq 700$, for both chamber centres. A first feature of this plot is that both chambers show the same values of $\sigma_n^*$ at each $Re$, giving evidence of no evolution of the flow field statistics between chambers with different locations.

More, for the velocity time histories shown in Figure 4.23 and Figure 4.24, the dimensionless mixing intensity also evolves continuously from the lowest to the highest Reynolds number. The major variation in $\sigma_n^*$ occurs between $Re = 100$ and $Re = 150$, which clearly shows an evolution in the flow field dynamics after the regime transition at the critical Reynolds
number. Further evidence of this evolution range will be later provided in the power spectra analysis in Section 4.4.2.4. In the range of $200 \leq Re \leq 700$, no sharp increase in $\sigma^*_n$ occurs, indicating that no further flow evolution exist.

![Diagram](image)

**Figure 4.25** Evolution of $\sigma^*_n$ at the chamber 1 and chamber 2 centres with Reynolds number.

4.4.2.4 Power Spectra Analysis

Since from the direct comparison of the time series shown in Section 4.4.2.2 little information is extracted regarding the effect of the Reynolds number, here the dynamic analysis of the system in the frequency domain is performed. The transformation from the time domain into the frequency domain is accomplished by computing the frequency power spectra of the time series from the Fourier Transform.

The Fourier transform establishes the relationship between a *time data series* and its representation in the frequency domain. For discrete time series, the transformation from the time domain into the frequency domain is done using the *Discrete Fourier Transform*, DFT.

An infinite-range Fourier transform of a given time record $x(t)$ is defined by the complex-valued quantity (Bendat and Piersol, 1993)

$$\tilde{X}(f) = \int_{-\infty}^{\infty} x(t)e^{-j2\pi ft} dt$$  \hspace{1cm} (4.35)
where \( f \) is the frequency. By restricting the limits to a finite time interval of \( x(t) \), say in the range \((0, t_f)\), the finite-range Fourier transform is defined as

\[
\tilde{X}(f, t_f) = \int_0^{t_f} x(t) e^{-j2\pi ft} \, dt
\]  

(4.36)

Sampling the record \( x(t) \) at \( n_{\text{samples}} \) equally spaced points \( \Delta t \) apart, considering the initial point of the record to be \( t_0 = 0 \), so that \( t_i = i \Delta t \), and denoting the data values as

\[
x_i = x(i \Delta t) \quad i = 0, 1, 2, ..., n_{\text{samples}} - 1
\]  

(4.37)

Equation 4.36 can be written in the discrete form

\[
\tilde{X}(f, t_f) = \Delta t \sum_{i=0}^{n_{\text{samples}}-1} x_i e^{-j2\pi fi/\Delta t} \quad i = 0, 1, 2, ..., n_{\text{samples}} - 1
\]  

(4.38)

Using the discrete frequency values for the computation of \( \tilde{X}(f, t_f) \)

\[
f = \frac{k}{t_f} = \frac{k}{n_{\text{samples}} \Delta t} \quad k = 0, 1, 2, ..., n_{\text{samples}} - 1
\]  

(4.39)

the final form of the DFT, \( \tilde{X} \), is given by

\[
\tilde{X} = \frac{\tilde{X}(f, t_f)}{\Delta t} = \sum_{i=0}^{n_{\text{samples}}-1} x_i e^{-j2\pi ki/n_{\text{samples}}} \quad k = 0, 1, 2, ..., n_{\text{samples}} - 1
\]  

(4.40)

Notice that the DFT is independent of the sampling rate and the results are unique only for \( \Delta t = n_{\text{samples}}/2 \) since the Nyquist cut-off frequency occurs at this point.

For the computation of the DFT an improved algorithm that reduces the number of numeric operations is used, the Fast Fourier Transform (FFT) (Hearn and Metcalfe, 1995). The FFT of a time series yields a complex number series that is used to compute the power spectrum. The power spectrum is given by

\[
\tilde{G}(f) = \frac{2}{t_f} |\tilde{X}(f, t_f)|^2
\]  

(4.41)
From Equation 4.40, the power spectrum becomes

\[
\tilde{G}(f) = \frac{2}{n_{\text{samples}} \Delta t} \left| \tilde{X}(f,t) \right|^2 = \frac{2 \Delta t}{n_{\text{samples}}} \left| \tilde{X}^2 \right|
\]  

(4.42)

In this work all power spectra were normalised by their integral, i.e.,

\[
\tilde{G}^* = \frac{\tilde{G}(f)}{\int \tilde{G}(f) df}
\]

(4.43)

The FFT was obtained with the LabView™ software using its built-in library.

Figure 4.26 and Figure 4.27 show the power spectra of the \( \upsilon_n^* \) time histories at both probe points, for Reynolds numbers in the range of \( 100 \leq Re \leq 700 \). To allow a direct comparison for different values of \( Re \), the power spectra are presented in terms of the dimensionless frequency, \( f^* \), defined as

\[
f^* = \frac{fd}{\upsilon_{in}}
\]

(4.44)

where \( f \) is the flow field oscillation frequency, \( d \) is the channels width and \( \upsilon_{in} \) is the inlet channels velocity.
Figure 4.26  Normalised power spectra of $u_n^*$ at the chamber 1 and chamber 2 centres for Reynolds numbers ranging from $Re = 100$ to $Re = 300$. 
Figure 4.27 Normalised power spectra of $u_n^*$ at the chamber 1 and chamber 2 centres for Reynolds numbers ranging from $Re = 500$ to $Re = 700$.

The Strouhal number, $St$, at each $Re$, and for each probe point, is directly obtained as

$$St = \frac{f^*}{f^*_{\text{max}}}$$  \hspace{1cm} (4.45)

where $f^*_{\text{max}}$ is the value of dimensionless oscillation frequency at which the power spectrum presents the highest energy value. Figure 4.28 shows the Strouhal numbers for Reynolds numbers in the range of $100 \leq Re \leq 700$. The line in this figure corresponds to the geometry-based predicted Strouhal number according to Section 4.5.

For Reynolds numbers in the range $100 \leq Re \leq 300$, Figure 4.26 clearly shows a single strong energy peak in the power spectra, indicating that the velocity values oscillate with a well-defined frequency.

Further, from $Re = 100$ to $Re = 150$, the Strouhal number increases sharply (see Figure 4.28), indicating a strong evolution in the flow dynamics, which is also supported by the mixing intensity evolution with the Reynolds number, shown in Figure 4.25. For Reynolds numbers
in the range of $150 \leq Re \leq 300$, the values of $St$ are nearly unchanged, supporting the assumption referred in Section 4.4.2.2 that no evolution in the flow occurs.

For Reynolds numbers above $Re = 300$, the typical $St$ peak loses definition and the power spectra present a spread of energy through a range of frequencies, making the identification of the flow field oscillation frequency, and thus of the Strouhal number, a difficult task. The onset of new oscillatory states for Reynolds numbers in the range $500 \leq Re \leq 700$ is probably due to an increase in the jets turbulence, induced by the decreasing influence of viscous forces and corresponding increasing interaction between the different flow field structures: jets and vortices.

The power spectra for both chambers at each $Re$ are similar, giving further support to the evidence of no flow field statistics evolution between chambers, as mentioned in Section 4.4.2.3. Furthermore, this fact also shows the inexistence of spatial evolution of the flow field dynamics between chambers.

The small variability of $St$ with $Re$, shown in Figure 4.28, is strong evidence that the oscillation frequency values directly scale with $u_{in}$.

![Figure 4.28](image)

*Figure 4.28*  *Strouhal numbers from CFD simulations against Reynolds number.*
4.4.2.5 Cross-Correlograms

The cross-correlation of two sets of data describes the general dependency of one set of data on the other. Cross-correlation function measurements have many important applications, including measurement of time delays, determination of transmission paths or detection and recovery of a known signal in noise. Considering a pair of time data series \( x(t) \) and \( y(t) \) over an observation period \( t_r \), the cross-correlation is defined as (Bendat and Piersol, 1993)

\[
R_{12}(\xi) = \lim_{t_r \to \infty} \frac{1}{t_r} \int_0^{t_r} x(t) y(t + \xi) dt
\]  

(4.46)

where \( t \) is the time and \( \xi \) is the lag between the two time records.

The function \( R_{12}(\xi) \) may assume positive or negative values, presenting a maximum value at a time \( \xi \) that does not necessarily has to be zero, so both positive and negative lags are of interest. It is possible to compute \( R_{12}(\xi) \) for negative values of \( \xi \), interchanging \( x(t) \) and \( y(t) \), as

\[
R_{12}(-\xi) = R_{21}(\xi)
\]  

(4.47)

The plot of \( R_{12}(\xi) \) against \( \xi \) for a pair of data sets is called the cross-correlogram. Sharp positive and negative peaks of \( R_{12}(\xi) \) indicate the existence of strong correlation between \( x(t) \) and \( y(t) \) for specific \( \xi \) values, while for values of \( R_{12}(\xi) \) equal to zero \( x(t) \) and \( y(t) \) are said to be uncorrelated.

Since in this work the history records are not continuous in time, a discrete version of the cross-correlation is used instead. This function, referred to as the discrete cross-correlation function, is defined as

\[
R_{12}(\xi) = \frac{1}{t_T} \sum_{t=0}^{t_T} x(t) y(t + \xi), \quad \xi \in \left[0, \frac{t_T}{2}\right]
\]  

(4.48)

The function \( R_{12}(\xi) \) was computed using the IMSL™ routine CCF/DCCF in a program compiled in Absoft™ Pro Fortran for Mac™ OS X v8.0.

Recalling Equation 4.46, the cross-correlation can be interpreted as a function that relates \( x(t) \) and \( y(t) \) presenting the following behaviour: when \( x(t) = y(t + \xi) \) both time data series data are in phase and \( R_{12}(\xi) \) reaches a maximum; on the other hand when \( x(t) = -y(t + \xi) \) the series are out of phase and \( R_{12}(\xi) \) reaches a minimum. Hence, for two measuring points apart
in space, the lag time at the maximum value of the cross-correlation, $\xi^*$, is the time shift caused by the system for a known wave to travel between the two points. For lag times values which are integer multiples of $\xi^*$, local maxima of $R_{13}(\hat{\xi})$ occur. These aspects of the cross-correlation function are of crucial significance in the following results discussion.

The simultaneous availability of $u^*_n$ time series at two separately positions, chamber 1 and chamber 2 centres, allows their cross-correlation, and therefore computing the time it takes for a wave to travel between the two chamber centres. In addition, the cross-correlation function provides information concerning the synchronization between the behaviour of both velocity time series, namely if the series are in phase or out of phase.

Figure 4.29 and Figure 4.30 show the cross-correlograms of $u^*_n$ at the two probe points, for Reynolds numbers above the critical Reynolds number, ranging from $Re = 100$ to $Re = 200$ and from $Re = 300$ to $Re = 700$, respectively.

In Figure 4.29, all cross-correlograms persist periodically over all time displacements with the same frequency as the underlying time series, showing clearly that the $u^*_n$ time series at both positions are strongly coupled. The maximum of $R_{13}(\hat{\xi})$ occurs for $\hat{\xi} = 0$, indicating that both time series are in phase.

Furthermore, for Reynolds numbers ranging from $Re = 100$ to $Re = 200$, $\hat{\xi} = 0$ is at the same time a local maximum and the global maximum of function $R_{13}(\hat{\xi})$. This important aspect, together with the decaying shape of the cross-correlation plots, supports the assumption that both time series are similar, for the exception of a narrow-band random noise. In fact, the resemblance between both $u^*_n$ time series for $Re = 100$, 150 and 200 is patent in Figure 4.23 and Figure 4.24.

In Figure 4.30 the cross-correlograms display sharper peaks at certain time displacements, indicating the existence of strong correlation for those specific time displacements. However, as observed for lower Reynolds numbers, for Reynolds numbers in the range of $Re = 300$ to $Re = 700$ the local maximum and global maximum of function $R_{13}(\hat{\xi})$ occurs at $\hat{\xi} = 0$.

Contrary to Figure 4.29, the cross-correlograms in Figure 4.30 have no longer a well-defined decaying form, as a result of the presence of underlying frequencies to the typical flow field oscillation frequency, marking the beginning of flow field regimes with no repeatability. In spite of the increasing randomness in the flow field dynamics, also noticeable in the normalized power spectra analysis in Section 4.4.2.4, the spatial synchronization is maintained. This constitutes final evidence of no statistical or dynamic evolution of the flow field between chambers.
Figure 4.29  Cross-correlograms of $v_{q}^{*}$ at the chamber 1 and chamber 2 centres for Reynolds numbers ranging from $Re = 100$ to $Re = 200$. 
Figure 4.30 Cross-correlograms of $v_1^*$ at the chamber 1 and chamber 2 centres for Reynolds numbers ranging from $Re = 300$ to $Re = 700$. 
4.4.2.6 Pressure Drop

For the steady state simulations, the network total pressure drop, $\Delta p_{\text{steady state}}$, is given by

$$
\Delta p_{\text{steady state}} = \langle P_1 \rangle - \langle P_0 \rangle
$$

(4.49)

where $\langle P_1 \rangle$ and $\langle P_0 \rangle$ are the average pressure over all inlet and outlet channels, respectively.

For the transient simulations, the network total pressure drop, $\Delta p_{\text{transient}}$, becomes

$$
\Delta p_{\text{transient}} = \frac{1}{n_{\text{samples}}} \sum_{i=1}^{n_{\text{samples}}} (\langle P_1(i) \rangle - \langle P_0(i) \rangle)
$$

(4.50)

where $n_{\text{samples}}$ is the total number of time instants considered and $\langle P_1(i) \rangle$ and $\langle P_0(i) \rangle$ are the average pressure over all inlet and outlet channels, respectively, at a time instant $i$.

Figure 4.31 shows the total pressure drop from steady state simulations and transient simulations for various Reynolds numbers. Transient simulations were performed up to $10\tau$, but only the last $7.5\tau$ of the time series were taken into account for the pressure drop calculations.

![Figure 4.31 Network total pressure drop from CFD simulations.](image)

For $Re \geq 100$, the flow in the transient state simulations field was seen to always evolve to a fully self-sustained oscillatory behaviour state, with increasing velocity fluctuations causing
increasing energy losses by viscous dissipation inside the fluid, resulting in higher pressure drop values than those obtained for the steady state simulations, wherein only the wall frictional effects are present. For \( Re < 100 \), the pressure drop from both steady state simulations and transient simulations exactly overlap, as can be seen in Figure 4.31. Thus, the pressure drop from the steady state simulations may be considered, for all Reynolds numbers, a good indication of the fraction of pressure drop due to the network walls frictional energy losses.

4.5 Geometry-Based Flow Dynamics Prediction

Typical frequencies of oscillation of \( v'_n \) were observed in Section 4.4.2.4 for the range of \( 100 \leq Re \leq 700 \). The small variation of \( Str \) with \( Re \), shown in Figure 4.28, points to the hypothesis that the typical oscillation frequencies are associated to the well-defined network structure.

To check the validity of this hypothesis, the Strouhal numbers are calculated, assuming that the typical oscillation frequencies are ruled by a geometry-based mechanism. The geometry-based prediction of the Strouhal numbers is then compared with Strouhal numbers from the CFD simulation time series.

A simple relationship between geometry and flow field oscillation frequency, based on the mean residence time of one chamber, \( \tau_{chamber\,2D} \), the generated frequency, \( f_{2D} \), is given by

\[
    f_{2D} = \frac{1}{\tau_{chamber\,2D}} = \frac{2q_{in\,2D}}{V_{chamber\,2D}} 
\]

(4.51)

where \( q_{in\,2D} \) is the flow rate at each inlet channel defined as

\[
    q_{in\,2D} = u_{in} \, d \, z 
\]

(4.52)

and \( V_{chamber\,2D} \) is the volume of the chamber, approximately defined as

\[
    V_{chamber\,2D} = \pi \left( \frac{D}{2} \right)^2 \, z 
\]

(4.53)

where \( u_{in} \) is the inlet channels velocity, \( d \) is the inlet channels width, \( D \) is the chamber diameter and \( z \) is a third dimension normal to the 2D channel. Replacing Equation 4.52 and
Equation 4.53 into Equation 4.51, the generated frequency becomes equal to

\[ f_{2D} = \frac{8u_{in}d}{\pi D^2} \quad (4.54) \]

The geometry-based predicted Strouhal number, \( St_{2D} \), for the simulated network dimensions, \( d = 1.5 \times 10^{-3} \text{ m} \) and \( D = 7 \times 10^{-3} \text{ m} \), is then

\[ St_{2D} = f_{2D} \frac{d}{u_{in}} = \frac{8}{\pi} \left( \frac{d}{D} \right)^2 = 0.117 \quad (4.55) \]

Figure 4.28 shows the plot of the CFD simulation values of \( St \), for chamber 1 and chamber 2, and the geometry-based predicted \( St \) value, \( St_{2D} \). It is clear that the geometry-based flow dynamics prediction hypothesis describes the system behaviour between \( 150 \leq Re \leq 300 \) where typical oscillation frequency values are easily identified (Figure 4.27). For higher Reynolds numbers a typical well-defined oscillation frequency cannot be immediately obtained from the power spectra, as shown in Figure 4.27, since the oscillatory behaviour becomes more random. Nevertheless, for \( 500 \leq Re \leq 700 \), higher energy values occur for oscillation frequencies of \( St \approx 0.125 \) and this maximum relative deviation of no more than 7\% does not invalidate the hypothesis that the underlying frequency mechanism remains the same. Thus the initial assumption that the system typical oscillation frequency is ruled by a geometric-based mechanism is valid in the range of simulated Reynolds numbers.

### 4.6 Hydrodynamic Scales

Under isotropic homogeneous turbulence it is possible to compute the smallest length and time scales for the hydrodynamics known as the Kolmogorov scales of length and time. Although this is not the case, it was decided to compute the hydrodynamic scales of length and time to verify the adequacy of the computational grid and temporal discretization (see Section 4.3) to the present problem.

The Kolmogorov scale of length, \( \eta_k \), and Kolmogorov scale of time, \( \tau_k \), are defined, respectively, as (Tennekes and Lumley, 1972)

\[ \eta_k = \left( \frac{v^3}{\varepsilon_{turbulent}} \right)^{\frac{1}{4}} \quad (4.56) \]

and
\[ \tau_k = \left( \frac{v}{\varepsilon_{turbulent}} \right)^{1/2} \]  (4.57)

where \( v \) is the kinematic viscosity and \( \varepsilon_{turbulent} \) is the rate of dissipation of turbulent kinetic energy estimated as (Baladyga and Bourne, 1999)

\[ \varepsilon_{turbulent} = \frac{P_{mixing}}{V_{network}} \]  (4.58)

\( P_{mixing} \) is the mixing power consumption, given by

\[ P_{mixing} = \Delta p_{turbulent} q_f \]  (4.59)

where \( \Delta p_{turbulent} \) is the network turbulent pressure drop and \( q_T \) is the total flow rate. For a given Reynolds number, \( \Delta p_{turbulent} \) can be determined from the difference between the network total pressure drop from the CFD transient simulations, \( \Delta p_{transient} \), and network total pressure drop from the steady state simulations, \( \Delta p_{steady-state} \). Thus,

\[ \varepsilon_{turbulent} = \Delta p_{turbulent} \frac{\tau}{\rho} \]  (4.60)

From Equation 4.56 and Equation 4.57 are calculated the Kolmogorov length and time scales at each Reynolds number ranging from \( 100 \leq Re \leq 700 \). Both Kolmogorov length and time scales attain continuously lower values as the Reynolds number is increased, ranging, respectively, from 0.489 mm to 0.071 mm and from 0.239 s to 0.005 s.

According to Libby (1996) acceptable accuracy in DNS, Direct Numeric Simulation, is obtained if the grid spacing is four to six times greater than the Kolmogorov length scale. In the present work, the computational grid spacing was found to be 0.20 to 1.41 times larger than the Kolmogorov length scale, for \( Re = 100 \) and \( Re = 700 \), respectively. Furthermore, the time steps used in the temporal discretization were correspondingly 18.5 to 62.2 times smaller than the Kolmogorov time scale. Hence, the simulations presented here can be considered as DNS, and so it is not required to proceed with grid and time step sensitivity numerical analysis. This analysis will be again shown to be unnecessary from the good experimental validation results presented in Chapter 5.
4.7 Conclusions

In this chapter the flow field inside a regular network of chambers and channels such as the NETMIX® model, was characterized from CFD simulation. This type of approach has the unique advantage of giving all the hydrodynamic variables at every point and time. More, as shown from hydrodynamic scales analysis, the CFD simulations here presented follow under the category of DNS. Since DNS of flows are exact reproductions of the reality without any kind of model, these simulations may also be called numerical experiments (Givi and Mcmurtry, 1988).

From the presented simulations two types of flow field structures are clearly identified: jets and vortices. These structures are observed trough the range of simulated Reynolds numbers, and the main differences in the flow field is that the jets exhibit a self-sustainable oscillatory behaviour above a certain value of Reynolds number, $Re = 100$, defined as the critical Reynolds number.

Below the critical Reynolds number the system has the capability of damping any imposed perturbation, tending always to a steady state flow regime. For $Re \geq 100$, the system, after perturbed, is no longer capable of returning to the initial departing steady state, always evolving to a self-sustained oscillatory regime.

The flow field dynamics was studied from the time histories, mixing intensity and power spectra analysis. From this study, it is observed that the main flow features are roughly maintained, for both chambers, in the range of Reynolds numbers $100 \leq Re \leq 700$.

From the mixing intensity studies, a continuously increase of the flow field dynamics was observed. After the critical Reynolds number, and in the range of $Re = 100$ to $Re = 150$, there is strong evidence of a continuous and strong evolution of the flow field dynamics, after which, in the range of $150 \leq Re \leq 700$, the only observed trend is in the direction of a slight monotonically increase in the mixing intensity with $Re$.

From the power spectra analysis it was shown that above the critical Reynolds number the flow field oscillates with typical well-defined frequencies. The dimensionless oscillation frequency, defined by the Strouhal number, was kept almost constant with $Re$, and thus the typical frequencies scale directly with the velocity at the inlet channels. Supported on this
feature, it was later shown that the sole mechanism dictating the frequency of the flow field oscillation is the mean residence time in each chamber.

Furthermore, a trend of increasing randomness of the flow field oscillation is observed with the increasing Reynolds number, which is in good agreement with the observations from mixing intensity studies.

The spatial evolution of the flow field dynamics was studied from cross-correlation of velocity time series at two different locations. From this analysis it was quantitatively proved the observation that the flow field between chambers is strongly coupled, with the normal velocity time histories at both probe points found to be in phase.

In conclusion, from the simulated flow field it seems clear that the proposed network structure presents, above a critical but low Reynolds number, a strong flow field dynamics that promotes mixing with high energetic efficiency. Although the simulations here presented were shown to be DNS, the concluding validation of the simulated flow field and its role on mixing mechanisms is assessed in the following chapter.
5. MIXING AND CHEMICAL REACTION

5.1 Introduction

Mixing and chemical reaction are coexisting and interrelated phenomena in many chemical static mixers. The manner in which initially segregated reactants are brought together can have a great impact on the evolution of a chemical reaction. Inefficient mixing usually has a deleterious effect on both the yield and the selectivity of reaction, by slowing the formation of desired products and enhancing the generation of undesired materials. This aspect is most important when unwanted products must be separated in downstream processes, since the cost and dimensioning of such separation processes is directly related with the amount of impurities present (Ottino, 1994; Zalc and Muzzio, 1999). Thus, the availability of a model suitable to describe mixing and chemical reaction on a static mixer can translate into maximising the creation of the desired product and minimising the cost of downstream purification processes.

The NETMIX® model introduced in Chapter 3 is certainly attractive because of its simplicity and modest computational demands, but the practical value of such model of mixing and chemical reaction has to be rated, finally, on the basis of its ability to adequately predict experimental static mixer data.

In Chapter 4 a systematic CFD study in a regular 2D network of chambers and channels was conducted, supporting the mixing viability in a NETMIX® model based structure. CFD
involves the analysis of fluid flow and related phenomena such as mixing using numerical solution methods. Despite being a very powerful and versatile tool for the analysis and solution of problems which are of considerable interest in chemical engineering, CFD does not completely replaces experimental work (Kuipers and van Swaaij, 1997), being imperative that the results from CFD analysis are compared with experiments to assess the validity of the 2D CFD model to describe a 3D network structure. The comparison should allow the model validation, if the same dynamic behaviours are observed from the 3D experiments and 2D CFD simulations.

The twofold purpose to consider the validity of the 2D CFD model and the NETMIX® model in light of experimental data, along with the mixing efficiency evidenced from CFD analysis in Chapter 4 for the simulated network structure, conducted to the design and construction of a pilot NETMIX® unit.

Section 5.2 concerns specific information and details regarding the NETMIX® unit and experimental setup, and must be considered a prerequisite to the following sections. After the presentation of the experimental setup the basis are set for the presentation and interpretation of the tracer experiments and pressure experiments data, done in Section 5.3 and Section 5.4, respectively.

The used non-intrusive tracer flow visualization technique assures that results obtained correspond to the actual undisturbed flow. The possibility of capturing images of dynamic flow field instantaneous patterns at several time instants allows the comparison of the dynamic experimental data with the CFD results shown in Chapter 4 and thus the CFD model validation. More, the experimental work in Section 5.3 further contributes to the knowledge of the influence of the Reynolds number in the system dynamic behaviour.

In Section 5.4 pressure experiments results are presented and compared with the 2D CFD simulations in Chapter 4 to consider the validity of the NETMIX® model and the CFD model to describe the behaviour of the NETMIX® static mixer in terms of pressure drop.

Imaging experiments in Section 5.3 and chemical reaction experiments in Section 5.5 lead support for the NETMIX® model evaluation in Section 5.6 as macromixing and micromixing and chemical reaction descriptive model for the NETMIX® static mixer. The final conclusions from this chapter are presented in Section 5.7.
5.2 Experimental Setup

Section 5.2.1 starts with a basic description of the designed pilot NETMIX\textsuperscript{®} unit, where all experiments were carried out. In Section 5.2.2, the imaging equipment used is described along with the explanation of its components function and operation principles. Finally, Section 5.2.4 presents a brief description of the stopped-flow spectrometer, used in the chemical reaction experiments.

5.2.1 The NETMIX\textsuperscript{®} Unit

All experiments were conducted in a pilot NETMIX\textsuperscript{®} unit composed of a Plexiglas\textsuperscript{®} static mixing device, the NETMIX\textsuperscript{®} static mixer, four independent feeding reservoirs, one discharging reservoir, two pump systems and tubing with all necessary fittings. The core of the unit is the NETMIX\textsuperscript{®} static mixer and all accessory equipment serves the sole purpose of delivering fluid with a precise flow rate control. Technical drawings of the NETMIX\textsuperscript{®} static mixer are shown in Figure 5.1 and some installation views of the pilot NETMIX\textsuperscript{®} unit are shown in the photographs of Figure 5.2.

The NETMIX\textsuperscript{®} static mixer has a NETMIX\textsuperscript{®} model based structure, see Chapter 3, with $n_x = 49$ rows of spherical chambers connected by an oblique arrangement of cylindrical channels, each channel at an angle of $\phi = 45^\circ$ with the main flow direction, the $x$-axis. Each row alternates between 15 and 16 chambers, starting the first row with 15 chambers. By definition, the number of columns in a NETMIX\textsuperscript{®} static mixer, $n_y$, is the maximum number of chambers in a row. Therefore, in the present case $n_y = 16$.

Chambers in the first row are called inlet chambers, while the last row chambers are referred as outlet chambers. Each inlet and outlet chamber includes two opposed channels, in a direction normal to the static mixer plane, named respectively the inlet channels and the outlet channels. This assembly results in a total of 30 inlet channels and 30 outlet channels.

The characteristic dimensions of the chambers and channels are the same as those used in CFD simulation, i.e., chambers diameter $D = 7.000$ mm, channels diameter $d = 1.500$ mm, and oblique distance between two neighbouring chamber centres $L^\prime = 10.000$ mm.

The NETMIX\textsuperscript{®} static mixer void volume and segregation parameter are $V_{NETMIX} = 143\,600 \pm 70$ mm$^3$ and $\alpha_{NETMIX} = 0.052$, respectively.
Figure 5.1  NETMIX® static mixer technical drawings.
1 - NETMIX® unit mounting structure
2 - NETMIX® static mixer
3 - NETMIX® static mixer inlet channels
4 - NETMIX® static mixer discharging channels
5 - Feeding reservoirs
6 - Discharging reservoir
7 - Pump systems

Figure 5.2  Photographs of the pilot NETMIX® unit.
The 3D void structure of the static mixer was created from two machined Plexiglas® sheets joined together by polymerisation. The polymerisation reaction was initiated using chloroform which was subsequently vacuum removed.

Each Plexiglas® sheet forms half of the network matrix and half spheres and half cylinders were machined using a CNC (Computer Numerical Controlled) table, ensuring an alignment and dimensional precision of the chambers and channels up to ±0.001 mm. The fluids are driven to the NETMIX® static mixer using two Ismatec® MCP Standard pump systems; each consisting of a drive ISM404, a pump-head ISM724 and an extension block ISM185. Both pump-head and extension block have 6 rollers and 16 cassettes, although only 15 cassettes were actually used, as explained next. Each cassette was equipped with a Tygon® ST tube with internal diameter 1.85 mm.

To achieve the highest level of feeding control, each front and back side of the NETMIX® static mixer is fed from a single pump system, ensuring in this way an equal flow rate in all the 15 inlet channels on the same side.

Each MCP Standard pump system is capable of delivering from 3.15 ml min⁻¹ to 750.15 ml min⁻¹ per channel, at 20 °C, and to develop a maximum differential pressure of 1.0 bar. The flow rate is manually controlled through the driver speed controller, ranging from 1 rpm to 240 rpm, with a resolution of 0.1 rpm.

For the static mixer discharge, only one of the two available outlet channels per outlet chamber was used. The atmospheric fluid discharge is made at a single level in order to avoid preferential flow induced by pressure gradients.

### 5.2.2 Imaging

The components of the TSI® imaging equipment used in the flow visualisation experiments are described next. The system consists of a Charge-Coupled Device, CCD, high-speed camera (see Section 5.2.2.1), a synchroniser (see Section 5.2.2.2), and a computer for image acquisition and components control. The control and data acquisition parameters are set using the graphical interface of the software Insight®, from TSI®. For this work a 880 MHz Pentium® III computer with 512 MB RAM was used. Photographs of the imaging equipment components are shown in Figure 5.3.
5.2.2.1 The CCD Camera

The CCD camera model is a PIVCAM 10-30 from TSI®, with 1024 (H) × 1024 (V) pixels, each pixel with 8 bits definition, and a maximum frame rate of 30 Hz. The captured frames are transferred from the camera to the computer memory through a PCI card, the Frame Grabber (TSI® model 600067). Possible camera control settings in the software Insight® are: Free Run, Triggered Exposure and Triggered Double Exposure.

5.2.2.2 The Synchroniser

To capture flow field images, the CCD camera must be triggered with the correct sequence and timing. The Synchroniser (TSI® model 610032) performs this task, offering full computer
control using an RS-232 interface, tying the CCD camera and PC computer together as an integrated and automated system. The frame grabber receives the trigger signal from the Synchronizer, and starts acquiring a sequence of captures, with a user-defined frame rate. The maximum number of images that can be acquired depends on the camera type and memory option selected. This timing master camera setup is referred in the software *Insight*® as the *synchronizer triggered* mode, and is the appropriate for the acquisition of single frame sequences.

### 5.2.3 Pressure Measurements

In this section, the VALIDYNE® system used for the network pressure head loss measurements is described. The system consists of a pressure transducer and a carrier demodulator module installed in a model MC1-10T module case with a plug-in digital meter model PM212-1.

#### 5.2.3.1 The Pressure Transducer

Measurements of the NETMIX® static mixer total pressure drop were carried out using a variable reluctance pressure transducer (VALIDYNE® model DP-15). This fast response transducer uses interchangeable membranes that allow measurements in various pressure ranges. A diaphragm with working range from 0 Pa up to 860 Pa and sensitivity close to 1 Pa was used in the present work.

#### 5.2.3.2 The Carrier Demodulator Module

The VALIDYNE® model CD19A is a high-gain carrier demodulator, plug-in module for use in model MC1-10T module case. It provides transducer excitation, and amplifies and demodulates its output signal. Output frequency response is controlled by a low-pass active filter, and is switch selectable from 1 Hz to 1 kHz.

The CD19A power requirements of 5 V rms at 3 kHz carrier and ±15 V DC are supplied from the MC1-10T module case.

### 5.2.4 Chemical Reaction: The Stopped-Flow Reaction Analyser

A Microvolume Stopped-Flow Reaction Analyser, model SX.18MV-R from Applied Photophysics®, was used for the chemical reaction experiments. This reaction analyser is a
complete and fully functional stopped-flow system, providing the user with single mixing, single wavelength absorbance and fluorescence detection capability.

The SX.18MV-R shown in Figure 5.4 consists of a sample handling unit, a spectrometer and a 32-bit RISC® workstation, as described next.

5.2.4.1 The Sample Handling Unit

The sample handling unit is used with the purpose of delivering the samples to analyse into the SX.18MV-R optical detection cell. The optical detection cell has two orthogonal viewing ports made of silica, giving a choice of $\delta = 2$ mm or $\delta = 10$ mm optical path lengths.

The handling unit consists of two drive syringes (filled by two reservoir syringes) whose plungers are moved by a pneumatic ram operated at a pressure of 8 bar. This unit and the optical cell are both immersed in a thermostatic bath. Downstream of the driving syringes, the samples are fed into the optical cell.

5.2.4.2 The Spectrometer

The SX.18 MV-R spectrometer consists of a light source, a monochromator, photomultipliers and a photometric controller.

The light source uses a 150 watt gap shortened xenon bulb and includes a housing, a Safe-Start Igniter and is powered by the power controlled lamp supply.

The programmable grating monochromator (Czerny-Turner optical configuration) has continuously variable bi-lateral slits (allowing the bandpass to be varied from below 0.5 nm up to 37 nm) and an holographic diffraction grating blazed at 250 nm. The monochromator is fitted with a stepper motor drive and wavelength selection is controlled from the workstation. The light output from the monochromator is coupled to the viewport on the Stopped-Flow sample handling unit via a spectrosil light guide.

The photomultipliers are attached to the appropriate viewports on the Stopped-Flow sample handling unit, providing an operation range of 200 nm to beyond 870 nm.

The Photometric Controller produces the variable high voltage for the photomultipliers. Setting of the high voltage is under direct control of the spectrometer workstation. In addition, the Photometric Controller provides signal conditioning circuits through which the detector
signals pass prior to digitalisation. These facilities comprise interchangeable gain and electronic filters, under direct software control.

5.2.4.3 The Workstation and Data Acquisition

The workstation function is diverse. It provides direct control of spectrometer activity and data acquisition together with data manipulation and analysis. The CPU of the workstation is an ARM 32-bit RISC processor with 4 MB RAM. In addition to the workstation there is a photometric unit that digitalises the signal output from the photomultipliers.

![Photograph of the Microvolume Stopped-Flow Reaction Analyser](image)

1 - Sample handling unit
2 - Lamp power supply
3 - Safe-Start igniter
4 - 150 Watt xenon arc lamp
5 - Monochromator
6 - Photometric controller
7 - Workstation
8 - Photomultipliers

*Figure 5.4 Photographs of the Microvolume Stopped-Flow Reaction Analyser, model SX.18MV-R from Applied Photophysics®.*

5.3 Tracer Experiments

The experimental conditions for the set of tracer experiments performed in this work are reported in Section 5.3.1. The imaging experiments are presented in Section 5.3.2 and
discussed in Section 5.3.3. Finally, Section 5.3.4 presents the comparison between the experimental results and the 2D model CFD simulation results.

### 5.3.1 Experimental Conditions

The tracer flow visualization experiments were conducted in steady state, for Reynolds numbers ranging from $Re = 25$ to $Re = 700$. The static mixer steady state is considered attained after no further evolution is visually observed in its global behaviour. The list of the imposed settings using two Ismatec® MCP Standard pump systems is presented in Table 5.1.

<table>
<thead>
<tr>
<th>$Re$</th>
<th>speed [min$^{-1}$]</th>
<th>$q_{re}$ [ml min$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>8.5</td>
<td>1.741</td>
</tr>
<tr>
<td>37.5</td>
<td>12.7</td>
<td>2.646</td>
</tr>
<tr>
<td>50</td>
<td>16.9</td>
<td>3.521</td>
</tr>
<tr>
<td>75</td>
<td>25.4</td>
<td>5.292</td>
</tr>
<tr>
<td>100</td>
<td>33.9</td>
<td>7.064</td>
</tr>
<tr>
<td>150</td>
<td>50.9</td>
<td>10.60</td>
</tr>
<tr>
<td>200</td>
<td>67.9</td>
<td>14.14</td>
</tr>
<tr>
<td>300</td>
<td>101.8</td>
<td>21.21</td>
</tr>
<tr>
<td>500</td>
<td>169.6</td>
<td>35.34</td>
</tr>
<tr>
<td>700</td>
<td>237.5</td>
<td>49.49</td>
</tr>
</tbody>
</table>

Tap water was used as working fluid, at ambient pressure and air-conditioning controlled temperature of $20.0 \pm 0.5$ °C. A dye, methylene blue, was used to trace both streams delivered into the NETMIX® static mixer central inlet chamber (see Figure 5.5).

A practically uniform illumination and a good light dispersion were obtained using a white photo reflector located between the static mixer and a halogen lamp.

The viscosity of both coloured and uncoloured liquid solutions was considered constant and equal to $\mu = 1.0 \times 10^{-3}$ Pa s.
5.3.2 Flow Visualisation

The tracer experiments allow a qualitative analysis of the NETMIX® static mixer mixing performance as a function of the Reynolds number. Macromixing can be studied through visualization of the steady state overall patterns, and micromixing through local visualization of flow patterns, up to the smallest scales present, inside individual static mixer chambers.

Image acquisition is performed in the plane containing the chambers and channels centres. Since this plane has a geometry similar to the 2D model used in the CFD simulations, it allows immediate and direct comparison of the experimental data with the CFD results presented in Chapter 4.

5.3.2.1 Macromixing

Macromixing concerns the spread of the material throughout the static mixer, and its assessment is done from the visualisation of the tracer spread patterns in the NETMIX® static mixer, shown in Figure 5.6, Figure 5.7 and Figure 5.8, for the range of Reynolds numbers, $25 \leq Re \leq 700$, in steady state.

From Figure 5.6, it is observable that for $Re = 25$ and $Re = 37.5$ the same final steady state is achieved, indicating that no influence of the Reynolds number on the dynamic behaviour of the static mixer exists in this operating range. Except for the first three bottom chambers rows, where the plume presents a $45^\circ$ aperture, no further spread of tracer occurs up to the exit. This initial plume aperture is most probably resulting from pumps induced perturbations in the flow, after which, outside the pumps influence region, the plume keeps a uniform width. This plume behaviour indicates that pump influence is restricted to the inlet neighbouring region, being shortly dumped afterwards. The quick dissipation of perturbation
occurring in the static mixer makes impractical the use of pulsed flow to overcome minimum Reynolds limits for mixing. The non-spreading of the plume can only be caused by a complete lack of mixing inside the chambers, i.e. each stream flows in its original entrance side of the chamber, completely segregated from the opposed stream.

Increasing the Reynolds number from $Re = 37.5$ to $Re = 50$ an overall change of tracer spreading patterns is observed. At $Re = 50$, see Figure 5.7, the plume consistently opens from the bottom to the top of the static mixer, denoting a flow field transition to the onset of mixing mechanisms inside each chamber. For the range of studied Reynolds numbers above the flow field regime transition, Figure 5.7 and Figure 5.8 show a continuously increasing of the plume aperture, up to the physical limit of 45°. More, the overall tracer flow patterns become practically indistinguishable above $Re = 200$, as can be seen in Figure 5.8.

The continuous increase of the plume spread was already expectable from CFD simulation results shown in previous chapter, namely from the continuous increase of mixing intensity with $Re$.

Figure 5.6  Tracer experiments for Reynolds numbers $Re = 25$ and $Re = 37.5$: photographs of the NETMIX® static mixer in steady state for a single central injection point.
Figure 5.7  Tracer experiments for Reynolds numbers ranging from $Re = 50$ to $Re = 150$: photographs of the NETMIX® static mixer in steady state for a single central injection point.
Figure 5.8  Tracer experiments for Reynolds numbers ranging from $Re = 200$ to $Re = 700$: photographs of the NETMIX® static mixer in steady state for a single central injection point.
5.3.2.2 Micromixing

Micromixing is associated to the homogenisation of the mixture at the smallest scales. Therefore, micromixing assessment can be achieved through local visualization of mixing inside the chambers.

The dyed fluid forms an evolving plume from the single injection chamber towards the static mixer outlet, as can be seen from Figure 5.6 to Figure 5.8. Since flow patterns are only observable at chambers where clear and dyed fluid enters separately, the positioning of the imaging acquisition frame was set for each $Re$ to obtain the best contrast images, i.e., scanned chambers are in the interface between dyed and clear streams and sufficiently distanced from the pumps influence region and static mixer borders. Figure 5.9 shows an example of one frame acquired using the PIVCAM 10-30 camera. When scanning different positions, care was taken to ensure that at least two interface chambers are simultaneously acquired, allowing their comparison at the same exactly time instants. At each flow condition and scanning position, an ensemble of 200 frames with a frequency of 30 Hz was captured.

![Figure 5.9](image)

**Figure 5.9** Typical digital frame obtained with the PIVCAM 10-30 camera for the tracer experiments.

The scanned region comprehends a length of 25.20 mm by a width of 25.20 mm, thus a resolution of 24.61 $\mu$m/pixel. Such resolution permits the visualization of scales smaller than the Kolmogorov length scale found in Chapter 4 from CFD simulations. Since DNS of flow was made, the computed length scale is assumed valid, and therefore an effective imaging of micromixing is attained.

Figure 5.10 to Figure 5.25 present the dynamic flow pattern sequences inside two
neighbouring chambers, identified as chamber 1 and chamber 2 (see Figure 5.9), for the range of Reynolds numbers \( Re = 37.5 \) to \( Re = 700 \). To enhance mixing visualization, images were post-processed by indexing each gray level to a colour level ranging from white to blue.

Single chamber imaging shown the same flow patterns up to \( Re = 50 \), as expected from the overall patterns of tracer spreading shown in Figure 5.6. Therefore, bellow \( Re = 50 \) images at a single Reynolds number, \( Re = 37.5 \), are presented. Figure 5.10 and Figure 5.11 show the flow field patterns for \( Re = 37.5 \). At this operating condition there is almost complete segregation between the two halves of the chamber, i.e., total absence of convective transport between the dyed and clear streams. This particular flow pattern is the cause of no plume spreading towards the static mixer top, at \( Re < 50 \), as was observed in Figure 5.6.

For \( Re = 50 \), Figure 5.12 and Figure 5.13 indicate the existence of a flow regime transition, where mixing mechanisms are observed inside the chambers, resulting in some mixture degree between both inlet streams. The two types of flow field structures already identified in the CFD studies, jets and vortices, become also clearly visible. Moreover, the jets are now impinging approximately at the chambers centre. Further analysis of the sequence of frames shows that the interface between the dyed and clear streams is continuously changing with time, showing that the flow field presents a self-sustained oscillatory behaviour. Comparing chamber 1 and chamber 2, it is further observed that the two chambers present consistently the same flow patterns, for all the imaged times.

In the range of Reynolds numbers \( 50 < Re \leq 200 \), see Figure 5.12 to Figure 5.19, there is a clear increase in the mixing dynamics, with the interface oscillation amplitude growing with \( Re \). Interface oscillation causes both streams to be constantly engulfed by the vortices structures located near the top and bottom wall of each chamber. These structures are not clearly seen from the tracer experiments frames, but were identified during the dynamic visualisation of the tracer experiments and seem to be consistent with the flow field maps from CFD. It is also observed that chamber 1 and chamber 2 maintain the same flow patterns, for all the imaged times, but now with some minor underlying loss of synchronization as \( Re \) is increased. This flow field feature will be further discussed in Section 5.3.3.

The increase of mixing dynamics progressively turns the chamber homogenisation nearly instantaneous, with the tracer flow patterns above \( Re = 200 \) becoming featureless, see Figure 5.20 to Figure 5.25. The quasi-instantaneous homogenisation denotes very intensive mixing inside the chambers, which is studied in Section 5.5 through the use of test reactions for micromixing characterisation.
Figure 5.10  Tracer experiments at $Re = 37.5$: post-processed digital frames of chamber 1.

Figure 5.11  Tracer experiments at $Re = 37.5$: post-processed digital frames of chamber 2.
Figure 5.12  Tracer experiments at Re = 50: post-processed digital frames of chamber 1.

Figure 5.13  Tracer experiments at Re = 50: post-processed digital frames of chamber 2.
Figure 5.14  Tracer experiments at Re = 75: post-processed digital frames of chamber 1.

Figure 5.15  Tracer experiments at Re = 75: post-processed digital frames of chamber 2.
Figure 5.16  Tracer experiments at \( Re = 100 \): post-processed digital frames of chamber 1.

Figure 5.17  Tracer experiments at \( Re = 100 \): post-processed digital frames of chamber 2.
Figure 5.18  Tracer experiments at $Re = 150$: post-processed digital frames of chamber 1.

Figure 5.19  Tracer experiments at $Re = 150$: post-processed digital frames of chamber 2.
Figure 5.20  Tracer experiments at $Re = 200$: post-processed digital frames of chamber 1.

Figure 5.21  Tracer experiments at $Re = 200$: post-processed digital frames of chamber 2.
Figure 5.22  Tracer experiments at Re = 300: post-processed digital frames of chamber 1.

Figure 5.23  Tracer experiments at Re = 300: post-processed digital frames of chamber 2.
Figure 5.24  Tracer experiments at Re = 500: post-processed digital frames of chamber 1.

Figure 5.25  Tracer experiments at Re = 500: post-processed digital frames of chamber 2.
Figure 5.26 Tracer experiments at Re = 700: post-processed digital frames of chamber 1.

Figure 5.27 Tracer experiments at Re = 700: post-processed digital frames of chamber 2.
5.3.3 Dynamic Data Analysis

The snapshot images of the instantaneous flow field presented in the Section 5.3.2.2, allow a direct observation of the flow field dynamics for each Reynolds number. The evolution of the flow field can be drawn from the digital frames at different Reynolds numbers. As already observed from the CFD simulations presented in Chapter 4, flow visualization experiments evidenced the existence of typical flow field oscillation frequencies. Next, this phenomenon is analysed and its dependency with the Reynolds number established.

For purposes of review, the definitions of period and oscillation frequency of periodic data are now briefly introduced. The time required for one full oscillation is called the period, \( t_{\text{period}} \). The number of oscillations per unit time is called oscillation frequency, \( f \), and is related to the period by

\[
f = \frac{1}{t_{\text{period}}} \quad (5.1)
\]

As the frame acquisition rate was set to 30 Hz, the maximum error associated with the determination of each \( t_{\text{period}} \) is constant and equal to \( \pm 1/60 \) s, thus the NETMIX\textsuperscript{®} static mixer flow field oscillation frequency, \( f_{\text{NETMIX}} \), is within the range of

\[
f_{\text{min}} = \frac{1}{t_{\text{period}} + \frac{1}{60}} \quad (5.2)
\]

\[
f_{\text{max}} = \frac{1}{t_{\text{period}} - \frac{1}{60}} \quad (5.3)
\]

An intuitive examination of Figure 5.12 to Figure 5.19, shows the presence of a typical flow field oscillation frequency, with the periodic reappearance of the same flow field instantaneous patterns.

Table 5.2 presents the experimental periods and the corresponding observed oscillation frequencies for Reynolds numbers in the range \( 25 \leq Re \leq 200 \). Above \( Re = 200 \) the intense chamber homogenization makes unattainable to evaluate \( t_{\text{period}} \).
Table 5.2  \textit{NETMIX}® static mixer observed oscillation frequencies, from $25 \leq Re \leq 200$, using two Ismatec® MCP Standard pump systems.

<table>
<thead>
<tr>
<th>$Re$</th>
<th>$t_{\text{period}}$ [s]</th>
<th>$f_{\text{NETMIX}}$ [Hz]</th>
<th>$f_{\text{min}}$ [Hz]</th>
<th>$f_{\text{max}}$ [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-</td>
<td>0.000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>37.5</td>
<td>-</td>
<td>0.000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>0.533</td>
<td>1.875</td>
<td>1.819</td>
<td>1.937</td>
</tr>
<tr>
<td>75</td>
<td>0.400</td>
<td>2.500</td>
<td>2.400</td>
<td>2.609</td>
</tr>
<tr>
<td>100</td>
<td>0.267</td>
<td>3.750</td>
<td>3.525</td>
<td>3.995</td>
</tr>
<tr>
<td>150</td>
<td>0.200</td>
<td>5.000</td>
<td>4.615</td>
<td>5.455</td>
</tr>
<tr>
<td>200</td>
<td>0.133</td>
<td>7.500</td>
<td>6.682</td>
<td>8.596</td>
</tr>
</tbody>
</table>

The oscillation frequency, $f_{\text{NETMIX}}$, increases consistently with the Reynolds number, as it is clearly seen in the oscillation frequency against Reynolds number plot in Figure 5.28.

Since two Ismatec® MCP Standard pump systems were used for delivering fluid to the system, which results in a continuous degree of pulsation in flow, it was decided to scrutinize their influence in the oscillation frequency.

As described in Section 5.2.1, the pump-head ISM724 in the Ismatec® MCP Standard pump systems has 6 rollers, thus the \textit{induced oscillation frequency} in the flow, $f_{\text{induced}}$, is given by

$$f_{\text{induced}} = n_{\text{rollers}} \text{ speed}$$  \hfill (5.4)

where $n_{\text{rollers}}$ is the number of rollers, independently of the number of pump systems used.

In Figure 5.28 is also plotted the pumps induced oscillation frequency in the range of Reynolds numbers $25 \leq Re \leq 200$, showing coincident values from $f_{\text{induced}}$ and flow field oscillation frequency. It is then possible that the system pumps are determining the flow field oscillations. This would go against the hypothesis of flow perturbation fast dumping inside the static mixer, as postulated in Section 5.3.2.
Figure 5.28  Observed and induced oscillation frequencies against $Re$ for the case of two Ismatec® MCP Standard pump systems.

On the other hand, the fact that both induced and observed oscillation frequencies overlap may be merely a twist of fate. To confirm the nature of the oscillations, a new experiment was performed, consisting of achieving the same Reynolds number in the range of $25 \leq Re \leq 200$ using a single Ismatec® MCP Standard pump system. Table 5.3 presents the new experimental parameters set.

Table 5.3  Imposed settings for tracer experiments, from $25 \leq Re \leq 700$, using a single Ismatec® MCP Standard pump system.

<table>
<thead>
<tr>
<th>$Re$</th>
<th>speed [min$^{-1}$]</th>
<th>$q_{in}$ [ml/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>16.9</td>
<td>3.521</td>
</tr>
<tr>
<td>37.5</td>
<td>25.4</td>
<td>5.292</td>
</tr>
<tr>
<td>50</td>
<td>33.9</td>
<td>7.064</td>
</tr>
<tr>
<td>75</td>
<td>50.9</td>
<td>10.60</td>
</tr>
<tr>
<td>100</td>
<td>67.9</td>
<td>14.15</td>
</tr>
<tr>
<td>150</td>
<td>101.8</td>
<td>21.21</td>
</tr>
<tr>
<td>200</td>
<td>135.7</td>
<td>28.27</td>
</tr>
<tr>
<td>300</td>
<td>203.6</td>
<td>42.42</td>
</tr>
</tbody>
</table>
Figure 5.29 plots the induced oscillation frequencies for a single pump system, $f_{\text{induced}}$, given by Equation 5.4, with the observed flow field oscillation frequencies, $f_{\text{NETMIX}}$, for the studied range of Reynolds numbers. It is now clear that the flow field oscillation frequency is not determined by the pump pulsation. Moreover, Figure 5.28 and Figure 5.29 show that the flow field oscillation frequencies are maintained, regardless the number of pump feeding systems used.

The single dependency of the oscillation frequency on $Re$, regardless of external conditions, is strong evidence that this is a phenomenon intrinsic to the flow field.

![Graph showing oscillation frequencies against Re](image)

*Figure 5.29 Observed and induced oscillation frequencies against Re for the case of a single Ismatec® MCP Standard pump system.*

5.3.4 Comparison with CFD Data

In this section data from both experiments and simulations is compared, with the twofold purpose of greater insight into the flow field and validation of the CFD model. Comparison is made in terms of the Reynolds number for flow regime transition and in terms of the flow dynamics.

5.3.4.1 Critical Reynolds Number

For CFD simulations up to $Re = 100$, the system always evolved to a steady state, while in the experiments the flow regime transition Reynolds number, critical Reynolds number, was
shown to be $Re = 50$. The difference between the simulations and the experiments is now investigated from the relationship between the Reynolds number, based on the channels, for the 2D geometry, used in the CFD simulations, $Re_{2D}$, and for the 3D geometry in experiments, $Re_{3D}$.

Defining the *hydraulic diameter*, $d_H$, for a single channel as

$$d_H = \frac{4A}{P_w} \quad (5.5)$$

where $A$ is the cross-sectional area of the channel and $P_w$ is the length of the wetted perimeter of the channel cross section, the Reynolds number becomes

$$Re = \frac{\rho v_{in} d_H}{\mu} \quad (5.6)$$

where $v_{in}$ is the fluid velocity, $\rho$ is the fluid density and $\mu$ is the fluid viscosity.

For the 2D geometry, the hydraulic diameter, $d_{H,2D}$, is given by

$$d_{H,2D} = \frac{4d_z}{2(d + z)} = \frac{2dz}{d + z} \quad (5.7)$$

where $d$ is the channel width and $z$ is a third dimension normal to the 2D channel. As $z \to \infty$, $d_H \to 2d$, and the Reynolds number is given by

$$Re_{2D} = \lim_{z \to \infty} \frac{\rho v_{in} \left( \frac{2dz}{d + z} \right)}{\mu} = 2 \frac{\rho v_{in} d}{\mu} \quad (5.8)$$

For the 3D geometry, the hydraulic diameter, $d_{H,3D}$, is given by

$$d_{H,3D} = \frac{4 \left( \frac{\pi d^2}{4} \right)}{\pi d} = d \quad (5.9)$$

and thus the Reynolds number becomes

$$Re_{3D} = \frac{\rho v_{in} d}{\mu} \quad (5.10)$$
The relation between the two values of $Re$ is then

$$Re_{3D} = \frac{1}{2} Re_{2D}$$  \hspace{1cm} (5.11)

Hence, considering this relationship, the critical Reynolds number predicted from simulations to occur around $Re_{2D} = 100$ corresponds to $Re_{3D} = 50$, precisely matching the critical Reynolds number from the experiments.

5.3.4.2 Flow Dynamics

For Reynolds numbers at which the flow field is time dependent, from the dynamic evolution of the imaged flow field the Strouhal number can be obtained by

$$St_{NETMIX} = \frac{f_{NETMIX} d}{v_{in}}$$  \hspace{1cm} (5.12)

where $f_{NETMIX}$ is the flow field observed oscillation frequency, $d$ is the channels diameter and $v_{in}$ is the velocity at the inlet channels.

The Strouhal number allows a direct comparison between the typical frequencies at the different Reynolds numbers, checking if the changes of frequencies with $Re$ are only due to the increase of $v_{in}$.

The plot of the Strouhal number against Reynolds number is shown in Figure 5.30 where it can be seen that experimental data, $St_{NETMIX}$, is practically constant in the whole range of $Re$. Thus, although the oscillation frequencies increase with the Reynolds number in the range of $50 \leq Re \leq 200$ (Figure 5.28 or Figure 5.29), they scale directly with $v_{in}$.

The observed independence of $St_{NETMIX}$ on the channels velocity indicates that the flow field oscillations frequencies are determined by an underlying geometry mechanism (see Chapter 4). This hypothesis is supported by the fact that the oscillation frequency is spatially independent, see Section 5.3.2, and is studied next.

Recalling the simple relationship between geometry and flow field oscillation frequency, used in Chapter 4, the generated frequency, $f_{chamber\,3D}$, based in the mean residence time of one chamber, $\tau_{chamber\,3D}$, is
\[
\frac{f_{chamber\,3D}}{c_{chamber\,3D}} = \frac{1}{\tau_{chamber\,3D}} = \frac{2q_{in\,3D}}{V_{chamber\,3D}} \tag{5.13}
\]

where \(q_{in\,3D}\) is the flow rate at each inlet channel defined as

\[
q_{in\,3D} = u_{in}\pi \left(\frac{d}{2}\right)^2 \tag{5.14}
\]

and \(V_{chamber\,3D}\) is the volume of the chamber, approximately defined as

\[
V_{chamber\,3D} = \frac{4}{3}\pi \left(\frac{D}{2}\right)^3 \tag{5.15}
\]

where \(u_{in}\) is the inlet channels velocity, \(d\) is the inlet channels diameter and \(D\) is the chamber diameter.

Replacing Equation 5.14 and Equation 5.15 into Equation 5.13, the generated frequency becomes

\[
f_{chamber\,3D} = \frac{3u_{in}}{D} \left(\frac{d}{D}\right)^2 \tag{5.16}
\]

and the Strouhal number based on the volume of the chamber, \(St_{chamber\,3D}\), for \(d = 1.5 \times 10^{-3} \text{ m}\) and \(D = 7 \times 10^{-3} \text{ m}\) is obtained

\[
St_{chamber\,3D} = f_{chamber\,3D} \frac{d}{u_{in}} = 3\left(\frac{d}{D}\right)^3 \approx 0.030 \tag{5.17}
\]

Comparing this result with the experimentally observed Strouhal numbers, see Figure 5.30, it can be concluded that this is not the basic mechanism for the flow oscillations, probably due to the fact that the 2D geometry in Chapter 4, in which this analogy was previously established, is not a direct representation of the 3D static mixer. In the 3D geometry the streams do not enter throughout the whole chamber height, as in 2D geometry, see Figure 5.31a, and therefore the two inlet streams are probably mixing only in the channels plane fraction of the total chamber volume, acting the remaining fluid volume as lubricating. Figure 5.31b shows a dashed line delimited volume, the \textit{effective mixing volume}, which is confined by the upper and lower limits of the channels plane.
The assumption that the chambers effective mixing volume, $V_{\text{effective 3D}}$, is in fact determining the dynamics is checked next.

Replacing in Equation 5.13 the chamber total volume, $V_{\text{chamber 3D}}$, by the chamber effective mixing volume, $V_{\text{effective 3D}}$, the generated frequency, $f_{\text{effective 3D}}$, is given by

$$f_{\text{effective 3D}} = \frac{2a_{\text{in 3D}}}{V_{\text{effective 3D}}} \quad (5.18)$$

Since $V_{\text{effective 3D}}$ can be approximated by the volume of a cylinder with diameter equal to the chamber diameter, $D$, and thickness equal to the channels diameter, $d$, Equation 5.18 becomes

$$V_{\text{effective 3D}} = \pi d \left( \frac{D}{2} \right)^2 \quad (5.19)$$

Replacing Equation 5.19 into Equation 5.18, the generated frequency is given by

$$f_{\text{effective 3D}} = \frac{2 a_{\text{in}}}{d} \left( \frac{d}{D} \right)^2 \quad (5.20)$$
and the Strouhal number based on the chamber effective mixing volume, $St_{\text{effective}\ 3D}$, for $d = 1.5 \times 10^{-3}\ m$ and $D = 7 \times 10^{-3}\ m$, is

$$St_{\text{effective}\ 3D} = f_{\text{effective}\ 3D} \frac{d}{v_{in}} = 2 \left( \frac{d}{D} \right)^2 = 0.092 \quad (5.21)$$

From Figure 5.30 it can be seen that $St_{\text{effective}\ 3D}$ matches with reasonable accuracy the Strouhal numbers from the tracer experiments, $St_{\text{NETMIX}}$.

![Diagram of mixing chamber and channels](image)

(Figure 5.31) Mixing chamber and channels for: (a) 2D geometry used in CFD simulations; (b) experimental 3D geometry.

Although the values of $St_{2D}$, see Chapter 4, and of $St_{\text{effective}\ 3D}$ are different, they are associated to the same basic underlying mechanism, i.e., the mean residence time in the chambers effective mixing volume. The relationship between the values of $St$ for the two cases is then given by

$$\frac{St_{\text{effective}\ 3D}}{St_{2D}} = \frac{2 \left( \frac{d}{D} \right)^2}{\frac{8}{\pi} \left( \frac{d}{D} \right)^2} = \frac{\pi}{4} \quad (5.22)$$

From this study, a high degree of confidence on the 2D nature of the flow field was achieved. Further, as this effective mixing plane is coincident with the geometry of the 2D model used...
in CFD simulations, the simulation covers the physical range of interest for mixing, i.e., the static mixer axial cut, passing through its channels and chambers centres. The fact that the flow field has 2D nature validates the choice of the 2D model for the CFD simulation. Thus, the introduction of a third spatial coordinate, in the case of a 3D CFD model, would increase largely the computation time without significant insight into the flow field structures and dynamics.

5.4 Pressure Drop Experiments

For comparison with the NETMIX® model (see Chapter 3) and 2D CFD model (see Chapter 4) pressure drop experiments were conducted in the NETMIX® reactor. The experiments were conducted under the conditions described in Section 5.4.1, with results shown in Section 5.4.3. In Section 5.4.3 is also presented the comparison between the experimental results and the 2D model CFD simulations results. Finally, Section 5.4.4 is devoted to mixing energy analysis based on the measured pressure drop across the NETMIX® static mixer.

5.4.1 Experimental Conditions

The pressure experiments were conducted in steady state, for Reynolds numbers in the range $25 \leq Re \leq 700$. The list of the imposed settings using two Ismatec® MCP Standard pump systems is presented in Table 5.1. Tap water was used as working fluid, at ambient pressure and air-conditioning controlled temperature of $20.0 \pm 0.5 \degree C$.

All pressure measurements were made with one pressure transducer cavity open to the atmosphere and the other pressure transducer cavity connected to a pressure tap in the central inlet chamber. Pressure measurements with one cavity open to the atmosphere have the advantage of no interference between signals coming from two pressure taps. The connection between the pressure transducer and the pressure tap was made of LEGRIS® semi-rigid nylon tubing, model 1025P03 00 18, of internal diameter 1.8 mm.

The pressure transducer diaphragm was calibrated for the experimental conditions with the transducer already in place. All cables and wires were shielded to avoid additional magnetically induced noise. Moreover, care was taken to purge the air from the tubing connecting the pressure transducer to the pressure tap and from the related pressure cavity in order to avoid attenuation and non-linearity of the pressure signal.
5.4.2 Pressure Drop

Figure 5.32 shows the average values from total pressure drop measurements in the NETMIX® static mixer, $\Delta p_{NETMIX}^s$, as described in Section 5.4.1. For each Reynolds number, the acquisition of 200 s of data track was performed at a sampling frequency of 200 Hz.

Since the NETMIX® static mixer and 2D CFD model have different dimensions, the NETMIX® static mixer total pressure drop from the CFD simulations, $\Delta p_{correlated}^s$, is correlated to the 2D model pressure drop, $\Delta p_{transient}$, obtained from the CFD simulations in Chapter 4, by

$$\Delta p_{correlated} = \frac{n_{NETMIX}^s}{n_{2D}^s} \Delta p_{transient}$$  \hspace{1cm} (5.23)

where $n_{NETMIX}^s$ and $n_{2D}^s$ are the number of rows in the NETMIX® static mixer and in the 2D CFD model, respectively. The value of the Reynolds number must agree with the relation expressed by Equation 5.11, and so an equivalent Reynolds number, $Re_{eq}$, is defined for the CFD simulations as

$$Re_{eq} = \frac{1}{2} \frac{\rho v_{in} d}{\mu}.$$ \hspace{1cm} (5.24)

where $d$ is the channels width, and for the experiments is defined as

$$Re_{eq} = \frac{\rho v_{in} d}{\mu}.$$ \hspace{1cm} (5.25)

where $d$ is the channels diameter.

In Figure 5.32 it is plotted the NETMIX® static mixer CFD correlated total pressure drop against $Re_{eq}$. The origin of the difference between experimental and CFD pressure drop results is later analysed in Section 5.4.3 in view of the geometry differences between the 2D model and the 3D NETMIX® static mixer.

In order to compare these results with those obtained from the NETMIX® model described in Chapter 3, a regular network with NPBC and without HC was constructed with the exact dimensions of the NETMIX® static mixer, by removing one boundary chamber at every odd-numbered row and respective channels to implement the condition that network rows alternate between 15 and 16 chambers, starting the first row with 15 chambers.
The pressure drop in this network was determined from the NETMIX® model, which accounts only for frictional effects on the channels walls. Despite the assumptions introduced in Chapter 3, the pressure drop computed by the NETMIX® model, $\Delta p_{\text{model}}$, exactly fits the experimental pressure drop for $Re < 50$, as can be seen in Figure 5.32. Therefore, the NETMIX® model can be assumed to correctly predict, for all Reynolds numbers, the fraction of pressure drop due to the NETMIX® static mixer walls frictional energy losses.

![Figure 5.32](image)

**Figure 5.32**  \( \Delta p \text{ (Pa)} \) vs. \( Re_{eq} \). NETMIX® static mixer total pressure drop from the NETMIX® model, $\Delta p_{\text{model}}$, NETMIX® static mixer correlated total pressure drop from the CFD simulations, $\Delta p_{\text{correlated}}$, and NETMIX® static mixer total pressure drop from the experiments, $\Delta p_{\text{NETMIX}}$, against $Re_{eq}$.

### 5.4.3 Comparison with CFD Data

Figure 5.32 shows the values of the NETMIX® static mixer total pressure drop from the experiments and from the CFD simulations. As the $Re_{eq}$ increases, the CFD correlated total pressure drop is increasingly higher than the total experimental pressure drop. This discrepancy is next analysed in terms of the specific friction area of the 2D geometry used in the CFD simulations, $A_{\text{friction 2D}}$, and of the 3D geometry used in the experiments, $A_{\text{friction 3D}}$.

The first step for comparison is the definition of a dimensionless pressure drop, the Euler number, $Eu$, to eliminate the velocity differences between $Re_{2D}$ and $Re_{3D}$.
\[ \frac{Eu}{\rho v_{in}^2} = \Delta p \]  
\[ (5.26) \]

where \( v_{in} \) is the velocity at inlet channels.

Considering that the pressure drop is proportional to the specific friction area, \( A_{friction} \), defined as

\[ A_{friction} = \frac{A_{wall}}{V_{flow}} \]  
\[ (5.27) \]

where \( A_{wall} \) is the total friction area and \( V_{flow} \) is the geometric volume for flow.

The relation between \( Eu \) for both geometries is thus

\[ \frac{Eu_{2D}}{Eu_{3D}} = \frac{A_{friction \ 3D}}{A_{friction \ 2D}} = \frac{\left( \frac{A_{wall}}{V_{flow}} \right)_{3D}}{\left( \frac{A_{wall}}{V_{flow}} \right)_{2D}} \]  
\[ (5.28) \]

and for \( d = 1.5 \times 10^{-3} \) m and \( D = 7 \times 10^{-3} \) m,

\[ \frac{Eu_{2D}}{Eu_{3D}} = 1.640 \]  
\[ (5.29) \]

Defining then an equivalent Euler number, \( Eu_{eq} \), as

\[ Eu_{eq} = 1.640 Eu_{2D} = Eu_{3D} \]  
\[ (5.30) \]

direct comparison between CFD and experiments is now possible.

In Figure 5.33 are plotted the Euler number values from the CFD simulations against \( Re_{eq} \) from experiments. As it can be seen, CFD correlated values, \( Eu_{2D} \), are lower than those obtained from experiments, \( Eu_{3D} \). If computed Euler numbers are corrected according to Equation 5.30, data from experiments exactly fits the simulation values. This provides further validation to the 2D CFD simulations, which once accounted for the geometry differences, are
here proven to accurately describe the pressure drop behaviour for the NETMIX® static mixer.

Further, the correlated pressure drop from the CFD steady state simulations, $\Delta p_{\text{steady state}}$, (see Chapter 4), obtained from Equation 5.23, once expressed in terms of the Euler number and corrected by Equation 5.30, precisely matches data from the NETMIX® model, validating the assumption in Section 5.4.2 that the NETMIX® model can predict, for all Reynolds numbers, the fraction of pressure drop due to the NETMIX® static mixer walls frictional energy losses.

The pressure drop, as seen in Chapter 4, is directly related with energy for mixing, and so, there is a good agreement between experiments and CFD simulations also in terms of mixing energy consumption.

![Diagram](image)

**Figure 5.33** Values of Euler number from CFD simulations, $Eu_{2D}$, corrected values of Euler number from CFD simulations, $Eu_{eq}$, and values of Euler number from experiments, $Eu_{3D}$, against $Re_{eq}$.

### 5.4.4 Energy Analysis

A critical issue in mixing systems is the effective use of the delivered energy. The energy analysis next presented is based on the total pressure drop measurements from the NETMIX® static mixer.
5.4.4.1 Power Number

A common approach in the analysis of the power consumption in stirred tanks is to plot the power curve, that is the relationship between the power number and the Reynolds number, to express the power draw (e.g. Tanguy and Thibault, 2002). Power draw is the energy per time which is transferred from the mixing system impeller to the fluid. It is an integral quantity fundamental to mixing since energy is needed to cause fluid motion necessary for mixing (e.g. Tatterson, 1991). Although mainly approached through dimensional analysis and experimental measurements of torque (Harnby et al., 1997), power number calculation can be estimated using a drag-velocity analysis and the CFD simulations results, as described next.

The drag basis to power draw analysis is essentially mechanistic and approaches the calculation of power draw using a drag coefficient. Under turbulent flow conditions, the impeller blade of a stirred tank experiences two types of drag: frictional drag and pressure drag. The drag force, \( F_D \), can be expressed in terms of a drag coefficient, \( C_D \), as

\[
F_D = \frac{1}{2} C_D \rho A_{\text{impeller}} U^2
\]  

(5.31)

where \( A_{\text{impeller}} \) is the projected area of the impeller, \( U \) is the approach velocity of the fluid relative to the blade and \( \rho \) is the fluid density.

If the drag coefficient is assumed to be constant, then the drag force is proportional to the density, the velocity squared and the projected area

\[
F_D \propto \rho A_{\text{impeller}} U^2
\]  

(5.32)

Power, \( P \), is essentially force times velocity

\[
P \propto F_D U
\]  

(5.33)

By equating the velocity to the approach velocity of the fluid relative to the blade

\[
P \propto \rho A_{\text{impeller}} U^3
\]  

(5.34)

or in terms of a proportionality constant

\[
N_p = \frac{P}{\rho A_{\text{impeller}} U^3}
\]  

(5.35)
where \( N_p \) is the power number. The dimensionless power number is proportional to the ratio of power and power draw, i.e.,

\[
N_p = \frac{\text{total energy consumption}}{\text{mixing energy consumption}}
\]

(5.36)

Although it could be pointed out that the presented drag-velocity analysis does not take into account the effect of the flow rate in the power consumption for continuous-flow systems, Laity and Treybal (1957) found that effect to be negligible, for most applications.

The previous drag-velocity concept assumes that the power draw has to be transferred from the impeller to the surrounding fluid locally. The power, thus transferred, is dissipated in fluid mixing, wall friction and into the heating of the fluid.

Although in the NETMIX\textsuperscript{®} static mixer the continuous increase of mixing is solely due to the increase of \( Re \) and not from impellers application, an analogy with Equation 5.35 can be used to compute the power number, under the abusive assumption of turbulent flow conditions, as follows.

The power is given by

\[
P = \Delta p q_f
\]

(5.37)

where \( \Delta p \) is the total pressure drop and \( q_f \) is the total flow rate.

The power draw, power consumption in mixing, is given by

\[
P_{\text{mixing}} = \rho A_{\text{impeller}} U^3 = \Delta p_{\text{turbulent}} q_f
\]

(5.38)

where \( \Delta p_{\text{turbulent}} \) is the NETMIX\textsuperscript{®} static mixer turbulent pressure drop. For a given Reynolds number, \( \Delta p_{\text{turbulent}} \) can be determined from the difference between the experimental NETMIX\textsuperscript{®} static mixer total pressure drop, \( \Delta p_{\text{NETMIX}} \), and the pressure drop due to the NETMIX\textsuperscript{®} static mixer walls frictional energy losses, \( \Delta p_{\text{model}} \) (see Figure 5.32).

Replacing Equation 5.37 and Equation 5.38 into Equation 5.35, the power number for the NETMIX\textsuperscript{®} static mixer simply reduces to

\[
N_p = \frac{\Delta p_{\text{NETMIX}}}{\Delta p_{\text{turbulent}}} = \frac{\Delta p_{\text{NETMIX}}}{\Delta p_{\text{NETMIX}} - \Delta p_{\text{model}}}
\]

(5.39)
Figure 5.34 shows the power curve plot for the NETMIX® static mixer and for several stirred tank reactors with different impellers (Bates et al., 1963). When the Reynolds number is decreased up to the critical Reynolds number, \( Re = 50 \), and since \( \Delta p_{\text{turbulent}} \) tends to zero, it is possible to define in the NETMIX® static mixer an asymptote for \( N_p \) as

\[
\lim_{Re \to 50} N_p = +\infty
\]  

(5.40)

Therefore, for Reynolds numbers \( Re < 50 \) there is no energy consumption in mixing, meaning all energy is consumed in transport. For higher Reynolds number there is an increasing consumption of energy in mixing, tending to a state were the energy consumption in transport becomes negligible when compared with mixing consumed energy. It is then possible to define a second asymptote for the NETMIX® static mixer corresponding to

\[
\lim_{Re \to +\infty} N_p = 1
\]  

(5.41)

As it can be seen, for \( Re = 200 \) the NETMIX® static mixer power number has already decreased to 1.81, a value lower than most found in literature for stirred tanks (e.g. Bates et al., 1963; Bertrand et al., 1980; Papastefanos and Stamatoudis, 1989; Warmoeskerken and Smith, 1989), addressing the NETMIX® static mixer enhanced power draw efficiency.

![Figure 5.34](image-url)  

*Figure 5.34  Comparison of the power curve plot for the NETMIX® static mixer and for several stirred tank reactors with different impellers (Bates et al., 1963).*
5.4.4.2 Z Factor

It is common to interpret the pressure drop in static mixers by the Z factor (see Chapter 2) expressed as

$$Z = \frac{\Delta p_{\text{static mixer}}}{\Delta p_{\text{empty tube}}}$$ (5.42)

where $\Delta p_{\text{static mixer}}$ is the pressure drop through the static mixer and $\Delta p_{\text{empty tube}}$ is the pressure drop through an empty tube of equal length and diameter. Such formulation is convenient since it gives directly the ratio of pressure drops for installing static mixers in replacement of existing empty tubes.

Using Equation 5.42, the Z factor for the NETMIX® static mixer is given by

$$Z_{\text{NETMIX}} = \frac{\Delta p_{\text{NETMIX}}}{\Delta p_{\text{empty tube}}}$$ (5.43)

where $\Delta p_{\text{NETMIX}}$ is the experimental NETMIX® static mixer total pressure drop and $\Delta p_{\text{empty tube}}$ is for laminar regime (see Chapter 3) expressed as

$$\Delta p_{\text{empty tube}} = \frac{64}{Re} \left( \frac{8 \rho l_{\text{empty tube}} q_f}{\pi^2 d_{\text{empty tube}}^5} \right)$$ (5.44)

where $l_{\text{empty tube}}$ and $d_{\text{empty tube}}$ are the length and the diameter of the empty tube, respectively, determined by

$$l_{\text{empty tube}} = (n_x + 1) L^o \cos \phi$$ (5.45)

$$A_{\text{empty tube}} = \frac{\pi d_{\text{empty tube}}^2}{4} = 2 (n_y - 1) A_{in}$$ (5.46)

where $n_x$ and $n_y$ are the number of rows and columns in the NETMIX® static mixer, $L^o$ is the distance between the centres of two obliquely neighbouring chambers, $\phi$ is the angle formed between the channels and the $x$-axis, and $A_{\text{empty tube}}$ and $A_{in}$ are the empty tube and inlet channels cross-sectional areas, respectively.
Table 5.4 provides the Z factor values for the NETMIX® static mixer for Reynolds numbers $Re = 25$ to $Re = 700$. In this range of Reynolds numbers, the NETMIX® static mixer exhibits Z factor values lower than most commercially available static mixers (see Chapter 2), and therefore can be operated with smaller pressure drops and, consequently, with a reduced consumption of energy.

<table>
<thead>
<tr>
<th>$Re$</th>
<th>$Z_{NETMIX}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.304</td>
</tr>
<tr>
<td>37.5</td>
<td>2.302</td>
</tr>
<tr>
<td>50</td>
<td>2.304</td>
</tr>
<tr>
<td>75</td>
<td>2.447</td>
</tr>
<tr>
<td>100</td>
<td>2.747</td>
</tr>
<tr>
<td>150</td>
<td>3.508</td>
</tr>
<tr>
<td>200</td>
<td>4.342</td>
</tr>
<tr>
<td>300</td>
<td>5.790</td>
</tr>
<tr>
<td>500</td>
<td>8.049</td>
</tr>
<tr>
<td>700</td>
<td>10.15</td>
</tr>
</tbody>
</table>

### 5.5 Chemical Reaction Experiments

In order to study the mixing efficiency of the NETMIX® static mixer, a set of parallel or consecutive reactions can be used as test reaction, by exploiting the competition between two or more chemical reactions (Paul and Treybal, 1971; Bourne and Kozicki, 1977; Bourne, 1982; Bourne et al., 1990; Villermaux et al., 1992; Bourne and Yu, 1994; El-Hamouz and Mann, 1998).

In this work a consecutive competitive reaction system, the azo coupling of 1-naphthol ($A$) with diazotised sulphanilic acid ($B$) in dilute, aqueous, alkaline buffered solution was used for mixing studies.

This reaction, first proposed by Bourne (1981b), see Chapter 2, is schematically represented by
\[ A + B \rightarrow oR \quad \text{(very fast)} \]
\[ A + B \rightarrow pR \quad \text{(very fast)} \]
\[ oR + B \rightarrow S \quad \text{(fast)} \]
\[ pR + B \rightarrow S \quad \text{(fast)} \]

where \( oR, pR \) and \( S \) are 2-(4'‐sulphophenylazo)-1-naphthol, 4-(4'‐sulphophenylazo)-1-naphthol and 2,4-bis(4'‐sulphophenylazo)-1-naphthol, respectively. Its chemical kinetics are well known for aqueous solutions (Bourne et al., 1992a; Nunes et al., 2001), and the resulting products spectra are dependent on mixing (Bourne, 1983).

Since the reactants are uncoloured and the azo coupleings rapidly produce intense red colour, the first approach in this work was the visualisation of the products formation inside the static mixer. The extent of the reaction zones allows the estimation of the local and global spatial product distribution, for a given experimental set. The imaging experiments are presented in Section 5.5.1.

Furthermore, the study of mixing by the use of such reaction scheme has a twofold importance: first the azo coupling reaction is extremely sensitive to macromixing and micromixing, making its selectivity a good way to assess mixing; second it gives further knowledge on how to influence the product, as shown in Section 5.5.2.

### 5.5.1 Chemical Reaction Visualisation

The actual flow field role on micromixing is best assessed from chemical reaction visualisation, since the products formation only occurs when reactants contact at the molecular level. In addition, in overall terms, chemical reaction allows a clearer picture of the interaction between both inlet streams, in each chamber, since coloured products are only formed in the contact regions.

Mixing mechanisms are therefore further understood from visualisation studies with the chemical reaction above introduced.

#### 5.5.1.1 Experimental Conditions

Chemical reaction visualization experiments were conducted in steady state, for Reynolds numbers in the range of \( 50 \leq Re \leq 700 \). The two Ismatec® MCP pump systems
were used, under the settings shown in Table 5.1. The image acquisition is made in the plane containing the channels and chambers centres.

As in the tracer visualisation experiments, a practically uniform illumination and a better light dispersion were obtained using a white photo reflector located between the static mixer and the halogen lamp. Deionised water was used as working fluid, at ambient pressure and air-conditioning controlled temperature of 20.0 ± 0.5 °C. The viscosity of water and reactants solutions was considered constant and equal to \( \mu = 1.0 \times 10^{-3} \) Pa s.

The location of the injection points was set in such way that contact between reactants first occurs in a chamber above the pumps influence region (see Section 5.3.2). To this purpose, reactants \( A \) and \( B \) are separately injected, as shown in Figure 5.35. According to this scheme, and for \( Re \geq 50 \), the contacting chamber is located in the fourth row from inlet, as can be seen from Figure 5.6 to Figure 5.8.

Below \( Re = 50 \), the lack of mixing inside the chambers, shown in Section 5.3.2, forces reactants \( A \) and \( B \) to be maintained segregated from each other towards the NETMIX® static mixer exit, thus making the chemical reaction visualisation experiments, in that range of Reynolds numbers, an unviable proposition.

![Figure 5.35 Chemical reaction visualisation experiments injection scheme.](image)

### 5.5.1.2 Results

The azo couplings reaction products \( oR \), \( pR \) and \( S \) possess an intense red colour, although the \( S \) product colour is noticeably darker. By means of this colour difference, a micromixing assessment is obtained from the NETMIX® static mixer imaging during chemical reaction experiments.
From Figure 5.36 and Figure 5.37, the overall reaction patterns occurring in the NETMIX® static mixer are shown, in steady state at Reynolds numbers in the range of $50 \leq Re \leq 700$.

Besides the features already identified from the tracer experiments in Section 5.3.2, e.g., the increasing plume aperture with higher Reynolds numbers, the chemical reaction visualisation experiments revealed colour gradients inside the plume throughout both main flow and normal flow directions, resulting from the asymmetric $oR$, $pR$ and $S$ spatial distribution.

The fact that reactants $A$ and $B$ are separately injected in the static mixer, as shown in Figure 5.35, generates a concentration gradient along the normal flow direction for both chemical species. On the left side of the static mixer, $A$ is greatly predominant and so all $B$ arising is immediately consumed into $oR$ and $pR$, with only residual quantities of $S$ being possibly formed, thus the lighter red colour observed. Conversely, on the right side of the static mixer, as $B$ is in large excess, considerable quantity of $B$ remains unreacted even after complete consumption of $A$ into $oR$ and $pR$, thus promoting the production of $S$, which origins the darker red colour (see Figure 5.36 and Figure 5.37).

The increase in macromixing with Reynolds number (see Section 5.3.2) flattens the reactants concentration gradients, thus notoriously affecting the product distribution. On the left side of the static mixer, as the $Re$ is increased, the reduced but still present excess of $A$ always results in a complete and instantaneous consumption of $B$ into $oR$ and $pR$, and thus no visible colouring change occurs on that side of the plume. On the right side of the static mixer however, as the excess of reactant $B$ over $A$ diminishes for higher $Re$, the formation of product $S$ is prevented, thus the fading of the dark red colour on the left side of the plume and the increasing plume red colour homogenisation, as can be seen in Figure 5.37.

From the macromixing considerations of Section 5.3.2 an increasingly greater spatial spread of reactants with $Re$ was already expected. The continuous decrease of $S$ formation over certain spatial locations in the reaction experiments with the Reynolds number is thus evidence of both the increasingly greater spread of reactants $A$ and $B$ trough the static mixer, i.e., macromixing, and the increasingly reduction of local segregation, i.e., micromixing. Hence, these experiments clearly show an overall increase of mixing, both macromixing and micromixing, with $Re$. 
Figure 5.36  Chemical reaction visualisation experiments for Reynolds numbers ranging from $Re = 50$ to $Re = 150$: photographs of the NETMIX® static mixer in steady state.
Figure 5.37  Chemical reaction visualisation experiments for Reynolds numbers ranging from $Re = 200$ to $Re = 700$: photographs of the NETMIX\textsuperscript{\textregistered} static mixer in steady state.
Chemical reaction visualisation, while using the reaction proposed by Bourne et al. (1981b), faces a severe limitation ensuing the fact that the azo couplings rapidly produce intense red colour, becoming more and more difficult to distinguish the different flow structures present as reaction evolves.

Dynamic imaging sequences of chemical reaction, in a single chamber where the flow patterns are more clearly observable, i.e., in the chamber where both pure reactants A and B first contact, denoted as chamber 1, were taken for greater insight into the phenomenon underlying the evolution of mixing efficiency with Reynolds number. Figure 5.38 shows an example of one frame acquired using the PIVCAM 10-30 camera. For each flow condition, an ensemble of 200 frames was captured with a frequency of 30 Hz.

![Chamber 1](image)

*Figure 5.38 Typical digital frame obtained with the PIVCAM 10-30 camera, for the chemical reaction visualisation experiments.*

Again, to enhance mixing visualization, images were post-processed, indexing each gray level to a colour level ranging from white to red.

From the complete dynamic sequences, 8 snapshots at chosen time instants are shown for each Reynolds number in the range of \(50 \leq Re \leq 700\) in Figure 5.39 to Figure 5.46.
Figure 5.39 Chemical reaction experiments at $\text{Re} = 50$: post-processed digital frames of chamber 1.

Figure 5.40 Chemical reaction experiments at $\text{Re} = 75$: post-processed digital frames of chamber 1.
Figure 5.41 Chemical reaction experiments at $Re = 100$: post-processed digital frames of chamber 1.

Figure 5.42 Chemical reaction experiments at $Re = 150$: post-processed digital frames of chamber 1.
Figure 5.43  Chemical reaction experiments at $Re = 200$: post-processed digital frames of chamber 1.

Figure 5.44  Chemical reaction experiments at $Re = 300$: post-processed digital frames of chamber 1.
Figure 5.45 Chemical reaction experiments at $Re = 500$: post-processed digital frames of chamber 1.

Figure 5.46 Chemical reaction experiments at $Re = 700$: post-processed digital frames of chamber 1.
For $Re = 50$, product formation is restricted to the chamber central region. Further, at $Re = 50$, mixing is still insufficient to promote homogeneity of both reactant streams separately entering chamber 1, as can be seen in Figure 5.39. A strong red colour is only observable on the chamber 1 right side exit neighbouring chamber, resulting from the formation of $S$ driven by the excess of $B$ both on the right side of the chamber 1 and of the static mixer.

At $Re = 75$ a general widespread of product formation throughout the entire chamber is now observed, even tough the chamber 1 right side exit neighbouring chamber still presents a noticeably darker colour (see Figure 5.40). Although mixing was greatly improved, as is patent from the chamber 1 homogeneous appearance, in micromixing terms an excess of $B$ on the right side of the chamber still exists resulting in considerable more $S$ formation on the chamber 1 right side exit neighbouring chamber.

From $Re = 75$ to $Re = 100$ it is not possible to depict a significant mixing quality enhancement, as is shown in Figure 5.40 and Figure 5.41. Conversely, from $Re = 100$ to $Re = 200$, Figure 5.41 and Figure 5.43, a remarkably mixing improvement occurs expressed by a clear blurring between the red colour intensities of both chamber 1 left and right side exit neighbouring chambers.

For $300 \leq Re \leq 700$, no further improvements in mixing are observable, either for micromixing, Figure 5.44 to Figure 5.46, or for macromixing, Figure 5.37.

### 5.5.2 Mixing-Reaction Studies

From the previous hydrodynamic studies and chemical reaction visualisation experiments, the determining role of the Reynolds number on mixing was shown. More, from the imaging experiments in Section 5.5.1, the extent of the reaction zones allows the estimation of local and global spatial product distribution, for a given experimental set. Nevertheless, mixing quantification is only now introduced and applied to the set of experiments presented in Section 5.5.2.1.

The reaction rates of the fast consecutive competitive reaction system described by Equation 5.47 are sufficiently high, relative to the rate at which the reactants $A$ and $B$ are mixed, so that complete micromixing (homogenization down to the molecular scale) is often unattained. Therefore, the azo coupling reaction product distribution strongly depends upon the mixing intensity, i.e., upon the Reynolds number, and its selectivity becomes a suitable parameter for characterising mixing.
The maximum selectivities in \( oR \) and \( pR \) are obtained when the contact of \( A \) and \( B \) at the molecular level scale is done before significant reaction occurs, otherwise if the homogenisation is slower, the selectivities in \( oR \) and \( pR \) tend to zero. Adopting the formulation used by Bourne (1981b), the selectivity in \( S \), \( X_s \), is measured by determining \( C_{oR}^{\text{final}}, C_{pR}^{\text{final}} \) and \( C_S^{\text{final}} \) by spectrophotometry, and is expressed as

\[
X_s = \frac{2C_S^{\text{final}}}{C_{oR}^{\text{final}} + C_{pR}^{\text{final}} + 2C_S^{\text{final}}} \tag{5.48}
\]

\[
C_B^{\text{initial}} = C_B^{\text{final}} + C_{oR}^{\text{final}} + C_{pR}^{\text{final}} + 2C_S^{\text{final}} \tag{5.49}
\]

where \( C_B^{\text{initial}} \) and \( C_B^{\text{final}} \) are the initial and final reactant \( B \) concentrations, respectively, and \( C_{oR}^{\text{final}}, C_{pR}^{\text{final}} \) and \( C_S^{\text{final}} \) are the product concentrations after reaction.

For the problem here addressed, this particular chemical reaction experimental selectivities are presented in Section 5.5.2.2, for the experimental conditions in Section 5.5.2.1, and later compared with the NETMIX\textsuperscript{\textregistered} model predictions in Section 5.6.

### 5.5.2.1 Experimental Conditions

Several reactions are sufficiently slow so that their rates are determined by chemical kinetics. Reactants streams can therefore be well mixed before any significant conversion occurs, disregarding the need of detailed consideration on micromixing (Angst et al., 1984). Some reactions are, however, fast relative to mixing so that conversion occurs in reaction zones where steep concentration gradients are present, which has influence in product distribution (Bourne, 1982). In the azo coupling of 1-naphthol (\( A \)) with diazotised sulfanilic acid (\( B \)) the couplings are so fast that reaction is complete within few seconds. Thus, \( A \) and \( B \) were, for all experiments, separately fed into the NETMIX\textsuperscript{\textregistered} static mixer to assess only mixing within the static mixer, avoiding the external pre-mixing effects that would distort the results and their meaning.

To follow the course of the reactions in time, the instantaneous, volume-averaged concentrations could be measured (e.g. photometrically) as a function of length in the NETMIX\textsuperscript{\textregistered} static mixer, as was done by Bourne et al. (1982) using a plug-flow reactor in steady state for a single reaction. Such technique is difficult for two or more species, as in the present work, needing for example a scanning, multiple beam spectrophotometer. Thus, the product distribution was determined by spectrophotometry in the NETMIX\textsuperscript{\textregistered} static mixer outlet, as it will be described in Section 5.5.2.2.
To form significant quantities of $oR$ and $pR$, simplifying the determination of $oR$, $pR$ and $S$ after reaction, the initial stoichiometric ratio $\frac{C_A^{\text{initial}}}{C_B^{\text{initial}}}$ should be higher than 0.5, e.g. around 1. Ratios greatly in excess of 1 cause little $S$ formation and again analytical problems (Bourne et al., 1981b). Using a stoichiometric ratio $\frac{C_A^{\text{initial}}}{C_B^{\text{initial}}} > 0.5$ causes the reactant $B$ to become the limiting reactant (see Equation 5.47). In the present work, a stoichiometric ratio $\frac{C_A^{\text{initial}}}{C_B^{\text{initial}}} = 1.20$ was used for all azo couplings.

Recalling Equation 5.49, the quantity of $B$ added that is finally present in $R$ and $S$, $m$, is determined as

$$m = \frac{C_B^{\text{final}} + C_{oR}^{\text{final}} + C_{pR}^{\text{final}} + 2C_S^{\text{final}}}{C_B^{\text{initial}}}$$

(5.50)

thus providing a check on the mass balance.

Two types of experiments were conducted:

- since mixing consists of spatially re-arranging entities, the first approach was to maximise the reactants feed distribution, pre-mixed injection scheme, see Figure 5.47, strongly promoting the earliness of mixing;

- in the second type of experiments, focus was given to the study of mixing for different degrees of segregation in the reactants feed distributions, segregated injection schemes, see Figure 5.48.

Maximisation of reactants feed distribution is widely applied for instance in combustion chambers, aiming to accelerate mixing (Angst et al., 1982). Similarly, the pre-mixed injection scheme aims at accelerating mixing, establishing in this way the higher selectivity in $oR$ and $pR$ (smaller $X_s$) within reach for the NETMIX® static mixer, for a given hydrodynamic operating condition. Furthermore, provides a straight approach for mixing assessment at different values of $Re$.

The study of segregated injection schemes intends to find ways of controlling product distribution for the same hydrodynamic operating condition. Similar study was conducted by Bourne and Hilber (1990) to study the effect of the number of feed nozzles of reactant $B$ on the selectivity in $S$ in stirred tanks.
Figure 5.47  Pre-mixed injection scheme for chemical reaction experiments.

Figure 5.48  Segregated injection schemes for chemical reaction experiments: (a) segregated injection scheme 1; (b) segregated injection scheme 2; (c) segregated injection scheme 3.
Reactants 1-naphthol (p.a. ≥ 99.0%, Sigma-Aldrich GmbH, Germany) and sulphanilic acid (p.a. ≥ 99.0%, Fluka Chemie, Switzerland) were directly used. Diazotisation of sulphanilic acid was conducted in the temperature range of 3 °C to 5 °C with hydrochloric acid (min. 37%, Riedel-de Haën, Germany) and sodium nitrite (p.a. ≥ 99.0%, Riedel-de Haën, Germany) in 4% excess, and excess nitrite was destroyed after diazotisation by adding urea (p.a. ≥ 99.5%, Riedel-de Haën, Germany). 1-Naphthol was dissolved in deionised water, previously stripped of dissolved oxygen by a nitrogen stream. Fresh 1-naphthol and diazotised sulphanilic acid solutions were prepared every day and every half-day (Bourne et al., 1985), respectively, and stored in glass vessels under exclusion of light and at room temperature.

According to Bourne (1981b) at the optimum value of pH = 10 maximum reaction rates are attained. Therefore in this work 111.1 mol m⁻³ each sodium carbonate anhydrous and sodium hydrogen carbonate (p.a. ≥ 99.8% and p.a. ≥ 99.7%, Panreac Química, Spain, respectively) were used to buffer the 1-naphthol solutions, just before coupling, producing a pH of 9.9 and an ionic strength after mixing of I = 444.4 mol m⁻³.

Table 5.5 lists the reactants solutions concentrations fed into the static mixer, at 20 °C, according to the particular reactants injection scheme used. For the segregated injection schemes, a considerable difference between the concentrations of the two reactants is required to meet the condition of the overall feed stoichiometry $C_A^{\text{initial}} / C_B^{\text{initial}} = 1.20$. A column with the values of reactant A and B concentrations after mixing is introduced to assist the reader.

<table>
<thead>
<tr>
<th>Reactants injection scheme</th>
<th>Unmixed feed concentrations of A and B</th>
<th>Concentrations of A and B after mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-mixed injection scheme (see Figure 5.47)</td>
<td>$C_A^{\text{in}} = 0.450$ mol m⁻³, $C_B^{\text{in}} = 0.429$ mol m⁻³</td>
<td></td>
</tr>
<tr>
<td>Segregated injection scheme 1 (see Figure 5.48a)</td>
<td>$C_A^{\text{in}} = 0.257$ mol m⁻³, $C_B^{\text{in}} = 3.000$ mol m⁻³</td>
<td>$C_A^{\text{initial}} = 0.240$ mol m⁻³, $C_B^{\text{initial}} = 0.200$ mol m⁻³</td>
</tr>
<tr>
<td>Segregated injection scheme 2 (see Figure 5.48b)</td>
<td>$C_A^{\text{in}} = 0.277$ mol m⁻³, $C_B^{\text{in}} = 1.500$ mol m⁻³</td>
<td></td>
</tr>
<tr>
<td>Segregated injection scheme 3 (see Figure 5.48c)</td>
<td>$C_A^{\text{in}} = 0.300$ mol m⁻³, $C_B^{\text{in}} = 1.000$ mol m⁻³</td>
<td></td>
</tr>
</tbody>
</table>
As in the visualisation experiments, mixing-reaction experiments were conducted in steady state, using uniform flow rate distribution over all static mixer inlet channels. Pre-mixed injection scheme experiments were made at Reynolds numbers ranging from $Re = 50$ to $Re = 700$. Segregated injection schemes were only performed at $Re = 300$ and $Re = 500$, as reported in Section 5.5.2.2. The imposed settings using two Ismatec® MCP pump systems are presented in Table 5.1.

5.5.2.2 Results

The product distribution of Equation 5.47 defined by $X_s$ (see Equation 5.48) has been shown to be a suitable parameter for mixing characterisation (see for example, Bourne, 1982). Therefore, the product distribution was determined in the NETMIX® static mixer outlet for each hydrodynamic operating condition and reactants injection scheme studied. The procedure conducting to this determination and the experimental results obtained are reported next.

The reaction products $oR$, $pR$ and $S$, contrarily to the reactants $A$ and $B$, absorb visible light and thus can be quantitatively analysed by analysed by spectrophotometry, for which the SX.18MV-R Microvolume Stopped-Flow Reaction Analyser from Applied Photophysics® was used.

Figure 5.49 presents the extinction coefficients for the species $oR$, $pR$ and $S$ in the range of wavelengths $\lambda = 400$ nm to $\lambda = 650$ nm, calculated from the spectra of known concentration solutions, determined under the experimental conditions of this work (Nunes et al., 2001).

The products mixtures were analysed assuming that $oR$, $pR$ and $S$ absorb independently in the range of considered wave lengths (Bourne et al., 1981b) and that the Lambert-Beer law is valid at the concentration levels used.

Hence, at a given wavelength $\lambda$, the total absorbance $E$ over a path length $\delta$ is

$$E = \varepsilon_{oR} C_{oR}^{\text{final}} \delta + \varepsilon_{pR} C_{pR}^{\text{final}} \delta + \varepsilon_S C_S^{\text{final}} \delta \quad (5.51)$$

where $\varepsilon_{oR}$, $\varepsilon_{pR}$ and $\varepsilon_S$ are the extinction coefficients at wavelength $\lambda$ of $oR$, $pR$ and $S$, respectively, and $C_{oR}^{\text{final}}$, $C_{pR}^{\text{final}}$ and $C_S^{\text{final}}$ their concentrations.
Figure 5.49  Extinction coefficients of the species oR, pR and S at various wave lengths. $T = 20^\circ C$, $pH = 9.9$ and $I = 444.4$ mol m$^{-3}$. 
Figure 5.50 shows a representative plot of the total absorbance, over a path length \( \delta = 2 \text{ mm} \), of an \( oR \), \( pR \) and \( S \) mixture in the range of wavelengths \( \lambda = 400 \text{ nm to } \lambda = 650 \text{ nm} \).

\( C_{oR}^{\text{final}} \), \( C_{pR}^{\text{final}} \) and \( C_S^{\text{final}} \), as the changing coefficients in Equation 5.51, are determined by the best fit to the \( E \) experimental curve, using a LSF (Least Squares Fit).

![Graph showing absorbance vs wavelength](image)

**Figure 5.50** Total absorbance over a path length \( \delta = 2 \text{ mm} \) of an \( oR \), \( pR \) and \( S \) mixture at various wavelengths. Pre-mixed injection scheme, \( Re = 100 \), \( C_A^{\text{initial}} = 0.120 \text{ mol m}^{-3} \), \( C_A^{\text{initial}} / C_B^{\text{initial}} = 1.20 \), \( T = 20^\circ \text{C} \), \( pH = 9.9 \) and \( I = 444.4 \text{ mol m}^{-3} \).

For both pre-mixed and segregated injection schemes, and at every Reynolds numbers studied, samples were collected from all outlet channels of the NETMIX® static mixer. Each sample was immediately analysed twice, thus resulting in 30 absorbance measurements for each Reynolds number.

The two measurements served two purposes: first to ensure the spectrophotometric method reproducibility; second to verify if chemical reaction only occurred inside the static mixer, thus providing a quantification of mixing only inside the static mixer.

Further, for all reactants injection schemes in Table 5.5, two experiments were made at each Reynolds number, further ensuring the results reproducibility.

For the pre-mixed injection scheme, given that no concentration profile at the outlet channels was found to occur, values of \( C_{oR}^{\text{final}} \), \( C_{pR}^{\text{final}} \) and \( C_S^{\text{final}} \) are presented as arithmetic averages of all the measured concentrations values in each experiment, for each Reynolds number.
Table 5.6 presents the list of experiments and concentrations of $\alpha R$, $\rho R$ and $S$ measured at the outlet channels of the NETMIX static mixer, in the range of Reynolds number $50 \leq Re \leq 700$, using the pre-mixed injection scheme, $C_{A,\text{initial}} = 0.240$ mol m$^{-3}$, $C_{A,\text{initial}} / C_{B,\text{initial}} = 1.20$, $T = 20^\circ C$, pH = 9.9 and $I = 444.4$ mol m$^{-3}$.

<table>
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<tr>
<th>Re</th>
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<th>Exp. 2</th>
<th>Exp. 1</th>
<th>Exp. 2</th>
<th>m</th>
</tr>
</thead>
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<tr>
<td>50</td>
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<td>$C_{\rho R}$</td>
<td>$C_{S}$</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>0.0084±0.0001</td>
<td>0.1609±0.0016</td>
<td>0.0151±0.0002</td>
<td>99.75%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0083±0.0001</td>
<td>0.1596±0.0028</td>
<td>0.0153±0.0003</td>
<td>99.25%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>$C_{\alpha R}$</td>
<td>$C_{\rho R}$</td>
<td>$C_{S}$</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>0.0085±0.0001</td>
<td>0.1699±0.0032</td>
<td>0.0107±0.0002</td>
<td>99.93%</td>
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<td></td>
</tr>
<tr>
<td>0.0085±0.0002</td>
<td>0.1696±0.0034</td>
<td>0.0109±0.0003</td>
<td>99.95%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>$C_{\alpha R}$</td>
<td>$C_{\rho R}$</td>
<td>$C_{S}$</td>
<td>m</td>
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<tr>
<td>0.0086±0.0001</td>
<td>0.1747±0.0027</td>
<td>0.0083±0.0001</td>
<td>99.94%</td>
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<tr>
<td>0.0087±0.0002</td>
<td>0.1738±0.0033</td>
<td>0.0081±0.0001</td>
<td>99.35%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>$C_{\alpha R}$</td>
<td>$C_{\rho R}$</td>
<td>$C_{S}$</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>0.0087±0.0001</td>
<td>0.1810±0.0029</td>
<td>0.0045±0.0001</td>
<td>99.42%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0087±0.0002</td>
<td>0.1787±0.0056</td>
<td>0.0044±0.0001</td>
<td>98.10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>$C_{\alpha R}$</td>
<td>$C_{\rho R}$</td>
<td>$C_{S}$</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>0.0088±0.0000</td>
<td>0.1836±0.0011</td>
<td>0.0026±0.0000</td>
<td>98.83%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0089±0.0002</td>
<td>0.1818±0.0057</td>
<td>0.0026±0.0001</td>
<td>97.95%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>$C_{\alpha R}$</td>
<td>$C_{\rho R}$</td>
<td>$C_{S}$</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>0.0089±0.0001</td>
<td>0.1856±0.0012</td>
<td>0.0010±0.0000</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0.0089±0.0001</td>
<td>0.1858±0.0023</td>
<td>0.0010±0.0000</td>
<td>98.42%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>$C_{\alpha R}$</td>
<td>$C_{\rho R}$</td>
<td>$C_{S}$</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>0.0090±0.0001</td>
<td>0.1880±0.0035</td>
<td>0.0002±0.0000</td>
<td>98.70%</td>
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<td></td>
</tr>
<tr>
<td>0.0090±0.0000</td>
<td>0.1878±0.0000</td>
<td>0.0002±0.0000</td>
<td>98.60%</td>
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<td></td>
</tr>
<tr>
<td>400</td>
<td>$C_{\alpha R}$</td>
<td>$C_{\rho R}$</td>
<td>$C_{S}$</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>0.0091±0.0001</td>
<td>0.1889±0.0011</td>
<td>0.0002±0.0000</td>
<td>99.18%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0092±0.0002</td>
<td>0.1897±0.0032</td>
<td>0.0002±0.0000</td>
<td>99.64%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>$C_{\alpha R}$</td>
<td>$C_{\rho R}$</td>
<td>$C_{S}$</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>0.0092±0.0001</td>
<td>0.1897±0.0010</td>
<td>0.0002±0.0000</td>
<td>99.2%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0092±0.0002</td>
<td>0.1897±0.0043</td>
<td>0.0002±0.0000</td>
<td>99.63%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>$C_{\alpha R}$</td>
<td>$C_{\rho R}$</td>
<td>$C_{S}$</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>0.0093±0.0002</td>
<td>0.1897±0.0034</td>
<td>0.0002±0.0000</td>
<td>99.65%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0093±0.0002</td>
<td>0.1901±0.0043</td>
<td>0.0002±0.0000</td>
<td>99.87%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Between 97.95% to 99.95% of the quantity of $B$ added was found to be finally present as $\alpha R$, $\rho R$ and $S$, thus giving a check on the mass balance. In all these experiments the complete consumption of the limiting reactant $B$ was found to occur inside the NETMIX static mixer and no concentration evolution with time was observed.
Experimental measurements show that 4.347% to 5.252% of the 1-naphthol were converted to \( oR \) and 94.75% to 95.65% to \( pR \). Such results are in close agreement with the published data, Bourne et al. (1990) reported 7% of \( oR \) and 93% of \( pR \) and Nunes et al. (2001) reported 6% of \( oR \) and 94% of \( pR \) for azo couplings in non-viscous media.

The results of the mixing-reaction experiments for the pre-mixed injection scheme are shown in Figure 5.51. The line in this figure corresponds to the NETMIX\textsuperscript{®} model predicted data according to Section 5.6.2. In view of the experimental data, it is clear the major effect of the Reynolds number on macromixing and micromixing.

![Graph showing the relationship between Re and Xₜ](image)

**Figure 5.51**  Selectivity in \( S \) measured at the outlet channels of the NETMIX\textsuperscript{®} static mixer, in the range of Reynolds number \( 50 \leq Re \leq 700 \). Pre-mixed injection scheme, \( C_{A,\text{initial}} = 0.240 \text{ mol m}^{-3}, \quad C_{A,\text{initial}}/C_{B,\text{initial}} = 1.20, \quad T = 20^\circ\text{C}, \quad \text{pH} = 9.9 \) and \( f = 444.4 \text{ mol m}^{-3} \).

From \( Re = 50 \) to \( Re = 250 \), it is observed that \( X_S \) decays very rapidly to an asymptotic value of nearly zero for Reynolds numbers \( Re \geq 300 \). In terms of either macromixing and micromixing, this indicates a severe increase in the mixing intensity in the range of Reynolds numbers \( 50 \leq Re \leq 250 \), indicating for \( Re \geq 300 \) that the product...
distribution is no longer in a macromixing or micromixing controlled regime. Such conclusions are further supported in light of the results from flow visualisation, in Section 5.3.2, and chemical reaction visualisation, in Section 5.5.1, for $Re \geq 300$.

In Chapter 3, the effect of different reactants injection schemes in the selectivity in $S$ for consecutive competitive second-order reactions has been studied. The following experimental work aims to give a practical utility to that study, substantiating the use of segregated injection schemes to control and attain different product distribution for the same hydrodynamic operating condition. Experiments were carried out at Reynolds numbers $Re = 300$ and $Re = 500$, assuming, based on the previous experimental observations, that both hydrodynamic and mixing conditions present no further evolution with $Re$ in this range. The validity of this assumption is later discussed in Section 5.6.

Table 5.7 to Table 5.9 and Table 5.10 to Table 5.12 present the list of experiments and concentrations of $B$, $oR$, $pR$ and $S$ measured separately at each outlet channel of the NETMIX® static mixer, at $Re = 300$ and $Re = 500$, respectively, using the segregated injection schemes in Figure 5.48, for $C_{A}^{\text{initial}} = 0.240$ mol m$^{-3}$, $C_{A}^{\text{initial}} / C_{B}^{\text{initial}} = 1.20$, $T = 20^\circ$C, pH = 9.9 and $I = 444.4$ mol m$^{-3}$. Values of $C_{oR}^{\text{final}}$, $C_{pR}^{\text{final}}$ and $C_{S}^{\text{final}}$ are arithmetic averages of the two measured concentration values, for each reactants injection scheme and experiment.

Similarly to the pre-mixed injection scheme experiments, concentration evolution with time was not observed in these experiments, although now the limiting reactant B is not completely consumed inside the NETMIX® static mixer, except for the segregated injection scheme 3.

The quantity of $B$ found to be finally present in unreacted $B$, $oR$, $pR$ and $S$ was 98.33% to 100.5%, for $Re = 300$, and 98.45% to 100.0%, for $Re = 500$, thus giving a check on the mass balance. Values between 4.503% to 6.992% and 4.507% to 6.993% of $oR$ and 93.01% to 95.50% and 93.00% to 95.49% of $pR$ were obtained for $Re = 300$ and $Re = 500$, respectively.
Table 5.7  Concentrations of B, oR, pR and S measured at the outlet channels of the NETMIX® static mixer, at Reynolds number Re = 300. Segregated injection scheme 1, $C_{A_{\text{initial}}} = 0.240 \text{ mol m}^{-3}$, $C_{B_{\text{initial}}} / C_{P_{\text{initial}}} = 1.20$, $T = 20^\circ \text{C}$, pH = 9.9 and $I = 444.4 \text{ mol m}^{-3}$.

<table>
<thead>
<tr>
<th>Channel</th>
<th>Exp. 1</th>
<th>Exp. 2</th>
<th>Exp. 1</th>
<th>Exp. 2</th>
<th>Exp. 1</th>
<th>Exp. 2</th>
<th>Exp. 1</th>
<th>Exp. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{B_{\text{final}}} \text{ [mol m}^{-3}]$</td>
<td>$C_{oR_{\text{final}}} \text{ [mol m}^{-3}]$</td>
<td>$C_{pR_{\text{final}}} \text{ [mol m}^{-3}]$</td>
<td>$C_{S_{\text{final}}} \text{ [mol m}^{-3}]$</td>
<td>$C_{B_{\text{final}}} \text{ [mol m}^{-3}]$</td>
<td>$C_{oR_{\text{final}}} \text{ [mol m}^{-3}]$</td>
<td>$C_{pR_{\text{final}}} \text{ [mol m}^{-3}]$</td>
<td>$C_{S_{\text{final}}} \text{ [mol m}^{-3}]$</td>
</tr>
<tr>
<td>1</td>
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<td>0.0027</td>
<td>0.0444</td>
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<td>0.0000</td>
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<tr>
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<td>0.0042</td>
<td>0.0570</td>
<td>0.0145</td>
<td>0.0000</td>
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<td>0.0150</td>
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<tr>
<td>3</td>
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<td>0.0243</td>
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<td>0.0972</td>
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<td>0.0000</td>
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<td>0.0162</td>
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<tr>
<td>9</td>
<td>0.0163</td>
<td>0.0085</td>
<td>0.1373</td>
<td>0.0802</td>
<td>0.0178</td>
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<td>0.0000</td>
<td>0.0078</td>
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<td>0.0537</td>
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<tr>
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<td>0.0059</td>
<td>0.1058</td>
<td>0.0384</td>
<td>0.0000</td>
<td>0.0067</td>
<td>0.1007</td>
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<tr>
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<td>0.0233</td>
<td>0.0000</td>
<td>0.0055</td>
<td>0.0737</td>
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</tr>
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<td>0.0143</td>
<td>0.0000</td>
<td>0.0030</td>
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<td>0.0156</td>
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<td>0.0110</td>
<td>0.0000</td>
<td>0.0035</td>
<td>0.0468</td>
<td>0.0107</td>
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</table>
Table 5.8  Concentrations of B, pR, pR and S measured at the outlet channels of the NETMIX® static mixer, at Reynolds number Re = 300. Segregated injection scheme 2, $C_{A_{\text{initial}}}$ = 0.240 mol m$^{-3}$, $C_{A_{\text{initial}}}/C_{B_{\text{initial}}}$ = 1.20, $T = 20^\circ$C, pH = 9.9 and $I$ = 444.4 mol m$^{-3}$.

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<tr>
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Table 5.9  Concentrations of $B$, $oR$, $pR$ and $S$ measured at the outlet channels of the NETMIX® static mixer, at Reynolds number $Re = 300$. Segregated injection scheme 3, $C_{A,\text{initial}}^{\text{initial}} = 0.240$ mol m$^{-3}$, $C_{A,\text{initial}}^{\text{initial}} / C_{B,\text{initial}}^{\text{initial}} = 1.20$, $T = 20^\circ$C, pH = 9.9 and $I = 444.4$ mol m$^{-3}$.

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Table 5.10  Concentrations of B, oR, pR and S measured at the outlet channels of the NETMIX® static mixer, at Reynolds number \( Re = 500 \). Segregated injection scheme 1, \( C_{A_{\text{initial}}} = 0.240 \text{ mol m}^{-3}, \ C_{B_{\text{initial}}} / C_{A_{\text{initial}}} = 1.20, \ T = 20^\circ \text{C}, \ \text{pH} = 9.9 \) and \( I = 444.4 \text{ mol m}^{-3} \).

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Table 5.11 Concentrations of B, oR, pR and S measured at the outlet channels of the NETMIX® static mixer, at Reynolds number Re = 500. Segregated injection scheme 2, $C_{A_{initial}} = 0.240$ mol m$^{-3}$, $C_{A_{initial}} / C_{B_{initial}} = 1.20$, $T = 20^\circ$C, pH = 9.9 and $I = 444.4$ mol m$^{-3}$.

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Table 5.12  Concentrations of B, pR, qR and S measured at the outlet channels of the NETMIX™ static mixer, at Reynolds number \( Re = 500 \). Segregated injection scheme 3, \( C_{A_{\text{initial}}} = 0.240 \text{ mol m}^{-3}, \frac{C_{A_{\text{initial}}}}{C_{B_{\text{initial}}}} = 1.20 \), \( T = 20^\circ C \), pH = 9.9 and \( I = 444.4 \text{ mol m}^{-3} \).

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Figure 5.52 and Figure 5.53 show the profiles of $X_s$ measured along the outlet channels of the NETMIX® static mixer using segregated injection schemes for $Re = 300$ and $Re = 500$, respectively. From the inspection of the experimental results, several points can be made.

The reactants injection scheme strongly affects the selectivity in $S$ for the same Reynolds numbers, with $X_s$ markedly decreasing as the number of reactant $B$ injection zones is increased. This is in agreement with the qualitative predictions from Chapter 3, wherein $X_s$ is shown to be reduced as the initial state of effectiveness of mixing in the reactants is increased.

**Figure 5.52** Selectivity in $S$ measured at the outlet channels of the NETMIX® static mixer, at Reynolds number $Re = 300$. $C_{A_{\text{init}}} = 0.240$ mol m$^{-3}$, $C_{A_{\text{init}}}/C_{B_{\text{init}}} = 1.20$, $T = 20^\circ\text{C}$, pH $= 9.9$ and $I = 444.4$ mol m$^{-3}$.

**Figure 5.53** Selectivity in $S$ measured at the outlet channels of the NETMIX® static mixer, at Reynolds number $Re = 500$. $C_{A_{\text{init}}} = 0.240$ mol m$^{-3}$, $C_{A_{\text{init}}}/C_{B_{\text{init}}} = 1.20$, $T = 20^\circ\text{C}$, pH $= 9.9$ and $I = 444.4$ mol m$^{-3}$.
The profiles of $X_s$ along the outlet channels of the NETMIX® static mixer exhibit central symmetry. Since the segregated injection schemes used are centrally symmetric, as can be seen in Figure 5.48, this may constitute evidence that the flow rate inside all channels of the NETMIX® static mixer is uniform, hence endorsing the analogy to a pure resistive electrical circuit introduced in the hydrodynamic model in Chapter 3 to simulate the flow within such network structure.

Comparison between the profiles of $X_s$ for the same segregated injection scheme at $Re = 300$ and $Re = 500$ reveals similar spatial distributions, although the measured selectivities in $S$ are displaced towards lower values for $Re = 500$. Such decrease is in agreement with the qualitative predictions of the NETMIX® model concerning the effect of the Damköhler number on the $X_s$, as shown in Chapter 3.

The akin trend observed on the $X_s$ profiles for both Reynolds numbers further supports the previously introduced hypothesis of no hydrodynamic and mixing dependency on $Re$ between $Re = 300$ and $Re = 500$.

Furthermore, Figure 5.52 and Figure 5.53 show for both segregated injection scheme 1 and segregated injection scheme 2 the clear existence of a maximum value of $X_s$ located at the central outlet channel of the NETMIX® static mixer. It also follows for both $Re$ a flattening of the profile of $X_s$ along the outlet channels of the NETMIX® static mixer as the number of reactant $B$ injection zones is increased, with a nearly plane profile for the segregated injection scheme 3. These aspects are discussed in detail in next section.

Flat profiles of $X_s$ are obtained along the outlet channels of the NETMIX® static mixer both using the segregated injection scheme 3 and the pre-mixed injection scheme. Nevertheless, the mean selectivities in $S$ for the segregated injection scheme 3, $X_s = 0.0597$ and $X_s = 0.0424$, are remarkably larger than the corresponding selectivities for the pre-mixed injection scheme, $X_s = 0.0021$ and $X_s = 0.0019$, for $Re = 300$ and $Re = 500$, respectively. Therefore, the product distribution for the present reaction scheme is shown to be intimately dependent on the details of mixing-reaction interactions.

The present data provides firm and further basis for evaluating the NETMIX® model applicability to the NETMIX® static mixer, which is undertaken in next section.
5.6 Comparison with NETMIX® Model Data

At this point it is important to compare the data obtained using both the imaging and the mixing-reaction experiments with the NETMIX® model data. In Section 5.6.1, the overall mixing patterns in the NETMIX® static mixer are compared with a NETMIX® model simulation that is presented. In Section 5.6.2, the mixing-reaction experiments are compared with simulations in the inquest of the NETMIX® model to describe micromixing and chemical reaction in the NETMIX® static mixer.

5.6.1 Macromixing

Flow visualisation experiments in the NETMIX® static mixer provided detailed macromixing assessment in the range of Reynolds numbers $25 \leq Re \leq 700$, as can be seen in Section 5.3.2.

From the photographs of the NETMIX® static mixer, a continuously evolving tracer spread is observed for Reynolds numbers ranging from $Re = 25$ to $Re = 200$, while for Reynolds numbers $Re \geq 300$, the tracer plume aperture attains the limit of $45^\circ$, with any further evolution in the overall tracer patterns virtually impossible to differentiate.

Macromixing modelling in the NETMIX® model, see Chapter 3, is based both on the network structure and on the assumptions of perfectly mixed chambers and piston flow in the channels, with the hydrodynamics simulated using an analogy to a pure resistive electrical circuit, having hence no dependency on the Reynolds number.

Comparison between experimental and computed patterns is then required to appraise the ability of the NETMIX® model to correctly predict macromixing inside the NETMIX® static mixer. The regular network with NPBC and without HC constructed with the exact dimensions of the NETMIX® static mixer, see Section 5.4.2, was used for all NETMIX® model simulations.

Figure 5.54 compares the predicted and observed spread of tracer in the NETMIX® static mixer for a single central injection point. For the simulated concentration map in Figure 5.54a, a colour scale was built based on the successive dilution of the methylene blue solution used in the experimental tracer experiments.
The good match observed between the macromixing patterns from the NETMIX® model and from the NETMIX® static mixer provides a final validation to the NETMIX® model in Chapter 3 as a macromixing descriptive model for $Re \geq 300$. Thus, for $Re \geq 300$, the NETMIX® static mixer dimensionless RTD function, $E(\Theta)$, is assumed to follow Equation 3.44, from which can be shown that the NETMIX® static mixer behaviour approaches that of a plug-flow reactor. Knowledge of the RTD becomes a key parameter when static mixers are used as chemical reactors (Thakur et al., 2003).

Two mechanisms of macromixing were identified in the NETMIX® static mixer in Section 5.3.2.1: mixing inside the chambers and flow division. Mixing inside the chambers is the process whereby fluid concentrations impeding from different neighbouring chambers are repeatedly homogenised. Flow division occurs between successive rows of chambers since each chamber possesses two exit channels. These interrelated mechanisms are responsible for the 45° aperture of the plume and the halving of tracer concentrations along the rows at the plume boundaries, as can be seen in Figure 5.54b.
5.6.2 Micromixing and Chemical Reaction

To clearly interpret the mixing-reaction experiments, and compare them with the NETMIX® model data, it is important to have reliable chemical kinetic information.

Since the azo coupling of 1-naphthol (A) with diazotised sulphanilic acid (B) forms oR and pR simultaneously (see Equation 5.47), the reaction rate constants of these coupling reactions cannot be determined individually from kinetic runs, but instead a total reaction rate constant \( k_t = k_{1oR} + k_{1pR} \) is calculated (Nunes et al., 2001). In view of this, the consecutive competitive reaction system in Equation 5.47 is generally represented as a pair of consecutive competitive reactions

\[
\begin{align*}
A + B & \stackrel{k_1}{\rightarrow} R \quad \text{(very fast)} \\
B + R & \stackrel{k_2}{\rightarrow} S \quad \text{(fast)}
\end{align*}
\]

(5.52)

where \( k_1 \) and \( k_2 \) are the total reaction rate constants.

Bourne et al. (1981b; 1985; 1990), Baldyga and Bourne (1984), Wenger et al. (1992) and Nunes et al. (2001) reported results of stopped-flow kinetic experiments for these reactions. Nonetheless the wide range of published values for rate constants, all works report both azo coupling reactions to be irreversible and second order in concentration dependence so that

\[ -r_A = k_1 C_A C_R \]

(5.53)

and

\[ r_S = k_2 C_B C_R \]

(5.54)

Nunes et al. (2001) reported \( k_1 = 15.8 \times 10^3 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \) and \( k_2 = 2.7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \) at pH = 9.9 and \( T = 20^\circ \text{C} \), obtained in the SX.18MV-R Microvolume Stopped-Flow Reaction Analyser. These two values are used in all simulations below.

Since \( k_1 \) is three orders of magnitude higher than \( k_2 \), theoretical model predictions are found to be insensitive to modest variations in \( k_1 \) (Chang et al., 1986) but the same can not be said for \( k_2 \). Despite this problem, in the simulations below the two kinetics constants values reported by Nunes et al. (2001) were consistently used.

Aiming the validation of the NETMIX® model to describe mixing and reaction inside the NETMIX® static mixer, simulations were performed using the regular network with the same
geometry of the NETMIX® static mixer, see Section 5.4.2, and with the pre-mixed and segregated injection schemes in Figure 5.47 and Figure 5.48, respectively.

Figure 5.51 plots the computed and experimental selectivities in $S$ for Reynolds numbers in the range $50 \leq Re \leq 700$ for the pre-mixed injection scheme. For $Re \geq 300$ the NETMIX® model describes accurately the experimental results, thus providing strong evidence that likewise macromixing for $Re \geq 300$, micromixing is well described by the NETMIX® model.

In Section 5.3.4.2 it was argued that the effective mixing volume is confined by the upper and lower limits of the channels plane. However, the results in Figure 5.51 show that for $Re \geq 300$ experiments are well described by the NETMIX® model, which considers the complete volume of the chambers for mixing and chemical reaction. This suggests that the above assumption is only valid for $Re \leq 200$ and that for $Re \geq 300$ effective mixing volume coincides with the chamber total volume.

So far, the NETMIX® model comparison with experiments has focused on the pre-mixed injection scheme, suggesting an excellent agreement between measured and predicted data for $Re \geq 300$. For completeness, measured concentration profiles for the segregated injection schemes are next compared with the NETMIX® model calculations.

Computed concentrations of reactant $B$ and products $R$ and $S$ for the reaction scheme in Equation 5.52 using the NETMIX® model are presented and compared in Figure 5.55 and Figure 5.56 with the experimental data for each outlet channel and segregated injection scheme for $Re = 300$ and $Re = 500$, respectively. The inlet reactants concentrations for the simulations were set equal to the experimental values reported Table 5.5. The experimental concentration of product $R$, $C_{R}^{\text{final}}$, is assessed from Table 5.7 to Table 5.12 as

$$C_{R}^{\text{final}} = C_{oR}^{\text{final}} + C_{pR}^{\text{final}}$$  \hspace{1cm} (5.55)

where $C_{oR}^{\text{final}}$ and $C_{pR}^{\text{final}}$ are the concentrations of $oR$ and $pR$ measured spectrophotometrically.

It should be pointed out that no fitting or adjustable parameters or constants were used in these simulations. Agreement between experiments and NETMIX® model predictions is excellent for both Reynolds numbers $Re = 300$ and $Re = 500$, thus validating the assumptions in Chapter 3 that channels behave as PFRs and chambers behave as perfectly mixed CSTRs, exhibiting no hydrodynamic or mixing dependency on the Reynolds number.
Figure 5.55  Computed and experimental concentrations of B, R and S at the outlet channels of the NETMIX® static mixer at Reynolds number $Re = 300$. $C_{i,\text{initial}} = 0.240 \text{ mol m}^{-3}$, $C_{A,\text{initial}}/C_{B,\text{initial}} = 1.20$, $T = 20^\circ\text{C}$, pH = 9.9 and $I = 444.4 \text{ mol m}^{-3}$. 
Figure 5.56  Computed and experimental concentrations of B, R and S at the outlet channels of the NETMIX® static mixer at Reynolds number $Re = 500$. $C_{A}^{\text{initial}} = 0.240$ mol m$^{-3}$, $C_{A}^{\text{initial}} / C_{B}^{\text{initial}} = 1.20$, $T = 20^\circ\text{C}$, $\text{pH} = 9.9$ and $I = 444.4$ mol m$^{-3}$. 
The proper description of the effect of the reactants injection scheme on the concentration profiles at the outlet channels of the NETMIX® static mixer constitutes therefore final validation of the NETMIX® model as a macromixing and micromixing and chemical reaction descriptive model, for Reynolds numbers $Re \geq 300$.

The validation of the NETMIX® model as a macromixing and micromixing and chemical reaction descriptive model of the NETMIX® static mixer, allows trustworthy estimations of the concentration maps inside the NETMIX® static mixer, immediately accessible from computation.

Comparatively to experiments, a validated model offers the added advantage of complete knowledge of the concentrations maps, allowing deeper insight and investigation into the effect of local phenomena on the end result. Benefiting from this aspect, the already experimentally observed impact of the reactants injection scheme on the profiles of $X_s$ at the outlet channels of the NETMIX® static mixer, see Figure 5.52 and Figure 5.53, is next explained.

Figure 5.57 to Figure 5.59 show the computed concentration field maps of reactant $B$ and products $R$ and $S$ in the NETMIX® static mixer for the three segregated injection schemes at $Re = 300$. At higher Reynolds numbers, qualitatively similar behaviours occur.

*Figure 5.57  Computed concentration field maps of reactant $B$ and products $R$ and $S$ in the NETMIX® static mixer for the segregated injection scheme 1 at $Re = 300$.***
Figure 5.58  Computed concentration field maps of reactant B and products R and S in the NETMIX® static mixer for the segregated injection scheme 2 at $Re = 300$.

Figure 5.59  Computed concentration field maps of reactant B and products R and S in the NETMIX® static mixer for the segregated injection scheme 3 at $Re = 300$. 
The distribution of $R$ and $S$ is shown to be clearly depending on the details of the reactants $A$ and $B$ spatial distributions. The peaks of the distribution of $R$ occur in the contact region between reactants $A$ and $B$, with rich regions of $R$ delimiting the $B$ rich regions. Figure 5.57 and Figure 5.58 show this feature. When spatial inhomogeneity of $A$ and $B$ concentrations occur, excess of $B$ in presence of $A$ yields $R$ that is latter consumed into $S$. This is clearly the case, with the local maximum regions of $B$ overlapping for the three segregated injection schemes with local deficit regions of $R$. Such general behaviour for the case of a fast consecutive competitive reaction system was noted and qualitatively discussed by Levenspiel (1972) and Bourne and Toor (1977), with subsequent experimental studies (Paul and Treybal, 1971; Bourne et al., 1981a), and DNS simulations confirming the general validity of this observation (Chakrabarti et al., 1995).

Recalling Figure 5.52 and Figure 5.53, the experimental profiles of selectivity in $S$ for the cases of segregated injection scheme 1 and segregated injection scheme 2 display maximum values at the central outlet channel of the NETMIX® static mixer. Such feature is implicit from Figure 5.57 and Figure 5.58, noticing that for these reactants injections schemes, contact between reactants $A$ and $B$ is not sufficient to completely consume $B$ in the NETMIX® static mixer axis, thus resulting in great formation of $S$ in that region. On the other hand, the local maxima of $B$ in the static mixer axis promote the consumption of $R$, resulting in local minima of $R$, as also seen in Figure 5.52 and Figure 5.53.

For the segregated injection scheme 3, Figure 5.59 shows that local excess of reactant $B$ is rapidly faded, and therefore $S$ forms solely in the first rows of the NETMIX® static mixer, after which is spread throughout the static mixer, resulting in the almost flat profile of $X_s$ observed in the outlet channels.

The viability of using different reactants injection schemes as a key factor to control and attain different selectivities in $R$ and $S$ is shown experimentally through this study.

Since the fast consecutive competitive reactions offer a stringent test of reactive mixing (Li and Toor, 1986), the ability of the NETMIX® model to handle and describe extreme situations as the use of segregated injection schemes results in its final validation as a straightforward tool for product distribution design.
5.7 Conclusions

Qualitative analysis of the NETMIX® static mixer mixing efficiency was assessed through tracer flow visualisation experiments in the range of Reynolds numbers $25 \leq Re \leq 700$. The importance of the work presented lies in the fact that it contributes to the knowledge of the influence of the operating $Re$ in the NETMIX® static mixer dynamic behaviour. From the present work it is clear the existence of a transition in the flow field regime at Reynolds number $Re = 50$, critical Reynolds number, with the onset of mixing mechanisms inside each chamber. For Reynolds numbers $Re < 50$, an almost complete segregation between the fluids in the two halves of the chamber is observed. Above the critical Reynolds number, a continuous increase in the mixing dynamics is observed, with quasi-instantaneous chamber homogenisation achieved for $Re > 200$.

Snapshot images of the instantaneous flow field from tracer experiments provide valuable information about the flow field dynamics in the NETMIX® static mixer for each Reynolds number for the validation of the 2D CFD model simulations. It was shown that the flow regime transition Reynolds number to the self-sustainable oscillatory regime and the typical flow field oscillation frequencies are correctly simulated from the 2D CFD model.

The relationship between the Reynolds number based on the channels, for the 2D geometry, used in the CFD simulations, and for the 3D geometry, used in the experiments, keeping the same ratio between inertial and viscous forces, is shown to be $Re_{3D} = 2 Re_{3D}$. The respective oscillation frequencies generated by the 2D and 3D flow structures are related as $St_{2D} = 1.3 St_{3D}$. More, from the oscillation frequency spatially independency and the practically constant value of the Strouhal number in the range of Reynolds numbers considered, it is shown that the sole mechanism dictating the frequency of the flow field oscillations is the mean residence time in the chambers effective mixing volume.

Pressure drop measurements further validated the 2D CFD model, which was seen to accurately describe the NETMIX® static mixer also in terms of pressure drop, once the geometry differences are accounted for. In addition, the NETMIX® model was shown to predict the NETMIX® static mixer pressure drop due to the frictional energy losses at the walls.

The power number and the Z factor values for the NETMIX® static mixer were established and compared to values available in the literature for different stirred tanks and static mixers,
respectively. For most cases the NETMIX® static mixer was found to achieve lower energy consumption.

A good match between the NETMIX® model and the NETMIX® static mixer macromixing patterns was shown from tracer flow visualisation experiments, validating the NETMIX® model in Chapter 3 as a macromixing descriptive model for $Re \geq 300$.

Greater insight in the mixing efficiency of the NETMIX® static mixer was achieved through chemical reactions experiments using as test reaction a fast consecutive competitive reaction system, the azo coupling of 1-naphthol with diazotised sulphanilic acid. Since the azo coupling reaction product distribution strongly depends upon the mixing intensity, the selectivity in $S$ can be used to further assess the NETMIX® model validity for mixing and reaction. Chemical reaction imaging provided further evidence on the overall increase of mixing, both macromixing and micromixing, with $Re$.

Experiments to determine the product distribution at the outlet channels NETMIX® static mixer were carried out for different Reynolds numbers and reactants injection schemes. Under the pre-mixed injection scheme, the selectivity in $S$ severely decreases in the range of Reynolds numbers $50 \leq Re \leq 250$, displaying nearly zero values for $Re \geq 300$. This indicates a severe increase in mixing intensity up to $Re = 300$, with the product distribution being no longer in a macromixing or micromixing controlled regime for higher Reynolds numbers. Likewise for macromixing, an excellent fit of mixing-reaction experimental data was obtained with the NETMIX® model for $Re \geq 300$.

NETMIX® model simulations in Chapter 3 showed a strong product distribution dependency on the reactants injection scheme. The feasibility of using segregated injection schemes as an operational and design parameter in the NETMIX® static mixer was experimentally shown for $Re = 300$ and $Re = 500$. Agreement between experiments and predictions was excellent for both Reynolds numbers, thus supporting for the NETMIX® static mixer the assumptions in the NETMIX® model that channels behave as PFRs and chambers behave as perfectly mixed CSTRs for $Re \geq 300$.

The agreement between chemical reaction experimental data and NETMIX® model predictions with segregated injection schemes provides a firm basis to its ultimate assertion as a macromixing and micromixing and chemical reaction descriptive model for the NETMIX® static mixer, under the appropriate conditions.
6. FINAL REMARKS

This chapter is divided in two sections. Section 6.1 summarises the main results and conclusions drawn from this work. Section 6.2 provides a list of suggestions for future work.

6.1 General Conclusions

A review on the state-of-the-art in the field of static mixers, including the most commonly used commercial static mixers and their applications, was provided in Chapter 2. From this review it is clear that static mixers have become standard equipment in the process industries, presenting an attractive alternative to conventional stirrers. However, despite their widespread use, research and development of new static mixers has been reduced, with most efforts aimed at characterising fluid flow and mixing performance of commercially available static mixers. Thus there is still much room for novel static mixer designs, making it possible to achieve a range of applications beyond those traditionally associated with static mixers.

In this context, the present work makes an important contribution to the current state-of-the-art by addressing the development of a new static mixing device, the NETMIX® static mixer, including its modelling, CFD simulation and experimental characterisation. Further, the usefulness of CFD in the design of new static mixers and in the study of the mixing mechanisms was clearly shown in this work.
In Chapter 3 the NETMIX® model was first introduced as a mixing and chemical reaction model. Using a combined network model and networks-of-zones model formulation, the NETMIX® model was shown to describe one conceivable way of coupling macromixing and micromixing in continuous flow systems. Chemical reaction simulations have shown good agreement between trends in NETMIX® model predictions and published experimental results. Further, the ability in the NETMIX® model to control macromixing and micromixing states, with resulting controlled outputs on both yield and selectivity of reaction, provided guidance to the development of a new static mixing device, the NETMIX® static mixer, with a NETMIX® model based network structure and capable of retaining its features.

In Chapter 4 the dynamic behaviour of the flow field in a regular network of channels and chambers such as the NETMIX® model, was studied by means of CFD simulation, aiming to check the viability of mixing in that structure.

From the CFD simulations with the 2D model in the range of $50 \leq Re \leq 700$ it was observed the existence of two flow field regimes. For $Re < 100$ there is no self-sustained evolution of the flow field and a final steady state flow regime is always identified. For Reynolds numbers $Re \geq 100$ the flow field tends to a fully developed self-sustained oscillatory state. The transition between the two regimes occurs in a sudden way at $Re = 100$, denoted as the critical Reynolds number.

From the normal velocity time histories for two probe points, the centres of chamber 1 and chamber 2, the mixing intensity, the power spectra and the cross-correlation function were computed for a greater insight into the flow field structures and dynamics.

Mixing intensity is here a measure of the fluctuations in the normal velocity component and was used as a measure of the mixing dynamics. Above the regime transition at $Re = 100$, the mixing intensity values continuously increase with the Reynolds number, showing an evolution in the flow field dynamics, with the major variation occurring between $Re = 100$ and $Re = 150$. Together with the flow field observation inside the chambers, the fact that both chamber 1 and chamber 2 show the same values of $\sigma_n^*$ at each $Re$ is evidence of no evolution of the flow field statistics between chambers with different locations, although some loss of synchronisation progressively occurs above $Re = 200$.

From the power spectra for both chambers in the range of $100 \leq Re \leq 300$, a single strong energy peak occurs, indicating that the flow field oscillates with a well-defined frequency.
From $Re = 100$ to $Re = 150$, the Strouhal number increases sharply, further supporting the assumption of strong evolution in the flow dynamics. For Reynolds numbers in the range of $150 \leq Re \leq 300$, the values of $St$ are kept approximately constant with $Re$ at $St \approx 0.125$. For Reynolds numbers above $Re = 300$, a slight increasing trend of $St$ towards higher Reynolds numbers is observed, with the typical $St$ peak losing definition and the power spectra presenting a spread of energy through a range of frequencies, marking the onset of new oscillatory states. Thus, the small variability of $St$ with $Re$ in the range of $150 \leq Re \leq 700$ is evidence that the main characteristic of the flow field are kept and so the mixing mechanisms. The fact that the power spectra for both chambers at each $Re$ are similar, gives further support to the evidence of no flow field statistics evolution between chambers.

Supported on the invariance of $St$ with $Re$, the hypothesis that the typical oscillations frequencies are ruled by a geometry-based mechanism was pointed out. It was shown that the sole mechanism dictating the frequency of the flow field oscillation is the mean residence time in each chamber.

From the cross-correlograms final evidence of no statistical or dynamic evolution of the flow field between chambers was obtained, with the normal velocity time histories at both probe points shown to be strongly coupled and in phase.

CFD simulations indicate that the proposed geometry presents, above a critical but low Reynolds number, a very strong flow field dynamics that promotes mixing with high energetic efficiency. In spite of the simulations presented in Chapter 4 have shown to be DNS, the final validation of the 2D CFD model to describe a 3D structure was attained in Chapter 5.

In Chapter 5 the pilot NETMIX® unit was experimentally characterised using tracer experiments, pressure drop experiments and chemical reaction experiments, with the twofold purpose to consider the validity of the CFD simulations in Chapter 4 and the NETMIX® model in Chapter 3.

Tracer experiments were conducted in the range of Reynolds numbers $25 \leq Re \leq 700$ and allowed a qualitative analysis of macromixing and micromixing in the NETMIX® static mixer through the visualisation of overall tracer spread patterns and local visualisation of mixing inside the chambers, respectively. From this experiments, the critical Reynolds number is seen to occur at $Re = 50$. For Reynolds numbers $Re < 50$, the almost complete lack of mixing
inside the chambers results in the non-spreading of the tracer plume towards the NETMIX® static mixer top. For Reynolds numbers $Re \geq 50$, the onset of mixing mechanisms inside the chambers causes a continuously increasing spread of the tracer plume aperture, up to the physical limit of $45^\circ$ for $Re = 200$. Above $Re = 200$ the overall tracer flow patterns become practically impossible to differentiate with a quasi-instantaneous homogenisation inside the chambers.

The different values obtained for the critical Reynolds number from CFD simulations and tracer experiments are due to the relation between the Reynolds numbers for the 2D model, used in CFD simulations, and for the 3D flow in the experiments. Thus, considering that relationship, the critical Reynolds number predicted from simulations precisely matches the critical Reynolds number from the experiments.

The snapshot images of the instantaneous flow field from tracer experiments in the range of Reynolds numbers $50 \leq Re \leq 200$ further evidenced the existence of a typical flow field oscillation frequency at $St = 0.081$. Although the values of $St$ from CFD simulations and from tracer experiments are different they are shown associated to the same mechanism in both cases, i.e., the mean residence time in the chambers effective mixing volume.

The simulation results presented in Chapter 4 were seen to reproduce correctly the dynamic behaviour identified in the tracer experiments in Chapter 5, validating the 2D CFD model. For further validation of the CFD simulations in Chapter 4 and energy consumption, the pressure drop across the NETMIX® static mixer was experimentally determined. The pressure drop behaviour of the NETMIX® static mixer was proven to be exactly described from the CFD simulation, once the geometry differences are accounted for. Furthermore, the NETMIX® static mixer was found for most cases to achieve lower energy consumption when compared with data available in literature for different stirred tanks and static mixers.

To study the mixing efficiency in the NETMIX® static mixer, a consecutive competitive reaction system, the azo coupling of 1-naphthol with diazotised sulphanilic acid, was used as test reaction. Chemical reaction visualisation experiments were conducted for Reynolds numbers in the range of $50 \leq Re \leq 700$, providing evidence on the overall increase of mixing, both macromixing and micromixing, with $Re$. For $Re = 50$, mixing inside the chambers is still insufficient to promote homogeneity of both reactant streams, restricting product formation to the chamber central region. For Reynolds numbers $75 \leq Re \leq 200$, micromixing is continuously enhanced and general widespread of product formation throughout the entire
chamber occurs. Similarly to the tracer experiments, no further mixing improvement is depicted from chemical reaction visualisation experiments for Reynolds numbers above $Re = 200$.

The extreme sensitivity of the azo coupling reaction used in this work makes its product distribution a suitable parameter for mixing characterisation. The product distribution, defined as the selectivity in $S$, was determined at the NETMIX® static mixer outlet for different Reynolds numbers and reactants injection schemes. From the pre-mixed injection scheme experiments, the lower selectivities in $S$ within reach for the NETMIX® static mixer were established at Reynolds numbers ranging from $Re = 50$ to $Re = 700$ and for the particular experimental conditions used. Pre-mixed injection scheme experiments further revealed a severe increase in the mixing intensity for $50 \leq Re \leq 250$, with the product distribution no longer being in a macromixing or micromixing controlled regime for $Re \geq 300$.

The viability of using different reactants injection schemes as a parameter to control and attain product distribution in the NETMIX® static mixer was experimentally established for $Re = 300$ and $Re = 500$.

The experimental data in this work provided a solid basis for the validation of the NETMIX® model as macromixing and micromixing and chemical reaction descriptive model for the NETMIX® static mixer, for $Re \geq 300$. The ability of the NETMIX® model to describe stringent situations such as the use of segregated injection schemes with test reactions extends its interest as a straightforward tool to make reliable estimates of the overall static mixer performance at the design stage. More, the NETMIX® model was shown to predict the NETMIX® static mixer pressure drop due to the frictional energy losses at the walls. Ultimately, combined with CFD simulations, the NETMIX® model reduces costs and ensures the NETMIX® static mixer meets or exceeds the product distribution requirements.

The NETMIX® static mixer is a novel type of static mixing device for continuous mode operation, with particular interest for the implementation of chemical reactions with conversion and selectivity control problems. The principle of operation of the NETMIX® static mixer, that is of manipulating flow fields through a particular structured design geometry, is straightforward and seems almost perfect in promoting a strong dynamics of mixing even at low Reynolds numbers. With this work, and further work here proposed, it should be possible to solve many of the problems inherent to the operation of static mixers
and widen their present range of application as efficient mixing devices. The NETMIX® static mixer has advanced to the stage were NETMIX® model data and CFD simulations can be coupled to rapidly produce optimal designs, in some sense, for a given application. In addition, other improvements of the NETMIX® static mixer, in comparison with other static mixers, are listed next.

- The structure of the NETMIX® static mixer is considerably simple.

- Possibility of easy inclusion of temperature, pressure and concentration sensors in the NETMIX® static mixer, without modifying its dynamics.

- The NETMIX® static mixer contains a high area for heat exchange. This characteristic can be used in temperature control, for highly endothermic or exothermic reactions, or when the reaction selectivity depends essentially on the operating conditions.

- The NETMIX® static mixer can be linked to a heat transfer unit, in a similar arrangement to a plate heat exchanger. The flow direction of fluids in the NETMIX® static mixer and in the heat transfer unit can easily be adjusted, in order to efficiently control the temperature in the interior of the NETMIX® static mixer.

- The NETMIX® static mixer can easily be constructed in different materials, with intensification of heat transfer and catalysis processes, through its walls.

- Chemical reaction can be controlled through the definition of different coating catalyst in different elements of the NETMIX® static mixer or in different NETMIX® static mixers associated in series or parallel.

- Ability to control the mixture and the mean residence time of the reactants.

- Easiness of implementation of different reactants injection schemes.

- Two or more NETMIX® static mixers can be associated in parallel or series. In this way, scale-up is immediate.

The innovations underlying the NETMIX® static mixer are currently in the process of applying for patent protection for Intellectual Property.
6.2 Future Work

The present work helps identify several important areas for future research. These areas are critical prerequisites for applying the NETMIX® model over a broader range of Reynolds numbers and or NETMIX® static mixer structures and for understanding of the physics of the flow in the NETMIX® static mixer and its implications for design and mixing efficiency. Specific suggestions are listed below.

- All NETMIX® model simulations, see Chapter 3, were presented for regular networks with PBC and without HC. Simulations should also be performed for regular networks with HC and for random sized networks with and without HC. The effect of removing chambers and or channels in a random or specified manner must be determined.

- The NETMIX® model should be amended to simulate the NETMIX® static mixer total pressure drop above the critical Reynolds number and the complicated dependence of mixing and chemical reaction on the Reynolds number. The availability of detailed experiments, however, is critical to the success of such a challenging undertaking.

- Particle tracking computations should be performed using the CFD model, see Chapter 4, providing valuable information, e.g. the RTD, the Poincaré maps or the stretching of fluid elements, to characterise mixing efficiency.

- LDA measurements for the flow field characterisation in the NETMIX® static mixer should be carried out. From the LDA measurements the spatial distribution of the averaged flow field and the intensity of mixing can be computed.

- CFD simulations offer an almost unlimited range of options for the paths to follow, since the costs involved are lower than those of building new experimental setups. In terms of the network structure, various modifications of the NETMIX® static mixer should be studied to identify likely mixing enhancing network structures. The effect of the network structure on the critical Reynolds number must be thoroughly considered.

- Given the CFD preliminary results concerning variant network structures, experiments should then be carried out in comparable NETMIX® static mixers to determine whether both NETMIX® model and CFD model are validated within the range of Reynolds numbers studied.
• Systematic studies addressing multiphase flow, flow of viscoelastic fluids, flow of fluids with different viscosities or flow of two, or more, immiscible fluids should also be considered.
REFERENCES


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