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Mixing and Controlled Combustion in NETmix

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To my official and
non-official supervisors

One Art

The art of losing isn't hard to master;
so many things seem filled with the intent
to be lost that their loss is no disaster.

Lose something every day. Accept the fluster
of lost door keys, the hour badly spent.
The art of losing isn't hard to master.

Then practice losing farther, losing faster:
places, and names, and where it was you meant
to travel. None of these will bring disaster.

I lost my mother's watch. And look! my last, or
next-to-last, of three loved houses went.
The art of losing isn't hard to master.

I lost two cities, lovely ones. And, vaster,
some realms I owned, two rivers, a continent.
I miss them, but it wasn't a disaster.

— Even losing you (the joking voice, a gesture
I love) I shan't have lied. It's evident
the art of losing's not too hard to master
though it may look like (*Write it!*) like disaster.

Elizabeth Bishop

Abstract

Combustion is behind a large number of daily activities, such as energy production and vehicles supply. However, these processes are associated to negative environmental impacts, namely pollution and global warming. In this way, it is imperative to find strategies to perform combustion, minimizing its harmful effects. *Controlled combustion* enables to perform combustion in strict conditions, having control over the reaction products. In this field, *lean combustion* has been gaining attention. In fact, the use of oxygen in excess makes this type of combustion a potential via to reduce pollutant emissions.

The products of chemical reactions are dependent on the hydrodynamics and mixing process of the reactants. In this way, it is of major relevance to fully characterize the flow prior to the performance of combustion. The size of the chemical reactor is another aspect that should be considered. In fact, the control of chemical reactions is easier if small devices are used, especially *micro* or *mesoreactors* (1 to 10 mm). In this work, combustion is performed for the first time in NETmix, a particular type of mesostructured reactor.

NETmix is a static mixer whose design is based on a network of mixing chambers interconnected by transport channels. This reactor has been used since 2005 for laboratorial and industrial applications, showing promising results in terms of reaction yields and heat transfer. The oscillating behaviour inside the mixing chambers enhances mixing in a laminar chaotic regime, which is fully characterized in this work.

To study the hydrodynamics and mixing process of NETmix prior to the simulation of combustion, macro and micromixing analysis is performed. For this, a new algorithm, Lagrangian Mixing Simulation (LMS) as well as two modified versions, Diffusive Lagrangian Mixing Simulation (DLMS) and Batch Lagrangian Mixing Simulation (BLMS), are developed. Along with Computational Fluid Dynamics (CFD) simulations, these methods enable to assess the chaotic mixing of NETmix and optimise the topology of the reactor to obtain nearly perfect mixing inside the NETmix chambers. According to this work, the optimal ratio between the chamber diameter and the channel width, D/d , is in the range $6.65 < D/d < 6.85$.

The optimised NETmix reduced model, ExtendedNUB, is used to simulate the hydrogen combustion with CFD simulations. Moreover, a new network model, NETcombustor, is developed to represent NETmix. The Lamellar Micromixing Model is also adapted for

combustion in NETmix. The prediction of the temperature inside the reactor as well as the composition of the products by the new models, NETcombustor and Lamellar Micromixing Model for Combustion, has less than 12% and 15% difference to the CFD results, respectively.

For *premixed* and *non-premixed* combustion, hotspots are formed inside NETmix. Moreover, the temperature of the hotspots decreases as the fuel in the reactive mixture is diluted by means of an inert or oxygen in excess. The analysis of combustion is made for different hydrogen reactive schemes with several diffusive and physical properties models. With NETcombustor, the injection scheme is also studied. Moreover, a combustion H₂-Air curve for NETmix is designed.

As a final approach, combustion is simulated in NETmix considering heat removal. From both models, CFD and NETcombustor, it is shown that the temperature inside the reactor can be controlled by heat transfer.

Resumo

A *combustão* está presente num vasto conjunto de atividades diárias, tais como a produção de energia e o funcionamento de veículos. Porém, estes processos têm um impacto ambiental negativo, nomeadamente ao nível da poluição e do aquecimento global. Assim, é da maior relevância encontrar soluções para operar as reações de combustão, minimizando os seus efeitos negativos. A *combustão controlada* tem tido um papel relevante uma vez que permite a realização de combustão em ambiente monitorizado, controlando os produtos reacionais emitidos. Nomeadamente, a *combustão pobre* tem ganho atenção nos últimos anos dado que a utilização de oxigénio em excesso permite reduzir as emissões poluentes.

Os produtos das reações químicas dependem da hidrodinâmica e do processo de mistura dos reagentes. Assim, é imperativo caracterizar o escoamento antes da implementação de reações de combustão. O tamanho do reator desempenha também um papel relevante nas reações químicas. De facto, o controlo das reações é mais simples se o reator for pequeno, nomeadamente tamanhos na escala *micro* e *meso* (1 a 10 mm). Neste trabalho, estudam-se pela primeira vez os processos de combustão no reator mesoestruturado NETmix.

O *NETmix* é um misturador estático cujo desenho se baseia numa rede de câmaras de mistura interligadas entre si por canais de transporte. Este reator é usado desde 2005 para aplicações quer laboratoriais quer industriais, tendo mostrado resultados promissores ao nível da transferência de massa e calor. O comportamento oscilatório do escoamento nas câmaras promove os processos de mistura num *regime laminar caótico*, extensivamente caracterizado neste trabalho.

Previamente à implementação de combustão no reator NETmix, a hidrodinâmica e os processos de mistura são estudados recorrendo a dois tipos de análise, macro e micro mistura. Para esse fim, desenvolve-se um novo algoritmo *Lagrangiano*, Lagrangian Mixing Simulation (LMS), assim como duas variantes do mesmo, Diffusive Lagrangian Mixing Simulation (DLMS) e Batch Lagrangian Mixing Simulation (BLMS). Em conjunto com análises de Dinâmica dos Fluidos Computacional (CFD), estes métodos Lagrangianos permitem a caracterização do escoamento caótico do NETmix e a otimização da topologia do reator com a finalidade de obter mistura praticamente perfeita no interior das câmaras. De acordo com este trabalho, a razão ótima entre o diâmetro das câmaras e a largura dos canais, D/d , está dentro do intervalo $6.65 < D/d < 6.85$.

Um modelo reduzido e otimizado do NETmix, o ExtendedNUB, utiliza-se para simular a combustão do hidrogénio com CFD. Mais ainda, um novo modelo de rede, o NETcombustor, é desenvolvido para representar o NETmix. O Lamellar Mixromixing Model é também adaptado para simular combustão no NETmix. A previsão da temperatura dentro do reator, assim como a composição dos produtos, pelos dois modelos novos, NETcombutor e Lamellar Mixromixing Model for Combustion, diferem menos de 12% e 15% dos resultados de CFD, respetivamente.

Para combustão *pré-misturada* e *não pré-misturada*, mostra-se que são formados *pontos quentes* no interior do NETmix. Além disso, a temperatura destes pontos diminui quando o combustível da mistura reacional é diluído por um inerte ou pela presença de oxigénio em excesso. A análise da combustão faz-se para diferentes esquemas reacionais do hidrogénio, utilizando diversos modelos de difusão e de propriedades físicas da mistura. No caso das simulações com o NETcombustor realiza-se também um estudo do esquema de injeção. Mais ainda, uma curva de combustão para o sistema H_2 -Ar no NETmix é elaborada.

Como estudo final, simula-se a combustão no NETmix considerando remoção de calor. Para as duas aproximações, com CFD e com o NETcombustor, mostra-se que a temperatura no interior do reator pode ser controlada através da transferência de calor.

Résumé

La combustion fait partie d'un grand nombre d'activités quotidiennes comme la production d'énergie et le fonctionnement des véhicules. Cependant, ces procédés sont associés à des impacts environnementaux négatifs, notamment la pollution et le réchauffement climatique. Ainsi, c'est impératif de trouver des stratégies pour faire des réactions de combustion en minimisant ses effets néfastes. La *combustion contrôlée* permet de réaliser la combustion dans des conditions strictes, facilitant le control des produits de la réaction. Sur ce domaine, la *combustion maigre* a attiré l'attention au cours des dernières années. En fait, l'utilisation de l'oxygène en excès permet de réduire les émissions polluantes.

Les produits des réactions chimiques sont dépendants de l'hydrodynamique et du procédé de mélange des réactants. Ainsi, c'est important the caractériser l'écoulement dans le réacteur avec détail avant de simuler les réactions de combustion. La taille du réacteur exerce aussi une grande influence sur le déroulement des réactions. En fait, c'est plus facile de contrôler les réactions si les dimensions du réacteur sont petites, notamment les *micro* et *méso* réacteurs (1 à 10 mm). Dans ce travail, la combustion est étudiée pour la première fois dans le réacteur méso-structuré NETmix.

Le *NETmix* est un mélangeur statique formé par un réseau de chambres de mélange interconnectées par des canaux de transport. Ce réacteur a été utilisée depuis 2005 pour des applications laboratoires et industrielles, montrant des résultats prometteurs de transfert de matière et d'énergie. Le comportement oscillatoire qui a lieu dans les chambres du NETmix favorise le mélange dans un *régime chaotique laminaire*, caractérisé en détail en ce travail.

Avant de simuler la combustion dans le NETmix, l'hydrodynamique et le procédé de mélange du réacteur sont analysés par des études de mélange macro et micro. Avec ce propos, un nouvel algorithme *Lagrangian*, le Lagrangian Mixing Simulation (LMS), aussi bien que deux variations du même, le Diffusive Lagrangian Mixing Simulation (DLMS) et le Batch Lagrangian Mixing Simulation (BLMS), sont développés. Avec des analyses de dynamique des fluides computationnelle (CFD), ces nouvelles méthodes permettent d'étudier le mélange chaotique du réacteur NETmix et optimiser la topologie du réacteur pour avoir un mélange presque parfait. D'après ce travail, le ratio optimal entre le diamètre des chambres et la largeur des canaux, D/d , appartient à la gamme $6.65 < D/d < 6.85$.

Un modèle réduit optimisé du réacteur NETmix, le ExtendedNUB, est utilisé pour simuler la combustion de l'hydrogène avec CFD. De plus, un nouveau modèle de réseau, le NETcombustor, est développé pour représenter le NETmix. Le Lamellar Micromixing Model est aussi adapté pour simuler des réactions de combustion dans le NETmix. La prédiction de la température de combustion aussi bien que la composition des produits par les deux modèles, NETcombustor et Lamellar Micromixing Model for Combustion, ont une différence de moins de 12% et 15% par rapport aux simulations de CFD, respectivement.

Pour la combustion a *prémélange* et *sans prémélange*, il se vérifie que des *points de chaleur* sont formés dans le réacteur NETmix. De plus, la température des points de chaleur diminue si le mélange réactionnel est dilué avec un gaz inerte ou avec de l'oxygène en excès. L'analyse de la combustion de l'hydrogène est faite pour des différents schémas réactionnelles, avec plusieurs modèles de diffusion et de prédiction des propriétés physiques du mélange. Avec le modèle NETcombustor, le schéma d'injections est aussi étudié. De plus, une courbe de combustion du système H₂-Air pour le NETmix est élaborée.

Dans l'étude final de cette thèse, la combustion est simulée dans le NETmix en considérant l'évacuation de la chaleur. Avec les deux modèles, CFD et NETcombustor, la température dans le réacteur peut être contrôlé par le transfert d'énergie.

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Notation

Roman Letters

a	exponential fitting parameter
$\mathcal{A}$	rate coefficient parameter
A	amplitude of modulation in active mixing, “inside” species in striation thickness algorithm
A_c	area of NETcombustor channels
A_j	area below v_x curve
b	rate coefficient parameter
b	exponential fitting parameter
$b1$	intercept of the tangent line at a particle i
$b2$	intercept of the tangent line at a particle j
B	“outside” species in striation thickness algorithm.
c	linear fitting parameter
c_p	specific heat capacity
C	Courant number
C_A	concentration of species A
C_i	molar concentration of species i
d	rate coefficient parameter
d	channel width of the NETmix reactor
$\mathcal{D}$	mass diffusivity
D	height of the mixing chamber in CIJ, chamber diameter in NETmix
D_h	hydraulic diameter
D_T	thermal diffusion coefficient
D_v^l	diameter of large vortices

D_v^s	diameter of small vortices
dx_j	initial distance between consecutive particles of BLMS
$\frac{\bar{D}}{\bar{D}t}$	mean substantial derivative
$\frac{\partial}{\partial t}$	partial derivative
E	energy
E_a	activation energy
f	frequency
$f(v)$	Probability Density Function of v
F	molar flow rate
gap	number of particles between the deleted particles and the particles at which new subsets are joined in DLMS
G	surface
G_0	reference point of surface G
h	specific enthalpy
H	width of the mixing chamber in CIJ reactor
I_s	intensity of segregation
I_{v_x}	turbulence intensity
j_{ix}	flux of component i
J	normalized gradient of G
k	turbulent kinetic energy
kb	backward rate coefficient
kf	forward rate coefficient
K_{in}	instantaneous rate coefficient
ℓ	turbulence length scale
l	channel length in the NETmix reactor
l_b	box size

ℓ_F	flame thickness
$\mathcal{L}$	characteristic dimension
$L1$	tangent line at particle j
m	mass of fuel or oxygen
$m1$	slope of the tangent line at a particle i
$m2$	slope of the tangent line at a particle j
$\mathcal{M}$	molecular mass of the mixture
$\mathcal{M}_F$	molecular mass of fuel
$\mathcal{M}_O$	molecular mass of oxygen
n	number of moles of fuel or oxygen
n_b	number of boxes
np	number of particles in LMS
n_b^l	number of blue particles that exit the mixing chamber on the left side
n_b^r	number of blue particles that exit the mixing chamber on the right side
n_r^l	number of red particles that exit the mixing chamber on the left side
n_r^r	number of red particles that exit the mixing chamber on the right side
n_x	number of rows of the NETmix reactor
n_y	number of columns of the NETmix reactor
$\mathcal{N}$	fractal or attractor dimension
N	dimension of vectors $p1$ and $p2$
$Npoints$	number of points of DFT
p	pressure
P	exit conditional probability
p_{gap}	minimum number of particles between consecutive split points in DLMS
p_n	last particle at the inlet in BLMS
P_b^l	exit conditional probability of blue particles exiting the mixing chamber on the left side

P_b^r	exit conditional probability of blue particles exiting the mixing chamber on the right side
P_r^l	exit conditional probability of red particles exiting the mixing chamber on the left side
P_r^r	exit conditional probability of red particles exiting the mixing chamber on the right side
p_1	first particle at the inlet in BLMS
$\mathcal{P}$	momentum
p^*	fluctuation component of pressure
$\langle p \rangle$	mean pressure
P1	point (0,0) in CIJ reactor
P2	point (0, $2.5 \times 10^{-3}\text{m}$) in CIJ reactor
P3	point (0, $2.5 \times 10^{-2}\text{m}$) in CIJ reactor
p1	vector with particles j to be deleted
p2	vector with particles k to be deleted
Q	heat of combustion
r	distance between two points
rc	component rate
r_i	rate of reaction i
r_{inf}	infinite reaction rate
R	ideal gas constant
$R(r)$	correlation coefficient
R^2	squared correlation coefficient
s	length of the interface of particles
s_0	initial interfacial area in LMS
S	striation thickness
s_F	flame speed

S_i	strip thickness in strip method
s_L	laminar burning velocity
s_p	local length around a particle
S_s	scale of segregation
S_0	initial strip thickness in strip method, initial striation thickness in LMS
t	time
t_f	LMS final time
t_F	flame time
t_{max}	final time
t_η	Kolmogorov time scale
T	temperature
$\mathcal{U}$	characteristic velocity scale
$\mathcal{U}_F$	flame speed
$\mathcal{U}_\eta$	Kolmogorov velocity scale
ν	sample variable corresponding to velocity v
V	network volume
$\mathbf{v0}$	inlet mesh cells velocity vector in BLMS
W	CIJ injectors width
x	x-coordinate
x_c	x-coordinate of the intersection of the lines with slopes $m1$ and $m2$
x_p	x-coordinate of particles
$\mathbf{X}$	position vector of particles or markers
X_i	conversion of reactant i
$\mathbf{x0}$	inlet mesh cells vector with position coordinates
y	y-coordinate, molar fraction
y_c	y-coordinate of the intersection of the lines with slopes $m1$ and $m2$

y_p	y -coordinate of particles
Y	mass fraction
Z	conserved scalar
Z_F	mass fraction of the elements from the fuel stream at any point of the mixture
$Z_{F,1}$	mass fraction of fuel in the fuel stream
Z_O	mass fraction of oxygen from the oxidizer stream at any point of the mixture
$Z_{O,2}$	mass fraction of oxygen in the oxidizer stream

Greek letters

α	interfacial area generation
α_p	local interfacial area generation
β	contribution parameter
ΔA	difference between consecutive areas
ΔH_f°	enthalpy of formation
ΔS_f°	entropy of formation
Δt	time step
Δx	maximum hedge of the quadrilateral elements of the mesh
Δx_i^0	initial space between markers in strip method
ε	dissipation rate
ϵ	vorticity
ϵ^*	normalized vorticity
ζ	strain rate
ζ^*	normalized strain rate
η	Kolmogorov scale
θ	equivalence ratio
λ	Lyapunov exponent, thermal conductivity

μ	viscosity
μ_j^{in}	viscosity of inlet j mixture in the NETcombustor network
ν	kinematic viscosity
ν_F	stoichiometric coefficient of fuel F
ν_O	stoichiometric coefficient of oxygen O
ξ	minimum convective mixing scale
ρ	density
ρ_j^{in}	density of inlet j mixture in the NETcombustor network
ρ_{out}	molar density
$\sigma_{C_A}^2$	variance of C_A
σ_i	Lennard-Jones parameters
τ	residence time
τ_c	residence time in one NETmix chamber
τ_ℓ	time scale of larger eddies in turbulent flows
τ_η	Kolmogorov time scale
T	tensor
u'	turbulence intensity (Flamelet models)
$\mathbf{u}$	velocity vector
u	velocity
$\bar{u}$	velocity average
u_{inj}	velocity of the injection
$\overline{u_{inj}}$	surface and time averaged velocity of the injection
u_{max}	maximum velocity
u_x	x -velocity
u_x^*	normalized x -velocity
u_y	y -velocity

v_y^*	normalized y-velocity
$\overline{v_y}'$	cumulative average y-velocity
v_j^{in}	inlet j velocity of the NETcombustor network
$\gamma_x(f)$	Fourier transform of v_x
φ	phase displacement between opposed jets
ϕ	typical frequency in active mixing, connection angle in NETmix
χ	scalar dissipation rate
ω	depth of the NETmix reactor
$\psi(\mathbf{x},t)$	stretching function
Ω	cell in the mapping method
Ω_D	diffusion collision integral

Dimensionless Numbers

C	Courant number
Da	Damköhler number
Ka	Karlovitz number
Le	Lewis number
Re	Reynolds number
St	Strouhal number

Abbreviations

BLMS	Batch Lagrangian Mixing Simulation
CCS	Carbon Capture and Storage
CIJ	Confined Impinging Jets
CDF	Cumulative Distribution Function
CFD	Computational Fluid Dynamics
CPU	Central Processing Unit

CSTR	Continuous Stirred-Tank Reactor
DFT	Discrete Fourier Transform
DLMS	Diffusive Lagrangian Mixing Simulation
FFT	Fast Fourier Transform
FT	Fischer-Tropsch
LMS	Lagrangian Mixing Simulation
MOF	Metal Organic Frameworks
PDE	Partial Differential Equation
PDF	Probability Density Function
RIM	Reaction Injection Moulding
UDF	User Defined Function

Chapter I – Introduction

I.1 Motivation and Relevance

Combustion, “the process of burning something”, is present in most daily activities. The lighting up of the stove to cook, the fireplace in winter or the lighted candles on a birthday cake are processes that only exist due to combustion.

In 2020, the worldwide energy production of 1.6×10^5 TWh, came mostly from the combustion of oil and coal (Enerdata 2021). In Portugal, more than a half of the energy (gas and electricity) production is obtained from the combustion of coal and gas (EDP 2021). One crucial application of combustion is the use of fuel for vehicles. In 2019, the world fuel consumption reached 137 TWh, mostly natural gas, crude oil and coal (Our World in Data 2021).

The first evidence of the control of fire by man dates to one million years ago by a member of the *Homo* genus (James 1989). Since then, the importance of fire for livelihood was recognized and as the human species evolved, several theories about the combustion process have been developed. The requirement of oxygen for combustion to occur was noticed by Guericke, in 1650, who showed that a candle would not burn in a container with no air inside (Spangenburg and Moser 1993). The first theory to explain the process of combustion was developed in 1667 when Becher started the Phlogiston theory, which was later dismissed. According to the Phlogiston theory, the *phlogisticated* substances contain *phlogistons*, a fire-like element, which can burn until they become *dephlogisticated* by the process of losing phlogistons, which are absorbed by the air (Conant 1964). *Combustion*, as known today, was not discovered until 1772 by Lavoisier who realized that combustion occurred if a particular component of air, oxygen, named by Lavoisier as “la portion respirable de l’air”, was mixed with certain compounds, such as coal or hydrogen (Lavoisier 1789). In the early 19th century, Sir Humphry Davy performed experiments which enabled to measure flame temperatures. However, the influence of chemical kinetics and thermochemistry on combustion flames was not shown until the 20th century (Encyclopædia Britannica 2019). Nowadays, it is of general knowledge that combustion occurs if the *comburent*, i.e., oxygen, is mixed with the *combustible*, i.e., fuel, under specific conditions such as the temperature and the spatial arrangement where mixing takes place (Carrà et al. 2008).

With the growing awareness of environmental issues, such as global warming and pollution, the modelling of combustion, especially the modelling of *controlled combustion*, has become of major importance. Lately, the concept of *lean combustion*, i.e., combustion performed with a

reduced amount of fuel in relation to oxygen, has been gaining attention, aiming the decrease of NO_x emissions (Rankin et al. 2008).

The modelling of combustion has been done previously through two main methods: Probability Density Functions, PDF, (Vassilatos and Toor 1965, Pope 1985, Givi and McMurty 1988) and Flamelet models (Peters 1984, Peters 1995, Peters 2000). As an example, the PDF method has already been applied to model non-premixed methane jets flames (Chen et al. 1989) and to study the NO formation in non-premixed Hydrogen-Air jet flames (Chen et al. 1992). The flamelet models have been used to study several systems, such as the formation of NO_x and soot (Peters 1995, Pitsh 1998), and the formation of pollutants in gas-turbine combustors (Barths et al. 1998). More recently, the system Methane-Air was studied using concentric tubes (Carbonell et al. 2009). In this work, the combustion of hydrogen will be modelled using Computational Fluid Dynamics (CFD), the Lamellar Micromixing Model, which will be adapted to combustion for the first time, and NETcombustor, a new model that will be developed.

The reaction process of combustion is intrinsically linked to the mixing of the reactants. As stated by Ottino, “Mixing, or some form of interspecies contact, is an essential antecedent of mutual diffusion. Diffusion in turn is an antecedent of chemical reaction” (Ottino 1980). The first step to control reactions is then to understand the mixing process of the chemical species. In this way, the contribution of this work to perform controlled combustion starts by the development of a numerical algorithm, Lagrangian Mixing Simulation (LMS), as well as two variants of the original method, that will be used to characterize mixing in chemical reactors. Moreover, the algorithm will be coupled to the Lamellar Micromixing Model to perform its adaptation to combustion. LMS has already been used to quantify mixing in Confined Impinging Jets (Matos et al. 2018, Matos et al. 2020) and in a plate-plate rheometer (Brito et al. 2022).

The control of chemical reactions is easier if small devices are used. In this way, *micro* or *mesoreactors*, i.e., devices in the scale of 1 to 10 mm, will be used to perform combustion. In fact, reactors at this scale have a great heat transfer capacity and enable a larger control over the mixing scales (Hessel and Lowe 2003, Ottino and Wiggins 2004). In this work, combustion will be studied in a particular type of mesostructured device, the NETmix reactor.

NETmix is a static mixer patented in 2005 (Lopes et al. 2005). The design of the reactor is based on a network of mixing chambers interconnected by transport channels (Lopes et al. 2005). The mixing chambers are elements with a circular footprint which can be cylinders or spheres, the channels that connect the chambers are cylindrical or prismatic. The centre of these elements lay in a 2D plane. The fluids enter the NETmix reactor through separated inlets placed at the bottom row of the network and exit through a set of outlets at the top row. Figure I.1 shows the NETmix

network and flow patterns from a tracer CFD simulation (Fonte et al. 2013) for a *chaotic flow regime*, which will be extensively characterized in this work. The NETmix flow is shown in the video `NETmix_flow_tracer.mov` (Fonte et al. 2013) of the folder *Mixing_and_Controlled_Combustion_in_NETmix_videos*.

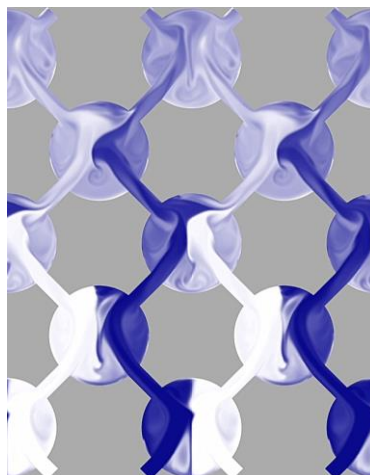


Figure I.1 NETmix network and flow pattern (Fonte et al. 2013).

In NETmix, it is possible to control macro and micromixing, which can be manipulated to improve the performance of the reactor. Moreover, the periodic nature of the NETmix design enables a direct scale-up from laboratory to industrial devices by numbering-up the network (Laranjeira 2005, Laranjeira et al. 2009).

Since 2008, an industrial NETmix prototype is used at Fluidinova S.A. (fluidinova.com) for the continuous large-scale production of synthetic nanocrystalline hydroxyapatite (Lopes et al. 2006, Silva et al. 2008, Gomes et al. 2009). Between 2011 and 2013, a laboratorial NETmix device was developed (Gomes et al. 2011, Fonte et al. 2013) to perform pressure drop measurements and laboratory flow studies, such as hydrodynamics and multiphasic analysis (Fernandes et al. 2021). Since 2017, NETmix has been used for microencapsulation for textile applications (Moreira et al. 2020), Pickering emulsions (Ribeiro et al. 2021) and metal-organic frameworks (MOF) production.

Recently, studies of heat transfer in NETmix have shown that the NETmix heat transfer capacity is ca. two and four orders of magnitude higher than the conventional Tubular and Jacketed Stirred Tank reactors, respectively, as shown in Figure I.2 (Costa et al. 2017).

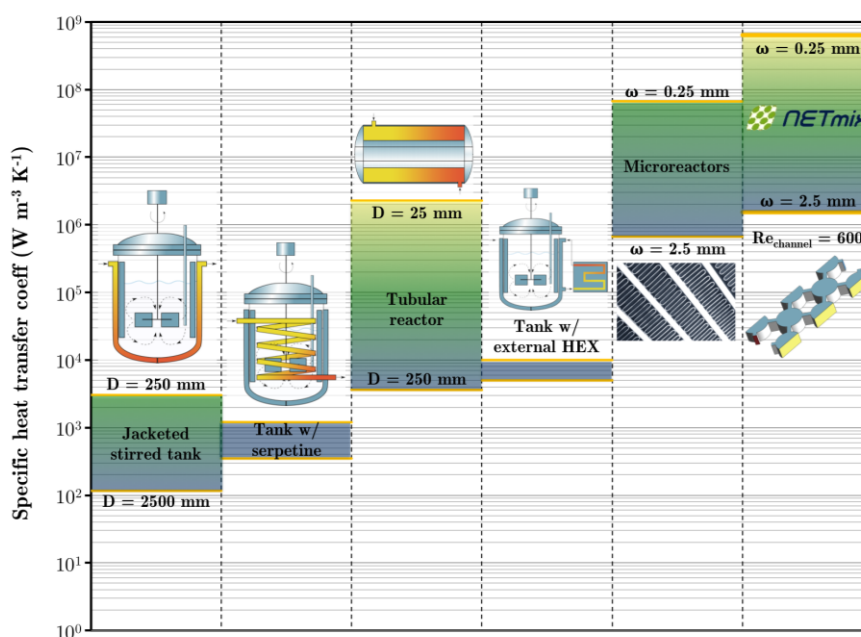


Figure I.2 Specific heat transfer capacity of different devices (Costa et al. 2017).

The simplicity of the NETmix design enables the scale-up and the coupling of devices such as heating and radiation plates. In this way, it is possible to have a major control of heat and mass transfer (Costa 2017), which has been widening the applications of this technology.

Since 2016, a photocatalytic NETmix was designed (Lima et al. 2016) which is used to perform photocatalysis studies such as kinetic modelling (Marinho et al. 2017, Santos et al. 2019, Santos et al. 2021) and ozonation (Filho et al. 2019). Since 2017, at the CoLAB NET4CO₂ (<https://www.net4co2.pt/index.php>), NETmix devices coupled to heat exchangers have been developed for the continuous production of CO₂ hydrates (Costa et al. 2017, Lopes et al. 2018, Lopes et al. 2019).

The promising results of NETmix in processes that involve heat transfer make this technology appealing to combustion applications. In this work, it will be shown that the NETmix properties in terms of mixing, mass and heat transfer are related with the *chaoticity* of the system which will be fully characterized. The NETmix reactor will then be used to perform combustion.

I.2 Objectives and Layout

As previously shown, NETmix has a higher heat transfer capacity when compared to commonly used devices. In this way, improved efficiencies of the process are expected, enabling the performance of combustion with lower temperatures ($T < 1300$ °C), preventing the formation of pollutants as NO_x.

In this work, combustion will be simulated in the NETmix reactor for the first time. To study combustion, Computational Fluid Dynamics (CFD) simulations will be used, and a new model, NETcombustor, will be developed. Moreover, the Lamellar Micromixing Model will be adapted to combustion.

Since the reactive systems are highly dependent on the flow hydrodynamics and on the mixing of the reactants, the NETmix chaotic system will be fully characterized prior to the simulation of combustion. CFD simulations will be used as well as Lagrangian methods. For that, new algorithms will be developed: Lagrangian Mixing Simulation (LMS), Diffusive Lagrangian mixing Simulation (DLMS) and Batch Lagrangian Mixing Simulation (BLMS).

To accomplish the objectives above mentioned, Chapter II to Chapter IV are dedicated to hydrodynamics and mixing characterization; Chapter V to Chapter VII are focused on the simulation of combustion. The content of this work is divided as follows:

In Chapter II, CFD will be used to characterize the hydrodynamics in NETmix and in the confined Impinging Jets (CIJ) reactor. To represent NETmix, a 2D reduced geometry will be numerically validated, the ExtendedNUB model, including the construction of a new symmetrical mesh grid.

Chapter III is dedicated to the quantification of mixing scales. For that, new Lagrangian algorithms will be developed: Lagrangian Mixing Simulation (LMS) and Diffusive Lagrangian mixing Simulation (DLMS). For the numerical validation of these models, the CIJ reactor will be used. LMS and DLMS enable the quantification of scales through the measurement of the interfacial area generation and the striation thickness, for which an algorithm was also developed. LMS and DLMS will be applied to characterize passive and active mixing in CIJ.

In Chapter IV, the NETmix topology will be optimised. Two approaches will be used, a macromixing approach and a micromixing approach. For the macromixing studies, a modification of LMS will be developed, the Batch Lagrangian Mixing Simulation (BLMS) algorithm, which will be used to optimise the ratio between the chamber diameter and the channel width, D/d , of NETmix. For the micromixing characterization, tracer CFD simulations will be used for the numerical validation of BLMS. Moreover, LMS will be applied to the NETmix chambers in order to quantify the mixing scales from the interfacial area generation and the striation thickness measurement. The NETmix chaotic system will be fully characterized. For that, hydrodynamics studies of the velocity, vorticity and strain rate will be performed, as well as phase diagrams, Poincaré maps and spectral analysis.

The simulation of combustion in NETmix starts in Chapter V. In the beginning of the chapter, the ExtendedNUB model is numerically validated for gases. CFD simulations will then be used to

study the hydrogen combustion for premixed and non-premixed mixtures. Different reactive schemes will be applied: the global reaction scheme with and without the reverse rate and the 19-reactions scheme. The influence of the mixture properties will be analysed, as well as the choice of the diffusion model. The difference between transient and steady-state approaches will also be studied. In the end of the chapter, the Lamellar Micromixing Model will be adapted to simulate combustion in NETmix. The results will be compared to the CFD simulations.

Chapter VI is focused on a technological perspective. A new model, NETcombustor, will be developed to represent a full NETmix network and perform combustion studies. The global scheme of hydrogen will be applied with and without the reverse rate. Premixed and non-premixed mixtures will be simulated, and the results will be compared with the CFD simulations. A study of the injection scheme will also be performed. To end the chapter, a combustion curve for the system H_2 -Air will be designed for NETmix.

In Chapter VII, heat removal from NETmix will be included in the simulations of combustion. Two approaches will be used: a micro-scale analysis, in which CFD simulations will be performed with ExtendedNUB considering convection through the walls; and a macro-scale analysis, in which the energy equation of NETcombustor will be adapted to consider the heat transfer.

To conclude, in Chapter VIII, the summary and contributions of this work are reviewed. Moreover, future studies to follow this line of research are suggested.

Chapter II – Flow Hydrodynamics

The degree and mechanisms of mixing, which in turn depend on the flow hydrodynamics, exert an influence in chemical reactions and in their outcome products. In this way, the flow is as important as the chemistry, and it is imperative to fully understand its hydrodynamics before incrementing the complexity of the system by adding the chemical reaction.

Chapter II is dedicated to hydrodynamics studies in the mesostructured reactors that will be used in this work: NETmix and Confined Impinging Jets (CIJ). The CIJ reactor will be used for the numerical validation of the Lagrangian algorithms that will be presented in Chapter III. The NETmix reactor will be used to perform all the other studies of this work.

In this chapter, the State of the Art of fluid dynamics modelling will be presented, focusing on laminar and turbulent flows, followed by a bibliography review on the NETmix and CIJ reactors. The flow hydrodynamics in the CIJ and NETmix reactors will then be characterized using CFD simulations. For the CIJ reactor, a 2D model, validated in previous work, will be used. The CFD model and boundary conditions will be explained, and the results analysed. The CIJ reactor will be used to simulate active and passive mixing. To compare the results, a spectral analysis will be made. For the NETmix reactor, a new 2D model, ExtendedNUB, will be numerically validated and used to simulate the flow dynamics. The 2D model will be described as well as the boundary conditions.

II.1 State of the Art

II.1.1 Fluid Dynamics

It is possible to distinguish two flow regimes: *steady* and *dynamic* flows. In steady flows, the pressure, density and velocity components of the particles of a certain fluid, that are subjected to a flow, do not change with time at any point of the stream. In dynamic flows, the stream properties depend on the *flow time*.

In a flow, the momentum can be transferred in two ways, the *molecular momentum transport*, which is related with the viscous forces, and the *advective momentum transport*, which is proportional to the gradients of the velocity of the flow. The relation between the inertial and viscous forces of the flow is given by the Reynolds number.

The Reynolds number, Re , is a characteristic of the flow and can be defined as

$$Re = \frac{\rho \mathcal{L} \mathcal{V}}{\mu} \quad (\text{II.1})$$

in which $\mathcal{L}$ and $\mathcal{V}$ are the characteristic length scale and velocity (depending on the geometry of the flow), respectively. ρ and μ are the density and viscosity of the fluid.

Flows are divided in two main regimes which can be assessed from the Reynolds number. In a pipe flow, for $Re < 2100$, the flow is in a *laminar regime*. For $Re > 4500$, the flow is clearly in the *turbulent regime*. Laminar regimes are characterized by an “orderly” flow composed of several adjacent layers of fluid, called *laminae*. In contrast, turbulent regimes have “disorganized” or *chaotic* flow formed of *coherent structures*, i.e., vortices. In the Laminar regime, the viscous forces are dominant. Thus, to achieve a turbulent regime, the inertial forces need to be much larger. (Bird et al. 2002). Figure II.1 shows a schematic representation of laminar and turbulent flows.

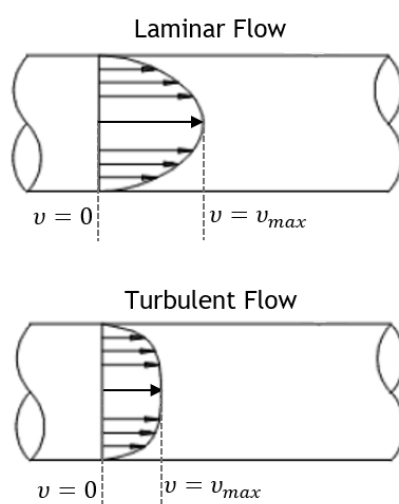


Figure II.1 Laminar vs turbulent flow (adapted from DOE Fundamentals Handbook 1992).

Under peculiar situations, that depend on the geometry of the reactor where mixing will occur and on the initial and boundary conditions of the flow, it is possible to reach chaotic behaviour in the laminar flow regime, i.e., for $Re < 2100$ the flow is not orderly. In that case, chaotic structures such as vortices will be developed. This behaviour is called *laminar chaotic regime*, which will be further analysed in this work in Chapter IV.

To assess if a flow is chaotic or not, the Lyapunov exponents can be applied. Considering two particles in a flow that are initially separated by r_0 , if the flow is chaotic the separation, r , is exponential

$$|r(t)| = e^{\lambda t} |r_0| \quad (\text{II.2})$$

in which λ is the Lyapunov exponent. If $\lambda > 0$ the system is chaotic (Eckman 1985).

II.1.1.1 Modelling of Laminar Flows

Two main equations are used to model laminar flow regimes, the *equation of continuity* for the mass balance and the *equation of motion* for the momentum balance (Bird 2002).

In 3D, the equation of continuity is written as

$$\frac{\partial \rho}{\partial t} = - \left(\frac{\partial}{\partial x} \rho v_x + \frac{\partial}{\partial y} \rho v_y + \frac{\partial}{\partial z} \rho v_z \right) \quad (\text{II.3})$$

in which ρ is the density of the fluid and v_x, v_y, v_z are the components of the velocity.

The condensed form of the equation of continuity is

$$\frac{\partial \rho}{\partial t} = -(\nabla \cdot \rho \mathbf{v}) \quad (\text{II.4})$$

in which $\mathbf{v}$ is the velocity vector.

For incompressible fluids, i.e., fluids with constant density, the continuity equation simplifies to

$$\nabla \cdot \mathbf{v} = 0 \quad (\text{II.5})$$

in which $\nabla \cdot \mathbf{v}$ is the divergence of $\mathbf{v}$.

The equations of the conservation of momentum in fluids are written as follows

$$\frac{\partial}{\partial t} \rho v_x = - \left(\frac{\partial}{\partial x} \delta_{xx} + \frac{\partial}{\partial x} \delta_{yx} + \frac{\partial}{\partial x} \delta_{zx} \right) \quad (\text{II.6a})$$

$$\frac{\partial}{\partial t} \rho v_y = - \left(\frac{\partial}{\partial x} \delta_{xy} + \frac{\partial}{\partial x} \delta_{yy} + \frac{\partial}{\partial x} \delta_{zy} \right) \quad (\text{II.6b})$$

$$\frac{\partial}{\partial t} \rho v_z = - \left(\frac{\partial}{\partial x} \delta_{xz} + \frac{\partial}{\partial x} \delta_{yz} + \frac{\partial}{\partial x} \delta_{zz} \right) \quad (\text{II.6c})$$

For fluids with constant density and viscosity, the tensor, δ , can be expressed by

$$\delta = \rho \mathbf{v} \mathbf{v} + \nabla p - \mu (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) \quad (\text{II.7})$$

in which $\nabla \mathbf{v}$ is the gradient of $\mathbf{v}$ and $(\nabla \mathbf{v})^T$ is the transpose of the velocity gradient. p is the pressure.

In the condensed form, the equation of motion becomes

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\rho \mathbf{v} \cdot \nabla \mathbf{v} - \nabla p + \mu \nabla^2 \mathbf{v} \quad (\text{II.8})$$

in which p is the pressure and $\nabla^2 \mathbf{v}$ is the Laplacian of $\mathbf{v}$.

If the previous equation is written using the substantial derivative, $\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$, the *Navier-Stokes equation* is obtained in its most condensed form (Navier 1827, Stokes 1845):

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla p + \mu \nabla^2 \mathbf{v} \quad (\text{II.9})$$

II.1.1.2 Modelling of Turbulent Flows

Turbulent flows are characterized by a random evolution of the velocity field at each position and flow time. Motion in turbulent flows occurs at a large range of scales due to the formation and “disappearing” of eddies. The larger scales have a size close to the width of the flow which is dependent of the flow boundary conditions.

The energy of larger eddies is transferred, and smaller eddies are formed. This process, known as *energy cascade*, is repeated until the effects of the kinematic viscosity become considerable and the smallest scales are reached. The energy of the largest eddies is in the order of $\mathcal{V}^2$, in which $\mathcal{V}$ is the characteristic velocity (see Section II.1.1). The rate at which that energy is transferred to the smaller eddies is the *dissipation rate*, ε , which is in the order of $\mathcal{V}^3 / \ell$, in which ℓ is the size of the eddies. The timescale of the larger eddies is given by $\tau_\ell = \ell / \mathcal{V}$ (Pope 2000). Note that, as the length scale decreases, the Reynolds number becomes smaller.

The smallest flow scale in turbulent flows is the Kolmogorov scale. The length, velocity and time scales are defined as

$$\eta = \left(\frac{\nu^3}{\varepsilon} \right)^{1/4} \quad (\text{II.10})$$

$$\mathcal{V}_\eta = (\nu \varepsilon)^{1/4} \quad (\text{II.11})$$

$$\tau_\eta = \left(\frac{\nu}{\varepsilon} \right)^{1/2} \quad (\text{II.12})$$

in which $\nu = \mu / \rho$ is the kinematic viscosity.

Several methods to model turbulent flows have already been developed such as Direct Numerical Simulation (DNS), Large Eddy Simulation (LES), Reynolds-averaged Navier-Stokes (RANS) and Probability Density Function (PDF).

The Direct Numerical Simulation (DNS) method solves the Navier-Stokes equations to compute the instantaneous velocity of the flow.

For Newtonian fluids, i.e., fluids with constant viscosity, independently of the stress to which the fluid is subjected to, the Navier-Stokes equation can be written as

$$\frac{D\mathbf{v}}{Dt} = -\frac{1}{\rho}\nabla p + \nu\nabla^2\mathbf{v} \quad (\text{II.13})$$

in which $\mathbf{v}$ is the velocity vector, p is the pressure and $\nu = \mu/\rho$ is the kinematic viscosity. μ and ρ are the viscosity and density of the fluid, respectively.

Note that Equation II.13 contains the advective term at the left and the pressure and diffusivity terms at the right.

In the DNS method, all the scales of the flow are resolved. As the turbulent flow is composed of different length-scales, which have distinct timescales, DNS is very demanding in terms of computing resources and computation time which increase as the Reynolds number gets larger (Pope 2000). The application of the DNS method is then dependent on the computational resources which determines the size of the grid that is used for the discretization of the domain. Frequently, the grids are not small enough to comprise all the flow scales. Thus, the smallest scales, in most engineering problems, are not possible to simulate with DNS.

In the Large Eddy Simulation (LES) method, the Navier-Stokes equations are only used to compute larger length-scales which are less demanding in computational terms. The smaller scales are then simulated using models. The first model was proposed by Smagorinsky (1963). In 1980, Bardina, Ferziger and Reynolds proposed the *scale-similarity model* (Berselli et al. 2006). Later, Germano et al. (1991) proposed the *dynamic model* which was extended by Lilly (1992) and Meneveau et al. (1996). More recently, new models for LES were developed by Kajishima and Nomachi (2006) and Veloudis et al. (2008).

Another approach to simulate turbulent flows is the Reynolds-Averaged Navier-Stokes (RANS) method which uses the Reynolds stresses to compute the mean velocity field.

The velocity, v , can be decomposed into its mean, $\langle v \rangle$, and fluctuation, v^* , in the form: $v^* = v - \langle v \rangle$. The Reynolds-Averaged Navier-Stokes (RANS) equation is then written as

$$\frac{\overline{D}\langle v_j \rangle}{\overline{D}t} = \nu \nabla^2 \langle v_j \rangle - \frac{\partial \langle v_j^* v_i^* \rangle}{\partial x_i} - \frac{1}{\rho} \frac{\partial \langle p \rangle}{\partial x_i} \quad (\text{II.14})$$

in which $\frac{\bar{D}}{\bar{D}t} = \frac{\partial}{\partial t} + \langle v \rangle \cdot \nabla$ is the mean substantial derivative. The covariances of the velocities, $\langle v_j^* v_i^* \rangle$, are called *Reynolds Stresses*. Half of the Reynolds stress is the *turbulent kinetic energy*, $k = \frac{1}{2} \langle v_j^* v_i^* \rangle = \frac{1}{2} \langle \mathbf{v}^* \cdot \mathbf{v}^* \rangle$.

In similarity with Equation II.13, the Reynolds equation, II.14, contains the advective term at the left-hand side and the pressure and diffusivity terms at the right-hand side.

In the Reynolds equations, the Reynolds stresses can be computed through the *turbulent-viscosity hypothesis* which was introduced by Boussinesq (1877) or directly from the Reynolds-stress transport equations.

In the turbulent-viscosity hypothesis approach, the most used model in CFD is the *k – ε model* (Jones and Launder 1972, Launder and Sharma 1974) which is based on two equations, one for the dissipation rate, ε , and another for the turbulent kinetic energy, k . Other turbulent-viscosity models are, for example, the *k – ω model* (Wilcox 1993) and the *Spalart-Allmaras model* (1994).

If the Reynolds-stress approach is considered, the transport equation for the Reynold stresses is solved to calculate the Reynolds stress and the dissipation rate, ε . The first model that implementd this method was *Rotta's model* (1951) which later led to the development of other models (Pope 2000).

Statistical Description of Turbulence

The Probability Density Function (PDF) method is an approach that is used to model turbulent flows.

Since turbulent flows have an irregular variation of the velocity flow field which can be seen as a “random process”, it is not possible to predict with certainty the behaviour of the flow. An alternative to describe turbulent flows is then the use of *probabilities*, P (between 0 and 1), which are a measure of the likeliness of an event to happen. As an example, the probability of the event B “the velocity field, v , is smaller than v_b ” is written as

$$P = P(B) = P\{v < v_b\} \quad (\text{II.15})$$

in which $v(x, t)$ is the velocity field and v_b is a value of the sample space variable, v , corresponding to the velocity v .

The probability of any event can be given by the Cumulative Distribution Function (CDF), $F(v) \equiv P\{v < v\}$. The previous example of Equation II.15 can be written as

$$P = P(B) = P\{v < v_b\} = F(v_b) \quad (\text{II.16})$$

The Probability Density Function (PDF) is given by

$$f(v) \equiv \frac{\partial F(v)}{\partial v} \quad (\text{II.17})$$

in which $f(v)$ represents the PDF of the velocity v .

Applying the $f(v)$ concept in the previous example, Equation II.16 is equal to

$$P = P(B) = P\{v < v_b\} = F(v_b) = \int_0^{v_b} f(v) dv \quad (\text{II.18})$$

The use of PDFs to model turbulent flows is much simpler than solving the RANS or Navier-Stokes equations, described in the above-mentioned methods.

The PDF transport equation can be written as

$$\frac{\partial f}{\partial t} + v_i \frac{\partial f}{\partial x_i} = \frac{1}{\rho} \frac{\partial \langle p \rangle}{\partial x_i} \frac{\partial f}{\partial v_i} - \frac{\partial}{\partial v_i} \left[f \langle v \nabla^2 v_i - \frac{1}{\rho} \frac{\partial p^*}{\partial x_i} \rangle \right] \quad (\text{II.19})$$

in which p^* is the fluctuation component of the pressure, $p^* = p - \langle p \rangle$ and $\langle p \rangle$ is the mean pressure. $\nu = \mu/\rho$ is the kinematic viscosity, in which μ and ρ are the viscosity and density of the fluid, respectively.

Note that, the previous equation has the advective term at the right-hand side and the pressure and viscosity terms at the left-hand side.

To model the viscosity and the fluctuation component of the pressure, which appear at the right side, the most used model in the Generalized Langevin Model (GLM) proposed by Pope (1983b). Other models are the Simplified Langevin Model (SLM), the isotropization-of-production model, the Haworth-Pope model and the Lagrangian IP model (LIMP) (Pope 2000).

II.1.2 Mesostructured Reactors

Mesomixers are devices in the scale of 1 to 10 mm that enable mixing scales in the order of micrometers. *Micromixers* have a scale smaller than 1 mm, which is related with better heat transfer capacity and ease of controlling mixing scales. However, especially in industry, it might not be possible to reduce the size of the reactor to achieve the microscale. In this way, mesostructured reactors are a good alternative (Ottino and Wiggins 2004). In this work, two types of meso-reactors will be used: the Confined Impinging Jets (CIJ) reactor and the NETmix reactor.

II.1.2.1 Confined Impinging Jets Reactor (CIJ)

CIJs are widely used for Reaction Injection Moulding (RIM) for polyurethane processing (Keuerleber 1971, Lee et al. 1980, Baldyga and Bourne 1983) and have been extensively studied over the last two decades (Santos et al. 2005, Erkoç et al. 2007, Li et al. 2015). CIJs consist of a cylindrical mixing chamber (generally having a diameter, $D \approx 10$ mm, and height, $H \approx 50$ mm) with two opposed injectors (diameter, $W \approx 1.5$ mm) placed at $D/2$ from the closed top of the mixing chamber. The headspace above the injectors promotes the onset of chaotic flow regimes at injection Reynolds numbers above 100 (Santos and Sultan 2013, Santos et al. 2009, Fonte et al. 2011, and Tu et al. 2015). The Reynolds number at the inlet in CIJs is defined as $Re = \rho W \overline{v_{inj}} / \mu$, where $\overline{v_{inj}}$ is the surface and time averaged velocity of the fluid at the injector, W is the diameter of the injector, ρ and μ are the density and viscosity of the fluid, respectively (Malguarnera and Suh, 1977). For injection Reynolds numbers larger than 120, CIJs present a *laminar chaotic flow regime*, characterised by extreme dynamics of mixing in which vortices being shed from the impingement of the opposed jets engulf the fluids. The locally generated vortices have a scale that is initially set around $D/2$ which engulfs into larger vortices, with scale D , that flow in tandem and with alternate spins towards the outlet of the mixing chamber (Santos et al. 2009, Gonçalves et al. 2017). Previous studies have shown that to occur mixing the impingement point of the opposed jets needs to be in the axis of the injectors (Fonte 2012, Brito et al. 2018). Figure II.2 shows the transition to the Laminar chaotic flow regime in the CIJ reactor between $Re = 104$ and 150 from tracer experiments with Planar Laser Induced Fluorescence (PLIF).

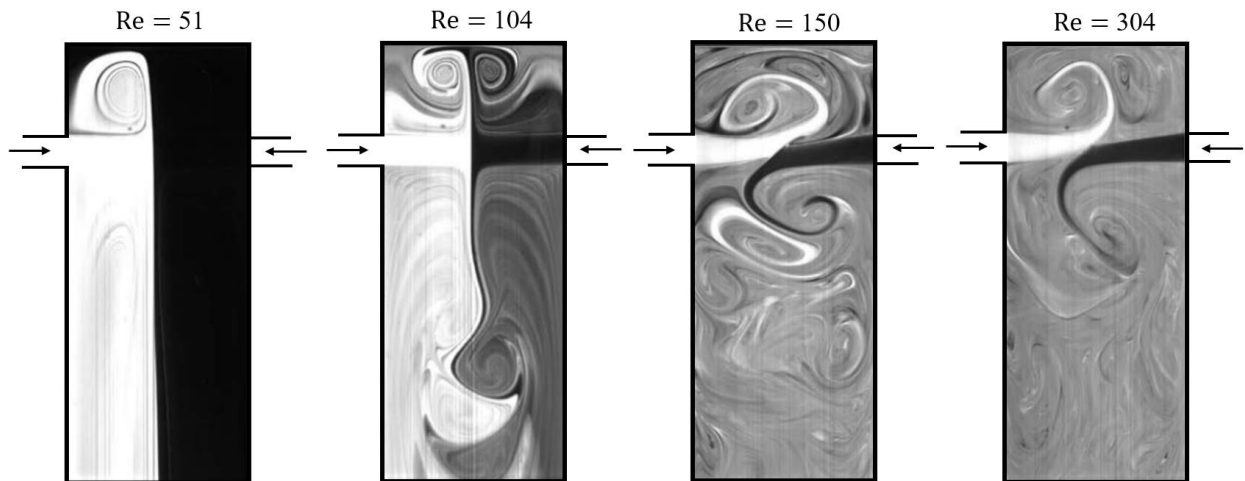


Figure II.2 PLIF tracer experiment in the CIJ reactor at different Re (adapted from Fonte 2012).

CIJs mixing dynamics in chaotic flow regimes are well described from 2D flow physics regarding flow scales, the occurrence of coherent structures and the energy transfer between scales (Kraichnan 1967, Santos et al. 2009, Santos et al. 2010, Gonçalves et al. 2017). In fact, the flow

in the CIJ reactor is mainly affected by the dynamics of the opposed jets in a plane defined by the axis of the injectors and chambers which enables to use 2D simulations to describe the 3D reactor (Matos et al. 2018, Sultan et al. 2019).

CIJs have previously been simulated using *passive* and *active* mixing (Erkoç et al. 2016, Li et al. 2013, Li et al. 2016, Kravtsova et al. 2018). Contrary to passive mixing, in active mixing the flow rate at the inlet jets is modulated, enhancing mixing. It has been shown that for lower Re number, using active mixing, it is possible to attain the same *degree* of mixing of higher Re numbers with passive mixing. Moreover, active mixing can be used to control mixing scales (Erkoç et al. 2016).

CIJ Geometry

The 2D CIJ model was numerically and experimentally validated in previous works (Santos et al. 2009, Santos et al. 2010, Gonçalves et al. 2017). The CIJ reactor is composed of two opposed inlets (inlet 1 and inlet 2) and one outlet. The width and height of the mixing chamber are $H = 5.0 \times 10^{-2}$ m and $D = 1.0 \times 10^{-2}$ m, respectively, and the injectors have a width, $W = 1.5 \times 10^{-3}$ m. The residence time is defined as $\tau = \frac{HD}{2W\overline{v_{inj}}}$, where $\overline{v_{inj}}$ is the time and spaced average inlet velocity at each injector. In Figure II.3, the point P1 is in the origin of the axis with coordinates $(x, y) = (0, 0)$, points P2 and P3 are at $(x, y) = (2.5 \times 10^{-3}$ m, 0) and $(x, y) = (2.5 \times 10^{-2}$ m, 0), respectively.

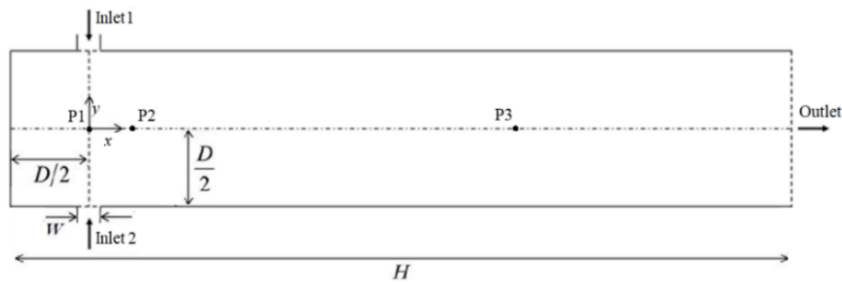


Figure II.3 Geometry of the 2D CIJ reactor (Matos et al. 2018).

II.1.2.2 NETmix Reactor

NETmix is a static mixer patented in 2005. The design of the reactor is based on a network of mixing chambers interconnected by transport channels (Lopes et al. 2005). The mixing chambers are elements with a circular footprint which can be cylinders or spheres, the channels that connect the chambers are cylindrical or prismatic. The centre of these elements lays in a 2D plane.

The first NETmix device was designed in 2005 with a network of spherical chambers connected by cylindrical channels (Laranjeira 2005). In 2008, an industrial prototype was built at Fluidinova

S.A. (fluidinova.com) for the continuous large-scale production of synthetic nano-hydroxyapatite (Lopes et al. 2006, Silva et al. 2008). CFD studies have shown that the mixing mechanisms in NETmix are well described from 2D simulations (Gomes 2011). In this way, other NETmix units were developed using cylindrical chambers and prismatic channels (Gomes 2011). Nowadays, the NETmix network is etched in plates, making it particularly suited for coupling other devices such as heating and radiation plates. The diameter of the chambers and channels was varied between different NETmix devices which enables to switch from a micro to a meso device. In this way, it is possible to have a better control of the heat and mass transfer (Costa, 2017) which has been widening the applications of this technology. Since 2016, a photocatalytic NETmix was designed (Lima et al. 2016) which is used to perform photocatalysis studies such as kinetic modelling (Marinho et al. 2017, Santos et al. 2019, Santos et al. 2021) and ozonation (Filho et al. 2019). In 2017, a NETmix device coupled to heat exchangers was developed for the continuous production of CO₂ hydrates (Costa et al. 2017, Lopes et al. 2018, Lopes et al. 2019). The NETmix reactor has also been used for microencapsulation (Moreira et al. 2020) and Pickering emulsions (Ribeiro et al. 2021). A review of the NETmix technology and its applications is made in Section VI.1.1.

The fluid enters in the NETmix network at the inlets of the bottom row and exits the reactor at the top outlets. In Figure I.1 (see Section I.1), is shown the NETmix network and its flow pattern. In the NETmix reactor, the channels conduct the fluids to the chambers where mixing occurs. The Reynolds number at the inlet channels in the NETmix reactor is defined as $Re = \frac{\rho 2d v_{inj}}{\mu}$, in which v_{inj} is the velocity of the fluid at the injector, d is the diameter of the injector, ρ and μ are the density and viscosity of the fluid, respectively. The NETmix reactor works according to the mixing principle of the CIJ reactor, described in the previous section. The impingement point of the inlet jets promotes the shedding of vortices which enhances mixing. If the collision zone of the jets of the CIJ reactor is repeated in series and parallel, a pattern close to the NETmix concept is obtained, as visible in Figure II.4. The evolution of the NETmix design is shown in Section VI.1.1. As will be shown further in this work, for both reactors, vortices are formed at the top and bottom of the impingement point. In the case of the NETmix reactor, the impingement point coincides approximately with the centre of the mixing chambers.

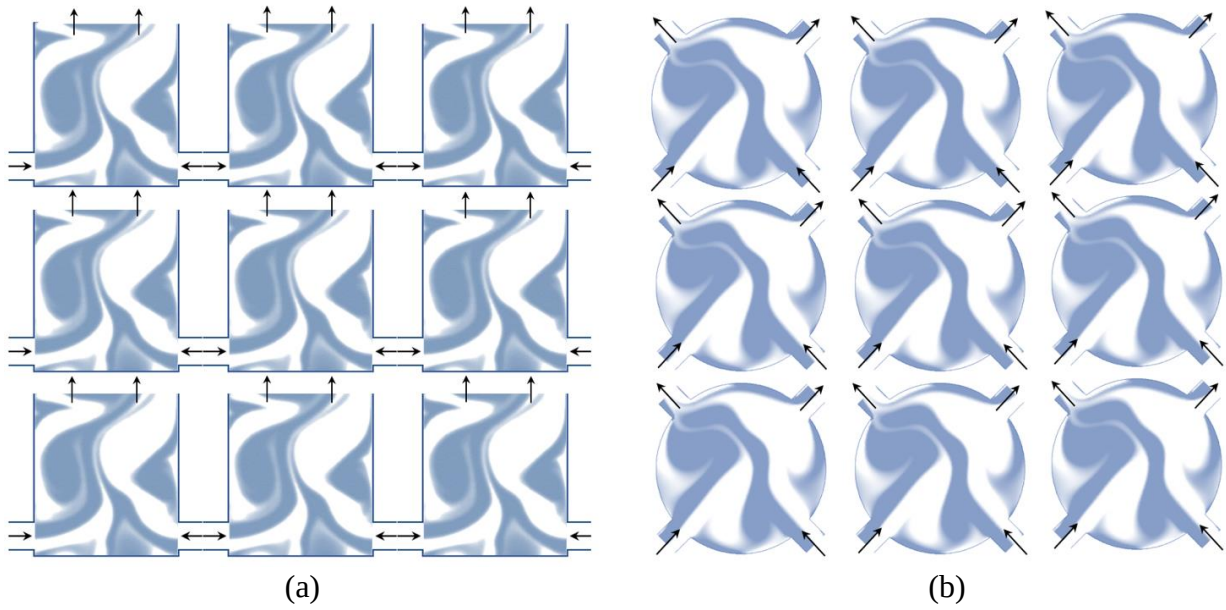


Figure II.4 (a) Portion of a CIJ reactor. (b) NETmix chambers in series and parallel.

Above the critical Reynolds number, the impinging point of the inlet jets inside the NETmix chambers promotes an oscillating behaviour characterized by vortex shedding (Laranjeira et al. 2009, Laranjeira et al. 2011). The engulfment of the vortices that are formed especially at the top and bottom of the chambers is responsible for mixing. Tracer CFD simulations performed in previous works have shown the transition between the laminar and the chaotic flow regimes. An example is shown in Figure II.5 for a NETmix chamber with the Multi-inlet NETmix 2D device dimensions (see Chapter VI). It is visible that for $Re = 200$ the oscillating behaviour is subtle, and the oscillation of the inlet jets is still not visible. At $Re = 300$, the oscillation is clearly visible as well as the vortex shedding (Gomes 2011).

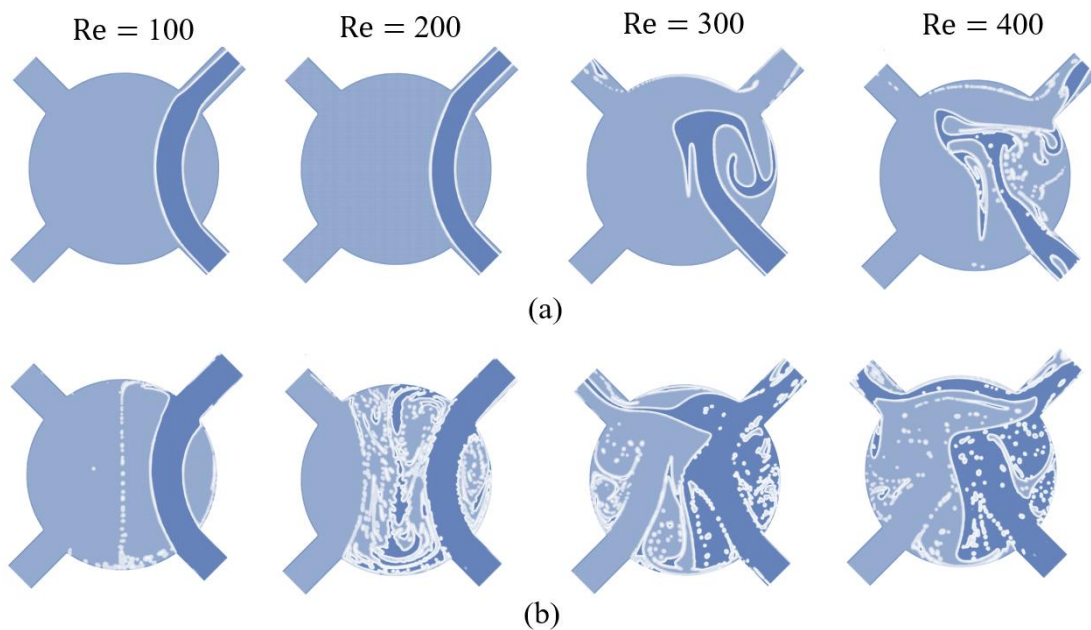


Figure II.5 Tracer CFD simulation in one NETmix chamber at: (a) t_l s and (b) $t_l + 13.2$ s flow time, for different Re numbers. Tracer fluid is in dark blue (adapted from Gomes 2011).

The influence of Re is also noticeable on the network simulation. As shown in Figure II.6, for Re below the critical value, the oscillating behaviour is not enough to mix the fluids on the NETmix columns that are at the side of the inlet chamber. For Re above the critical value, in the second row of chambers, mixing is already visible in the adjacent columns. From the fourth row of chambers, it is no longer possible to distinguish the mixing pattern of the NETmix chambers due to the occurrence of a quasi-homogenization (Laranjeira et al. 2011, Gomes 2011).

In previous works, it was shown that the *injection scheme*, i.e., the inlets of the bottom row at which the mixing fluids are injected, and the *network size*, i.e., the number of rows and columns of chambers, have an influence on the way mixing occurs through the network. Tracer experiments, simulations and test reactions have shown that at Re above the critical value, a quasi-homogenization is always verified from a certain row of chambers (Laranjeira 2005, Laranjeira et al. 2009, Laranjeira et al. 2011, Gomes 2011).

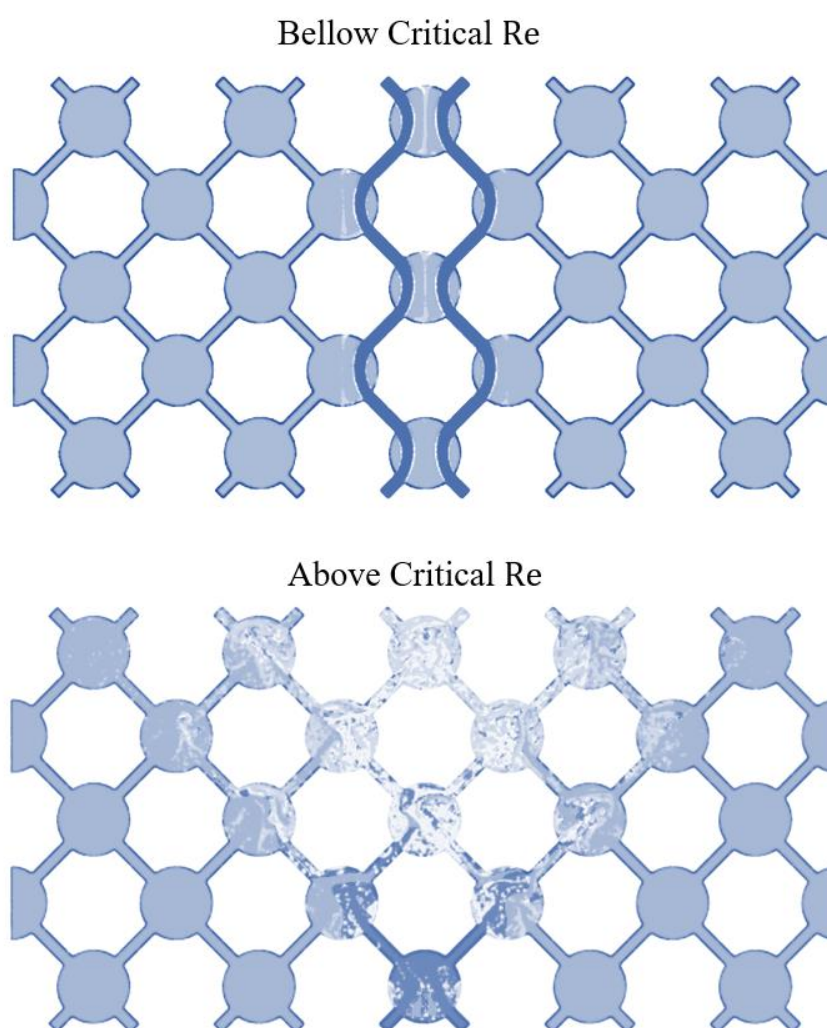


Figure II.6 Tracer CFD simulation in a NETmix network below and above the critical Re . Tracer fluid is in dark blue (adapted from Gomes 2011).

NETmix Network

The NETmix model was numerically and experimentally validated in previous works (Laranjeira et al. 2009, Laranjeira et al. 2011). The NETmix network (Figure II.7a) is composed of cylindrical chambers with diameter, D , interconnected by prismatic channels with width, d , and length, l , at an angle of 45° (Lopes et al. 2005, Laranjeira 2005, Gomes 2011). This network can be obtained by the repetition of the NETmix unit cell shown in Figure II.7b, where ω is the depth of the reactor. The NETmix network was developed with a 3D model and studies have shown that, as the mixing mechanisms are mainly 2D in the xy plane (Gomes 2011), it is possible to represent the mixing dynamics with accuracy using a 2D model.

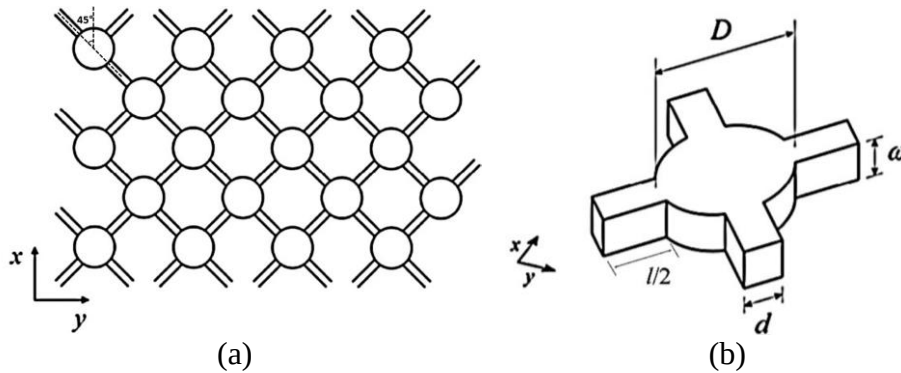


Figure II.7 Schematic representation of: (a) the NETmix network and (b) the NETmix unit cell (adapted from Fonte et al. 2013).

Previous works have shown that the geometry and the flow of NETmix obey to a repetitive pattern, as visible in Figure I.1 (Section I.1), which enables to simulate a portion of the network to study the NETmix reactor (Fonte et al. 2013, Costa et al. 2017).

In 2013, Fonte developed a 3D geometry that consisted in 3 *full chambers* interconnected to 6 *half chambers*, the NETmix Unit Block (NUB) shown in Figure II.8a. In his Master thesis, Torres (2017) studied the possibility of simulating reduced 2D geometries of NETmix. One of the models, ExtendedNUB, consisted in a repetition of 2 NUBs (Figure II.8b). The ExtendedNUB geometry has two bottom inlets and two top outlets and is composed of four *full chambers*, C2, C4, C6 and C8, (see Figure II.8b) and 5 *half chambers*. This geometry will be numerically validated further in this work.

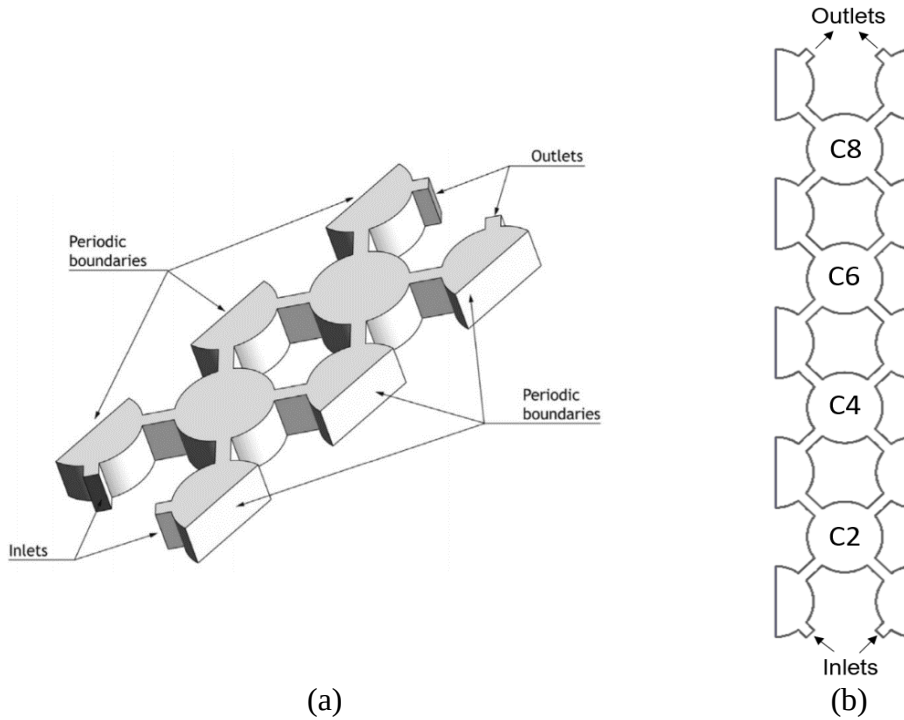


Figure II.8 Schematic representation of: (a) NUB (Fonte et al. 2013) and (b) ExtendedNUB.

II.2 Hydrodynamics Characterization in the CIJ Reactor

To characterize the hydrodynamics in the CIJ reactor, the 2D CIJ geometry, previously described in Section II.1.2.1, was used. The flow was simulated using CFD. This section starts by describing the CFD model, followed by the flow field simulation and the analysis of the results.

II.2.1 CFD Model and Boundary Conditions

The 2D CFD model of CIJ was validated in previous works (Santos et al. 2009, Santos et al. 2010, Gonçalves et al. 2017). To simulate the dynamic flow field in the CIJ reactor, the 2D domain of the geometry presented in Figure II.3 was discretized with a structured regular mesh of quadrilateral elements with edge length, $\Delta x = 5.0 \times 10^{-5}$ m. The commercial finite volume CFD software ANSYS® FLUENT™ was used to solve the mass and momentum conservation equations (Equation II.5 and II.8).

The transient calculations were performed with the First Order Implicit method. For the pressure-velocity coupling, the Coupled method was used. The spatial discretization was performed with the Least Squares Cell Based algorithm for the gradient, PRESTO! For the pressure and Second Order Upwind for the momentum. The convergence criterion for the maximum residuals of continuity and momentum is 10^{-4} and 10^{-6} , respectively. The time step, $\Delta t = 8.3 \times 10^{-6}$ s, was

chosen, according to the Courant number, $C = \frac{v_{max}\Delta t}{\Delta x} = 1$, in which $v_{max} = \frac{3}{2}v_{inj}$ and $v_{max} = 6$ m/s. Thus, $\overline{v_{inj}} = 4$ m/s. The residence time is $\tau = \frac{HD}{2W\overline{v_{inj}}} = 4.2 \times 10^{-2}$ s.

To simulate the passive mixing cases, a fully developed parabolic velocity profile was considered at the inlets. For inlet1 (see Figure II.3) the y -velocity component along the x -coordinate is given by

$$v_y(x) = \frac{3}{2}\overline{v_{inj}} \left(1 - \left(\frac{x}{W/2} \right)^2 \right) \quad (\text{II.20})$$

in which $\overline{v_{inj}}$ is the space averaged velocity, and the x -velocity component, v_x , is zero.

The velocity profile at inlet 2 is symmetrical to the profile at inlet 1: $v_y \left(x, y = \frac{D}{2} \right) = -v_y \left(x, y = -\frac{D}{2} \right)$.

To simulate active mixing, the flow rates of the jets are modulated with a sine function, which is set by defining the inlet velocity profile as

$$v_y(x, t) = (1 + A \sin(2\pi f t + \varphi)) \frac{3}{2}\overline{v_{inj}} \left(1 - \left(\frac{x}{W/2} \right)^2 \right) \quad (\text{II.21})$$

where A is the amplitude, f is the frequency, $\varphi = \pi$ is the phase displacement between the opposed jets flow rate and t is the time.

At the walls, the velocity components are set to zero. A constant and uniform pressure profile is imposed at the outlet (Matos et al. 2018).

The simulations were performed using a fluid with constant density, $\rho = 1000$ kg/m³. The viscosity, μ , was varied according to the Reynolds number, as shown in Table II.1.

Table II.1 Viscosity of the fluid as function of the Reynolds number.

Re vs μ	
Re	μ (kg/(m s))
100	6×10^{-2}
300	2×10^{-2}
600	1×10^{-2}

II.2.2 Flow Field CFD Simulation in the 2D CIJ Reactor

Using the 2D CIJ model that was previously described, the dynamic flow was simulated in the reactor for passive and active mixing.

Passive Mixing

Passive mixing was simulated for $Re = 100, 300$ and 600 . The maps of the z -component of the vorticity at 10τ are represented in Figure II.9.

If the Re number ($Re = 100$) is below the critical value (ca. 120), the vorticity map (Figure II.9a) shows a symmetric steady flow where the opposed jets impinge with each other at the mixing chamber axis and are bent towards the outlet. As the jets flow towards the outlet without engulfing the surrounding fluid, mixing is not promoted by chaotic advection. This behaviour is characteristic of steady flows. In contrast, if the inlet Re is above the critical value ($Re = 300$ and $Re = 600$), the vorticity maps (Figure II.9b and Figure II.9c) show that the opposed jets are engulfed by vortices formed immediately downstream the inlet jets of the mixing chamber. Further, fully developed vortices, extending throughout the entire mixing chamber width, are formed. This intense formation of vortices characterises a fully developed chaotic flow regime, where mixing is promoted by the street of vortices that evolves from the impingement point of the inlet jets towards the outlet (Santos et al. 2005, Santos et al. 2009 and Fonte et al. 2012). *Smaller vortices* with a vortex diameter, $D_v \approx D/2$, are formed in the region $0 < x < D/2$. *Fully developed vortices*, $D_v \approx D$, are formed from the engulfment of smaller vortices in the region $D/2 < x < 3D/2$ (Figure II.9b and Figure II.9c). Comparing Figure II.9b to Figure II.9c, it is visible that for higher Reynolds numbers the vortices are formed closer to the inlets. Nevertheless, the overall flow patterns are quite similar.

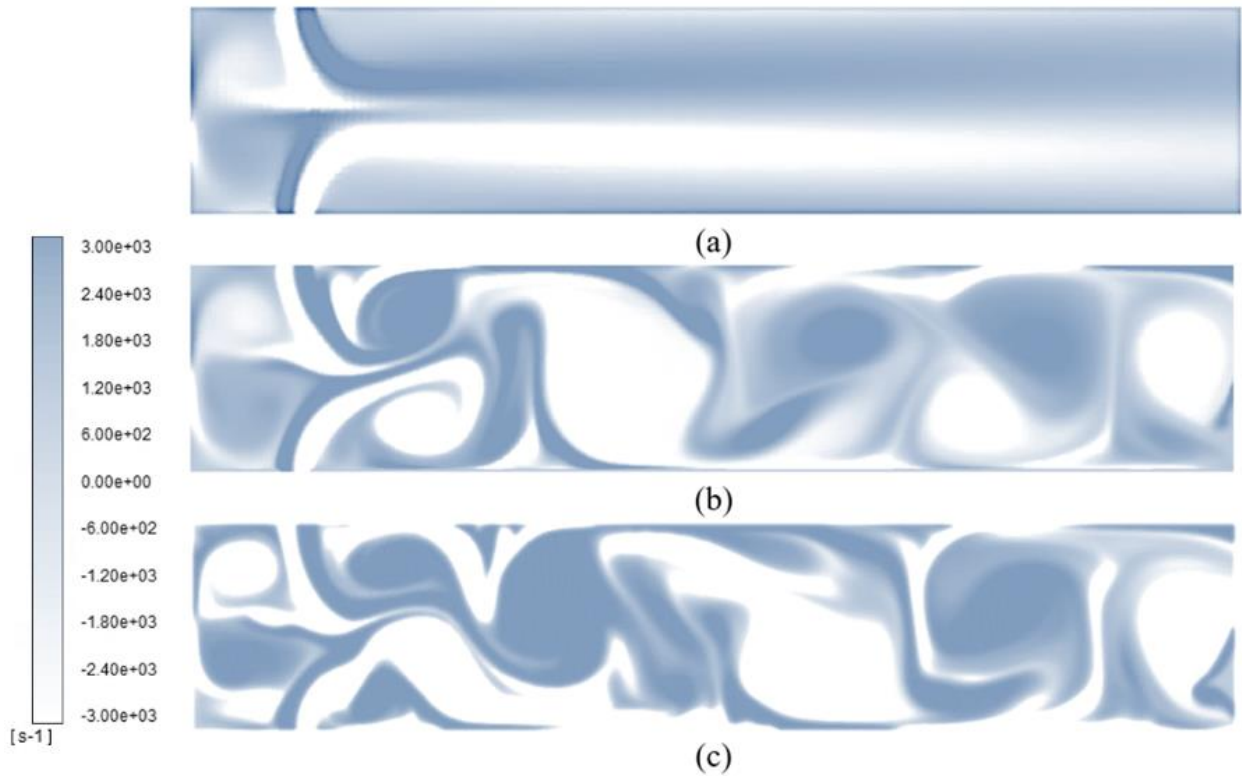


Figure II.9 Map of the z-component of the vorticity at 10τ in a 2D CIJ reactor for: (a) $Re = 100$, (b) $Re = 300$ and (c) $Re = 600$.

Active Mixing

As previously stated, in active mixing the velocity of the inlet jets is modulated, enhancing mixing. Active mixing was simulated in the 2D CIJ reactor for $Re = 300$ with a phase displacement of $\varphi = \pi$ between the modulation of the opposed jets. The study was performed with two frequencies, $f = 267 \text{ Hz}$ ($f = \phi$) and $f = 80 \text{ Hz}$ ($f = 3\phi/10$) and two amplitudes, $A = 0.5$ and $A = 1.0$. The maps of the z-component of the vorticity are shown in Figure II.10.

For active mixing, the vortex diameter, D_v , is related with the pulsation frequency through the Strouhal number, defined in CIJs as $St = fW/\overline{v_{inj}}$ (Wood et al. 1991, Santos et al. 2009, Gonçalves et al. 2017), where f is the frequency of the flow oscillations, determined from the generation rate of the vortices that are formed downstream the inlet jets. For the smaller vortices, at P1, the vortex diameter is related to the Strouhal number as $D_v^s = \sqrt{\frac{4W^2}{2\pi St}}$, which results in a diameter of ca. 3.8 mm (visible at P1 of Figure II.10a) with $St = 0.1$ ($f = 267 \text{ Hz}$). For the larger vortices, formed at downstream positions, P3, the vortex diameter is related to the Strouhal

number by $D_v^l = \sqrt{\frac{4W^2}{\pi St}}$, which gives a diameter of ca. 9.8 mm for $St = 0.03$ ($f = 80$ Hz). The relation between the Strouhal values is given by $St_{P1} = \frac{3}{10} St_{P3}$ (Santos et al. (2009)).

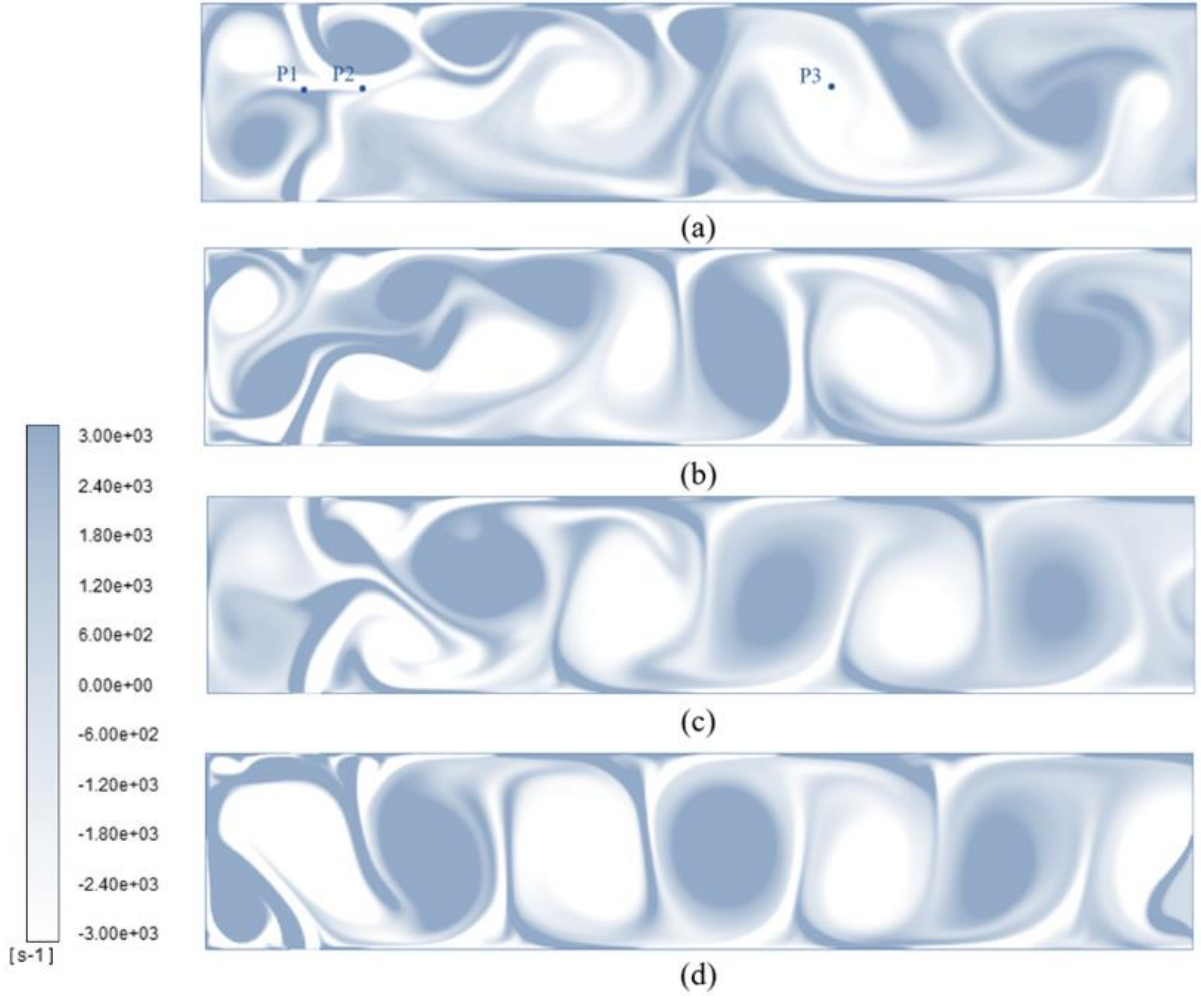


Figure II.10 Map of the z-component of the vorticity at 10τ in a 2D CIJ reactor for $Re = 300$ with: (a) $f = \phi$ and $A = 0.5$, (b) $f = \phi$ and $A = 1.0$, (c) $f = 3\phi/10$ and $A = 0.5$, and (d) $f = 3\phi/10$ and $A = 1.0$.

II.2.3 Spectral Analysis of Passive and Active Mixing

The spectral analysis was performed for the dynamic y-velocity, $v_y(t_k)$, using the Discrete Fourier Transform (DFT), according to

$$r_y(f) = \frac{1}{N_{points}} \left| \sum_{k=1}^{N_{points}-1} v_y(t_k) e^{-i2\pi f t_k} \right| \quad (II.22)$$

where f is the frequency, t_k is the time and $N_{points} = 5000$. The velocity data corresponds to 5τ , which were recorded after an initial simulation period of 5τ (the flow takes ca. 1.8τ to attain a

fully developed chaotic flow regime as shown by Santos et al. 2010). The spectral analysis was made at P1, P2 and P3 (see Figure II.3).

The spectral analysis of passive mixing is shown in Figure II.11a. It is visible that the highest energy peak for passive mixing ($Re = 300$) at P1 and P2 is approximately $Y_y(f) = 0.1$ m/s, and $Y_y(f) = 0.27$ m/s, respectively, obtained at ca. $f = 267$ Hz. At P3, the highest peak, approximately $Y_y(f) = 0.5$ m/s, is originated by the passage of fully developed vortices (see Figure II.9b and Figure II.9c) at ca. 50 Hz.

The spectral analysis of active mixing cases is shown in Figure II.11b and in Figure II.11c. These spectra show two distinct patterns. While in Figure II.11b the spectrum shows several energy peaks and a wide spread of energy throughout several frequencies, in Figure II.11c, the spectral energy is concentrated at a particular frequency, i.e., the flow is at resonance. For a modulation frequency, $f = \phi$, even with the highest modulation amplitude, $A = 1$, the system does not engage into an overall resonance. In fact, Figure II.11b shows the existence of several frequencies other than the modulation frequency, ϕ . From $x = 0$ to D , the formation of smaller vortices occurs, which engulf into fully developed vortices from $x = D$ to the outlet of the chamber (Figure II.11b). The evolution of the scale of the vortices originates spectral peaks at different frequencies: the smaller vortices originate peaks at $f = \phi$ and the fully developed vortices at $f = 3\phi/10$ (Table II.2).

For a modulation frequency $f = 3\phi/10$, the highest energy peak is always obtained at $f = 3\phi/10$ throughout the mixing chamber (Figure II.11c). In fact, $f = 3\phi/10$ is the frequency generated by the flow of pairs of vortices with diameter $D_v = D$, causing a resonance phenomenon which makes these structures dominant in the entire chamber, even at the contact point of the jets (Figure II.10d). If the amplitude of the modulation is increased, the value of the energy peak increases. With $A = 1$, the energy peak is close to $\overline{v_{inj}}$ of the modulation (Figure II.11c).

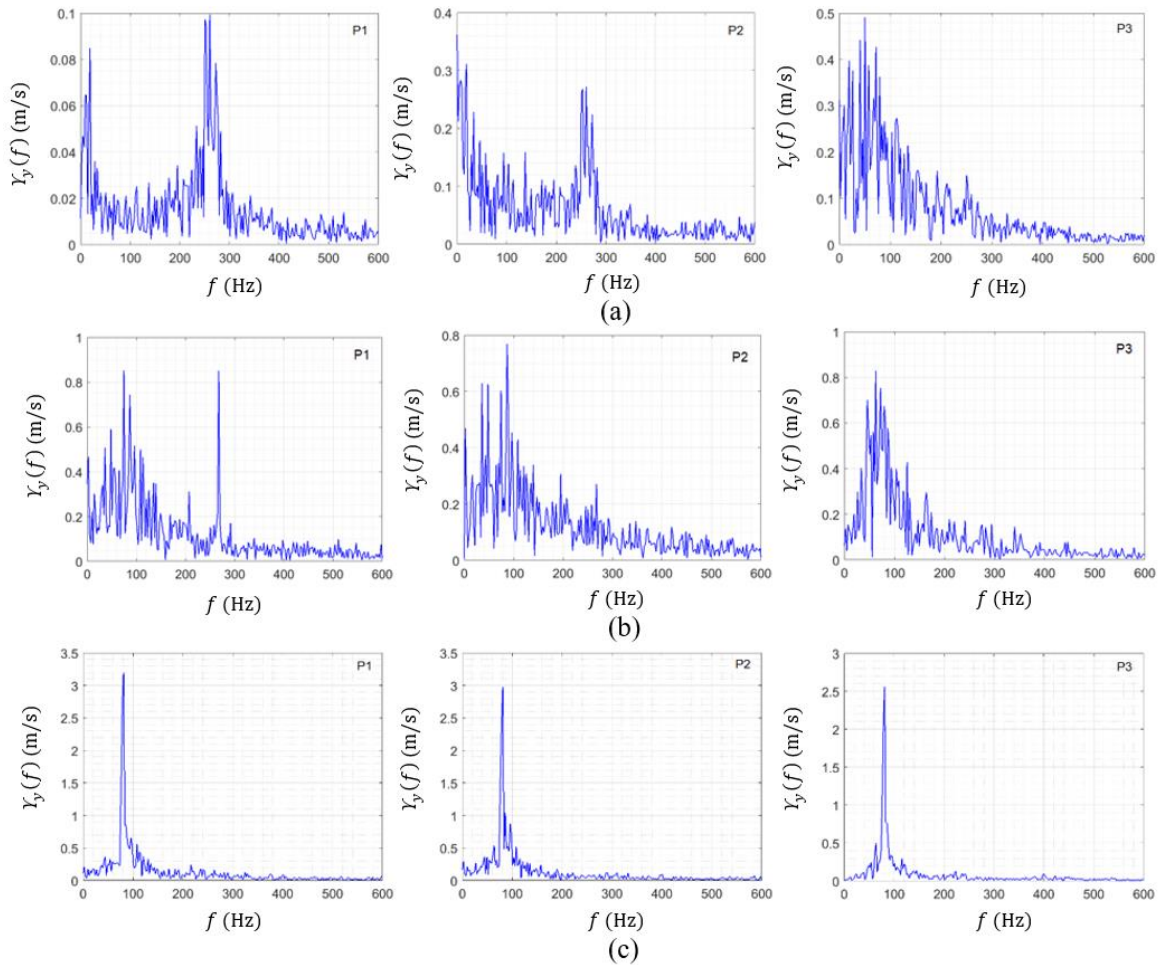


Figure II.11 Spectral analysis at P1, P2 and P3 during 10τ at $Re = 300$ for: (a) passive mixing, (b) active mixing with $f = \phi$ and $A = 1.0$, and (c) active mixing with $f = 3\phi/10$ and $A = 1.0$.

Table II.2 Spectral analysis of active mixing.

Spectral Analysis					
			$Y_y(f)$ (m/s)		
			P1	P2	P3
Passive mixing for $Re = 300$			0.1	0.27	0.5 (at $2\phi/10$)
Active mixing for $Re = 300$	$f = \phi$	$A = 0.5$	0.47 (at $3\phi/10$)	0.68	0.66 (at $3\phi/10$)
		$A = 1.0$	0.86	0.78 (at $3\phi/10$)	0.83 (at $3\phi/10$)
	$f = 3\phi/10$	$A = 0.5$	0.21	1.92	1.99
		$A = 1.0$	3.2	2.99	2.58

II.3 Hydrodynamics Characterization in the NETmix Reactor

To characterize the hydrodynamics of the flow in the NETmix reactor, a new 2D reduced geometry, ExtendedNUB, will be used. The CFD model will be presented as well as the simulation results which will enable to numerically validate the model.

II.3.1 2D ExtendedNUB Geometry

The ExtendedNUB geometry, already presented in section II.1.2.2, is a NETmix reduced-geometric model which has two bottom inlets and two top outlets. It is composed of four *full chambers* (C2, C4, C6 and C8), five *half chambers* and nine lines of outlet channels (left channels, $l1$ to $l9$ and right channels, $r1$ to $r9$), as shown in Figure II.12.

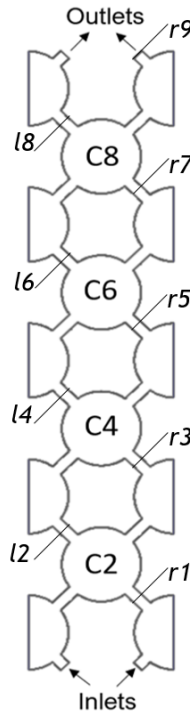


Figure II.12 Schematic representation of the 2D ExtendedNUB geometry.

II.3.2 CFD Model and Boundary Conditions

The 2D domain was discretized with a symmetric mesh in relation to the x and y axis, using ANSYS® ICEM CFD™. A quarter of chamber is shown in Figure II.13. The cell elements have an average edge length, $\Delta x = 1.7 \times 10^{-5}$ m and the complete mesh has 1.4×10^5 elements. Note that, asymmetric meshes with a similar average edge length were validated in previous works to simulate NETmix (Fonte et al. 2013, Costa et al. 2017).

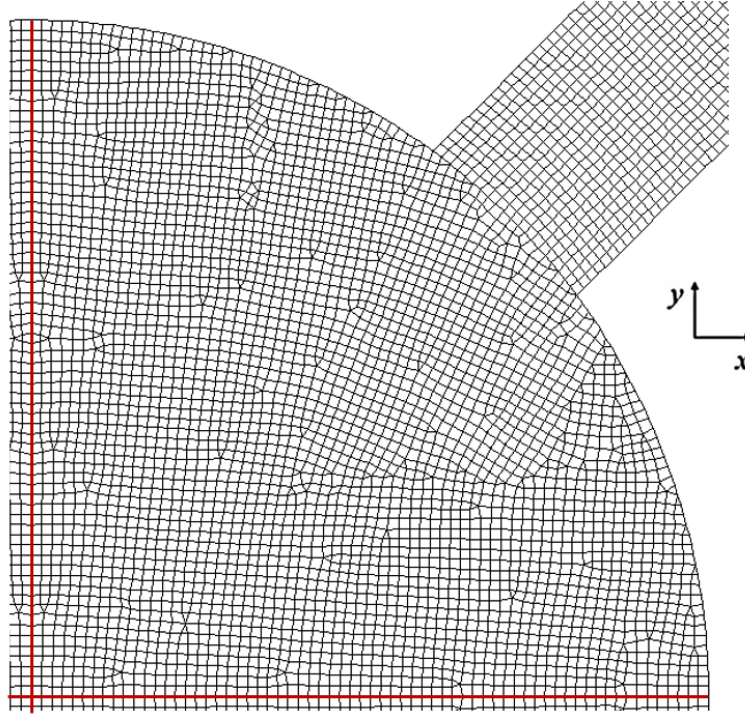


Figure II.13 Meshing in a quart of one NETmix chamber.

The commercial finite volume CFD software ANSYS® FLUENT™ was used to solve the mass and momentum conservation equations for the ExtendedNUB model, respectively defined as

$$\nabla \cdot \mathbf{v} = 0 \quad (\text{II.23a})$$

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + \mu \nabla^2 \mathbf{v} \quad (\text{II.23b})$$

where $\mathbf{v}$ is the velocity vector, p is the pressure, ρ and μ are the density and viscosity of the fluid, respectively. The transient calculations were performed with the First Order Implicit method. For the pressure-velocity coupling, the SIMPLEC method was used. The spatial discretization was performed with the Least Squares Cell Based algorithm for the gradient, PRESTO! For the pressure and Third-Order MUSCL for the momentum. The convergence criterion for the maximum residuals of continuity and momentum is 10^{-5} .

At the inlets, a constant velocity is imposed, v_{inj} , which is obtained from the Reynolds number, according to

$$v_{inj} = \frac{\mu Re}{\rho D_h} \quad (\text{II.24})$$

where $D_h = 2d$ is the hydraulic diameter for the 2D geometry (considering an infinite depth of the equivalent 3D geometry, $\omega \rightarrow \infty$), $\rho = 998.2 \text{ kg/m}^3$ and $\mu = 1.0 \text{ mPa s}$. At the outlets, a constant and uniform pressure profile is used.

It is possible to use reduced geometries with one column to represent the NETmix network if periodic boundaries are imposed at the half chambers (see Figure II.8 and Figure II.12). A periodic boundary condition is then set at each pair of half lateral chambers. The x and y -velocity components are set to zero at the walls.

To perform the transient CFD simulations, the initial solution was obtained by setting all variables to zero.

II.3.3 2D ExtendedNUB Model Numerical Validation

In Computational Fluid Dynamics (CFD), the simulation of the NETmix mixing dynamics in each chamber is subject to the boundary conditions that are imposed to the model. In this way, the reduced geometry needs to ensure that the mixing characteristics are not significantly affected by the model conditions. The *Turbulence intensity* is related with the intensity of the fluctuation of the velocity which is associated to the enhance of mixing that occurs in laminar chaotic or turbulent flows (Pope 2000, Matos et al. 2021), such as the NETmix flow. Turbulence intensity studies will then be used for the numerical validation the ExtendedNUB model.

For the numerical validation of the 2D ExtendedNUB model, the dynamic flow field was simulated for a geometry with a chamber diameter, $D = 6.65 \times 10^{-3}$ m, channel length, $l = 2.0 \times 10^{-3}$ m and channel width, $d = 1.0 \times 10^{-3}$ m. Several Reynolds numbers were set between 100 to 340 from the variation of the velocity of the inlet. The time step was calculated to maintain the Courant number, $C = \frac{v_{inj} \Delta t}{\Delta x} = 1$. The inlet velocity, v_{inj} and the time step size, Δt , for each Re are shown in Table II.3.

Table II.3 Inlet parameters as function of Re.

Inlet Parameters		
Re	v_{inj} (m/s)	Δt (s)
140	7.02×10^{-2}	2.44×10^{-4}
180	9.03×10^{-2}	1.90×10^{-4}
220	1.10×10^{-1}	1.55×10^{-4}
260	1.31×10^{-2}	1.31×10^{-4}
300	1.51×10^{-2}	1.14×10^{-4}

The residence time in one NETmix chamber is given by $\tau_c = \frac{\pi D^2}{8v_{inj}d} = 0.12$ s, for the above-mentioned dimensions. The residence time of the entire ExtendedNUB is $\tau = 1.1$ s.

In CFD simulations, the oscillating behaviour, previously referred in Section I.1 (Figure I.1), takes approximately 8τ (10 s flow time) to be reached as will be shown in Section IV.3.2. To perform the turbulence intensity analysis, the simulation was run during 16τ (17 s flow time).

The contour plot of the z-component of the vorticity for the 2D ExtendedNUB simulation with $Re = 300$ is shown in Figure II.14a. The vorticity map shows the chaotic flow regime, characterized by an oscillating behaviour inside the NETmix chambers, along with the vortex formation on the top, bottom and sides of each chamber. The overall mixing pattern is similar to the CFD tracer flow shown in Figure I.1. In contrast, if the Reynolds number, $Re = 100$, is below the critical Reynolds (ca. 120 for this geometry), the flow is steady. The oscillating behaviour inside the chambers is not visible since no vortices are formed, as shown in Figure II.14b. For a Re number below the critical value, the z-component of the vorticity decreases one order of magnitude.

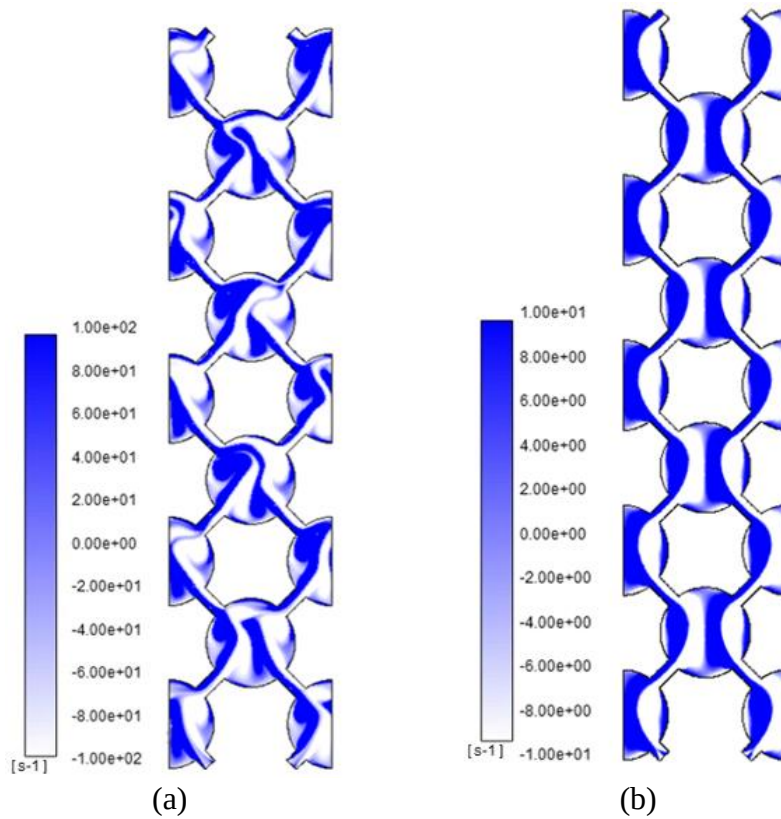


Figure II.14 Map of the z-component of the vorticity in 2D ExtendedNUB at 16τ for: (a) $Re = 300$ and (b) $Re = 100$.

When boundary conditions are imposed to a reduced model, it is necessary to ensure that mixing inside the chambers, that will be used to perform further analysis, are not affected. As described in the previous section, at the inlet, the velocity is constant. At the outlet, the constant and uniform pressure imposes that the flow lines are normal to the surface, which causes damping of the flow. Turbulence intensity, I_{v_x} , studies were performed in the centre of the full chambers C2, C4, C6 and C8, in the direction of the oscillations, to understand how they are affected by the boundary conditions.

The turbulence intensity is defined by

$$I_{v_x} = \frac{1}{v_{inj}} \sqrt{\frac{\sum_{i=1}^n t_i (v_{x_i} - \bar{v}_x)^2}{\sum_{i=1}^n t_i}} \quad (\text{II.25})$$

where v_{inj} is velocity at the inlet, v_{x_i} is the x -component of the velocity at several flow times, $\bar{v}_x$ is the average of v_{x_i} and t_i is the flow time.

Figure II.15 shows that for all Reynold numbers, the turbulent intensity is higher than zero. Thus, the Reynolds is above the critical value and the oscillating behaviour occurs inside the chambers, as visible in Figure II.14a. As the Re, 140 to 260, becomes apart from the critical value (ca. 120), the turbulence intensity increases, as expected. In fact, at higher Reynolds, the vortices are more developed, as visible in Figure II.16 which shows the maps of the velocity for $\text{Re} = 140$ and $\text{Re} = 260$. At $\text{Re} = 140$, the oscillations are similar for all the chambers (Figure II.16a). Thus, the intensity of turbulence does not differ from C2 to C8, as shown in Figure II.15. At $\text{Re} = 260$, Figure II.16b shows that in the top chambers, C6 and C8, the formation of vortices is enhanced. The intensity of turbulence is then higher, as visible in Figure II.15.

For $\text{Re} = 300$, the oscillating behaviour of ExtendedNUB is fully developed. In Figure II.15, is it visible that the turbulence intensity starts with a low value in the first full chamber, C2, since the oscillations are still being developed due to the proximity to the inlets. In chamber C4, the turbulence intensity increases, and attains its maximum in chamber C6. In chamber C8, the turbulence intensity decreases due to the effect of the outlet boundary condition which dampens the oscillations. For Re between 140 and 300, the turbulence intensity graphic shows that $\text{Re} = 300$ is the case with the lowest effect of the outlet boundary condition since the turbulence intensity of chamber C6 is higher than in C8. The numerical validation of the ExtendedNUB model will be verified in Section IV.3.2.

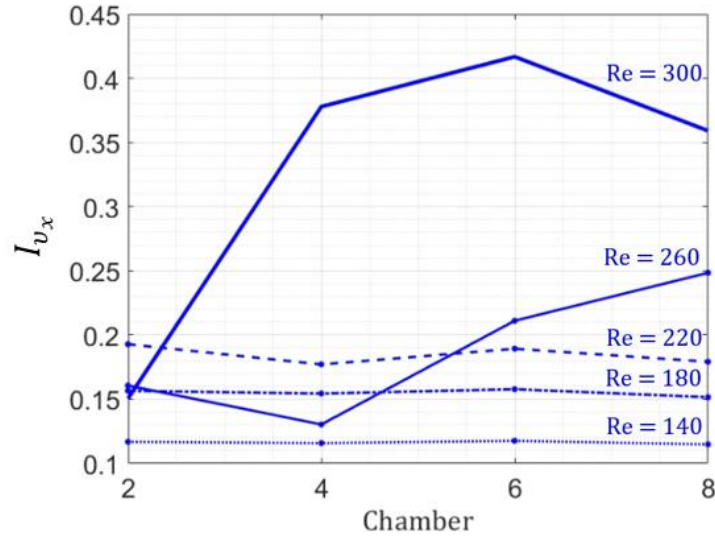


Figure II.15 Turbulence intensity in the centre of the ExtendedNUB chambers C2, C4, C6 and C8 for $D/d = 6.65$, at $Re = 140, 180, 220, 260$ and 300 .

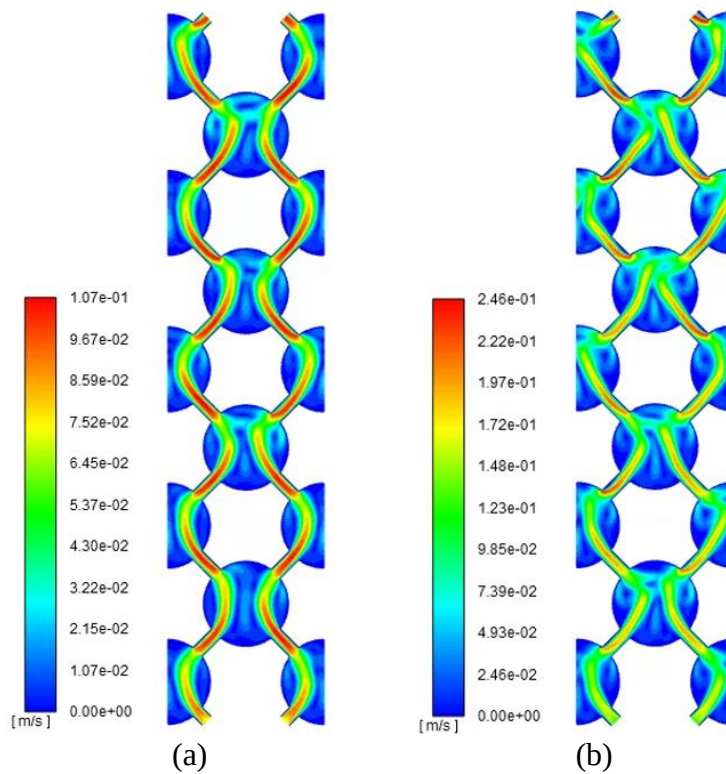


Figure II.16 Velocity maps for $D/d = 6.65$, at: (a) $Re = 140$ and (b) $Re = 260$.

A detailed analysis of the hydrodynamics in each chamber and channel is performed further in this work in Section IV.3.3.4 and Section V.2. The analysis of an enlarged reduced model of NETmix is done in Appendix B.

II.4 Computational Aspects

The mesh grid of CIJ was built using ANSYS® Workbench V19.2. The meshing process was performed in a x64-based processor Intel® Core™ i7-2600 with 4 cores at 3.40 GHz and 8 GB of RAM. The mesh grid of ExtendedNUB was built using ANSYS® ICEM™ V19.2. The meshing process was performed in a x64-based processor Intel® Xeon® X5687 with 8 cores at 3.60 GHz and 24 GB of RAM.

The CFD simulations of CIJ and ExtendedNUB were performed using the software ANSYS® FLUENT™ V19.2. The simulations were run in 2 nodes of a computational cluster (FEUP) Intel® Xeon® with 16 cores at 2.1 GHz and 64 GB of RAM. A 2D CIJ simulation takes ca. 5 days to run 10τ , 0.42 s flow time (5.1×10^4 time steps). A 2D ExtendedNUB simulation takes ca. 3 days to run 16τ , 17 s flow time (1.5×10^5 time steps).

For the CIJ simulation, a User Defined Function (UDF) was used for the inlet velocity profile. The programming code is shown in Appendix D.1.

The data was saved from ANSYS® FLUENT™ in files with ASCII format. The data processing was made in MATLAB® R2018a. The conversion of the data in ASCII format to files .mat and their processing are shown in Appendix D.2.

II.5 Conclusions

2D CFD simulations of the CIJ reactor were performed for passive and active mixing. The analysis of the vorticity maps of passive mixing has shown the difference between using an inlet Re below the critical value which leads to a steady flow; and an inlet Re above the critical value which onsets the formation of vortices, characteristic of chaotic flows. From the spectral analysis, it was shown that the modulation of the velocity at the inlets enhances mixing. In fact, the number of interferent frequencies decreases for a lower modulation frequency with a higher amplitude. The spectrum presents discrete frequencies with a larger principal frequency.

A 2D reduced model to represent the NETmix reactor was numerically validated, the ExtendedNUB model. For this geometry, a new symmetrical mesh was designed. The vorticity map showed a mixing pattern in ExtendedNUB similar to the mixing pattern of NETmix, which is characterized by a chaotic flow with vortex formation at the top, bottom and sides of the mixing chambers. The turbulence intensity study has shown that the turbulence intensity is higher in chamber C6 at $Re = 300$. In this way, this chamber is not affected by the boundary conditions of the model.

Chapter III – Quantification of Mixing Scales

The behaviour of a chemical reaction depends on the mixing of the reactants. The better mixing is characterized, the easiest is to control the chemical reaction, which is the purpose of this work.

In the previous chapter, the flow hydrodynamics was characterized in the CIJ and NETmix reactors. From the CFD results, it is possible to understand and visualize the overall mechanisms and structures that are responsible for mixing. However, the smaller scales that have a major influence in mixing, which in turn will determine the outcome of the reaction, are not well represented. In this way, this chapter is dedicated to the quantification of mixing scales.

In the State of the Art of Chapter III, mixing concepts will be reviewed as well as several Lagrangian techniques that have already been developed to characterize mixing scales. After that, a new Lagrangian algorithm, Lagrangian Mixing Simulation (LMS), will be developed and numerically validated, using the 2D CIJ model. LMS will be used to characterize passive mixing in the CIJ reactor, through the calculation of the interfacial area generation and striation thickness. For the computation of the striation thickness, a new methodology will be developed. To study active mixing in the CIJ reactor, a modified version of LMS will be presented, Diffusive Lagrangian Mixing Simulation (DLMS). The LMS and DLMS results will be compared with the flow dynamics of the CFD simulations of Chapter II.

LMS will be used further in this work, in Chapter IV, to characterize micromixing in NETmix. Moreover, the interfacial area generation and striation thickness will be calculated in the NETmix chambers. In Chapter V, DLMS will be applied to quantify the mixing scales in combustion and LMS will be used to adapt the Lamellar Micromixing Model to simulate combustion in the NETmix chambers.

III.1 State of the Art

Micromixing represents the mechanisms through which mixing at a microscopic scale occurs, being promoted by the smaller scale eddies. *Macromixing* shows the overall patterns of the distribution of fluids from larger flow scales.

Mixing in reactors relies on advective mechanisms such as stretching and folding of the fluids/gases being mixed. When the material is stretched and folded, the formation of *striae* or *laminae* occurs, increasing the interfacial area between the fluids being mixed (Ottino 1980,

Ottino 1990). The growth of the interfacial area is associated to a decrease of the *Striation thickness* represented in Figure III.1.

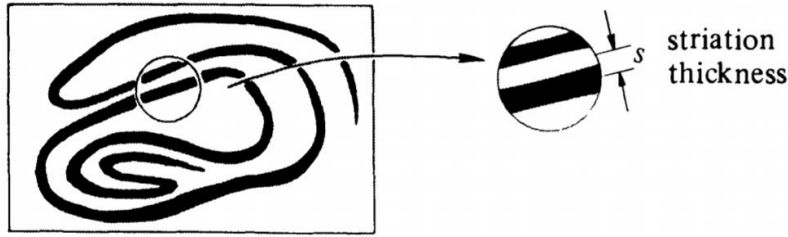


Figure III.1 Striation thickness (adapted from Ottino 1989).

The striation thickness is a quarter of the *Scale of segregation*, a concept introduced by Danckwerts (1952).

The scale of segregation, S_s represents the degree of homogeneity of the mixture and is defined as

$$S_s = \int_0^\infty R(r) dr \quad (\text{III.1})$$

in which $R(r)$ is the mean correlation coefficient between two points of the mixture distanced by r .

Another quantity that is frequently used to characterize the degree of mixing is the *Intensity of Segregation* which measures the deviation from the mean concentration of the species A and B in the mixture (Santos et al. 2012). The intensity of segregation is defined as

$$I_s = \frac{\sigma^2 C_A}{\overline{C_A} \overline{C_B}} \quad (\text{III.2})$$

in which $\sigma^2_{C_A}$ is the variance of the concentration, C , of species A. $\overline{C_A}$ and $\overline{C_B}$ are the mean concentrations of A and B, respectively.

A review of the intensity and scale of segregation concepts, including several approaches of application was presented by Kukukova et al. (2009). The intensity of segregation has already been used to study mixing in Reaction Injection Moulding (RIM) machines (Santos et al. 2005) and in T-jets (Sultan et al. 2012). Alberini et al. (2014) used the intensity and scale of segregation to analyse mixing in KM static mixers.

III.1.1 Lagrangian Methods to Quantify Mixing Scales

In chaotic laminar flows, the scale of segregation rapidly decreases to values lower than the computational grid used in *Eulerian methods*, i.e., methods where the fluid is considered as a

whole, preventing the quantification of the smaller mixing scales. In this way, *Lagrangian methods*, i.e., methods that consider discrete elements that go with the fluid (markers), are of major importance to study chaotic flows.

In Lagrangian methods, the tracking of the flow is based on the motion equation

$$\frac{d\mathbf{x}}{dt} = \mathbf{v}(\mathbf{x}, t) \quad (\text{III.3})$$

in which $\mathbf{x}$ is the vector with the coordinates of the markers, $\mathbf{v}$ is the velocity vector and t is the time.

Several Lagrangian methods have been previously used in order to characterize mixing. Hyman (1984) described Lagrangian approaches that could be implemented for the simulation of mixing in a flow field in order to overcome the limitations of Eulerian methods on the spatial resolution of mixing scales. In those approaches, the simulation of mixing is decoupled from the flow simulation and focused on the contact region of the fluids being mixed. These approaches are then called *interface tracking methods*, which can be divided in three categories: moving mesh methods, surface tracking methods and volume tracking methods. Although these techniques have been proposed since the 80s for fully resolved simulation of mixing (Hyman 1984, Franjione and Ottino 1987), there is only a limited number of published works.

Meshing methods were mainly implemented by the group at Eindhoven University of Technology (Anderson and Meijer 2000, Galaktionov et al. 2002, Singh et al. 2009). The mapping method, presented by Anderson and Meijer (2000), uses a deformable grid to track the flow front. A cell of the grid is filled with markers which are tracked from the starting cell, Ω_j , to the recipient cell Ω_i , as shown in Figure III.2.

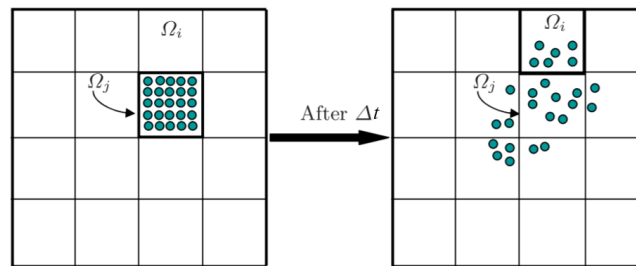


Figure III.2 Tracking of markers from Ω_j to Ω_i for Δt flow time (adapted from Anderson and Meijer 2000).

This method has been used to study cavity flows, the SMX mixer (Anderson and Meijer 2000, Singh et al. 2009) and sine flows (Schlick et al. 2013). Later, the extended mapping method was developed, enabling the measurement of the interfacial area through the area tensor (Galaktionov et al. 2002).

Villermaux and Meunier (2010) developed the Diffusive strip method, a *surface tracking method*, which uses passive scalar markers to simulate the advection of a strip in a flow. As shown in Figure III.3, the markers, x , are initially spaced of Δx_i^0 and the strip has a thickness of S_0 . In the absence of diffusion, as the flow time increases, the strip is stretched, i.e., the markers become apart from each other, and gets thinner, i.e., the striation thickness decreases. This method has been used to reconstruct the scalar field of a passive tracer with diffusion and to study flows in a point vortex and sine flows.

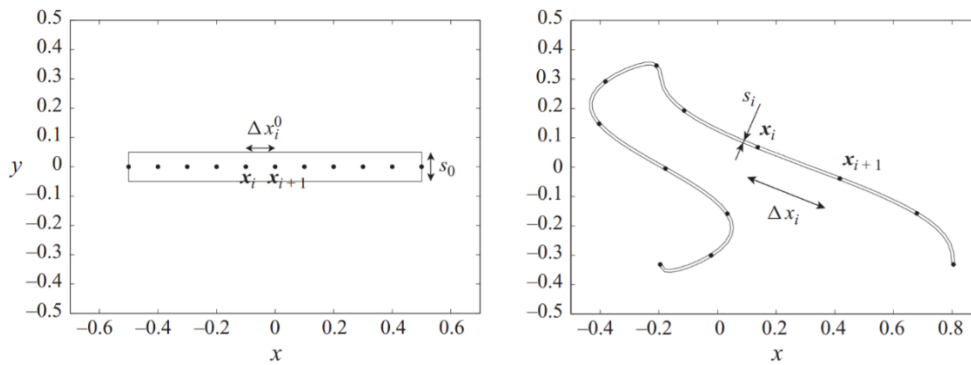


Figure III.3 Evolution of a strip (adapted form Meunier and Villermaux 2010).

III.2 Lagrangian Mixing Simulation (LMS)

During the mixing process, the interfacial area between the fluids being mixed increases and the striation thickness decreases. Ottino (1989) pointed out that the best mixing conditions correspond to the situation where chaotic flows originate exponential stretching, and the mixing of two fluids can be quantified by the stretching of a line that defines the interfacial area. However, the smaller scales, associated with the reduction of the laminae dimensions as the exponential area grows, demand computational resources which were not available at that time. Ottino (1989) reported that in the mixing simulations “the manifolds will not appear as continuous lines which they are, but as a series of disconnected dots”. Moreover, “computations based on the discretization of the velocity field provide only a crude picture of the flow”, as visible in Figure III.4 (Ottino 1995). In Figure III.5 is shown the application of the motion equation, through Taylor series, to track the flow of a bubble under a time-periodic perturbation (Ottino 1990).

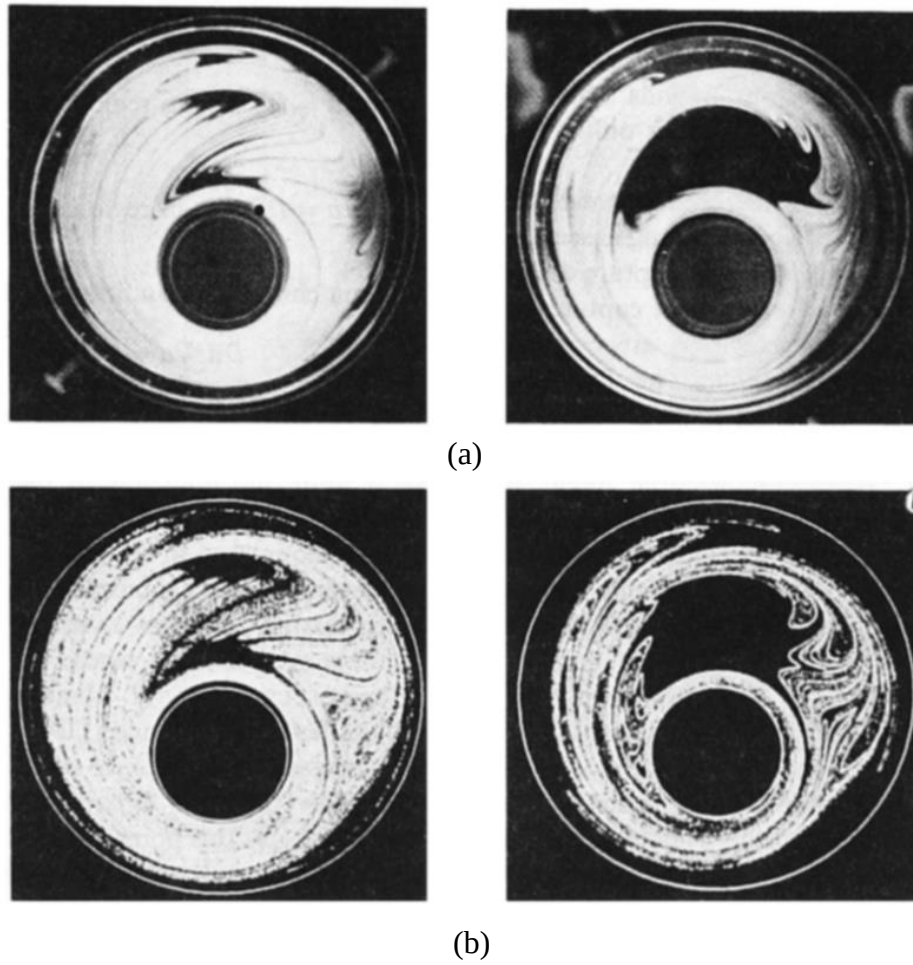


Figure III.4 Comparison between: (a) experiments and (b) flow simulation (from Ottino 1995).

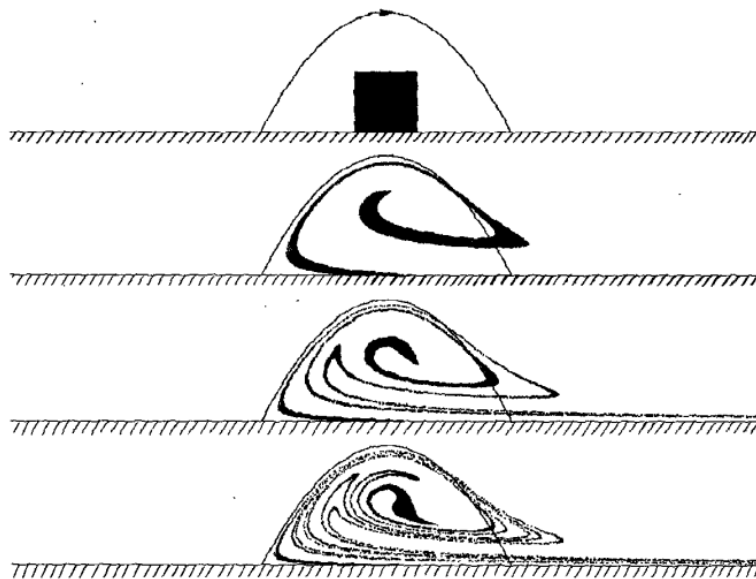


Figure III.5 Tracking of a bubble under a time-periodic perturbation (from Ottino 1990).

LMS is a numerical algorithm developed to characterize mixing through the measurement of the interface between the mixing fluids. Differently from the Lagrangian methods that were described previously, LMS can be applied to continuous aperiodic flows, issuing from more than one inlet.

In LMS, the filling front of fluid is tracked by particles. The particles are first positioned at the inlet of the reactor over the Eulerian velocity field obtained from the CFD simulation. The position of the particles evolves according to the 2D transient velocity data for each time step, forming an interface that grows along with the flow time. The interface of particles can be used to perform the computation of mixing properties such as the interfacial area generation and striation thickness, enabling to quantify mixing.

The position matrix of the particles at each time step, $\mathbf{X}_{i,j}$, is given by

$$\mathbf{X}_{i,j} = \mathbf{X}_{i-1,j} + \mathbf{v}_{i-1,j} \Delta t_{LMS} \quad (\text{III.4})$$

in which Δt_{LMS} is the time step of LMS and $\mathbf{v}$ is a matrix with the velocities of the particles. i represents the time and j the particle.

As the particles are advected by the chaotic flow they grow apart from each other. In order to prevent this distancing, which would compromise the accurate tracking of the flow, a new particle is inserted when the distance between two consecutive particles becomes larger than r , i.e.,

$$|\mathbf{X}_{i,j} - \mathbf{X}_{i,j+1}| > r \quad (\text{III.5})$$

where r is a parameter of the LMS method (Matos et al. 2018). The value of r will be discussed further in this work.

LMS Implementation

To exemplify the implementation of the LMS method, the 2D CIJ case at $Re = 600$ with $\Delta t_{LMS} = 8.3 \times 10^{-5}$ s and $r = 1.0 \times 10^{-4}$ m was used. Note that, the LMS time step is tenfold the time step of the CFD simulation, $\Delta t_{LMS} = 10 \Delta t$, since the CFD velocity fields, over which the particles are tracked, were recorded at each $10 \Delta t$.

The particles are initially positioned over the velocity field at 10τ which was recorded from the CFD simulation. The initial particles, $np = 18$, were equally distributed at the top inlet (Inlet 1 of Figure II.3), completely comprising the length of the inlet from $(x, y) = (-7.5 \times 10^{-4} \text{ m}, 5.0 \times 10^{-3} \text{ m})$ to $(x, y) = (7.5 \times 10^{-4} \text{ m}, 5.0 \times 10^{-3} \text{ m})$, which are the coordinates of the first and last particles, respectively (see Figure III.6). The simulation was performed during 0.28τ (0.012 s flow time),

at which the particles had already started to exit the chamber, i.e., the tip of the interface formed by the particles attains the outlet of the chamber at 0.045 m (Figure III.7).

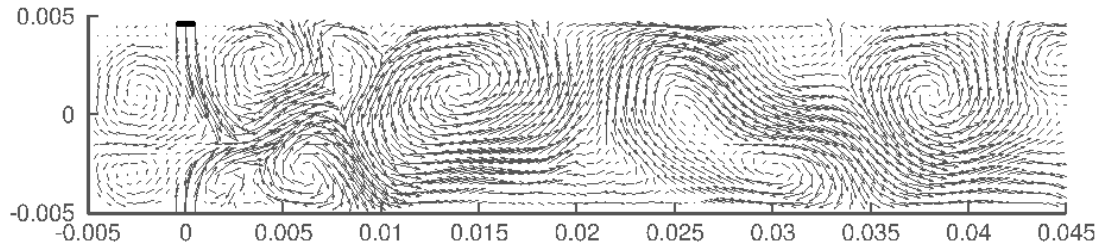


Figure III.6 Particles positioned at Inlet 1 over the 2D CIJ flow field for $Re = 600$ at 10τ .

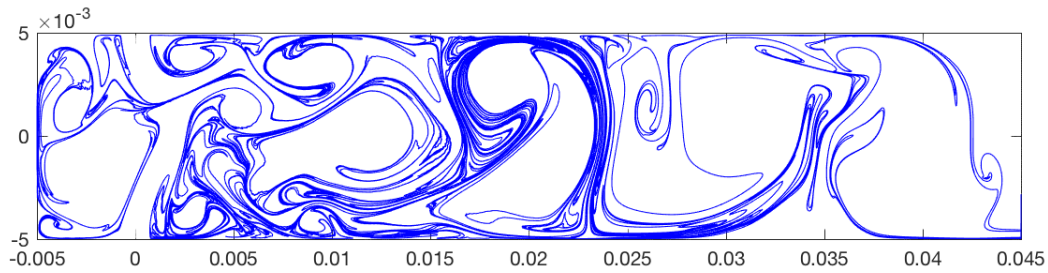


Figure III.7 Particle tracking in the 2D CIJ reactor for $Re = 600$ at 10.28τ .

The complete LMS tracking is shown in the video `LMS_re_600.mp4` of the folder *Mixing_and_Controlled_Combustion_in_NETmix_videos*.

Parameter r Analysis

The maximum separation between consecutive particles, r , was analysed to assess its influence on the simulation results. The initial number of particles, np , is a function of r . An example of LMS for different values of r is shown in Figure III.8, using the 2D CIJ case for $Re = 600$. Four r values were tested: $5.0 \times 10^{-5}\text{ m}$, $1.0 \times 10^{-4}\text{ m}$, $2.0 \times 10^{-4}\text{ m}$ and $5.0 \times 10^{-3}\text{ m}$ which correspond to np equal to 9, 18, 25 and 36, respectively. Δt was equal to $8.3 \times 10^{-5}\text{ s}$.

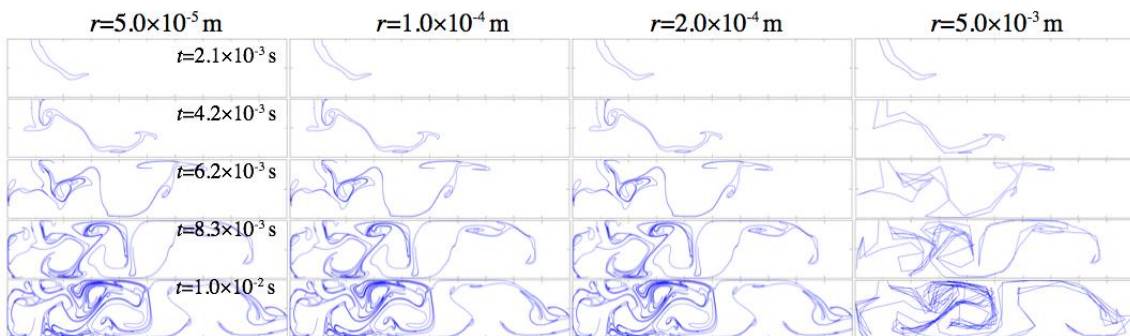


Figure III.8 LMS in 2D CIJ for $Re = 600$ with several r values at different flow time.

As shown in Figure III.8, for $r < 2.0 \times 10^{-4}\text{ m}$ the particles provide a representation of the mixing dynamics that is independent of r . Since there is no difference in the flow features between lower

values, $r = 5.0 \times 10^{-5}$ m and $r = 2.0 \times 10^{-4}$ m, the model is numerically validated. For larger values of $r > 2.0 \times 10^{-4}$ m, the tracking of the fluid is not accurate, yielding a filling front with sharp edges. In this way, to perform the simulations of this work, $r = 1.0 \times 10^{-4}$ m and $np = 18$.

III.2.1 LMS Algorithm

The LMS algorithm is summarized as follows:

1. Specify np , Δt , r and t_{max} ;
2. Load the first velocity field file;
3. Position the particles over the inlet;
4. Calculate the distance between two consecutive particles $|\mathbf{X}_{i,j} - \mathbf{X}_{i,j+1}|$;
5. Insert a new particle between particles j and $j+1$ if $|\mathbf{X}_{i,j} - \mathbf{X}_{i,j+1}| > r$;
6. Recalculate the number of particles, np ;
7. Load the velocity field of the next iteration;
8. Calculate the velocities of the particles with *interp2*;
9. Recalculate the position of the particles with Equation II.4;
10. Repeat steps 4 to 9 until t_{max} is attained.

III.2.2 LMS Algorithm Block Diagram

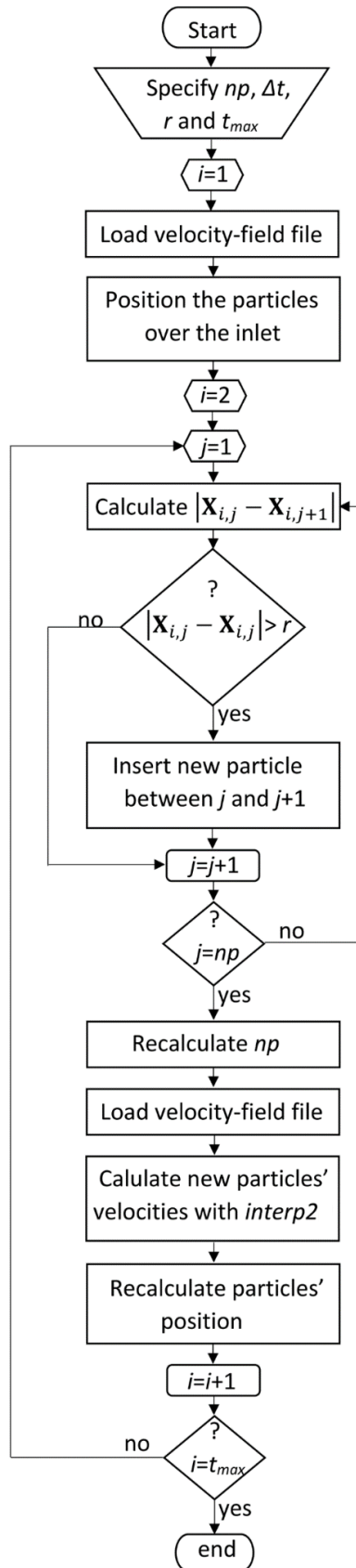


Figure III.9 LMS algorithm block diagram.

III.3 Interfacial Area Generation Calculation Procedure

The interfacial area generation can be computed by measuring the length, s , of the interface that is formed by the LMS particles,

$$s = \sum_{i=1}^{np} |\mathbf{x}_{i,j} - \mathbf{x}_{i,j+1}| \quad (\text{III.6})$$

where np is the total number of particles.

The non-dimensional interfacial area, α is given by

$$\alpha = \frac{s}{s_0} \quad (\text{III.7})$$

in which s_0 is the initial length of the interface of particles which depends on the inlet of the reactor (Matos et al. 2018).

III.4 Striation Thickness Algorithm

As shown in Figure III.7, the particle tracking interface grows and folds along with the simulation time, creating thin layers delimited by the tracking line. The scale of these layers is a measure of the mixing scale, which can be calculated using the intersection of the line perpendicular to the tangent at each particle j , i.e., the line defined by two adjacent particles, $j-1$ and $j+1$, with the *closest interface*. A close-up of Figure III.7 is shown in Figure III.10, in which the dot represents a particle j of the *main interface*, and the arrow represents its intersection with the closest interface. The distance, S , represents the thickness of one layer (striation thickness) which is $\frac{1}{4}$ of the scale of segregation (Tadmor and Gogos, 2009).

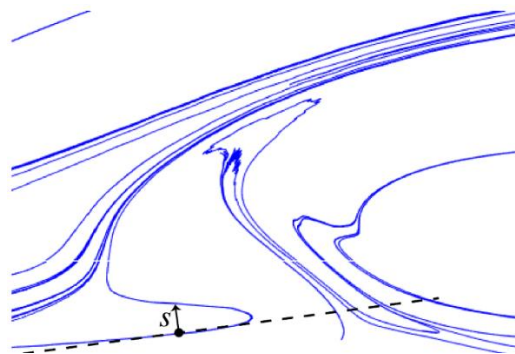


Figure III.10 Striation thickness.

The striation thickness algorithm is summarized in the following steps:

1. Calculate the slope, m , of the tangent to the current particle j (coordinates x_{p_j} and y_{p_j}), using particles $j+1$ and $j-1$;
2. Calculate the slope, $m_1 = -1/m$, which is perpendicular to the tangent obtained in Step 1, and the intercepts, b_1 , through particle j . *line1* is defined as $y = m_1x + b_1$;
3. Define a domain around particle j in which particles k are apart less than 1.0×10^{-4} m from particle j ;
4. Inside the domain defined in Step 3, calculate a tangent line with slope m_2 , and intercepts, b_2 , at each particle k (using particles $k+1$ and $k-1$). *Line2* is defined as $y = m_2x + b_2$ for each particle k ;
5. For each particle k of the domain defined in Step 3, determine the intersection (x_{c_k} and y_{c_k} coordinates) of *line1* from Step 2 with *line2* from Step 4;
6. For the current particle j , find the minimum distance, S , between its coordinates (x_{p_j} and y_{p_j}) and the coordinates of the intersections with particles k (x_{c_k} and y_{c_k}) of Step 5:

$$S = \min \left(\sqrt{(x_{p_j} - x_{c_k})^2 + (y_{p_j} - y_{c_k})^2} \right);$$

7. Repeat Steps 1 to 6 for all particles j ;

An illustration of this procedure is given in Figure III.11.

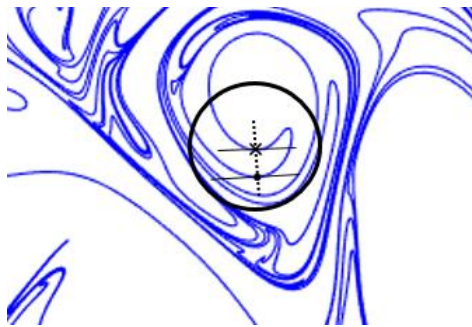


Figure III.11 Striation thickness calculation procedure (× represents current particle j , and • represents a particle k).

Note that, as the particles are in ascending order, the slope m_1 in particle j is in the opposite direction of slope m_2 in particle k . Thus, m_1 and m_2 have opposite signs, as well as the lines that are normal to them (Matos et al. 2018). This topic will be discussed further in this work.

III.5 Diffusive Lagrangian Mixing Simulation (DLMS)

DLMS is an adaptation of LMS which considers the diffusive scales. A limitation of the LMS algorithm is related with the increase of the CPU time due to a larger number of particles (see Section III.7.1 and Section III.7.2). In fact, for active mixing cases, where the number of particles increases exponentially, the CPU time of LMS can compromise the simulation, as will be shown further in this work. Moreover, LMS computes mixing scales below the physical limit, which is not realistic (Matos et al. 2018). DLMS is then an improved version of LMS to overcome these issues (Matos et al. 2020).

As show in Figure III.7, the interface of particles is folded, forming several layers between which the striation thickness can be measured. At certain zones of the reactor, the layers are so close to each other that it is not possible to distinguish them, only a blue region can be identified. If the striation thickness is measured at those locals, its value is lower than the physical limit, i.e., the scales are at the diffusional region, which is not relevant for the tracking (see Section III.6.2). In DLMS, the striation thickness is evaluated at each location and time step. If the striation thickness is below the minimum advective mixing scale, ξ , the interface between the fluids being mixed is split at that location and two closed subregions are formed. Since portions of the interface are deleted, the number of particles decreases improving the CPU time, as will be shown in Section III.7.2. Moreover, DLMS gives a realistic approach of the simulation of the mixing features. In fact, below ξ a homogenization occurs, and it is not relevant to simulate the interface between the fluids.

Figure III.12 shows the beginning of DLMS in the 2D CIJ reactor at $Re = 600$, where the interface of particles is split when $\xi < 1.0 \times 10^{-3}$ m. This condition leads to the formation of several blobs which are already visible at 1.5×10^{-3} s. Note that the tips of the blobs are an exception to the elimination procedure of particles. As the particles at the tips are very close to each other, the blobs that would be formed would be very small. In this way, the particles at the tips of the blobs are not deleted and new blobs will not be formed. This enables the existence of mixing structures below ξ at certain regions, as shown in the striation thickness of each blob which is slightly below 10^{-3} m, as visible in Figure III.12.

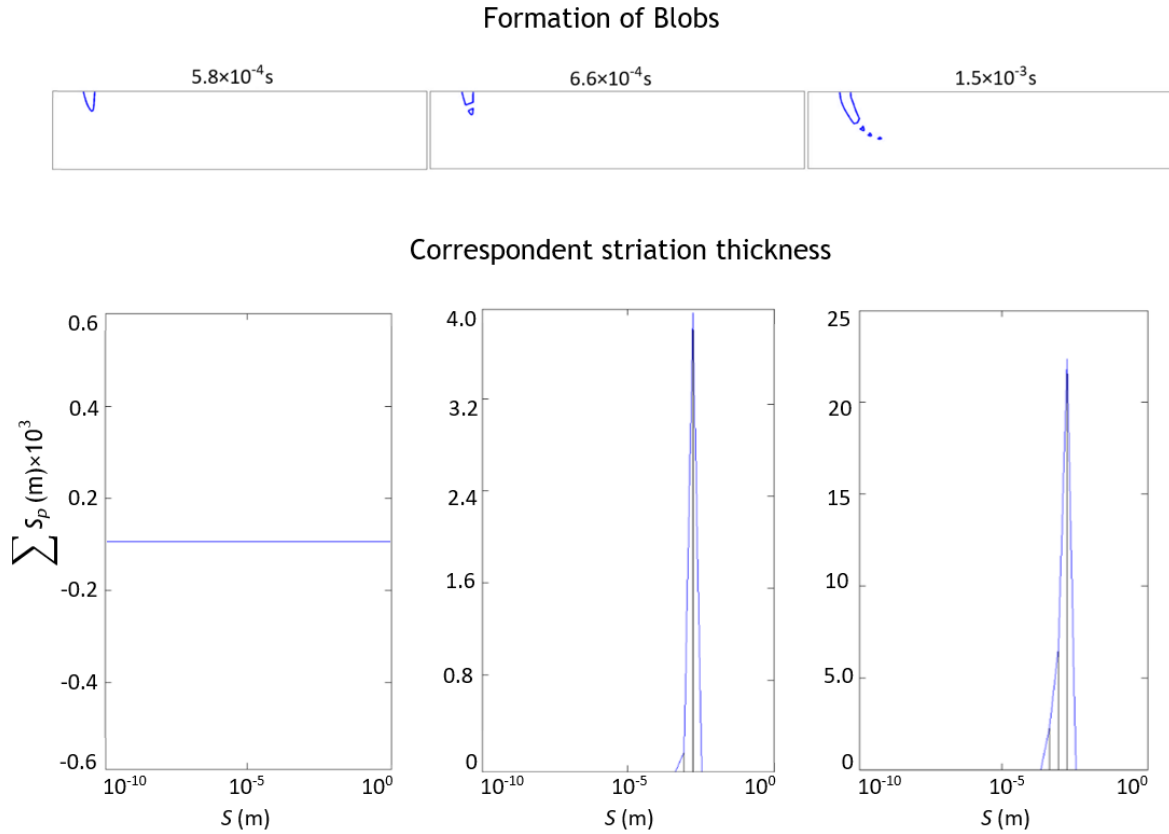


Figure III.12 Dynamic evolution of DLMS in the 2D CIJ reactor, at $Re = 600$ with $\xi = 1.0 \times 10^{-3} \text{ m}$, and correspondent striation thickness (Matos et al. 2018).

In the DLMS algorithm, the striation thickness, S , is calculated (at each time step) for each particle j . For that, a line, $L1$, tangent to the interface of the fluids in j is defined, using particles $j-1$ and $j+1$. Line, $L2$, that passes through particle j and is normal to $L1$ is then calculated. The intersection of $L2$ with the closest interface gives the striation thickness, S (see Section III.4). Since this intersection may not be exactly over a particle, the particle that is closest to the intersection, designated k , is considered (see Figure III.13).

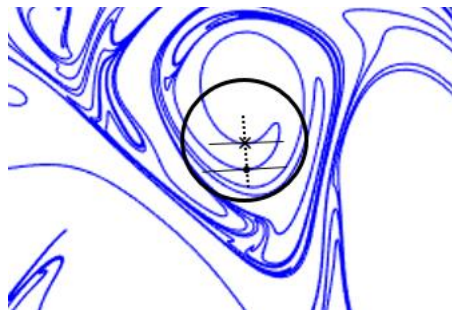


Figure III.13 Striation thickness calculation procedure, $\times$ represents current particle j , and $\bullet$ represents a particle k (Matos et al. 2018).

If $S < \xi$, the interface is split and particles j and k are deleted. The subsets of the initial interface are then closed, using an interpolation between the values (positions) of the particles that are at the end of those subsets (Figure III.14).

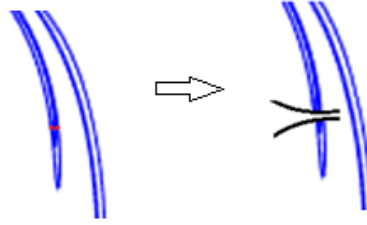


Figure III.14 Elimination of particles j and k (red dots), and formation of two new subsets.

Considering the interface around particle j :

$$j-3 \dots j-2 \dots j-1 \dots j \dots j+1 \dots j+2 \dots j+3 \quad (\text{III.8})$$

and the interface around particle k :

$$k-3 \dots k-2 \dots k-1 \dots k \dots k+1 \dots k+2 \dots k+3 \quad (\text{III.9})$$

the interfacial area is collapsed at this region, which consists in deleting particles j and k , forming two new subsets according to:

$$j-3 \dots j-2 \dots j-1 \dots k+1 \dots k+2 \dots k+3 \quad (\text{III.10})$$

and

$$j+3 \dots j+2 \dots j+1 \dots k-1 \dots k-2 \dots k-3 \quad (\text{III.11})$$

In addition to the threshold value, ξ , the DLMS algorithm has two new parameters, gap and p_{gap} , which were added to the original LMS in order to have an accurate formation of the subsets of particles.

Parameter gap

When the mixing interface is eliminated at a pair of particles $j - k$, since the striation thickness is presumably smaller than ξ in the surrounding area, the parameter gap sets a vicinity around each rupture region that is erased. This procedure makes the separation interface clear and prevents two separate regions to stay closer than r . In this way, the parameter gap is inserted to control whether the separation between the subsets is created at the rupture points j and k (i.e., $j-1$ to $k+1$ and $j+1$ to $k-1$) or if a larger extent of interfacial region is deleted, e.g., if $gap = 3$, the reconstructed portion around j and k would be: $j-3$ to $k+3$, and $j+3$ to $k-3$.

Frequently, around a pair of particles j and k which have a striation thickness $S < \xi$, due to fluid stretching effects, the two interfacial regions are parallel and the adjacent particles have S close to ξ . In this way, $gap = 3$ for the cases of this work. In fact, it was observed that this value enables to reduce significantly the number of subsequent rupture regions, which would compromise the CPU time, and is conservative enough to avoid the erase of large portions of the mixing interface, maintaining the accuracy of the tracking. The implementation of this parameter is shown in Figure III.15, in which is visible the difference between using gap or not.

Figure III.15 shows schematically the DLMS procedure at an interface defined by an interface with $np = 180$ particles. The pairs where $S < \xi$ (red dots) are: 10–123, 30–91 and 43–72. The interface is split at the marked points (red), originating 4 closed subsets. If gap is not used (Figure III.15a), the new subsets are closed immediately before and after the deleted particle: 9–124/11–122, 29–92/31–90 and 42–73/44–71. With $gap = 3$ (Figure III.15b), the subsets are closed at the 3rd particle before and after the deleted particle: 7–126/13–120, 27–94/33–88 and 40–75/46–69.

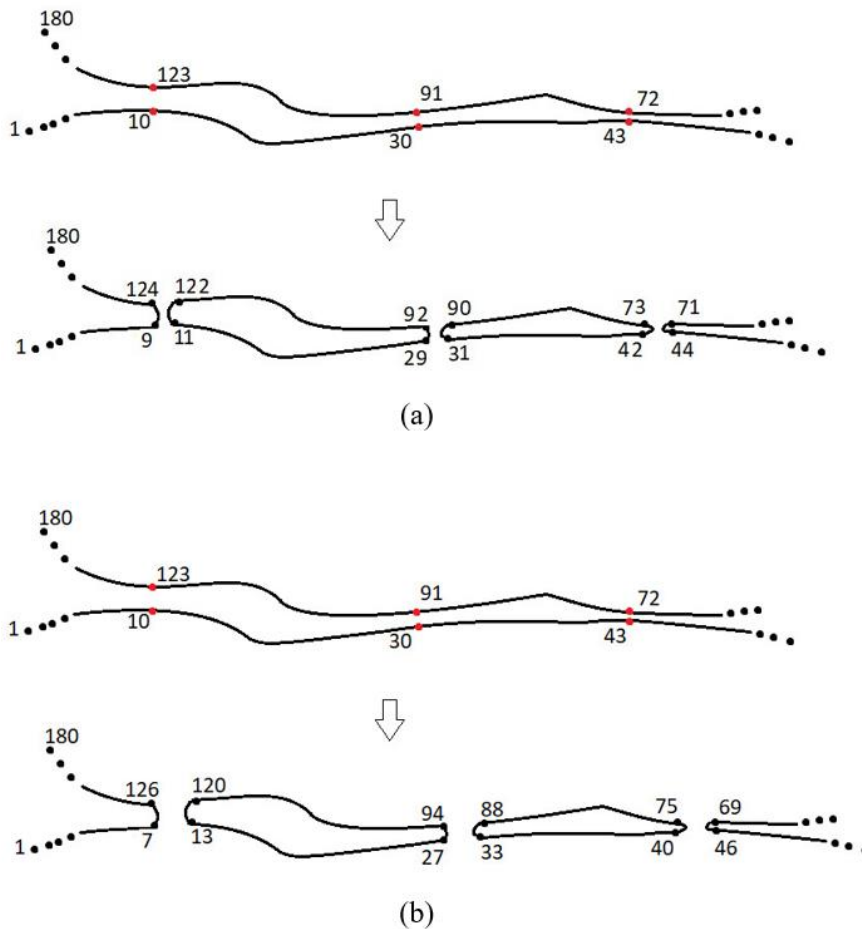


Figure III.15 Rupture of the filling front interface in the pairs of particles j (10, 30 and 43) and k (123, 91, 72) with $S < \xi$: (a) without gap , (b) with $gap = 3$.

The pairs of particles j and k where $S < \xi$ are stored in two vectors: particles j in $\mathbf{p1}$, and particles k in $\mathbf{p2}$. In the example of Figure III.15, $\mathbf{p1} = \{10, 30, 43\}$ and $\mathbf{p2} = \{123, 91, 72\}$. N is the dimension of the vectors $\mathbf{p1}$ and $\mathbf{p2}$. The blobs that will be formed after the splitting are stored in subsets of particles, $(\mathbf{X}_{i,j})_{subset\ n}$, created from the original array of the positions of the particles, $\mathbf{X}_{i,j}$. The total number of new subsets is $N + 1$.

The position vector of the particles that compose the first subset, $\mathbf{X}(i,j)_{subset\ 1}$, which is associated to the first pair of particles, $\mathbf{p1}(1)$ and $\mathbf{p2}(1)$ is given by

$$\mathbf{X}(i,j)_{subset\ 1} = \mathbf{X}(i,j = 1: \mathbf{p1}(1) - gap) \cup \mathbf{X}(i,j = \mathbf{p2}(1) + gap: np) \quad (\text{III.12})$$

The general expression for the position of the particles that form subsets $n = 2$ to $n = N$ is

$$\begin{aligned} \mathbf{X}(i,j)_{subset\ n} &= \mathbf{X}(i,j = \mathbf{p1}(n - 1) + gap: \mathbf{p1}(n) - gap) \\ &\cup \mathbf{X}(i,j = \mathbf{p2}(n) + gap: \mathbf{p2}(n - 1) - gap) \cup \mathbf{X}(i,j = \mathbf{p1}(n - 1) + gap) \end{aligned} \quad (\text{III.13})$$

Subset $N+1$ is given by

$$\begin{aligned} \mathbf{X}(i,j)_{subset\ N+1} &= \mathbf{X}(i,j = 1: \mathbf{p1}(N) + gap: \mathbf{p2}(N) - gap) \\ &\cup \mathbf{X}(i,j = \mathbf{p1}(N) + gap) \end{aligned} \quad (\text{III.14})$$

After the first split of the mixing interface, the analysis of the splitting points is performed for each subset separately. In this way, one subset of the initial interface will result in new subsets and so on.

Parameter p_{gap}

The parameter p_{gap} is introduced in DLMS to manage the generation of subsets of the mixing front tracking. Frequently, several points at a neighbourhood have approximately the same striation thickness, S , and if, $S < \xi$, new subsets will be formed, as previously discussed. The parameter p_{gap} introduces the criterion that two split points must be apart more than a certain number of tracking particles. If two rupture points are separated by less than a number of particles, p_{gap} , i.e., $\mathbf{p1}(n + 1) - \mathbf{p1}(n) < p_{gap}$, the subset is not formed at $(n + 1)$ and the split point is the next particle, $n + j$, where $\mathbf{p1}(n + j) - \mathbf{p1}(n) > p_{gap}$. The small subsets that would be formed between $\mathbf{p1}(n + j)$ and $\mathbf{p1}(n)$ if p_{gap} was not used are eliminated.

The effect of using p_{gap} is shown in Figure III.16. In Figure III.16a is represented the example of Figure III.15b ($gap = 3$) in which p_{gap} is not used. In Figure III.16b, $p_{gap} = 25$. It is visible that p_{gap} prevents the formation of many subsets with a small number of particles (between 20 and 50 particles) which would increase the computation time.

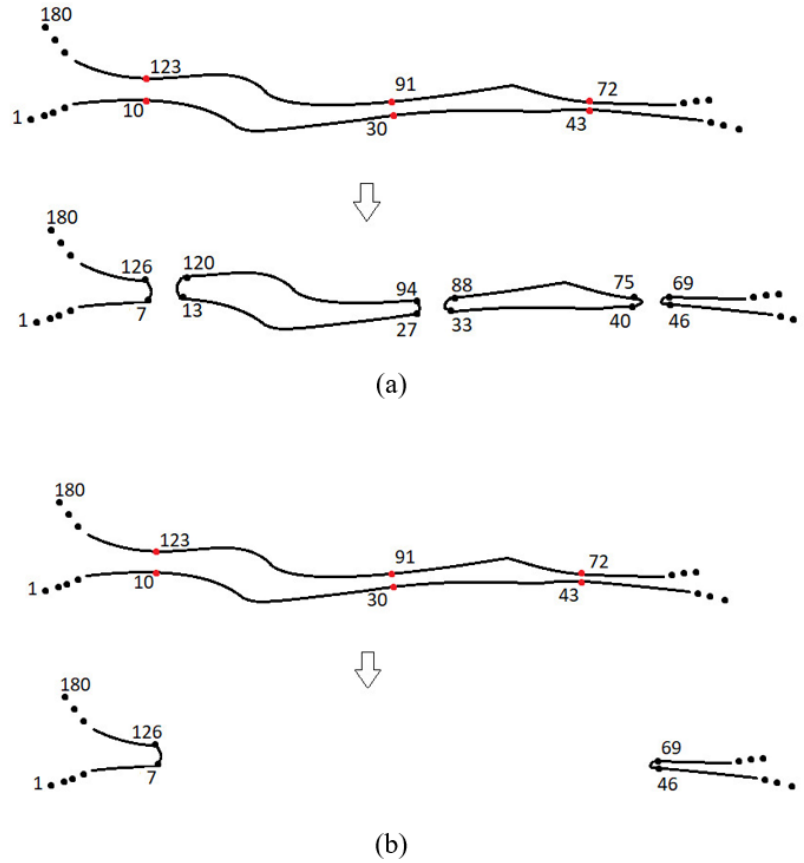


Figure III.16 Rupture of the filling front interface in the pairs of particles j (10, 30 and 43) and k (123, 91, 72) with $S < \xi$: (a) without p_{gap} , (b) with $p_{gap} = 25$.

Parameters gap and p_{gap} affect the number of matrix manipulations associated to the splitting of the tracking interface. If these values are kept small, they will not have impact on the flow visualization nor in the quantification of the interfacial area generation rate. Considering the maximum distance between the particles of the mixing front, $r = 10^{-4}$ m (LMS parameter), if $gap = 3$ and $p_{gap} = 100$, subsets smaller than $\cong 10$ mm are not generated, which is minimal in comparison to the total interface length of more than 150 m, as will be shown in Section III.6.1.

Parameter ξ Analysis

To analyse the influence of ξ , DLMS was applied to the 2D CIJ case for $Re = 600$. The initial number of particles, $np = 18$, were equally distributed at Inlet 1, particle 1 at $(x, y) = (-7.5 \times 10^{-4} \text{ m}, 5.0 \times 10^{-3} \text{ m})$, and particle np at $(x, y) = (7.5 \times 10^{-4} \text{ m}, 5.0 \times 10^{-3} \text{ m})$. The time step was set according to the CFD simulation, $\Delta t = 8.3 \times 10^{-6}$ s.

The DLMS parameters gap and p_{gap} , which are related with computational aspects concerning the number of matrix operations, should be conservative enough to control the number of formed

subsets without changing the values of the computed mixing statistics. The DLMS parameters were then set to $gap = 3$ and $p_{gap} = 100$.

For fast reactions, the diffusion time, $t_{Diff} \approx 10^{-3}$ s, is lower than the reaction time, $t_{Diff} \ll t_{React}$. Considering a diffusion coefficient of $\mathcal{D} = 10^{-9}$ m²/s (characteristic value for liquids), and the relation between t_{Diff} and $\mathcal{D}$ through the striation thickness, $t_{Diff} = \frac{S^2}{\mathcal{D}}$, it is possible to obtain a characteristic value of $S = 10^{-6}$ m. Thus, the mixing features should be simulated down to 10^{-6} m to enable the diffusion time to be faster than the reaction time. In this way, the threshold value, ξ , should be set to 10^{-6} m since lower values do not have a physical meaning.

This choice was assessed by analysing three values above the diffusion limit, $\xi = 10^{-3}$ m, 10^{-4} m and 10^{-5} m, and one value below the diffusion limit, $\xi = 10^{-7}$ m. Since the inlet of the reactor where the particles are injected is in the order of 10^{-3} m, the largest threshold value should be at least tenfold smaller. In fact, threshold values of 10^{-3} m led to the elimination of the filling front shortly upon entering the reactor, as shown in Figure III.12.

Figure III.17 shows the particle tracking at 0.01 s with DLMS, using $\xi = 10^{-4}$ m, $\xi = 10^{-5}$ m, $\xi = 10^{-6}$ m and $\xi = 10^{-7}$ m, and with LMS.

For $\xi = 10^{-6}$ m and $\xi = 10^{-7}$ m, two videos with the complete tracking with DLMS are shown in *Mixing_and_Controlled_Combustion_in_NETmix_videos*, DLMS_re_600_E_10_6.mp4 and DLMS_re_600_E_10_7.mp4.

In Figure III.17 is visible the convergence of the DLMS results towards LMS as the threshold decreases by one order of magnitude. For $\xi = 10^{-4}$ m, large portions of the interface are erased after a length of a mixing chamber width, D , from the impingement point of the jets. This shows a tenfold reduction of the mixing scales, from $W = 1.5 \times 10^{-3}$ m to $\xi = 10^{-4}$ m, over a length of $\approx D$. For smaller values of ξ , the visible length of the mixing front tracking increases between $\xi = 10^{-5}$ m and $\xi = 10^{-6}$ m. When the diffusion limit of 10^{-6} m is used several blobs are formed, although the erased portions of the mixing interface are very limited and spread throughout the mixer. For smaller threshold values, $\xi = 10^{-7}$ m, the breakage of the flow front is only observed in a few locations.

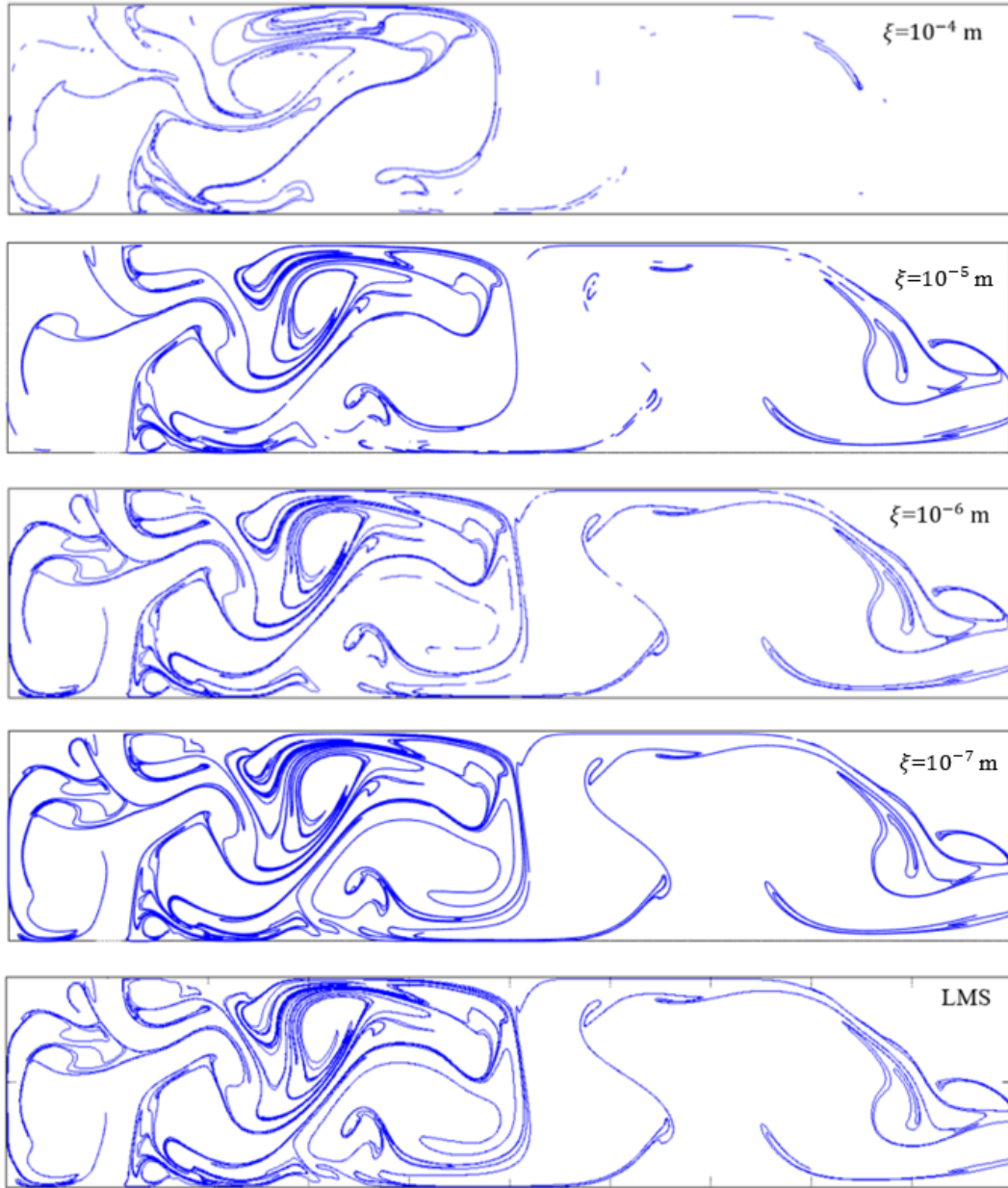


Figure III.17 LMS and DLMS simulations in the 2D CIJ reactor for $Re = 600$ at 0.01 s with $10^{-7} \text{ m} < \xi < 10^{-4} \text{ m}$.

A better analysis of the effect of the threshold value is obtained from the interfacial area generation measurement for each ξ . The interfacial area generation, α , is defined in Equations III.6 and III.7

$$\text{as } \alpha = \frac{\sum_{i=1}^{np} |\mathbf{x}_{i,j} - \mathbf{x}_{i,j+1}|}{s_0}, \text{ where } s_0 = W = 1.5 \times 10^{-3} \text{ m.}$$

The values of α are directly related to the evolution of the interfacial area in the early stages of LMS or DLMS. Since α is an exponential function of time, the specific generation of interfacial area is given by $b = \frac{1}{\alpha} \frac{d\alpha}{dt}$. The value of the curve exponent, b , is the specific rate of interfacial area generation.

With LMS, the growth of the interfacial area, α , for $Re = 600$ is given by $\alpha = ae^{bt}$, in which $a = 8.4 \pm 3.0$ and $b = 553 \text{ s}^{-1} \pm 35$. The standard deviation that is associated to each value of a and

b was obtained from 14 LMS runs, in which the particles injection was made at different flow time, varying from 0 s to 0.054 s with a step of 4.15×10^{-3} s between two consecutive LMS runs. For all runs, the fittings to the exponential curves have $R^2 = 0.999$ (Matos et al. 2018). This topic will be further discussed in Section III.6.

To compare with LMS, 14 runs of DLMS were also performed. The average values of b for the different thresholds are: $b = 375 \pm 26 \text{ s}^{-1}$, $419 \pm 38 \text{ s}^{-1}$, $521 \pm 12 \text{ s}^{-1}$ and $545 \pm 17 \text{ s}^{-1}$ for $\xi = 10^{-4} \text{ m}$, 10^{-5} m , 10^{-6} m and 10^{-7} m , respectively. The difference between the values of b computed from DLMS and LMS is 32%, 24%, 6% and 1%, for $\xi = 10^{-4} \text{ m}$, 10^{-5} m , 10^{-6} m and 10^{-7} m , respectively. As previously stated in the analysis of Figure III.17, as the threshold value decreases, the results are closer to the LMS simulation.

The threshold value in DLMS has an impact in the quantification of the specific rate of the interfacial area generation. In fact, the rate of creation of interfacial area is not the same for different mixing scales. In 2D CIJs, the injection jets have a mixing scale in the order of W . At upstream in the mixing chamber, the jets go round the vortices; at downstream locations, the fluid elements are striated through the vortex street. Thus, the cases where the quantification of mixing is mainly in upstream positions have a lower interfacial area generation rate. At downstream positions, the mixing dynamics are stronger and occur in regions where the fluids are already homogenised. In this way, the inclusion of a parameter that removes mixed fluids from the quantification of the mixing rates provides a more realistic benchmarking of mixers.

III.5.1 DLMS Algorithm

The DLMS algorithm is summarized as follows:

1. Set parameters: gap , ξ , p_{gap} , the number of iterations, n_{it} , the time step size, Δt , and the initial number of particles, np ;
2. Load the first velocity field file;
3. Position the particles (x and y coordinates) over the inlet;
4. Insert new particles if the interparticle distance becomes larger than $1.0 \times 10^{-4} \text{ m}$;
5. Calculate the velocity of the particles from the Eulerian field with a first order interpolation (See Section III.7.2.1);
6. Calculate the position of the particles with the LMS equation (Equation III.4);
7. Calculate the striation thickness, S , for all the particles (Matos et al. 2018);

8. Find the pairs of particles with $S < \xi$, delete the selected particles, and construct vectors **p1** and **p2**;
9. Split the interface of particles into several closed subsets, according to vectors **p1** and **p2**;
10. Load the velocity field file for the next time step;
11. Repeat Steps 4 to 8 until n_{it} is attained.

III.6 Quantification of Scales Applied to the CIJ Reactor

In order to quantify mixing in the CIJ reactor, LMS will be applied to passive mixing and DLMS to active mixing. The quantification of scales will be performed from the calculation of the interfacial area generation and striation thickness.

Passive Mixing

The LMS method was applied to passive mixing in the 2D CIJ reactor for $Re = 100, 300$ and 600 with $\Delta t = 8.3 \times 10^{-5}$ s and $r = 1.0 \times 10^{-4}$ m. The particles are initially positioned over the velocity field at 10τ which was recorded from the CFD simulation. The initial number of particles, $n_p = 18$, were equally distributed at the top inlet (Inlet 1 of Figure II.3), completely comprising the length from $(x, y) = (-7.5 \times 10^{-4} \text{ m}, 5.0 \times 10^{-3} \text{ m})$ to $(x, y) = (7.5 \times 10^{-4} \text{ m}, 5.0 \times 10^{-3} \text{ m})$ which are the coordinates of the first and last particle, respectively, as shown in Figure III.6. The results at flow time 0.022 s are in Figure III.18.

Comparing the LMS results for passive mixing, shown in Figure III.18, with the vorticity maps from CFD of Figure II.9, it is visible that the mixing features obtained with the particle tracking make an accurate representation of the flow.

The LMS tracking for passive mixing with $Re = 100, 300$ and 600 in the CIJ reactor is shown in the videos: `LMS_re_100.mp4`, `LMS_re_300.mp4`, `LMS_re_600.mp4` of the folder *Mixing_and_Controlled_Combustion_in_NETmix_videos*.

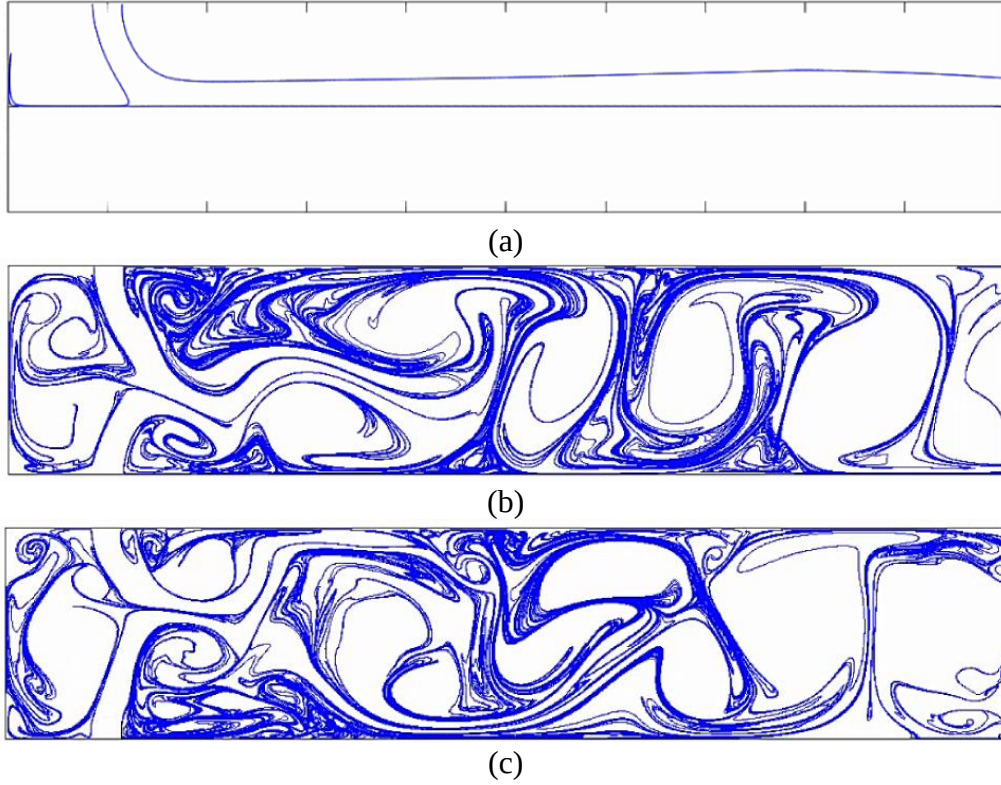


Figure III.18 LMS at 0.022 s in the 2D CIJ reactor for: (a) $Re = 100$, (b) $Re = 300$ and (c) $Re = 600$.

Active Mixing

The DLMS method was applied to active mixing in the 2D CIJ reactor for $Re = 300$ with a modulation frequency of $f = 80$ Hz ($\phi/3$) and 267 Hz (ϕ) and a modulation amplitude of $A = 0.5$ and 1.0. The algorithm parameters were: $\xi = 10^{-6}$ m, $\Delta t = 8.3 \times 10^{-5}$ s, $r = 1 \times 10^{-4}$ m, $gap = 3$ and $p_{gap} = 500$ (the value of p_{gap} was increased to 500 since the interfacial area is larger in active mixing). The particles are initially positioned over the velocity field at 10τ which was recorded from the CFD simulation. The initial particles, $np = 18$, were equally distributed at the top inlet (Inlet 1 of Figure II.3), completely comprising the length from $(x, y) = (-7.5 \times 10^{-4}$ m, 5.0×10^{-3} m) to $(x, y) = (7.5 \times 10^{-4}$ m, 5.0×10^{-3} m) which are the coordinates of the first and last particle, respectively, as shown in Figure III.6. The simulations were run until the first particles started to exit the mixing chamber, as shown in Figure III.19 (Matos et al. 2020).

Comparing the DLMS results of active mixing, shown in Figure III.19, with the vorticity maps from CFD of Figure II.10, it is visible that the mixing features obtained with the particle tracking make an accurate representation of the flow.

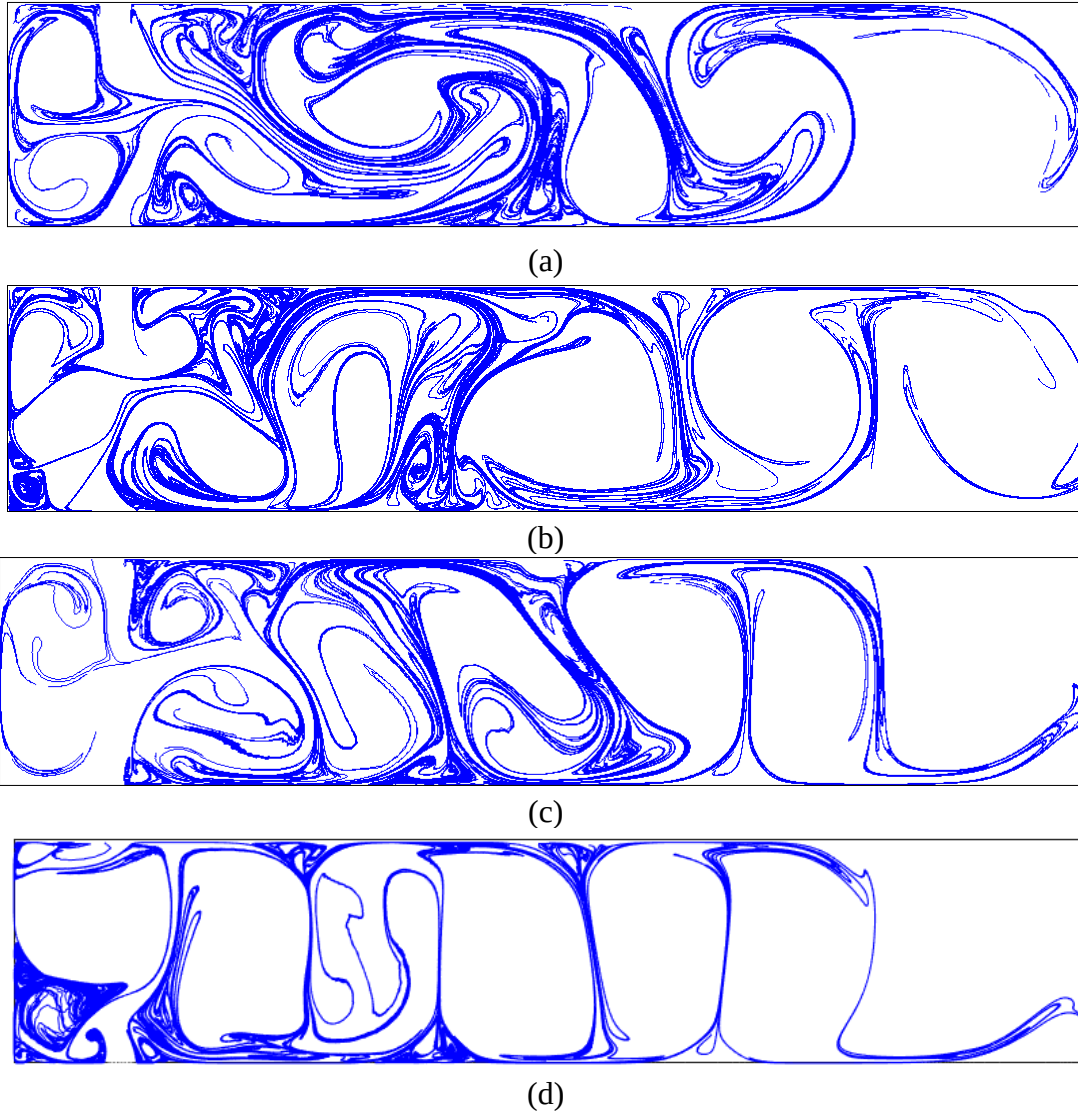


Figure III.19 DLMS of active mixing in 2D CIJ for $Re = 300$ with: (a) $f = \phi$, $A = 0.5$, (b) $f = \phi$, $A = 1.0$, (c) $f = 3\phi/10$, $A = 0.5$ and (d) $f = 3\phi/10$, $A = 1.0$.

The filling of the CIJ chamber, using DLMS is shown in the videos: DLMS_300_80_1.mp4, DLMS_300_80_05.mp4, DLMS_300_267_1.mp4 and DLMS_300_267_05.mp4 of the folder *Mixing_and_Controlled_Combustion_in_NETmix_videos*. The videos show the DLMS tracking together with the vorticity maps from CFD as well as the illustration of the modulation of the inlet velocity. The velocity is modulated at each inlet (in blue for the top inlet and in red for the bottom inlet) by $v^*(x, t) = 1 + A \sin(2\pi f t + \varphi)$. A video without modulation for $Re = 300$ is also included, DLMS_re_300.wmv. In the x -axis of the velocity modulation video, θ_{DLMS} is the DLMS time normalized by the residence time, $\tau = 4.2 \times 10^{-2}$ s.

III.6.1 Interfacial Area Generation Measurement

Passive Mixing in Dynamic Flows

To calculate the interfacial area generation (Equation III.6 and III.7 with $s_0 = W = 1.5 \times 10^{-3}$ m) for dynamic flows with $Re = 300$ and 600 , LMS ($r = 1.0 \times 10^{-4}$ m) was simulated for three different time steps: $\Delta t = 8.3 \times 10^{-5}$ s, $\Delta t = 2 \times 8.3 \times 10^{-5}$ s and $\Delta t = 8.3 \times 10^{-5} / 2$ s. As the flow is chaotic, small divergences on the position of the particles are greatly amplified. Thus, the time step is analysed to assess whether the overall dynamics of mixing are described by the same LMS indicators, a and b (Equation III.15), if the position of the particles is changed at each instant.

For each time step, 14 LMS runs were performed. In each LMS, the injection of particles is made at different flow time, varying from 0 s to 0.054 s with a step of 4.15×10^{-3} s between two consecutive LMS runs.

For dynamic flows at $Re = 300$ and 600 , α has an exponential grow. Thus, each LMS data was fitted to the equation

$$\alpha = ae^{bt} \quad (\text{III.15})$$

where a and b are the fitting parameters.

The exponential coefficient b corresponds to the Lyapunov exponent (Fonte et al. 2012); if $b > 0$, the flow is chaotic. Furthermore, this exponent is a measure of the interfacial area generation and can be used on reactors benchmarking. The coefficient a is related to the initial interfacial area generation; at $t = 0$, the interfacial area, α , should tend to the coefficient, a .

The rate of the interfacial area generation is given by $\frac{d\alpha}{dt}$ and represents the speed at which the interface of the fluids is stretched and folded, enabling mixing. As $\frac{d\alpha}{dt}$ is the time derivative of Equation III.15, it is also described by an exponential behaviour. The indicator b has the same meaning for both α and $\frac{d\alpha}{dt}$. The indicator a is the initial rate of the interfacial area generation for $\frac{d\alpha}{dt}$.

In Table III.1 and Table III.2, the average and standard deviation of the LMS indicators, a and b , is presented for each time step at $Re = 300$ and 600 , respectively. It is visible that the indicators, a and b , have no trend with Δt . Thus, the overall dynamics of mixing are described by the same LMS indicators if the position of the particles is changed at each instant.

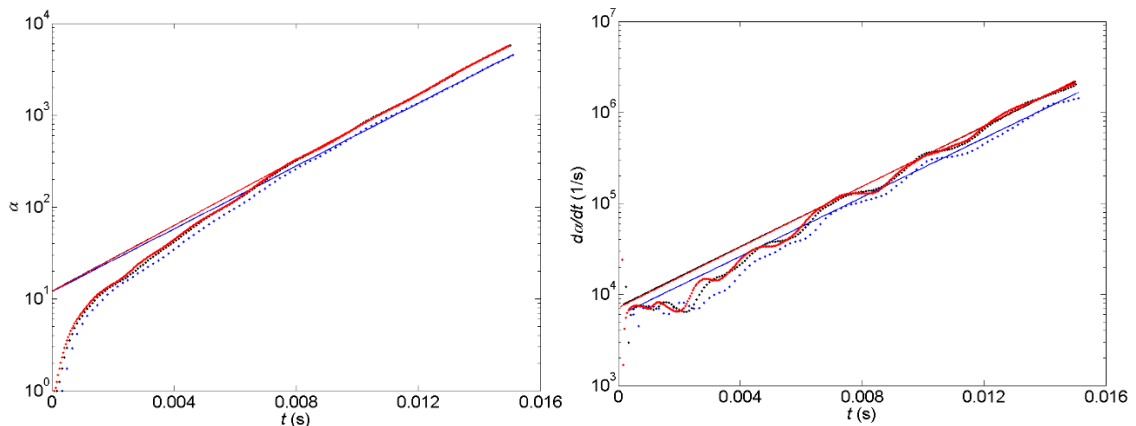
Table III.1 Exponential fitting parameters (average $\pm$ standard deviation) and squared correlation coefficient for different values of Δt , at Re = 300.

Exponential Fittings for Re = 300				
Δt (s)		$\bar{a}$	$\bar{b}$ (1/s)	$\bar{R}^2$
$8.3 \times 10^{-5} / 2$	α	14.3 ± 4.4	$4.13 \times 10^2 \pm 36$	0.999
	$\frac{d\alpha}{dt}$ (1/s)	$6.87 \times 10^3 \pm 3.70 \times 10^3$	$3.92 \times 10^2 \pm 37$	0.999
8.3×10^{-5}	α	13.2 ± 4.0	$4.05 \times 10^2 \pm 28$	0.999
	$\frac{d\alpha}{dt}$ (1/s)	$7.03 \times 10^3 \pm 2.00 \times 10^3$	$3.82 \times 10^2 \pm 22$	0.999
$2 \times 8.3 \times 10^{-5}$	α	15.9 ± 6.3	$3.90 \times 10^2 \pm 14$	0.999
	$\frac{d\alpha}{dt}$ (1/s)	$8.13 \times 10^3 \pm 5.18 \times 10^3$	$3.74 \times 10^2 \pm 34$	0.999

Table III.2 Exponential fitting parameters (average $\pm$ standard deviation) and squared correlation coefficient for different values of Δt , at Re = 600.

Exponential Fittings for Re = 600				
Δt (s)		$\bar{a}$	$\bar{b}$ (1/s)	$\bar{R}^2$
$8.3 \times 10^{-5} / 2$	α	8.7 ± 3.5	$5.53 \times 10^2 \pm 35$	0.998
	$\frac{d\alpha}{dt}$ (1/s)	$6.99 \times 10^3 \pm 2.98 \times 10^3$	$5.29 \times 10^2 \pm 46$	0.998
8.3×10^{-5}	α	9.2 ± 3.0	$5.55 \times 10^2 \pm 35$	0.998
	$\frac{d\alpha}{dt}$ (1/s)	$6.12 \times 10^3 \pm 3.13 \times 10^3$	$5.42 \times 10^2 \pm 64$	0.998
$2 \times 8.3 \times 10^{-5}$	α	7.2 ± 2.6	$5.52 \times 10^2 \pm 26$	0.998
	$\frac{d\alpha}{dt}$ (1/s)	$4.87 \times 10^3 \pm 2.11 \times 10^3$	$5.27 \times 10^2 \pm 41$	0.998

The exponential fitting, using the overall average for Re = 300 and 600, is given by $\alpha = 14.5e^{403t}$ and $\alpha = 8.4e^{553t}$, respectively. It is observed that when the Reynolds number increases, the value of $\bar{a}$ decreases and the value of $\bar{b}$ increases. Figure III.20 and Figure III.21 show the data of α and $\frac{d\alpha}{dt}$ for the first LMS, i.e., the injection of particles is made at flow time zero.

Figure III.20 Exponential fittings (full line) and LMS data (dotted line) for α and $\frac{d\alpha}{dt}$ in the 2D CIJ reactor at Re = 300, with different time step: $\Delta t = 8.3 \times 10^{-5}$ s in black, $\Delta t = 2 \times 8.3 \times 10^{-5}$ s in blue and $\Delta t = 8.3 \times 10^{-5} / 2$ s in red.

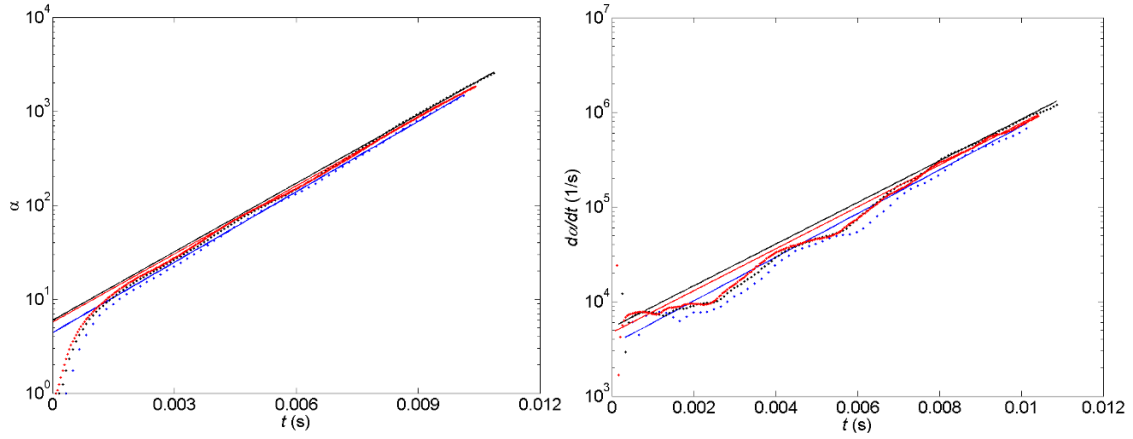


Figure III.21 Exponential fittings (full line) and LMS data (dotted line) for α and $\frac{d\alpha}{dt}$ in the 2D CIJ reactor at $Re = 600$, with different time step: $\Delta t = 8.3 \times 10^{-5}$ s in black, $\Delta t = 2 \times 8.3 \times 10^{-5}$ s in blue and $\Delta t = 8.3 \times 10^{-5} / 2$ s in red.

For both Re , the fittings have a correlation coefficient of 0.999 for α and 0.998 for $\frac{d\alpha}{dt}$. However, with the y-axis in logarithmic scale it is visible that in the beginning of LMS the values of α differ between the data and the fitting. In fact, α is obtained from the length of the interface of particles which, at start, is equal to the non-dimensional length of the inlet; thus, at $t = 0$, $\alpha = s/s_0 = 1$.

For low flow time, the behaviour of α and $\frac{d\alpha}{dt}$ show deviation to the exponential law. As the flow time increases, its value tends to the fitting. In fact, at the injection, the main flow feature is a parabolic jet; thus, the interfacial area generation is not described by an exponential growth law.

When the flow is chaotic, which is the case of this work for dynamic flow simulations with $Re = 300$ and 600 , the interfacial area generation between the fluids being mixed is exponential (Ottino 1980, Ottino 1989, Ottino 1990). Further in this section, the chaotic behaviour will be compared with a steady flow at $Re = 100$ and with a case in which a parabolic flow is always imposed.

Passive Mixing in Steady flows

To measure the interfacial area generation at $Re = 100$, LMS was used with the previous parameters: $\Delta t = 8.3 \times 10^{-5}$ s, $r = 1.0 \times 10^{-4}$ m and $np = 18$. The results have shown that the interfacial area generation is linear and can be given by

$$\alpha = ct \quad (III.16)$$

in which c is a parameter equal to $6.6 \times 10^3 \text{ s}^{-1}$. The value of c was obtained from a linear fitting to the simulation results.

Parabolic Flow

In this case, a parabolic flow is always imposed. The position of the particles along x with the time, t , is given by

$$y = v_{inj}t \left(1 - \frac{4x^2}{W^2}\right) \quad (\text{III.17})$$

in which v_{inj} is the velocity of the inlet, x represents the x -coordinate, y represents the y -coordinate, t represents the time and W is the length of the inlet.

To obtain the interfacial area generation, α_{s0} , the line integral, $ds = \sqrt{dx^2 + dy^2}$ was solved, and the results have shown that the value of α_{s0} is linear, according to

$$\alpha_{s0} = \oint v_{inj}t \left(1 - \frac{4x^2}{W^2}\right) ds = \frac{W}{2} \sqrt{\frac{36v_{inj}^2t^2}{W^2} + 1} + \frac{W^2}{36v_{inj}t} \ln \left(\frac{\sqrt{\frac{36v_{inj}^2t^2}{W^2} + 1} + \frac{6v_{inj}t}{W}}{\sqrt{\frac{36v_{inj}^2t^2}{W^2} + 1} - \frac{6v_{inj}t}{W}} \right) \quad (\text{III.18})$$

When $t \gg \frac{W}{v_{inj}}$, Equation III.18 reduces to

$$\alpha_{s0} \approx 3v_{inj}t \quad (\text{III.19})$$

Interfacial Area Generation Comparison

The comparison between the interfacial area generation obtained with the LMS method for dynamic and steady flows ($\Delta t = 8.3 \times 10^{-5}$ s) with the parabolic flow case is represented in Figure III.22.

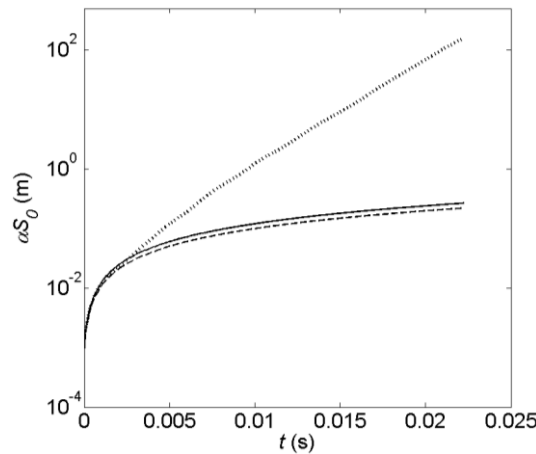


Figure III.22 α_{s0} (in logarithmic scale) of the 2D CIJ reactor at $Re = 300$ for: steady flow (dotted line), dynamic flow (dashed line), and parabolic flow (full line).

The comparison between parabolic and steady flows with dynamic or chaotic flows shows the difference between the interfacial area that is generated by a parabolic jet and the interfacial growth promoted by the vortex dynamics.

In Figure III.22 is visible that for the initial flow time, $t < 2.5 \times 10^{-4}$ s, αs_0 is similar for the three cases. In fact, the initial interfacial area is the same since, at the injection, the flow is a jet with a parabolic velocity profile, until the jets impingement point. As the flow time increases, steady-state and parabolic cases have a similar behaviour since the flow is a jet flowing nearly without disturbance. Differently, in chaotic flows, the vortex street formed downstream the jets impingement point engulfs the fluids, generating an exponential growth of the interfacial area.

At the LMS final time, 0.022 s, the value of αs_0 is larger than 150 m which corresponds to more than 3000 chamber lengths. It is concluded that the generation of interfacial area from the filling front injection is significantly less relevant than the vortices effect.

Active Mixing

As shown in the previous section, the indicators a and b obtained from several LMS runs have no trend with Δt . In this way, to study the interfacial area generation of active mixing cases, only one DLMS run was used. In Figure III.23 are shown the exponential fittings of the active mixing cases, which are compared with the passive mixing case at $Re = 300$. The fitting parameters are shown in Table III.3.

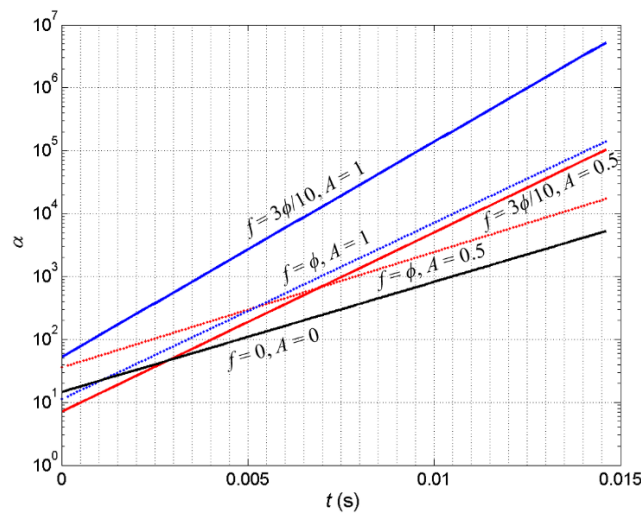


Figure III.23 α exponential fittings of the 2D CIJ reactor at $Re = 300$ for passive mixing with $f = 0$ and $A = 0$ (black), and for active mixing with: $f = \phi$ and $A = 0.5$ (dotted red), $f = \phi$ and $A = 1$ (dotted blue), $f = 3\phi/10$ and $A = 0.5$ (red), $f = 3\phi/10$ and $A = 1$ (blue).

Table III.3 Exponential fitting comparison for passive and active mixing.

Exponential Fittings				
			a	b (1/s)
Passive mixing for $Re = 300$			14.5 ± 4.0	$4.03 \times 10^2 \pm 28$
Active mixing for $Re = 300$	$f = \phi$	$A = 0.5$	35.9	4.23×10^2
		$A = 1.0$	11.2	6.46×10^2
	$f = 3\phi/10$	$A = 0.5$	7.1	6.56×10^2
		$A = 1.0$	52.0	7.88×10^2

The passive mixing case (black line) has a lower interfacial area, in the order of $a \cong 10^3$ at the end of the DLMS simulation, $\cong 0.015$ s. Active mixing with $f = \phi$ and $A = 0.5$ (red dotted line) generates an interfacial area slightly larger than the passive mixing case, at $\cong 0.015$ s. In fact, the fitting parameter b of these two cases has less than 5% difference. When the modulation amplitude doubles to 1, the system engages into resonance (see Figure II.11c) and the interfacial area generation increases one order of magnitude (blue dotted line). The increase in mixing dynamics is confirmed from the rise of b in 35%, when compared to the case with $A = 0.5$. For the case with modulation frequency $f = 3\phi/10$ and amplitude $A = 0.5$ (red line), the interfacial area is of the same order of magnitude (10^5 at $\cong 0.015$ s) of the previous case with $f = \phi$ and $A = 1$ (parameter b differs less than 2%). In fact, as previously shown in this work, when $f = 3\phi/10$ the diameter of the vortices extends throughout the entire width, D , of the mixing chamber. Thus, even with a smaller modulation amplitude, $A = 0.5$, the interfacial area generation is larger. For $f = 3\phi/10$, if A is doubled to 1, the interfacial area reaches an order of magnitude ca. 10^7 at the end of the DLMS simulation, which is more than one order of magnitude larger in relation to the case with $A = 0.5$, and four orders of magnitude larger than the passive mixing case.

The previous analysis shows that DLMS enables to benchmark active mixing through the interfacial area generation measurement, especially by the examination of parameter b which increases when the interfacial area generation is larger. Active mixing cases are associated to a high rate of interfacial area generation which implies a diminishment of the strias thickness (up to ca. 10^{-6} m). If a Eulerian method was to be used to study mixing dynamics, a grid with a larger number of elements, out of the reach of computational resources, would be needed to cover all the striation scales. In this way, it is not possible to differentiate active mixing cases from a Eulerian simulation with a passive tracer since the mixing scale is smaller than the computational grid (Erkoç et al. 2016, Matos et al. 2020). The use of Lagrangian techniques as DLMS enables to measure quantities lower than the computational grid for the characterization of the smallest mixing scales.

III.6.2 Striation Thickness Calculation

The striation thickness was calculated for all the particles of LMS for passive mixing with $Re = 300$ and 600 (see Figure III.24).

The local length of the interface around each particle, s_p , is given by

$$s_{p_{i,j}} = |\mathbf{X}_{i,j} - \mathbf{X}_{i,j+1}| \quad (\text{III.20})$$

in which i is constant and equal to the final time of the LMS simulation and j represents the particles.

Considering $\alpha = s/s_0$ (Equation III.7), it is possible to say that each particle has a *local interfacial area*, $\alpha_{p_j} = s_{p_j}/s_0$.

Since s_{p_j} is related with the degree of mixing, the normalized striation thickness, S/W , is used to weight s_{p_j} . In the distributions presented in Figure III.24, each class of S/W is related to $\sum s_p$ of the particles in that class.

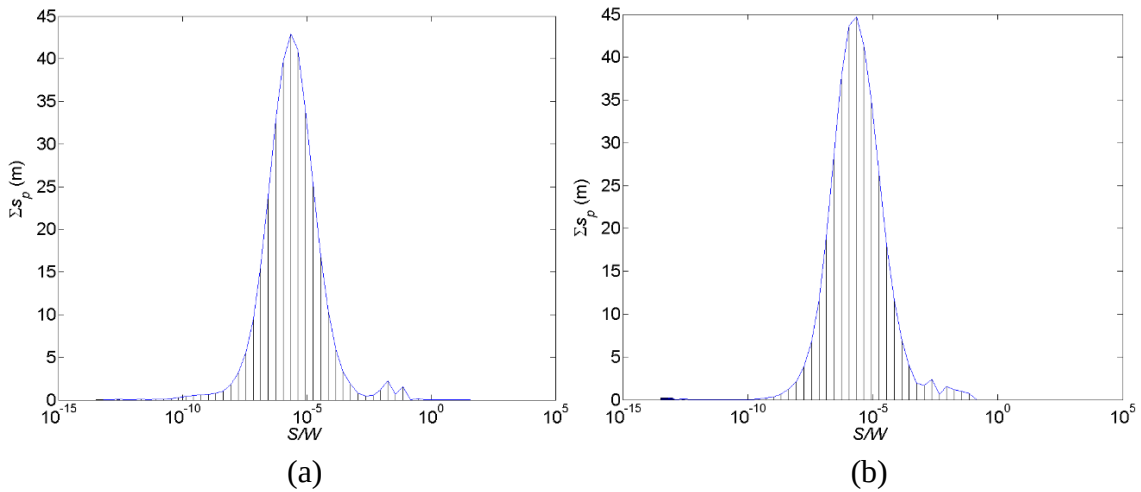


Figure III.24 Normalized striation thickness of the 2D CIJ reactor at: (a) $Re = 300$ and (b) $Re = 600$.

Figure III.24 shows that for both Re numbers the distribution of S with $\sum s_p$ is similar to a normal distribution centred at $\approx 10^{-5}$ m. The total *local length*, $\sum s_p$, is slightly larger for $Re = 600$ and its value is nearly 45 m.

LMS enables the simulation of values below the diffusional limits. The diffusion scale is given by $S \sim \sqrt{\mathcal{D} \Delta t}$; for $\Delta t \approx 10^{-4}$ s and $10^{-9} \text{ m}^2/\text{s} < \mathcal{D} < 10^{-11} \text{ m}^2/\text{s}$, the diffusion scale is in the range $10^{-8} \text{ m} < S < 10^{-6} \text{ m}$. Since the physical meaning is $\frac{S}{W} > 10^{-5}$ (see Section III.5), below this scale, both sides of the lamellae structure will merge. As LMS simulates $S < 10^{-8}$ m, mathematically, mixers can be compared beyond the physical limit of the diffusion scale.

The value of S can be predicted using a relation between S and α , proposed by Ranz (1979)

$$-\ln(\alpha) = \ln\left(\frac{S}{S_0}\right) \quad (\text{III.21})$$

in which S_0 is the initial striation thickness, $S_0 = W = 1.5 \times 10^{-3}$ m.

At the end of LMS, 0.022 s, $\alpha = 1.1 \times 10^5$. From Equation III.21, S/W is predicted to be 9.3×10^{-6} which corresponds to the central value, i.e., the most common value of S inside the chamber, of the distributions of Figure III.24. The method that was developed in this work for the calculation of the striation thickness is then numerically validated.

In the segregation scale, two zones can be identified, the “inside” and the “outside” of the filling front interface. The “inside” is the inner part of the interface that delimits the flow injection; the “outside” is the exterior side of that interface (see Figure III.25). Considering two species A and B , if the chamber is initially filled with B , when LMS starts A is constantly injected and mixed in the chamber. In this way, LMS defines a filling front in which the inner part, the “inside”, corresponds to A .

As it is only possible to compute the mixing scales, S , using the tracer with A , it is relevant to know whether S belongs to an “inside” or an “outside”.



Figure III.25 Identification of zones of the flow interface: “inside” (arrow, white zone) and “outside” (blue zone).

When the calculation of S is made by LMS, if the two particles (j and k) delimit an “inside”, the product of slopes of the tangent lines is negative. In contrast, if they delimit an “outside”, the product is positive. Note that if the product of the slopes is negative, particles j and k point to opposite directions. Thus, they belong to an interface that delimits an “inside” (which is the case presented in Figure III.11). If the product of the slopes is positive, the particles point to the same direction and delimit an “outside”.

The distribution of the mixing scales corresponding to positive and negative products is presented in Figure III.26 and in Figure III.27 for $Re = 300$ and 600 , respectively. For both Re , the distributions of the positive product (Figure III.26a and Figure III.27a) have two peaks; thus, the distribution of S is bimodal. The distributions of the negative product (Figure III.26b and Figure

III.27b) are similar to the distribution of S for all the LMS particles (see Figure III.24). In this way, most S data is from “insides”.

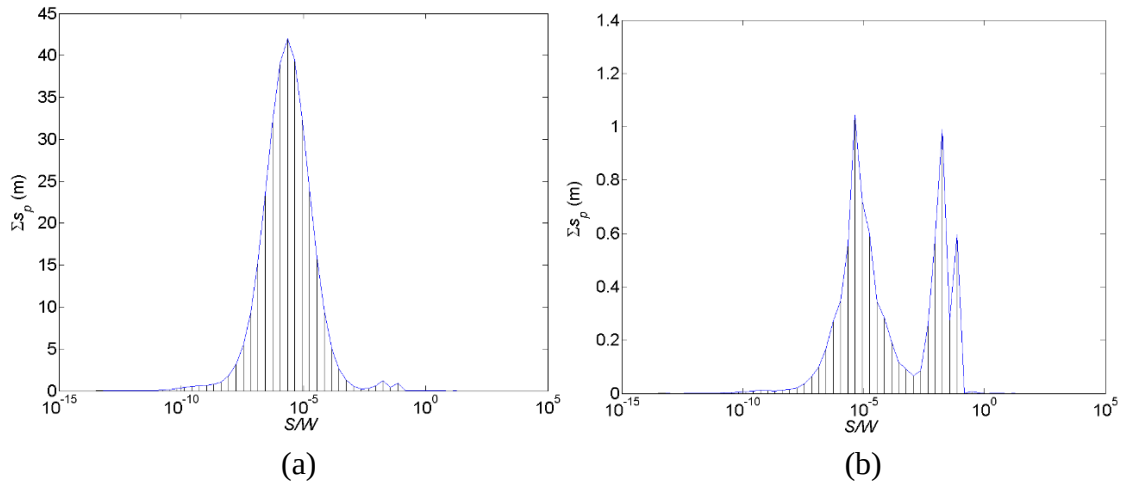


Figure III.26 Negative (a) and positive (b) product of slopes in the 2D CIJ reactor at $Re = 300$.

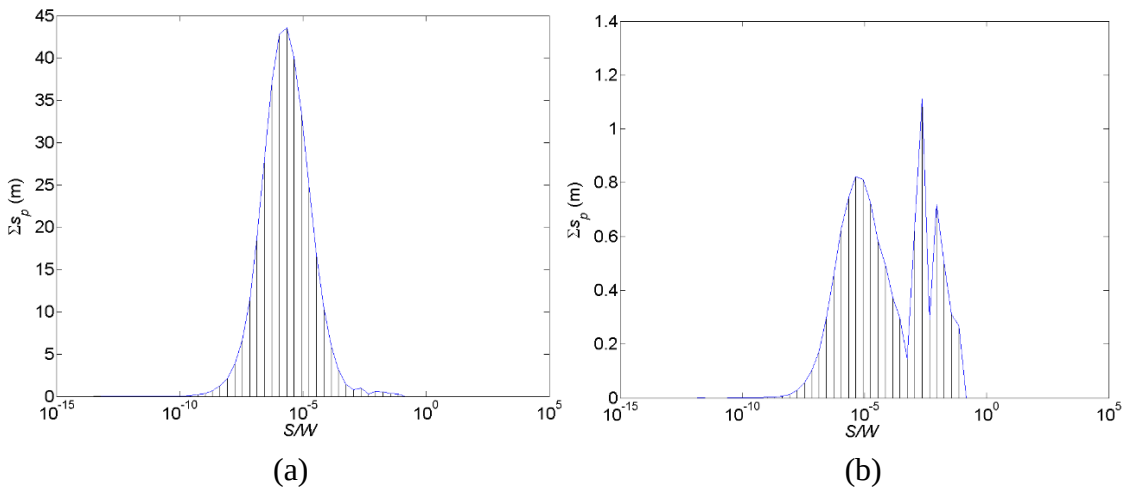


Figure III.27 Negative (a) and positive (b) product of slopes in the 2D CIJ reactor at $Re = 600$.

Analysing in detail the striation inside the chamber, it is possible to identify “peaks” which represent the tip of the filling front (Figure III.28). Since the line that is perpendicular to a tangent at particle j on these tips can be associated to artificially large values of mixing scales, the striation thickness at the tips will be studied.



Figure III.28 Identification of tips of the filling front.

The particles at the tips can be identified from the second derivative, which is larger. In the LMS interface, the second derivative at particle j is expressed as

$$f_j'' = \frac{y_{p_{j-1}} - 2y_{p_j} + y_{p_{j+1}}}{4(x_{p_{j+1}} - x_{p_{j-1}})^2} \quad (\text{III.22})$$

in which y_{p_j} and x_{p_j} are the y and x coordinates of particle j .

The distribution of the striation thickness computed at particles with $f_j'' > 10^{10}$ is represented in Figure III.29 for $\text{Re} = 300$ and 600 .

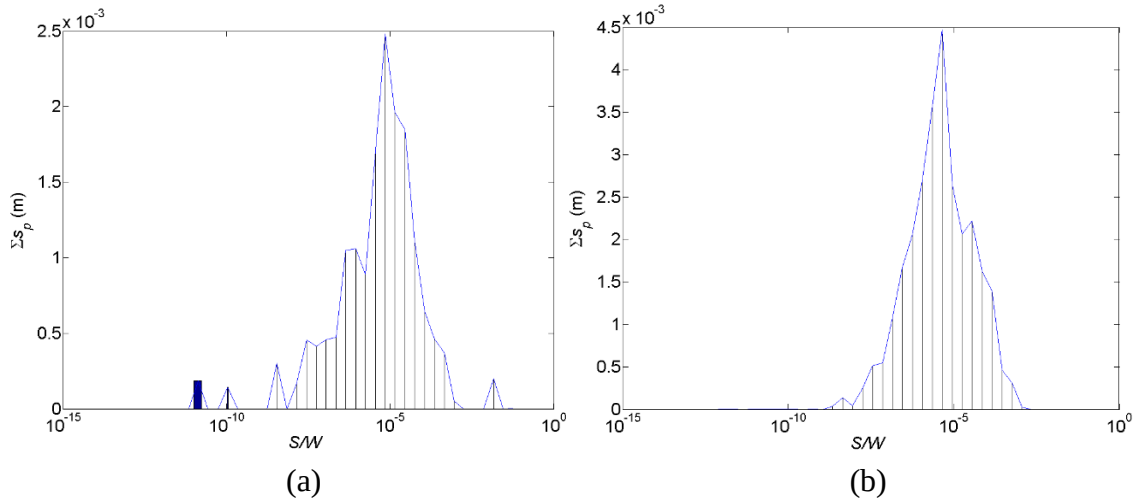


Figure III.29 S at particles with $f_j'' > 10^{10}$ for: (a) $\text{Re} = 300$ and (b) $\text{Re} = 600$, in the 2D CIJ reactor.

The central values, $S/W \cong 10^{-5}$, of the distributions of Figure III.29 are similar to the distributions that were previously presented. In this way, there is neither a biasing for “insides” or “outsides”, neither towards larger S/W values at the tips.

Furthermore, Figure III.29 shows that the number of particles in front tips is negligible and does not affect the calculation of the striation thickness. In fact, they represent 0.5 % and 1.5 % of the total number of particles for $\text{Re} = 300$ and 600 , respectively. In terms of $\sum s_p$, it is visible that its value, less than 5.0×10^{-3} m, is considerably smaller when compared with the value obtained with all the particles, nearly 45 m of total local interfacial area (see Figure III.24).

Figure III.29 shows that number of particles on tips is larger for $\text{Re} = 600$, comparing with $\text{Re} = 300$. The S values are similar for both Re numbers and $\sum \alpha_p$ is nearly the double for $\text{Re} = 600$.

III.6.2.1 LMS Comparison with the Lamellar Model for RIM

The results of the striation thickness calculation in the CIJ reactor with LMS for $Re = 300$ and 600 will be compared with a model proposed by Lee et al. (1980) for the calculation of the striation thickness in CIJ reactors.

The purpose of this model is to estimate the average striation thickness in Reaction Injection Moulding (RIM) lamellar structures. Considering no surface tension effects and that all the kinetic energy of the motion will disappear by viscous dissipation, the *equation of change for kinetic energy* (Bird et al. 2002) can be given by

$$\frac{d}{dt}\left(\frac{1}{2}\rho v^2\right) = -(\delta:\nabla\mathbf{v}) \quad (\text{III.23})$$

in which ρ is the density of the fluid, v is the velocity, δ represents the tensor and $\nabla\mathbf{v}$ is the gradient of the velocity.

Applying Newton's Law of Viscosity (Bird et al. 2002) for incompressible fluids, the equation assumes the form

$$\rho v^3 = -4\mu \frac{dv}{dt} \quad (\text{III.24})$$

in which μ is the viscosity of the fluid.

If the integration is performed with $v = v_{inj}$ at $t = 0$ (velocity at the injectors)

$$v^2 = \frac{v_{inj}^2}{1 + \rho v_{inj}^2 t / 2\mu} \quad (\text{III.25})$$

Considering the relation $\frac{dS}{dt} = -a(t)S$, between the stretching function $a(t)$ and the striation thickness, S , and $dv = a(t)dx$ (Ranz 1979, Lee 1980), it is possible to express the relation between S and the initial striation thickness, S_0 , after the integration of $\frac{d\ln(S)}{dt}$ (Lee 1980),

$$\frac{S}{S_0} = \left(1 + \frac{\rho v_{inj}^2 t}{2\mu}\right)^{-\frac{1}{2}} \quad (\text{III.26})$$

Equation III.26 was used to calculate S , considering $S_0 = W = 1.5 \times 10^{-3}$ m and the final time of LMS, $t = t_f = 0.022$ s. To compare with LMS, the average of S inside a region positioned at 5 mm from the outlet of the chamber was used (see Figure III.30).

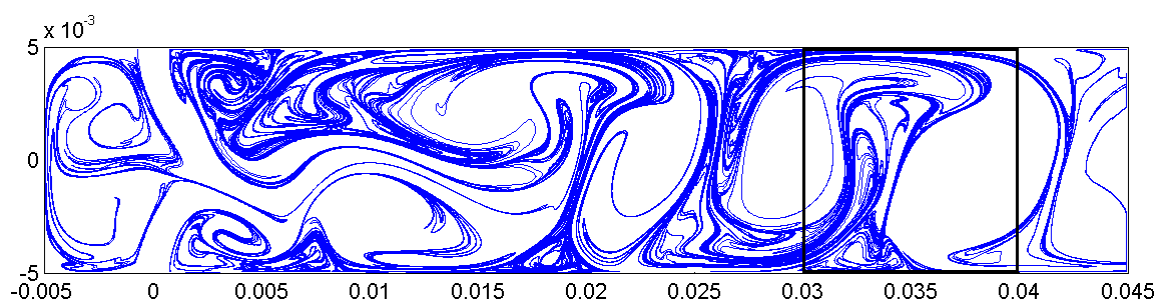


Figure III.30 LMS data for the striation thickness calculation at $Re = 300$ and $t_f = 0.022$ s.

The comparison is shown in Table III.4. As expected, LMS computes mixing scales smaller than the scales predicted by the Lamellar Model for RIM. The LMS and Lamellar Model results are apart approximately one order of magnitude for $Re = 300$ and approximately two orders of magnitude for $Re = 600$. This difference is acceptable since the considerations of both methods are quite different.

Table III.4 Comparison of S/W from LMS and Lamellar Model, at $Re = 300$ and 600 .

LMS vs Lamellar Model		
	LMS	Lamellar Model
Re = 300	2.9×10^{-3}	1.1×10^{-2}
Re = 600	3.4×10^{-4}	1.0×10^{-2}

III.7 Computational Aspects

The CFD simulations of CIJ that provided the velocity fields for LMS and DLMS were run in 2 nodes of a computational cluster (FEUP) Intel® Xeon® with 16 cores at 2.1 GHz and 64 GB of RAM. As in the previous chapter, a 2D CIJ simulation takes ca. 5 days to run 10τ , 0.42 s flow time (5.1×10^4 time steps).

III.7.1 LMS Analysis in CIJ

LMS was run in MATLAB® R2018a, using a x64-based processor Intel® Core™ i7-2600 with 4 cores at 3.40 GHz and 8 GB of RAM. The MATLAB® code of LMS for CIJ is shown in Appendix D.4.1.

In LMS, as the flow time increases, the length of the interface of particles grows and the number of particles gets larger. For chaotic flow regimes, the interfacial area generation is exponential which has implications in the LMS computation time.

For passive mixing, a LMS run until the particles exit the mixing chamber takes less than a minute to simulate. For $Re = 600$, the particles exit the reactor at iteration 127, which has ca. 6.3×10^4

particles (see Figure III.31a). From this point, the time that each iteration takes to run increases. For a full chamber (Figure III.31b), between iteration 226 and 227, LMS took 2 hours to perform the calculations with 3.0×10^6 particles.

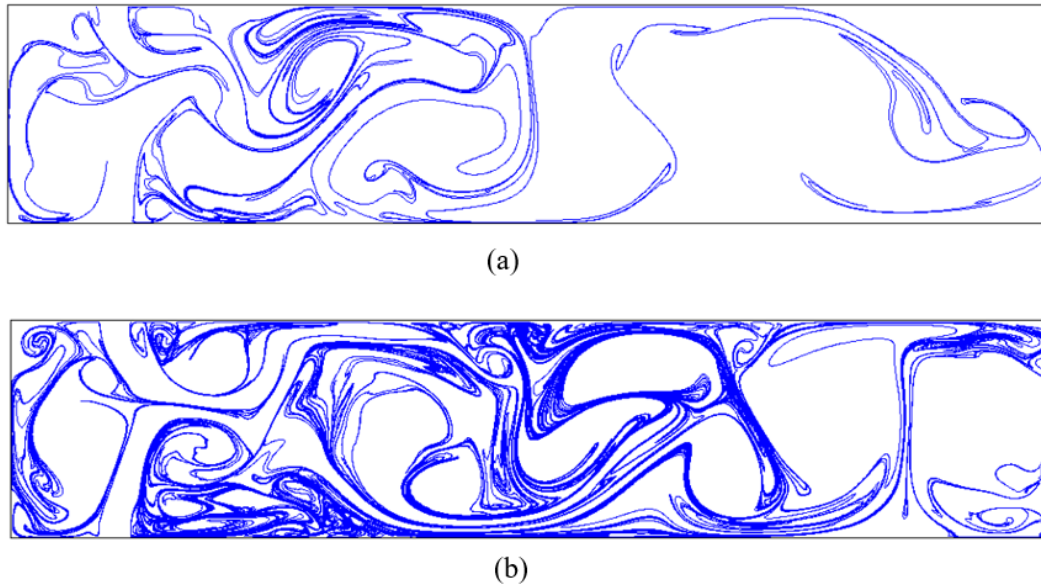


Figure III.31 LMS applied to the 2D CIJ reactor for $Re = 600$ at: (a) iteration 127 and (b) iteration 227.

Comparing with the 2D CFD simulations that were used to obtain the velocity fields, LMS takes significantly less time. In Table III.5, is shown the comparison of the CPU time (normalized by the flow time) between LMS (one simulation) and a CFD simulation (which takes approximately 5 days to run as sated in Section II.4). It is visible that the LMS CPU time is between one and two orders of magnitude lower than the CFD simulations. In this way, the additional time to study mixing, using LMS, is low when compared with the high computation time that would be associated with a mesh refining for CFD simulations in order to reach the smallest strias down to 10^{-6} m.

Table III.5 CPU time/flow time of LMS and CFD simulations, at $Re = 300$ and 600 .

	CPU Time	
	LMS	CFD
$Re = 300$	1.1×10^4	5.2×10^5
$Re = 600$	2.2×10^4	1.5×10^6

III.7.2 DLMS Analysis in CIJ

DLMS was run in the same device as LMS, a Desktop PC with a x64-based processor Intel® Core™ i7-2600 with 4 cores at 3.40 GHz and 8 GB of RAM. The MATLAB® code of DLMS is shown in Appendix D.5.

With the DLMS algorithm, it was possible to run 321 iterations of the 2D CIJ case for $Re = 600$ which corresponds to 0.027 s, ca. 30% more than the time simulated with the original LMS (see Figure III.32). The computation time for each time step (iteration) of LMS is more than the double of DLMS. As an example, iteration 184 (flow time = 0.015 s) takes 7 minutes with LMS and 3 minutes with DLMS.

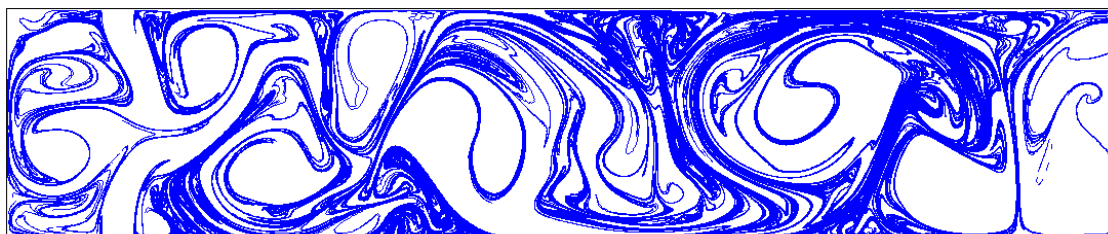


Figure III.32 DLMS in the 2D CIJ reactor for $Re = 600$ at 0.027 s.

III.7.2.1 Interpolation Comparison

At each iteration, the velocity of the particles is interpolated with the Eulerian velocity data obtained from the CFD simulation. Two interpolation schemes were used to obtain the local instantaneous velocity of the particles (step 5 of the DLMS algorithm): a first order interpolation, and a cubic spline using MATLAB[®] function *interp2* (which was used in LMS).

Both methods give approximately the same tracking of the mixing dynamics as shown in Figure III.33. Moreover, the interfacial area generation is similar for both cases as shown in Table III.6. In fact, parameter b of the interfacial area generation fitting ($\alpha = ae^{bt}$ obtained with data until 0.006 s flow time) differs less than 0.6 %.

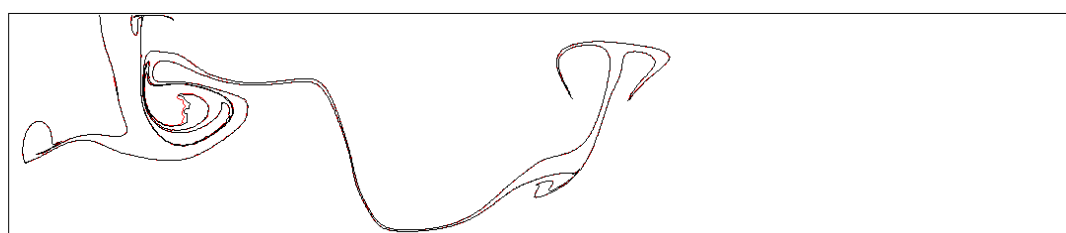


Figure III.33 Particle tracking for $Re = 600$ at 0.006 s. DLMS with first order interpolation in black, and DLMS with *interp2* in red.

Table III.6 Exponential fitting of DLMS with *interp2* and first order interpolation, at $Re = 600$.

Exponential Fittings		
	a	b (1/s)
DLMS with first order	4.8 ± 3.0	$5.87 \times 10^2 \pm 35$
DLMS with <i>interp2</i>	4.7 ± 3.0	$5.84 \times 10^2 \pm 35$

At the beginning of DLMS, e.g., iteration 69 which corresponds to 0.006 s, both algorithms are fast, ca. 17 seconds of total computing time. The CPU time of DLMS starts to increase when the vortex dynamics in the chamber develop, which implies a higher generation of interfacial area associated to a larger number of particles. In those cases, the choice of the interpolation method is significant. For larger flow time, e.g., iteration 184 to 185, corresponding to 0.015 s (Figure III.34), takes 60 minutes with *interp2*, and 3 minutes with a first order interpolation (Matos et al. 2020).

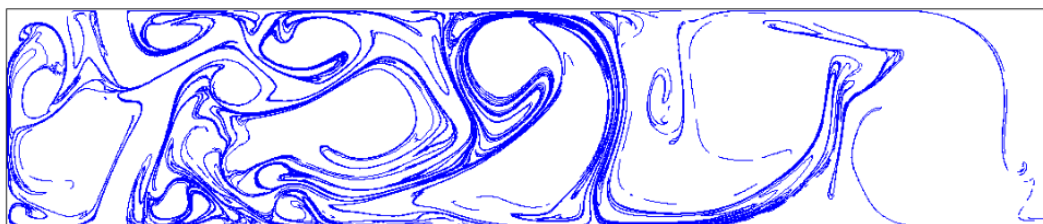


Figure III.34 Particle tracking with DLMS for Re = 600 at 0.015 s.

III.7.3 Striation Thickness Analysis in CIJ

The striation thickness algorithm was run in MATLAB® R2018a, using a x64-based processor Intel® Core™ i7-2600 with 4 cores at 3.40 GHz and 8 GB of RAM. The MATLAB® code for the striation thickness computation is shown in Appendix D.7. The computation of the striation thickness for all particles, 3.0×10^6 particles for Re = 600, at the final time of LMS, 0.022 s (iteration 227), takes approximately 1 day.

III.8 Conclusions

A new Lagrangian method to quantify mixing scales was developed, the Lagrangian Mixing Simulation (LMS) algorithm. This method uses particles to track the filling front of the fluids inside reactors. LMS was used to measure the interfacial generation and the striation thickness of flows. For the striation thickness, a new algorithm was also developed.

LMS was applied to passive mixing in the CIJ reactor. The LMS tracking has shown a pattern similar to the vorticity maps of CFD. For an inlet Re below the critical value the interfacial area generation is linear. For Re above the critical value, the interfacial area is exponential, characteristic of chaotic flows. The striation thickness of chaotic flows decreases to values lower than 10^{-6} m.

For flows with a larger generation of interfacial area, such as active mixing, a modified version of LMS was developed, the Diffusive Lagrangian Mixing Simulation (DLMS) algorithm. This method splits the filling front for mixing scales lower than a threshold value, ξ .

DLMS was applied to active mixing in the CIJ reactor. The mixing patterns of DLMS were similar to the CFD maps, showing that DLMS captures all the relevant features of mixing. The interfacial area generation measurement has shown that the interfacial area is larger as the frequency of modulation decreases and the amplitude of the modulation increases. This agrees with the higher energy of the principal frequency, mentioned in Chapter II.

Chapter IV – NETmix Topology Optimisation

In Chapter II, the reduced model ExtendedNUB was numerically validated and the CFD simulations have shown the overall mixing pattern of NETmix. In Chapter III, a new Lagrangian algorithm, LMS, was developed to characterize mixing scales. In this chapter, CFD simulations and LMS will be applied to perform detailed hydrodynamics studies in order to characterize mixing inside the NETmix chambers. From these studies, the NETmix network topology will be optimised in terms of the ratio between the chamber diameter and the channel width, D/d .

As will be shown further in this work, the NETmix system presents a chaotic behaviour. In this way, the State of the Art of this chapter is focused on reviewing important characteristics of chaotic systems. After that, a modified version of LMS, Batch Lagrangian Mixing Simulation (BLMS) will be developed to optimise the NETmix topology.

Considering one chamber of the NETmix reactor, “perfect” mixing occurs when the composition of the fluids exiting the mixing chamber is diluted by a factor of 2 in relation to the inlet composition. To optimise the NETmix network, BLMS will be applied to identify the topology where the outlet fraction is closest to 0.5.

The mixing properties of NETmix are related with its chaotic behaviour. To extend the knowledge of the *NETmix chaotic system*, hydrodynamics studies of the velocity, vorticity and strain rate will be performed. Phase diagrams as well as Poincaré maps will be analysed to assess the different states of chaotic behaviour of NETmix, which will be confirmed by a spectral analysis.

IV.1 State of the Art

IV.1.1 Chaotic Systems

Chaos is the word used to define systems with a non-periodic behaviour, the *chaotic systems*. In *deterministic* systems, the initial condition determines the response of the system. In contrast, chaotic systems have a random behaviour which depends on the initial conditions (Hilborn, 2001).

One of the most well-known chaotic systems was presented by Lorenz, who modelled the flow between plates at different temperatures. As parameters of the mathematical model were varied, Lorenz noticed that the system would respond differently, forming a “butterfly” shaped structure, as shown in Figure IV.1.

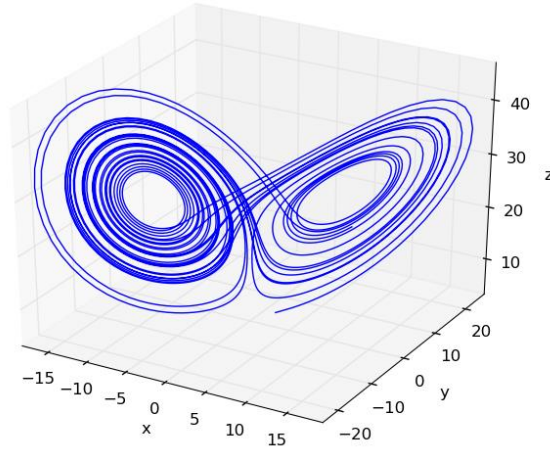


Figure IV.1 Lorenz attractor (from Gribble and Kistemaker 2012).

Figure IV.1 shows an apparent *periodic behaviour*, i.e., the trajectories of the system are repeated after a certain time, forming a similar path. The ensemble of points to which the trajectories approach as the number of iterations goes to infinity is the so-called *attractor* (Hilborn, 2001). Since the coordinates of the data points of the attractor are never repeated (hence the term *apparent periodic behaviour*), the shape of the attractor changes as new points (iterations) are added. In this way, the *line* that forms the attractor has a *fractal* dimension (Tamás 1992, Kenneth 2003).

A method that is frequently used to quantify the fractal dimension is the *box-counting dimension*. In this approach, “boxes” are used to measure the dimension, $\mathcal{N}$, of the attractor. The boxes are either a line with size l_b (for 1D cases), a square (2D) or a cube (3D) with edge, l_b . Considering a 2D attractor or fractal, the boxes are positioned over the points of the structure, as shown in Figure IV.2. The number of boxes, n_b , that are needed to cover all the points corresponds to the dimension of the fractal or attractor. As the size of the box, l_b , decreases, the number of boxes, n_b , increases. Ideally, $l_b \rightarrow 0$; thus, the accuracy of $\mathcal{N}$ depends on the computational resources. If $\mathcal{N}$ is an irrational number, the attractor is called *strange attractor* (Hilborn, 2001).

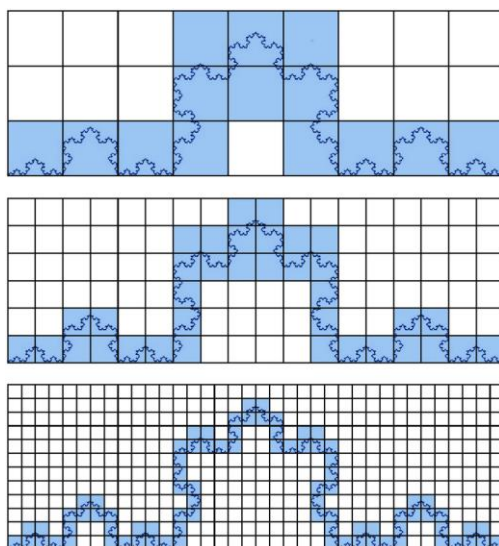


Figure IV.2 Box-counting method (from Pilgrim and Taylor 2018).

Chaotic systems are sensitive to “environmental” changes. The sudden alteration of the behaviour of the system due to parametrical changes is called *bifurcation*. In this way, the bifurcation delimits the transition between two distinct responses of the system.

The transition to chaos can occur in two distinct ways, via *Local Bifurcations*, in which the attractor can appear and disappear. Or via *Global Bifurcations*, in which the attractor is maintained. In both *routes*, the shape of the attractor can change if different parameters are used.

Of the local bifurcations makes part the *Quasi-periodicity*. The quasi-periodic behaviour is characterized by the presence of at least two different and discrete frequencies associated to the motion (Hilborn, 2001). When a control parameter is changed, if a second periodicity appears, a *Hopf bifurcation* occurs. In some cases, when the control parameter is changed further, the motion can become chaotic. If this happens, the route is called *Ruelle-Takens scenario* (Ruelle and Takens 1971).

Intermittency is another route in which the system gives chaotic responses alternated with apparently periodic behaviour. If the attractor suddenly disappears or changes its size as a control parameter is changed, a *crises bifurcation* occurs.

IV.2 NETmix Topology Optimisation – Macromixing

Mixing at larger scales, i.e., *macromixing*, can be assessed in the NETmix reactor through the visualization of the overall flow patterns using tracer simulations, which measure the relation between the inlet and the outlet fluid composition, as shown in Figure I.1. In each NETmix chamber, if the composition of the fluid that exits the mixing chamber is diluted by a factor of 2 in relation to the composition of the fluid that entered in the chamber, perfect mixing occurs. The

overall mixing capacity of the NETmix reactor is then 2^n , in which n represents the number of chambers. The composition of the fluid that exits the NETmix network at the top row is diluted 2^n times in relation to the composition of the fluid that entered in the NETmix network at the bottom row.

A way to evaluate the degree of mixing in the NETmix reactor is to use particles to monitor the distribution of the outlet fraction of the fluids being mixed. Considering one chamber, if the fraction of particles injected at the left inlet that exit the chamber through the right outlet is 0.5, the dilution factor is 2 and mixing is perfect. In this work, the algorithm Batch Lagrangian Mixing Simulations (BLMS) was developed to implement this methodology.

The mixing capacity of reactors is highly dependent on the device topology. Since its conception, it was noticeable that the configuration of the network has a major impact on the NETmix performance (Laranjeira 2005, Gomes 2011). One of the first works was focused on the connection between the chambers and channels. In 2005, to study the NETmix network design, Laranjeira used a network model where the chambers were modelled as perfectly mixing zones and the channels as perfect plug flow segregation zones. The results of the ratio between the volume of the channels and the volume whole network led to the present NETmix configuration, in which one chamber is connected to four channels at an angle of 45° . Previous works have also shown that macromixing and micromixing in NETmix depend on the number of chamber rows in the direction of the flow and on the injection scheme of the reactants (Laranjeira et al. 2009, Laranjeira et al. 2011).

In this work, the NETmix topology in terms of the ratio chamber diameter/channel width, D/d , will be optimised in order to achieve a dilution factor of 2 inside the NETmix chambers. For that, BLMS will be applied to the ExtendedNUB model to understand how mixing is influenced by the ratio D/d .

IV.2.1 Batch Lagrangian Mixing Simulation (BLMS)

Batch Lagrangian Mixing Simulations (BLMS) was developed from the Lagrangian Mixing Simulation (LMS) algorithm, presented previously in this work. In LMS, a continuous injection of particles is used to track the filling front of fluids, according to

$$\mathbf{X}_{i,j} = \mathbf{X}_{i-1,j} + \mathbf{v}_{i-1,j} \Delta t_{LMS} \quad (\text{IV.1})$$

in which $\mathbf{X}_{ij}$ is the matrix of the positions of the particles, Δt_{LMS} is the LMS time step (which is tenfold the Δt of the CFD simulation that provides the velocity fields) and $\mathbf{v}$ is a matrix with the velocities of the particles; i represents the time and j the particle.

The size of the position matrix of the particles, $\mathbf{X}_{ij}$, grows in LMS since new particles are inserted when two consecutive particles become apart more than 1.0×10^{-4} m. This step of inserting new particles is used to keep the accuracy of the tracking since the main objective of LMS is to characterize micromixing in which it is intended to represent all the mixing scales. In this way, with LMS it is not possible to follow the path of each particle since the identifiers of the particles, j , change when a new particle is inserted.

To overcome this issue, BLMS was developed. To quantify the degree of mixing in the NETmix reactor only macromixing needs to be analysed, i.e., the relation between the inlet and outlet of one mixing chamber. Thus, there is no need of representing all the mixing scales and fixed particles can be used. In this way, in BLMS the number of particles is constant at each injection which enables to follow the path of each particle from the injection to the outlet. When all the particles of the first injection, at flow time t_0 , have left the mixing chamber, a new injection starts at $t_0 + \Delta t_{BLMS}$, in which the BLMS time is tenfold the time step of the CFD simulation that provided the velocity fields, $\Delta t_{BLMS} = 10\Delta t$. Each injection is performed during n_i iterations, until all the particles have left the mixing chamber. The process is then restarted, and a new injection is performed at $t_0 + \Delta t_{BLMS} + \Delta t_{BLMS}$ and so on, until the total number of injections, nt , is reached. In this way, a series of injections are performed with interval Δt_{BLMS} until nt (Matos et al. 2021). The injection procedure is represented in Figure IV.3, in which two series of n_p particles (the number of particles will be discussed further in this section) are injected, a red series at the right inlet and a blue series at the left inlet. The example of Figure IV.3 shows BLMS applied to chamber C6 of the 2D ExtendedNUB model with $D/d = 6.65$ for $Re = 300$ (Matos et al. 2021).

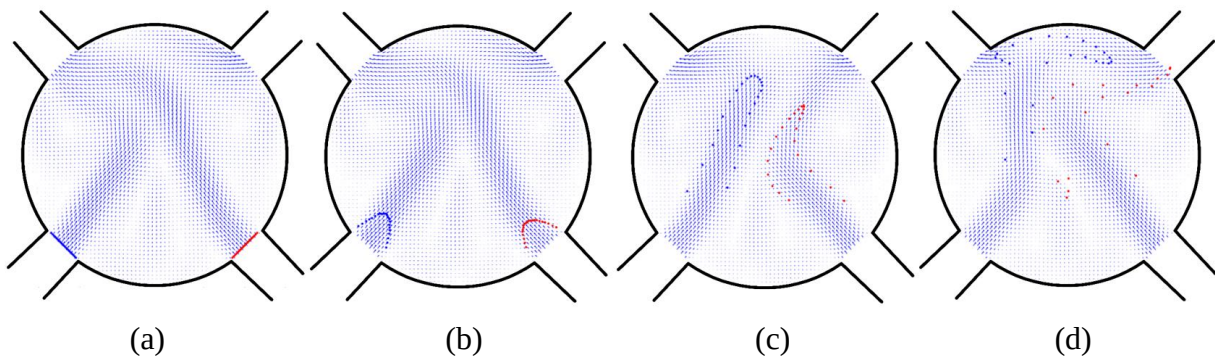


Figure IV.3 Injection of particles over the velocity field in one NETmix chamber.

In Figure IV.3, from (a) to (d) the velocity field vectors show an oscillating behaviour inside the mixing chamber. The oscillating behaviour is also visible on the path of the particles which follows the inlet streams (Figure IV.3b and Figure IV.3c) and is later engulfed by vortices (Figure IV.3d). In Figure IV.3d, it is possible to see the particles leaving the mixing chamber, which enables to register the number of blue and red particles that exit the mixing chamber through the left or right outlet. A full video of the injection of particles is shown in BLMS.mp4 of the *Mixing_and_Controlled_Combustion_in_NETmix_videos* folder.

In BLMS, the position of the particles at the inlets, Figure IV.3a, depends on the flow field, the zones with higher velocity have a larger density of particles. i.e., the distance between the particles is smaller. The velocity profile, v_{x_j} , at the inlets is close to a parabolic profile, as shown in Figure IV.4. The distance between two consecutive particles, d_{x_j} , was calculated in order to have $\frac{v_{x_j} + v_{x_{j-1}}}{2} dx_j = \text{constant}$. The algorithm for the calculation of the distance between the particles, d_{x_j} , for half of the domain, $P1$ to Pn , (the other half is symmetrical) is presented below (Matos et al. 2021).

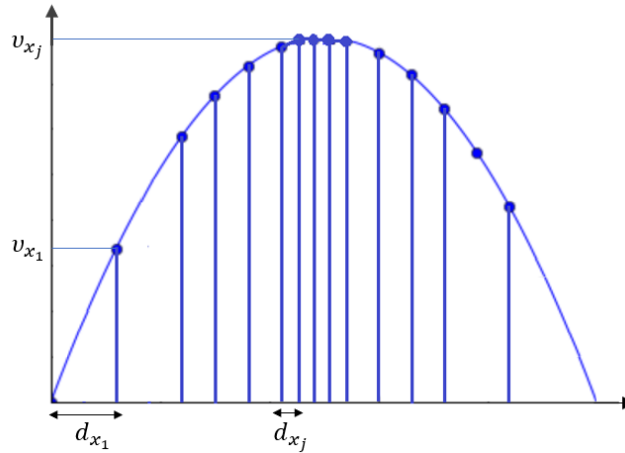


Figure IV.4 Scheme of the calculation procedure of dx_j .

Particles Distribution Over the Inlet Algorithm

1. Select the coordinates x and y for the first and last particles ($P1$ and Pn), according to the inlet channel coordinates;
2. Draw a line between $P1$ and Pn ;
3. Build vectors $\mathbf{x0}$ and $\mathbf{v0}$ with x -coordinates and x -velocities, respectively, of the mesh cells that are crossed by the line drawn in 2;
4. Start with $dx_j = 2.5 \times 10^{-5} \text{ m}$;

5. Obtain the position of particle $x_j = x_{j-1} + dx_j$;
6. Calculate the velocities of the particles from an interpolation with the velocity field, using *interp1*;
7. Calculate the area below the v_x curve: $A_j = \frac{v_{x_j} + v_{x_{j-1}}}{2} dx_j$;
8. Calculate the difference between consecutive areas: $\Delta A = |A_j - A_{j-1}|$;
9. Reduce dx_j by a factor of 10^{-7} m and repeat steps 5 to 8 for current particle j until consecutive areas are $\Delta A \leq 10^{-8} \text{ m}^2/\text{s}$;
10. Repeat steps 4 to 9 until the coordinates of Pn are reached;
11. The number of intervals, dx , that are needed to reach Pn is used to calculate half of the number of particles, $np = dx + 1$. The total number of particles after the symmetry is $np = 2(dx + 1)$.

Figure IV.5 shows the beginning of the particle tracking after one injection where is visible that on the tip of the parabolic profile, the density (number) of particles is larger.

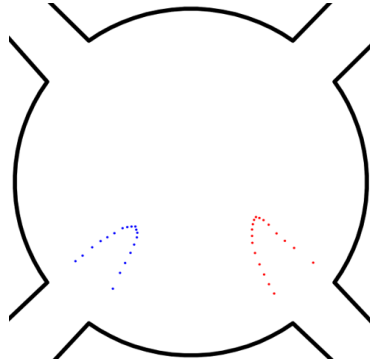


Figure IV.5. Profile of the injection of particles in one NETmix chamber.

IV.2.1.1 Bach Lagrangian Mixing Simulation (BLMS) Algorithm

The BLMS algorithm is presented next. The block diagram is shown in Figure IV.6.

1. Specify t_0 , np , Δt , ni and nt ;
2. Load the first velocity field file, $i = 1$, for the first injection, $n = 1$, at $t_0 + (n - 1)\Delta t_{BLMS}$;
3. Position the particles over the inlet;
4. Calculate the velocities of the particles with MATLAB[®] function *interp2*;
5. Recalculate the position of the particles with the LMS equation (Equation III.4);

6. Register the number of blue and red particles that exit the mixing chamber on the left or right outlet, n_b^l , n_b^r , n_r^l and n_r^r ;
7. Load the next velocity field, $i+1$, at $t_0 + (i - 1)\Delta t_{BLMS}$;
8. Repeat Steps 4 to 6 until $i = ni$;
9. Load the first velocity field file, $i = 1$, for the next injection, $n = n + 1$, which starts at time $t_0 + (n - 1)\Delta t_{BLMS}$;
10. Repeat Steps 3 to 8 until $n = nt$.

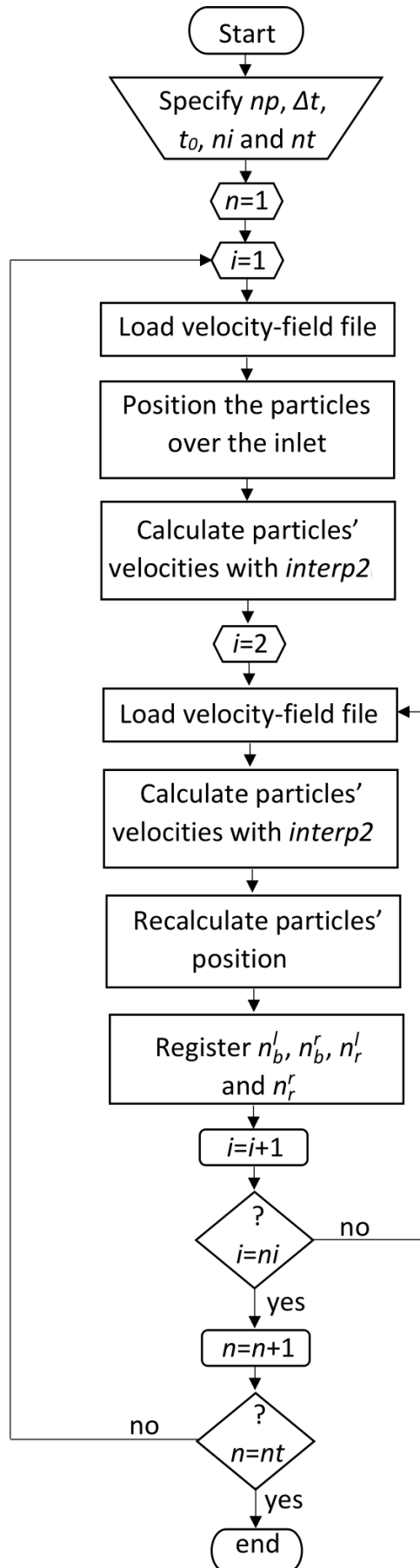


Figure IV.6 Batch Lagrangian Mixing Simulation (BLMS) block diagram (Matos et al. 2021).

IV.2.2 Study of the Ratio Chamber Diameter/Channel Width

To assess how the ratio, chamber diameter/channel width, D/d , influences mixing, BLMS was applied in the 2D ExtendedNUB model for several chamber diameters $6.25 \times 10^{-3} \text{ m} < D < 7.25 \times 10^{-3} \text{ m}$, the channel length, $l = 2.0 \times 10^{-3} \text{ m}$, and channel width, $d = 1.0 \times 10^{-3} \text{ m}$, were kept constants. For each D/d , a CFD simulation, with the model of Section II.3.3 (see Figure II.14a), was performed at $Re = 300$ to provide the velocity field for the injection of particles with BLMS. The velocity field data of chamber C6 was used to perform $nt = 5000$ injections, each one during 0.58 s flow time ($ni = 510$ iterations). The first injection was made at $t_0 = 17 \text{ s}$ flow time. The number of particles for each series depends on the ratio D/d and varied from 25 to 35.

To evaluate the particles distribution at the outlet, the exit conditional probabilities were computed. P_b^l is the probability of a blue particle exiting the mixing chamber on the left outlet, P_b^r is the probability of a blue particle exiting the mixing chamber on the right outlet, P_r^l is the probability of a red particle exiting the mixing chamber on the left outlet and P_r^r is the probability of a red particle exiting the mixing chamber on the right outlet. These probabilities were calculated according to

$$P_b^l = \frac{n_b^l}{n_b^l + n_b^r} \quad (\text{IV.2a})$$

$$P_b^r = \frac{n_b^r}{n_b^l + n_b^r} \quad (\text{IV.2b})$$

$$P_r^l = \frac{n_r^l}{n_r^l + n_r^r} \quad (\text{IV.2c})$$

$$P_r^r = \frac{n_r^r}{n_r^l + n_r^r} \quad (\text{IV.2d})$$

in which n_b^l is the number of blue particles that exit on the left outlet, n_b^r is the number of blue particles that exit on the right outlet, n_r^l is the number of red particles that exit on the left outlet and n_r^r is the number of red particles that exit on the right outlet (see Step 6 of the BLMS algorithm).

The results presented in Figure IV.7 show that the relation between macromixing in the NETmix chambers and the ratio D/d is represented by a butterfly shaped graphic centred at $D/d = 6.75$. For all the ratios, the graphic is symmetrical in relation to the line $P = 0.5$. For both, red and blue particles, the ratios $D/d = 6.65$ and $D/d = 6.85$ provide the best mixing since the exit conditional probabilities are very close to 0.5 which indicates that the dilution factor of 2 is attained. The exit

conditional probabilities are $P_b^l = 0.51$, $P_b^r = 0.49$, $P_r^l = 0.48$ and $P_r^r = 0.52$ for $D/d = 6.65$, and $P_b^l = 0.48$, $P_b^r = 0.51$, $P_r^l = 0.47$ and $P_r^r = 0.53$ for $D/d = 6.85$. In this way, the best ratio is $D/d = 6.65$ since the probabilities are closer to 0.5.

Analysing the results of all the ratios, $D/d = 6.75$ has an exit probability closest to 0.5. However, this is only verified for the blue particles. As the ratios move from the middle ratio $D/d = 6.75$ to the edges, $D/d = 6.25$ and $D/d = 7.25$, the probabilities move away from 0.5 and mixing is less good.

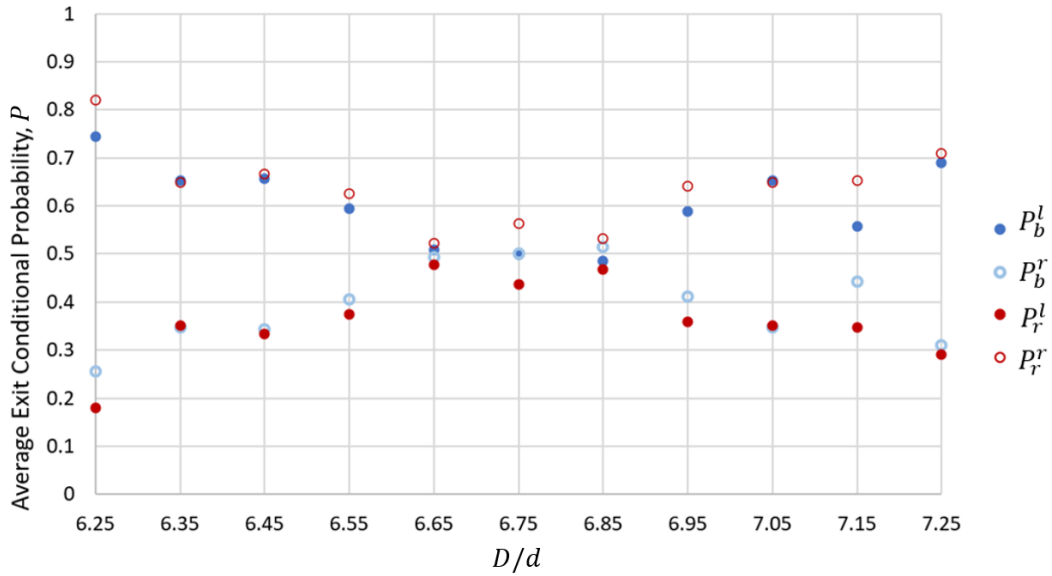


Figure IV.7 Exit conditional probability for $6.25 < D/d < 7.25$ in chamber C6 of ExtendedNUB at $Re = 300$.

IV.3 NETmix Topology Optimisation – Micromixing

In the previous section, *macromixing* studies, i.e., the relation between the inlets and the outlets of the NETmix reactor, were performed, which enabled to establish a range of $6.65 < D/d < 6.85$ with a nearly perfect degree of mixing. In this section, *micromixing*, i.e., mixing at smaller scales inside the NETmix chambers, will be analysed in detail in order to characterize the mechanisms that are responsible for mixing and assess their relation with the degree of mixing for different D/d . Micromixing studies will enable to quantify the mixing scales inside the NETmix chambers and characterize the chaotic laminar regime of the NETmix system. The oscillating behaviour of the inlet jets, represented in Figure IV.8, which is responsible for mixing, will also be evaluated.



Figure IV.8 Oscillation of the NETmix jets.

IV.3.1 Lagrangian Mixing Simulation (LMS) in the NETmix Reactor

To study micromixing in NETmix, the LMS algorithm was applied to chamber C6 of the ExtendedNUB geometry.

To start, the LMS particles are positioned at each inlet channel of chamber C6, over the CFD flow field: $np_l = 18$ blue particles at the left and $np_r = 18$ red particles at the right. The particles are equally distributed and completely comprise the length of the inlet, $d = 1.0 \times 10^{-3}$ m, as shown in Figure IV.9.

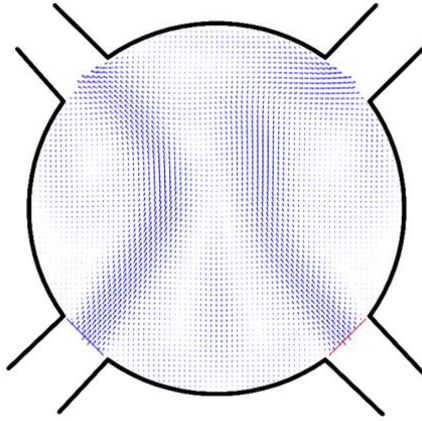


Figure IV.9 LMS particles at the inlet of chamber C6.

The particles are tracked along with the flow time, and their position is recorded in two matrices, $\mathbf{Xl}_{i,j}$ and $\mathbf{Xr}_{i,j}$, which contain the coordinates (x,y) of each particle. Each series is tracked separately, according to the LMS equation:

$$\mathbf{Xl}_{i,j} = \mathbf{Xl}_{i-1,j} + \mathbf{vl}_{i-1,j}\Delta t_{LMS} \quad (\text{IV.3a})$$

$$\mathbf{Xr}_{i,j} = \mathbf{Xr}_{i-1,j} + \mathbf{vr}_{i-1,j}\Delta t_{LMS} \quad (\text{IV.3b})$$

in which Δt_{LMS} is the LMS time step, $\mathbf{ul}$ and $\mathbf{ur}$ are the matrices of the velocity vectors; i represents the time step and j the particle number. When two consecutive particles become apart more than $r = 1.0 \times 10^{-4}$ m, a new particle is inserted at halfway of the two particles in order to accurately describe the interface between the mixing fluids (Matos et al. 2018).

Figure IV.10 shows the evolution of the mixing dynamics inside the NETmix chamber. It is visible that the interface of particles is folded and stretched, forming layers of striae. At the inlets, the profile is approximately parabolic as shown in Figure IV.10a. As the flow time increases, the inlet profile is no longer distinguishable and gives place to the vortex shedding that is promoted by the oscillating behaviour of the inlet jets. Figure IV.10b to Figure IV.10d show this oscillating behaviour which can be observed from the direction of the inlet jets that changes from the right (Figure IV.10b and Figure IV.10d) to the left (Figure IV.10c). Figure IV.10b shows the beginning of the vortices formation which are most visible at the sides of the mixing chamber. From Figure IV.10b to Figure IV.10d, the vortices continue to develop, increasing the interfacial area generation. The interface of particles becomes larger and folds according to the vortices. In Figure IV.10d, it is noticeable that the blue and red colours of the map are darker due to the overlap of the tracking interface, which is folded. In fact, a large number of striae are formed as mixing occurs. The length of the interface of particles as well as the striae size will be evaluated next.

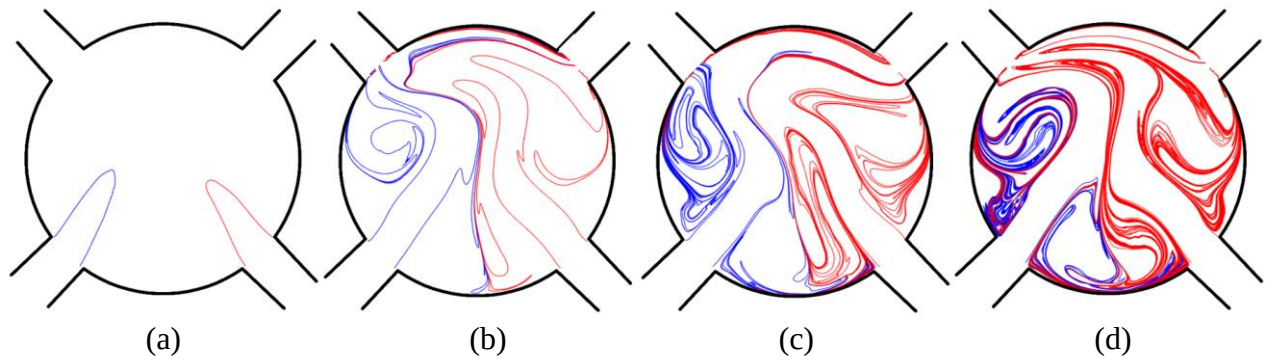


Figure IV.10 LMS particle tracking in chamber C6 of the ExtendedNUB geometry for $Re = 300$ at: (a) 17.01 s, (b) 17.03 s (c) 17.11 s and (d) 17.34 s.

The complete LMS tracking inside the NETmix chamber is shown in the video `LMS_NETmix.mp4` of the folder *Mixing_and_Controlled_Combustion_in_NETmix_videos*.

IV.3.1.1 Interfacial Area Generation Analysis and Striation Thickness Computation

Mixing implies the stretching and folding of the layers of striae which is accompanied by a reduction of the striation thickness and an increase of the interfacial area. The interfacial area is obtained by the length of the tracking interface, according to

$$\alpha = \frac{\sum_{i=1}^{np_l} |\mathbf{x}l_{i,j} - \mathbf{x}l_{i,j+1}| + \sum_{i=1}^{np_r} |\mathbf{x}r_{i,j} - \mathbf{x}r_{i,j+1}|}{s_0} \quad (\text{IV.4})$$

in which $s_0 = 2d = 2.0 \times 10^{-3}$ m, $np_l = 18$ and $np_r = 18$. Note that, in the case of NETmix, as two series of particles are used, the total α is obtained by the sum of the length of both series.

As shown in the previous section of this work, the topology of the NETmix reactor has a major impact on mixing. To analyse the chaoticity of the NETmix reactor and understand how this behaviour is related with the degree of mixing, the interfacial area generation will be calculated for $6.25 < D/d < 7.25$. The chamber diameter, D , was varied from 6.25×10^{-3} m to 7.25×10^{-3} m and the channel width and length were kept constants, $d = 1.0 \times 10^{-3}$ m and $l = 2.0 \times 10^{-3}$ m, respectively.

In chaotic flows, the interfacial area generation is exponential and can be represented by the fitting $\alpha = ae^{bt}$. The Lyapunov exponent $b > 0$ indicates that the system is chaotic (Matos et al. 2018). Figure IV.11 shows the exponential fitting, $\alpha = 63.9e^{20.9t}$ ($R^2 = 0.99$), to the interfacial area generation results for $D/d = 6.65$, during 3τ .

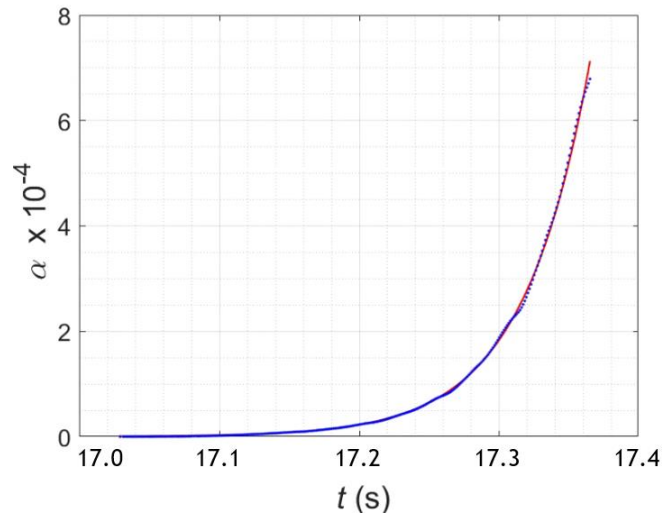


Figure IV.11 Interfacial area generation in chamber C6 during 3τ (simulation points in blue and fitting in red).

The value of parameter a is related to the early evolution of the interfacial area, at the beginning of the particle tracking with LMS. Since α is an exponential function of time, the specific generation of interfacial area is given by $b = \frac{1}{\alpha} \frac{d\alpha}{dt}$, which can be used to compare the interfacial area generation for $6.25 < D/d < 7.25$. Figure IV.12 shows the value of parameter b for each D/d . As shown in the previous section from the macromixing analysis of the NETmix reactor, the best mixing is obtained for the middle ratios $6.65 < D/d < 6.85$, in which $D/d = 6.65$ is the ratio with a dilution factor closer to 2 (exit probability $\cong 0.5$). From the analysis of Figure IV.12 and Figure IV.13, it is possible to conclude that the degree of mixing is associated to the interfacial area

generation. In fact, the best mixing range presents a higher exponential parameter, b . The case with the best mixing, $D/d = 6.65$, has the highest value of b (see Figure IV.12); thus, a larger interfacial area is generated, as shown in Figure IV.13. In both Figures, a peak is visible at $D/d = 6.65$, which coincides with the best mixing ratio according to the macromixing studies. For this ratio, the interfacial area generation is larger than 7×10^4 .

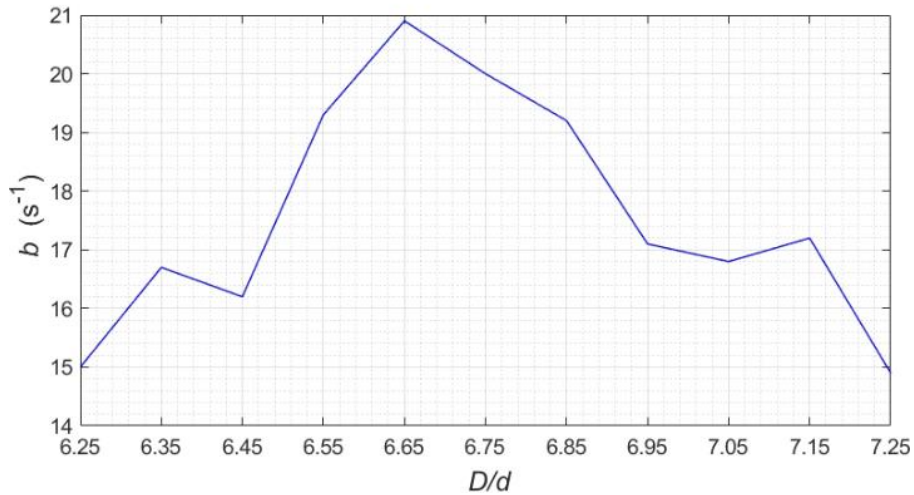


Figure IV.12 Parameter b in chamber C6 with $6.25 < D/d < 7.25$, during 3τ .

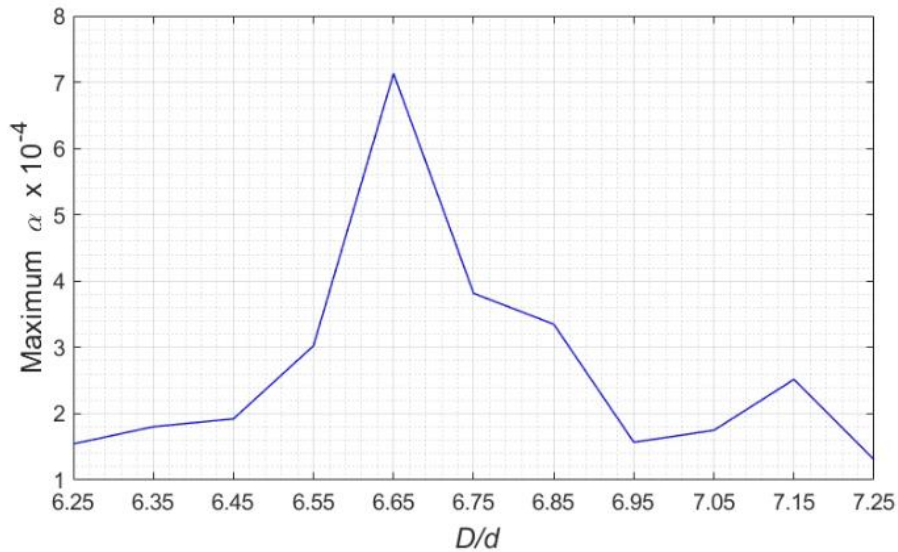


Figure IV.13 Maximum interfacial area generation in chamber C6 with $6.25 < D/d < 7.25$, during 3τ .

As previously explained, the interfacial area generation is associated to a reduction of the striation thickness, S . With LMS it is possible to measure S , considering the distance between two *parallel* layers of fluid (see Figure IV.14b).

As shown in Section III.6.2, the striation thickness was computed inside the Confined Impinging Jets (CIJ) reactor for all the LMS particles at the end of the tracking. However, in the NETmix reactor, since the inlet jets impinge near the centre of the chamber, the size of the jets (approximately 10^{-3} m) would have a major influence on the striation thickness distribution which

would not be representative of the small strias, responsible for the high degree of mixing of NETmix. In this way, the striation thickness will be calculated in eight locals of the mixing chamber C6. An example is shown in Figure IV.14a for $D/d = 6.65$ at 17.34 s. The strias of each local are shown in detail in Figure IV.15.

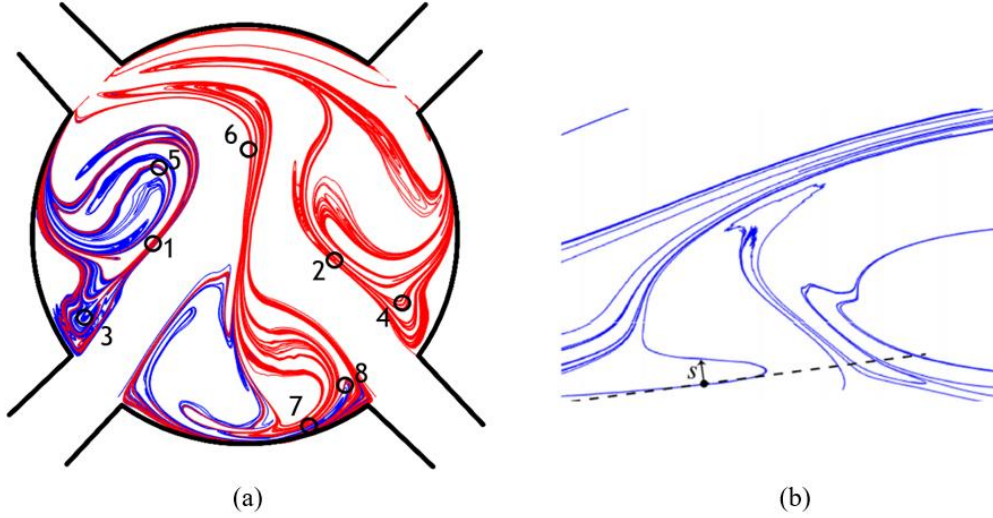


Figure IV.14 (a) Strias of chamber C6 for $D/d = 6.65$ at 17.34 s. (b) Striation Thickness, S , calculation procedure (Matos et al. 2018).

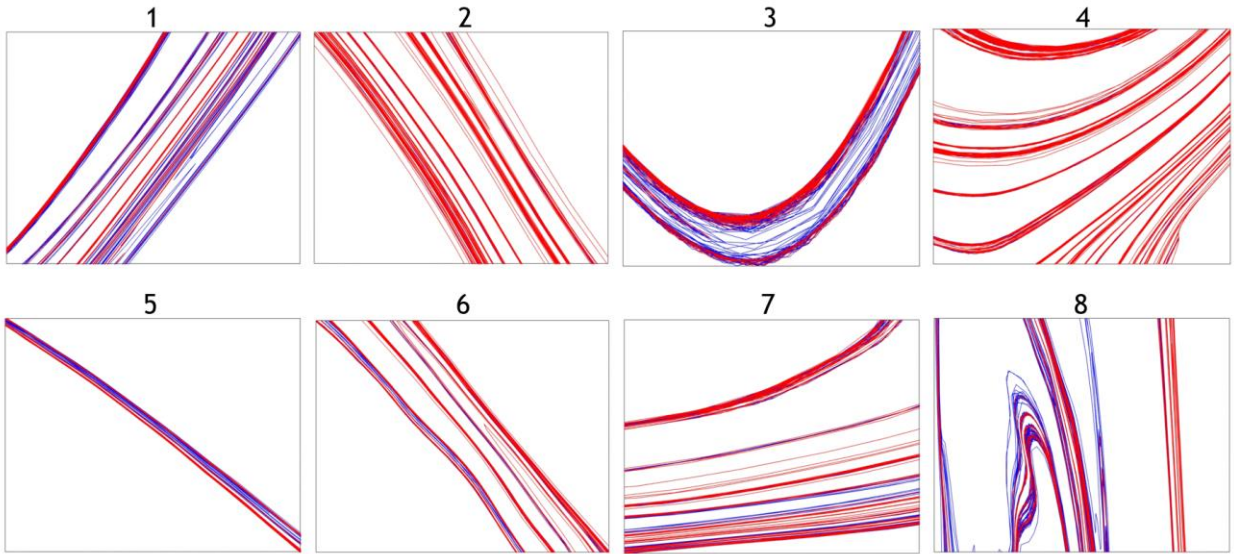


Figure IV.15 Strias of chamber C6 for $D/d = 6.65$ at 17.34 s.

The striation thickness distribution is shown in Figure IV.16 for $D/d = 6.65$. S was calculated in function of the local interfacial area, s_p , i.e., the length of the LMS interface around each particle (see Section III.6.2).

As expected for chaotic systems, the distribution is approximately normal, centred in 10^{-5} m which is the most common strias size. The smallest strias have an order of magnitude of 10^{-8} m (as explained in Section III.6, LMS can compute striation thicknesses below the threshold value of 10^{-6} m). The influence of the inlet jets is visible on the peak at $\cong 10^{-3}$ m, which results from the

calculation of S at the border strias (local 1, 2 and 6 of Figure IV.15). The striation thickness was calculated for $6.25 < D/d < 7.25$, using the same methodology, and the results have shown distributions similar to Figure IV.16.

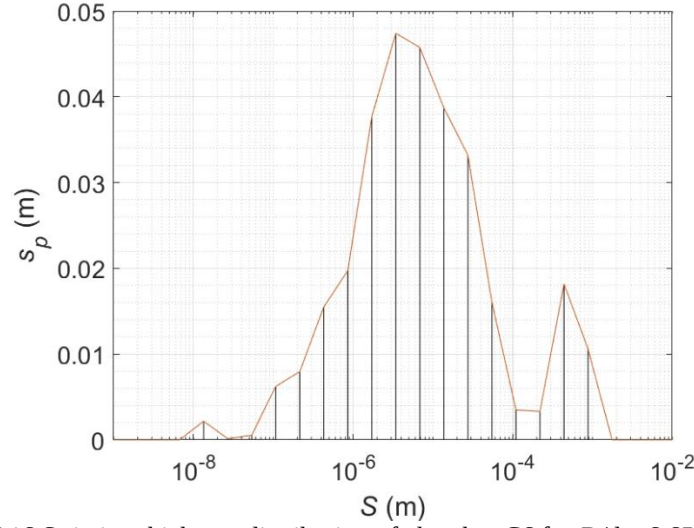


Figure IV.16 Striation thickness distribution of chamber C6 for $D/d = 6.65$ at 17.34 s.

IV.3.2 Tracer Simulation

As shown previously, the ratio $D/d = 6.65$ leads to the best mixing in NETmix. In this section, the ExtendedNUB geometry with this ratio is going to be used to perform a tracer simulation in order to confirm the capacity of BLMS to predict mixing and to conclude the numerical validation of the ExtendedNUB model.

The commercial finite volume CFD software ANSYS® FLUENT™ was used for the tracer simulation, considering the model described in Section II.3.2, with the additional species transport equation

$$\rho \left(\frac{\partial Y_i}{\partial t} + \nabla \cdot \mathbf{u} Y_i \right) = -\nabla \cdot \mathbf{J}_i \quad (\text{IV.5})$$

in which Y_i is the mass fraction of each species, i , and $\mathbf{J}_i$ is the diffusion flux vector, defined as

$$\mathbf{J}_i = -\rho \mathcal{D}_i \nabla Y_i \quad (\text{IV.6})$$

in which $\mathcal{D}_i = 10^{-9} \text{ m}^2/\text{s}$ is the mass diffusion coefficient of species i in the mixture.

The spatial discretization of the geometry is described in Section II.3.1.

The tracer simulation was performed at $\text{Re} = 300$ with the parameters of Section II.3.2. Two fluids, Fluid1 and Fluid2, with water properties were used. The reactor was initially filled with Fluid1 and Fluid2 was injected at the right inlet. Figure IV.17 shows the evolution of the molar fraction of Fluid2.

A video of the full tracer simulation, ExtendedNUB_tracer.mp4, is shown in the folder *Mixing_and_Controlled_Combustion_in_NETmix_videos*.

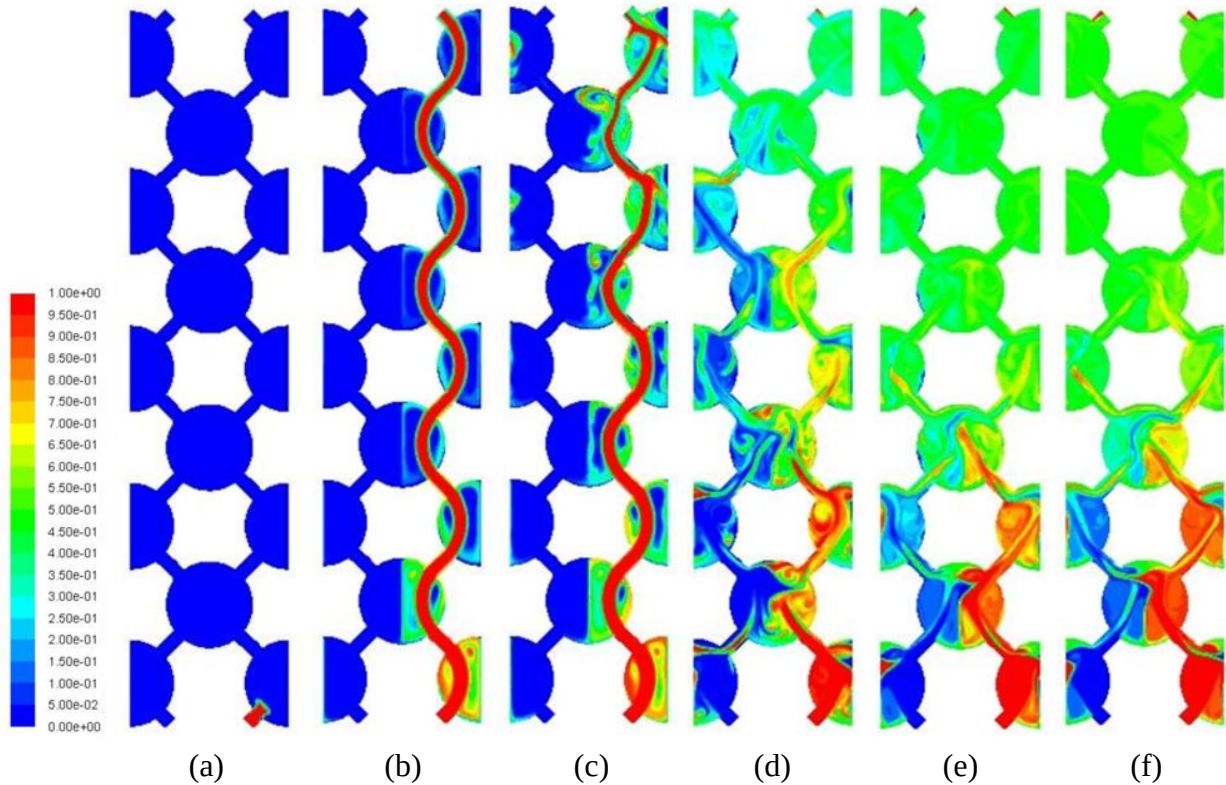


Figure IV.17 Molar fraction of Fluid2 in the ExtendedNUB geometry, for $Re = 300$, at: (a) 0.034 s, (b) 0.94 s, (c) 1.95 s, (d) 2.63 s, (e) 3.52 s and (f) 5.69 s.

Figure IV.17a shows the injection of Fluid2 at the right inlet. In Figure IV.17b, Fluid 2 is only present in the right side of the reactor since the oscillating behaviour of the NETmix jets is still being developed. In less than 2 s, mixing starts to occur and Fluid2 is visible in the left side of the reactor. The mixing process continues and in less than 6 seconds, the average of the molar fraction of Fluid2 in the top chambers, C6 and C8, is already close to 0.5, as shown in Figure IV.17f.

Figure IV.18 shows the history of the molar fraction of Fluid2 in the centre of chamber C6 in which is visible that, from approximately 6 s flow time, the molar fraction of Fluid2 tends to 0.5. The first 5 s correspond to the injection of Fluid2 which starts to occupy the reactor already filled with Fluid1.

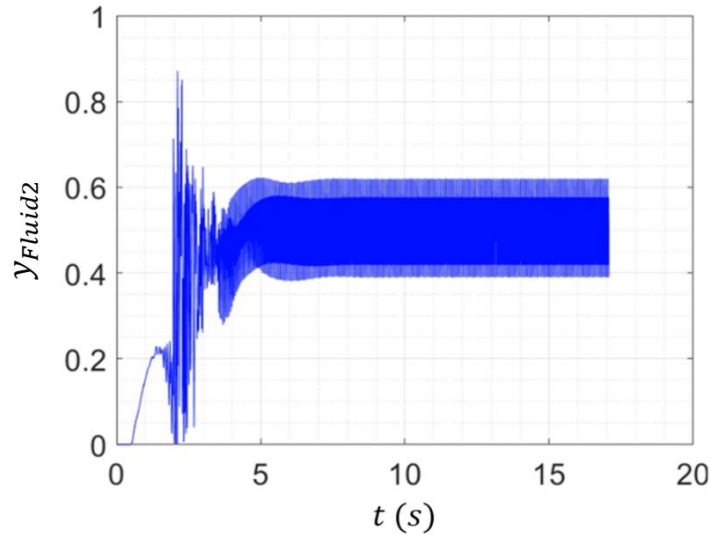


Figure IV.18 Molar fraction history of Fluid2 in the centre of C6 of the ExtendedNUB geometry, for $Re = 300$.

Although it takes ca. 6 s to have nearly perfect mixing inside the NETmix reactor, the oscillations take approximately 10 s to stabilize completely (as already mentioned in Section II.3.3). As shown in Figure IV.19, it is visible that, from 10 s, the oscillations have an *apparently periodic* behaviour, as will be discussed in the next section of this work.

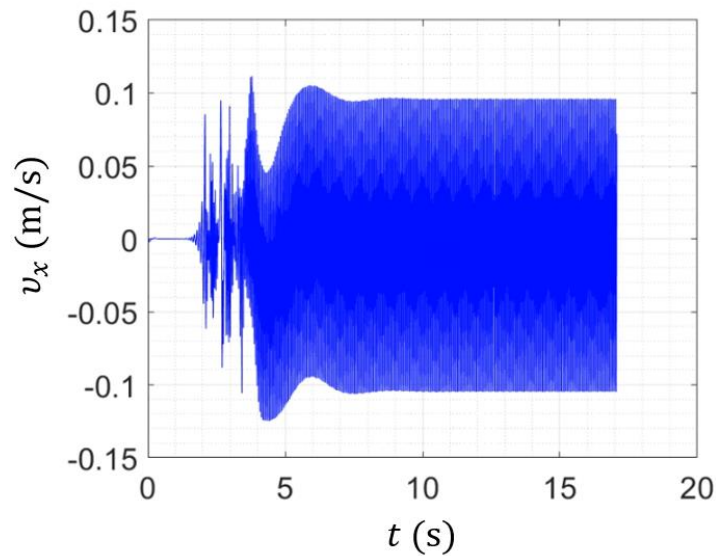


Figure IV.19 x-velocity history in the centre of chamber C6 of the ExtendedNUB geometry, for $Re = 300$.

In order to assess the mixing process of Fluid1 and Fluid2 inside the reactor, the average of the molar fractions between 10 s and 17 s flow time was evaluated in the centre of each channel at the right, r , and at the left, l (see Figure II.12). The result is shown in Figure IV.20 in which is visible that at the fifth row of channels the average molar fraction can be rounded to 0.5. From the fifth row of channels, the average molar fraction continues to approach 0.5, reaching exactly this value at row 8 which is maintained at row 9. In this way, the ExtendedNUB geometry has enough rows to represent the behaviour of a larger NETmix network since perfect mixing is

reached at the top row. Moreover, nearly perfect mixing is obtained from the fifth row of channels, i.e., before chamber C6.

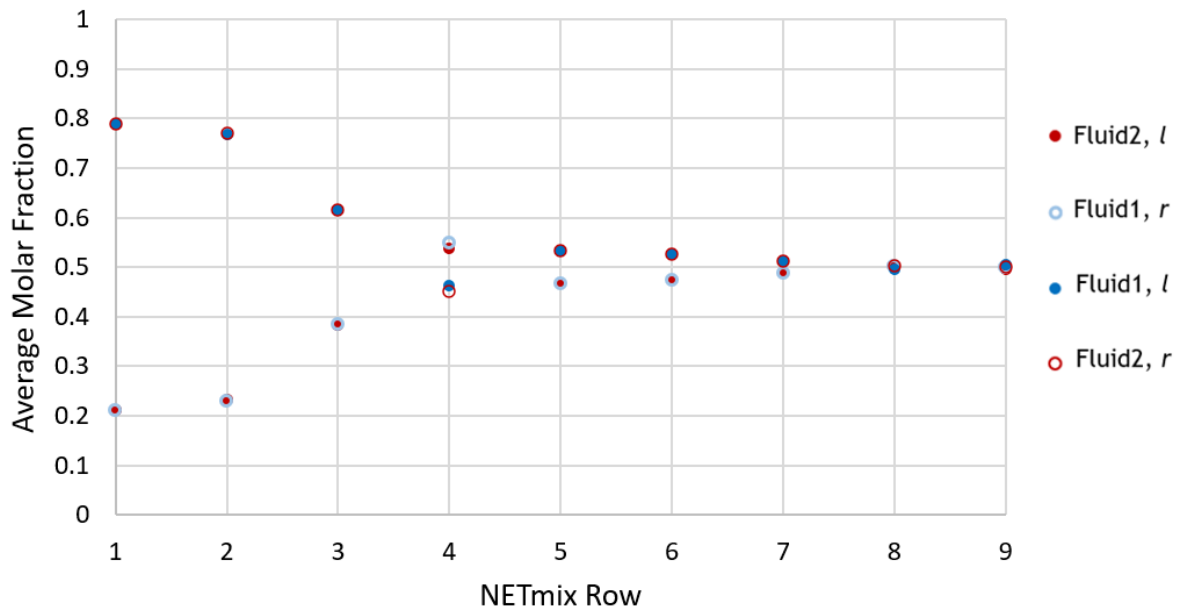


Figure IV.20 Average of the molar fraction of Fluid1 and Fluid2 in the centre of the left and right channels of the ExtendedNUB geometry, for $Re = 300$ between 10 s and 17 s flow time.

Table IV.1 shows the comparison between Fluid2 and the red particles of BLMS (both injected at the left); and the comparison between Fluid1 and the blue particles of BLMS (injected at the right). The difference of the molar fractions in the centre of chamber C6 between BLMS and the tracer simulation is less than 4%. In this way, the injection of particles is a good method to evaluate the performance of reactors.

Table IV.1 Comparison between BLMS and Tracer with CFD in chamber C6.

BLMS vs Tracer				
	<i>rr</i> / Fluid2, right	<i>rl</i> / Fluid2, left	<i>bl</i> / Fluid1, left	<i>br</i> / Fluid1, right
BLMS	0.52	0.48	0.51	0.49
Tracer	0.53	0.47	0.53	0.47

IV.3.3 Chaoticity of the NETmix System

In Section IV.3.1, it was shown that the NETmix system is chaotic from the interfacial area generation analysis, which is exponential. Moreover, previous studies from experiments and CFD simulations have shown that mixing inside the NETmix chambers has chaotic properties due to the vortex shedding that can be observed (Laranjeira et al. 2011, Fonte et al. 2013, Costa et al. 2017, Matos et al. 2021). Since chaotic features occur for a laminar regime at $Re = 300$, the NETmix system is in the *chaotic laminar regime*.

In this section, the chaotic behaviour of the NETmix system will be fully characterised. To understand the oscillating behaviour inside the NETmix chambers, velocity studies of v_x (lateral velocity) and v_y (velocity in the flow direction) will be performed. For that, in the CFD simulations that were previously presented, the velocities were registered in the centre of chamber C6 for $6.25 < D/d < 7.25$. Figure IV.21 shows the y -velocity plot for each diameter ratio, during ca. 5 s flow time (4τ). The amplitude of the velocities is shown in Table IV.2. As shown in the previous sections, as the system approaches the middle ratios, the dilution factor inside the NETmix chambers is close to 2 and better mixing occurs. This behaviour can also be observed on the histories of the velocity. For the smallest and largest ratios, $D/d = 6.25$ and 7.25 , the y -velocity has an irregular behaviour with an amplitude of approximately 0.2 m/s (see Table IV.2). As the ratios approach the middle values, the y -velocity history becomes regular with a smaller amplitude between 0.05 and 0.1 m/s (see Table IV.2). From $D/d = 6.35$ to 7.15 , the y -velocity has an *apparently periodic* behaviour since the “waves” formed by the oscillations seem to be repeated with a certain periodicity. For the best ratios $D/d = 6.65$ and $D/d = 6.85$, the period of the waves is smaller. The frequency of oscillation of the NETmix chambers will be analysed further in Section IV.3.3.3.

Table IV.2 Minimum and maximum y -velocity and x -velocity in chamber C6 for $6.25 < D/d < 7.25$, at $Re = 300$.

Amplitude of x-velocity and y-velocity				
D/d	$v_{y_{min}}$ (m/s)	$v_{y_{max}}$ (m/s)	$v_{x_{min}}$ (m/s)	$v_{x_{max}}$ (m/s)
6.25	-9.4×10^{-2}	1.5×10^{-1}	-1.2×10^{-1}	1.3×10^{-1}
6.35	2.7×10^{-3}	8.0×10^{-2}	-8.5×10^{-2}	4.9×10^{-2}
6.45	1.4×10^{-2}	7.1×10^{-2}	-8.0×10^{-2}	7.2×10^{-2}
6.55	4.4×10^{-2}	1.0×10^{-1}	-9.5×10^{-2}	8.8×10^{-2}
6.65	5.3×10^{-2}	1.2×10^{-1}	-1.0×10^{-1}	9.8×10^{-2}
6.75	4.7×10^{-2}	1.2×10^{-1}	-1.1×10^{-1}	1.1×10^{-1}
6.85	5.4×10^{-2}	1.2×10^{-1}	-9.9×10^{-2}	1.0×10^{-1}
6.95	2.5×10^{-3}	9.7×10^{-2}	-9.5×10^{-2}	1.0×10^{-1}
7.05	2.2×10^{-3}	1.0×10^{-1}	-1.0×10^{-1}	9.7×10^{-2}
7.15	2.2×10^{-3}	1.0×10^{-1}	-1.0×10^{-1}	1.1×10^{-1}
7.25	7.3×10^{-2}	1.2×10^{-1}	-1.5×10^{-1}	1.5×10^{-1}

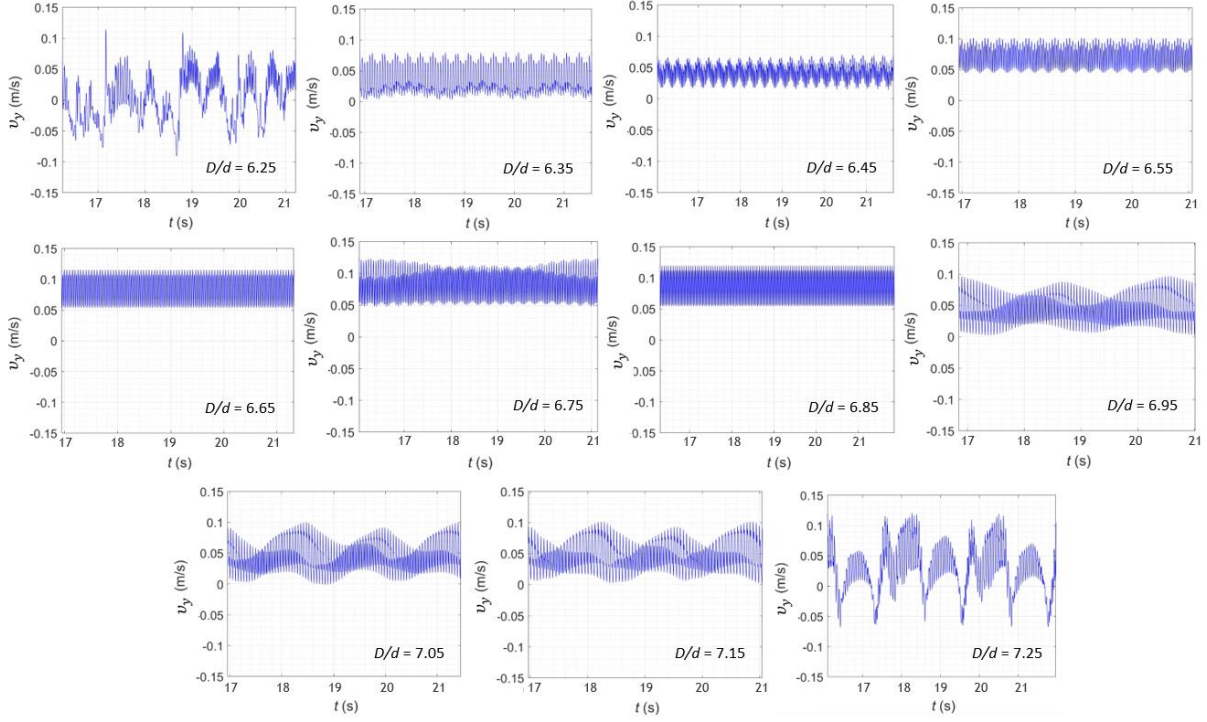


Figure IV.21 Histories of y-velocity in chamber C6 for $6.25 < D/d < 7.25$ at $Re = 300$, during 4τ .

Figure IV.22 shows the relation between v_x and v_y . The velocities were normalized according to $v^* = \frac{2(v-v_{min})}{(v_{max}-v_{min})} - 1$, and the values of $v_{x_{min}}$, $v_{x_{max}}$, $v_{y_{min}}$ and $v_{y_{max}}$ for each ratio, D/d , are in Table IV.2. Figure IV.22 shows that the ratios with worst mixing, $D/d = 6.25$ and 7.25 , which have an irregular velocity plot, are represented by an undefined structure. As the ratio D/d approaches the middle ratios, $6.55 < D/d < 6.85$, the phase diagram shows an 8 shaped structure. This representation is called a *strange attractor* since for an infinite number of iterations (flow time) the trajectory of the data points follows the same path. In this way, the phase diagrams show the existence of an apparently periodic behaviour, especially for the middle diameter ratios, since the 8 structure maintains its shape. This topic will be detailed in the next section of this work.

From Figure IV.22 it is possible to conclude that the ratios with the best mixing, $D/d = 6.65$ and $D/d = 6.85$, have a strange attractor with a thinner shape. In contrast, a less good mixing is represented by thicker strange attractors. Comparing Figure IV.21 with Figure IV.22, it is visible that the ratios with larger period waves are represented by a thicker strange attractor, while the best ratios with a smaller period present thin strange attractors.

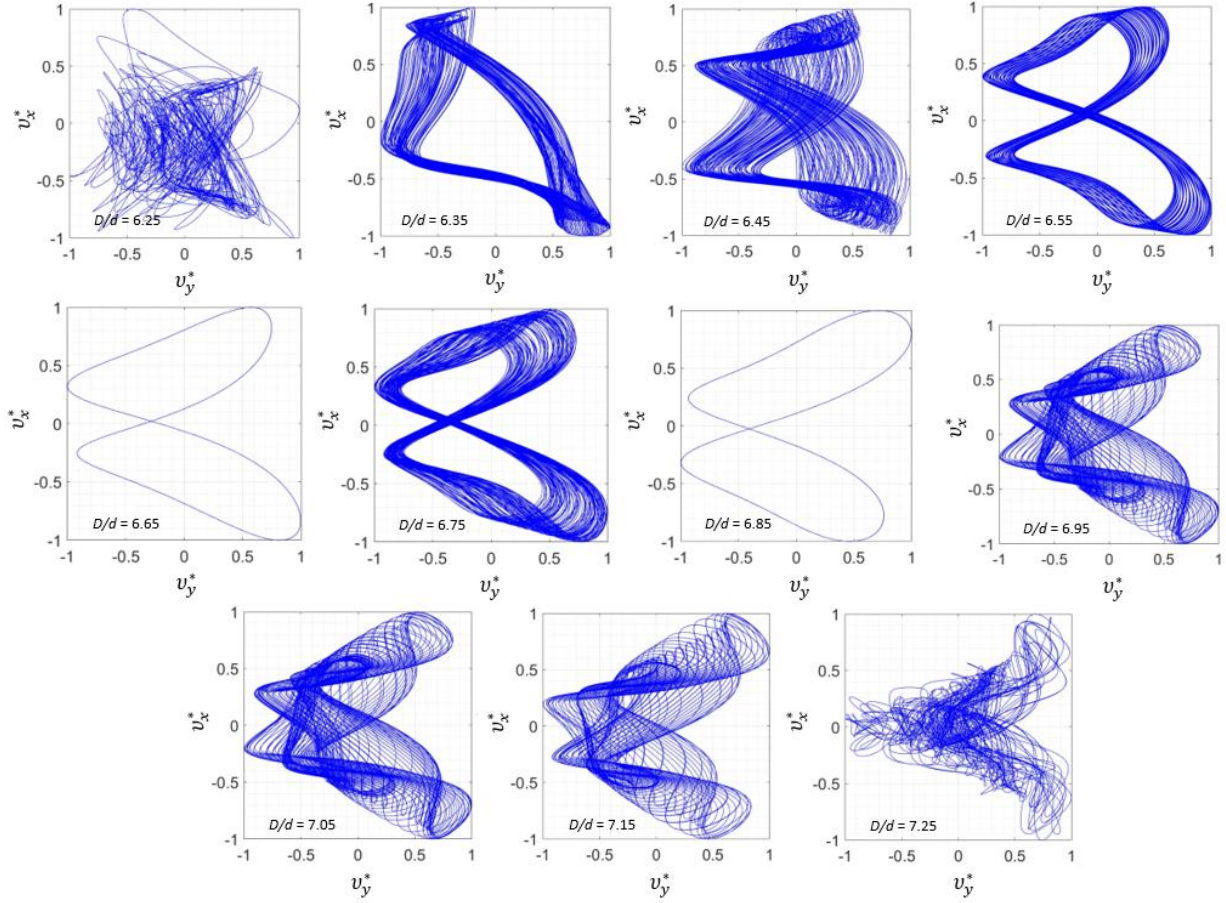


Figure IV.22 Phase diagrams of the normalized velocities, v_x^* and v_y^* , in chamber C6 for $6.25 < D/d < 7.25$, at $Re = 300$, during 4τ .

IV.3.3.1 Strange Attractor Analysis

As previously shown, the NETmix system can be represented by a strange attractor which shows an *apparently periodic* behaviour. To evaluate the chaoticity of system, the strain rate, $\zeta = \sqrt{\frac{2dv_x^2}{dx} + \frac{2dv_y^2}{dy} + \left(\frac{dv_x}{dy} + \frac{dv_y}{dx}\right)^2}$, and the vorticity, $\epsilon = \frac{dv_x}{dy} - \frac{dv_y}{dx}$, will be analysed. In fact, the strain rate is a measure of the deformation of the system due to the oscillatory behaviour, promoted by the inlet jets. The vorticity describes the spinning motion associated to the formation of vortices. To deepen the analysis of the NETmix strange attractor, phase diagrams of ζ vs ϵ were plotted for $6.25 < D/d < 7.25$. Figure IV.23 shows the phase diagrams in which the strain rate and the vorticity were normalized according to $\frac{2(\epsilon - \epsilon_{min})}{(\epsilon_{max} - \epsilon_{min})} - 1$. The values of ϵ_{min} , ϵ_{max} , ζ_{min} and ζ_{max} for each ratio, D/d , are in Table IV.3.

The relation between the strange attractors ζ^* vs ϵ^* of Figure IV.23 and the ratio, D/d , is similar to the result observed in Figure IV.22 for the strange attractors v_x^* vs v_y^* . As the ratio D/d approaches the middle ratios $6.65 < D/d < 6.85$, the phase diagram shows a W shaped structure.

For the ratios with the best mixing, $D/d = 6.65$ and $D/d = 6.85$, the strange attractor has a thinner shape. The strange attractor starts to take shape at $D/d = 6.35$. At $D/d = 6.45$, the shape is similar to a string suspended on four points, two at $\epsilon^* \cong 1$ and two at $\epsilon^* \cong 0.5$. The attractor is nearly symmetrical in relation to the axis $\zeta^* = 0$, forming a parabolic structure with a downward concavity. At $D/d = 6.55$, the attractor becomes slightly thinner, and the *parabola* vertex became apart from each other, giving place to a *W* shaped attractor. For $D/d = 6.65$ and $D/d = 6.85$ (dilution factor of 2), the attractors are very thin and almost symmetrical to each other: the *lasso* of the middle top tip is a at the right for $D/d = 6.65$ and at the left for $D/d = 6.85$. Although $D/d = 6.75$ is the middle ratio, the attractor is thicker. In fact, the results of macromixing, presented previously, have shown that the dilution factor is closer to 2 for $D/d = 6.65$ and for $D/d = 6.85$. Moreover, it was shown that the largest interfacial area generation is obtained for $D/d = 6.65$. It is then verified that more irregular oscillations lead to less good mixing and are associated with thicker strange attractors. For $6.95 < D/d < 7.15$, as the dilution factor becomes apart from 2, the attractor gets thicker and starts to assume a parabolic shape centred in $\zeta^* = 0$.

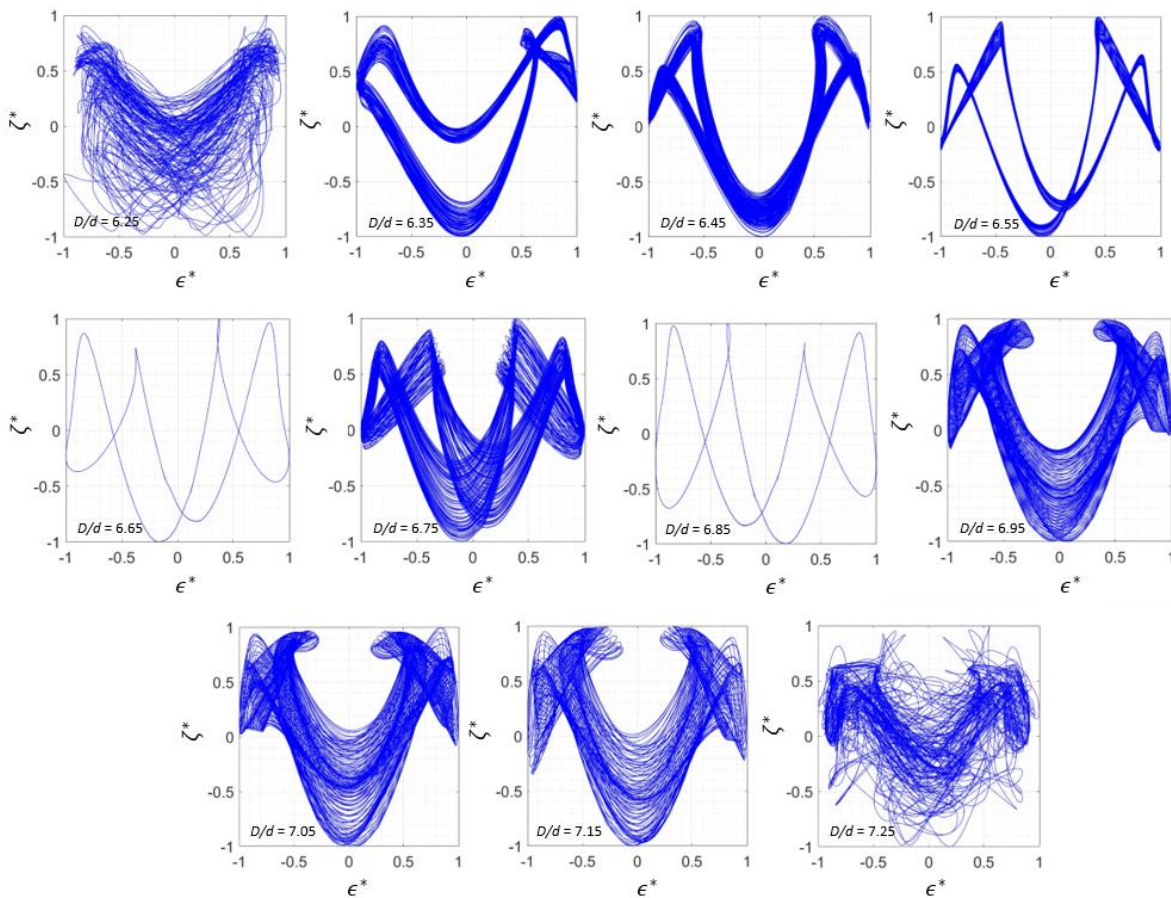


Figure IV.23 Phase diagrams of the normalized strain rate, ζ^* and vorticity ϵ^* in chamber C6 for $6.25 < D/d < 7.25$, at $Re = 300$ during 4τ .

Table IV.3 Minimum and maximum vorticity and strain rate in chamber C6 for $6.25 < D/d < 7.25$, at $Re = 300$.

Amplitude of Vorticity and Strain rate				
D/d	$\epsilon_{min} (s^{-1})$	$\epsilon_{max} (s^{-1})$	$\zeta_{min} (s^{-1})$	$\zeta_{max} (s^{-1})$
6.25	-3.7×10^2	3.6×10^2	1.2×10^0	4.5×10^2
6.35	-3.4×10^2	3.6×10^2	1.5×10^2	3.6×10^2
6.45	-3.5×10^2	3.7×10^2	1.8×10^2	3.8×10^2
6.55	-3.5×10^2	3.5×10^2	2.4×10^2	3.7×10^2
6.65	-3.5×10^2	3.4×10^2	2.8×10^2	3.6×10^2
6.75	-3.5×10^2	3.5×10^2	2.3×10^2	3.8×10^2
6.85	-3.3×10^2	3.4×10^2	2.8×10^2	3.6×10^2
6.95	-3.7×10^2	3.7×10^2	1.6×10^2	3.8×10^2
7.05	-3.7×10^2	3.8×10^2	1.4×10^2	3.8×10^2
7.15	-3.6×10^2	3.6×10^2	1.5×10^2	3.8×10^2
7.25	-3.6×10^2	3.7×10^2	3.8×10^1	4.4×10^2

Figure IV.21 to Figure IV.23 have shown that the NETmix system has an apparent periodic behaviour. In fact, the waves of the velocity plot have a repetitive pattern and the shape of the attractors is formed by a continuous line that follows a similar path. As an example, the construction of the attractor for $D/d = 6.75$ is analysed in Figure IV.24 at several intervals of flow time, $\Delta t = 0.2$ s, 0.4 s, 0.8 s, 1 s, 5 s and 10 s. Figure IV.24 shows the increment on the attractor size as Δt increases. For $\Delta t = 0.2$ s only 5 *lines* can be distinguished. If $\Delta t = 0.4$ s, the lines are distinguishable; however, it is not possible to count them clearly since the parabola vertex start to touch each other. For higher Δt , it not possible to distinguish the lines as they form a *net*. In this way, Figure IV.24 shows that the periodic behaviour of the NETmix reactor is only *apparent*. Although the data points of the attractor follow a similar path, they do not have the same coordinates.

The construction of the attractor is shown in the video, *Attractor_6_75.mp4*, of the folder *Mixing_and_Controlled_Combustion_in_NETmix_videos*.

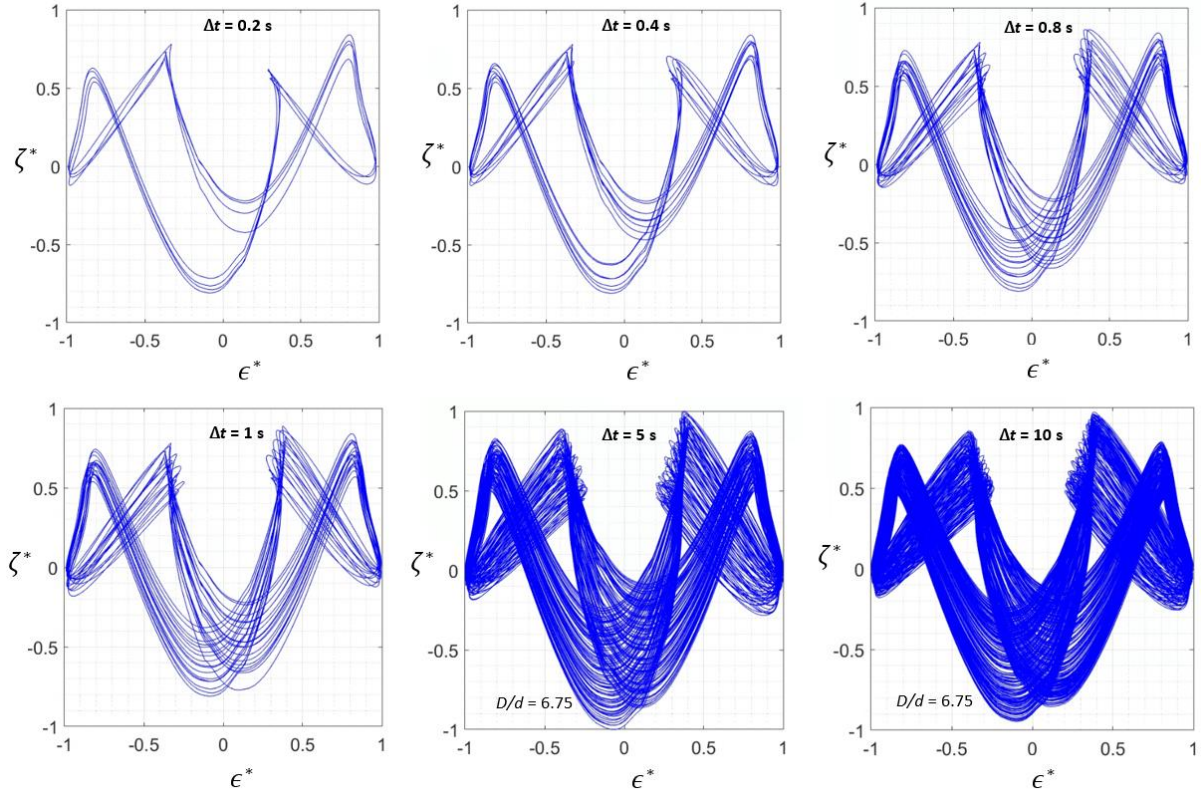


Figure IV.24 Phase diagrams of the normalized strain rate, ζ^* and vorticity ϵ^* in chamber C6 for $D/d = 6.75$ at $Re = 300$ with $\Delta t = 0.2$ s, 0.4 s, 0.8 s, 1 s, 5 s and 10 s.

As previously shown, $D/d = 6.75$ has a sufficiently thick attractor to be possible to distinguish the lines for low Δt . However, for thinner attractors such as $D/d = 6.65$ and $D/d = 6.85$, it is not possible to understand how the attractor is formed from phase the diagrams $\zeta^* vs \epsilon^*$. In order to perform a deeper analysis of the NETmix strange attractors, Poincaré maps will be constructed in the next subsections.

IV.3.3.2 Poincaré Maps

A *Poincaré map* is obtained from the intersection of a periodic or quasi-periodic orbit in the state space of a continuous dynamical system with a lower-dimensional subspace which is transversal to the flow of the system. This intersection is called *Poincaré section*. The Poincaré maps are a discrete dynamical system one dimension smaller than the original system. Since they preserve the periodic and quasi-periodic characteristics of the initial system, the Poincaré maps are very useful for the analysis of complex dynamic systems.

Poincaré maps were constructed for $6.35 < D/d < 7.15$. To build the Poincaré map, an “arm” of the attractor was chosen, as illustrated in Figure IV.25a for $D/d = 6.65$, where the line that intersects the attractor to obtain the Poincaré section is represented in red. In Figure IV.25b, a

close-up is shown where the series of the attractor are visible. The Poincaré section, i.e., intersection points of the attractor with the line, are shown in Figure IV.25c.

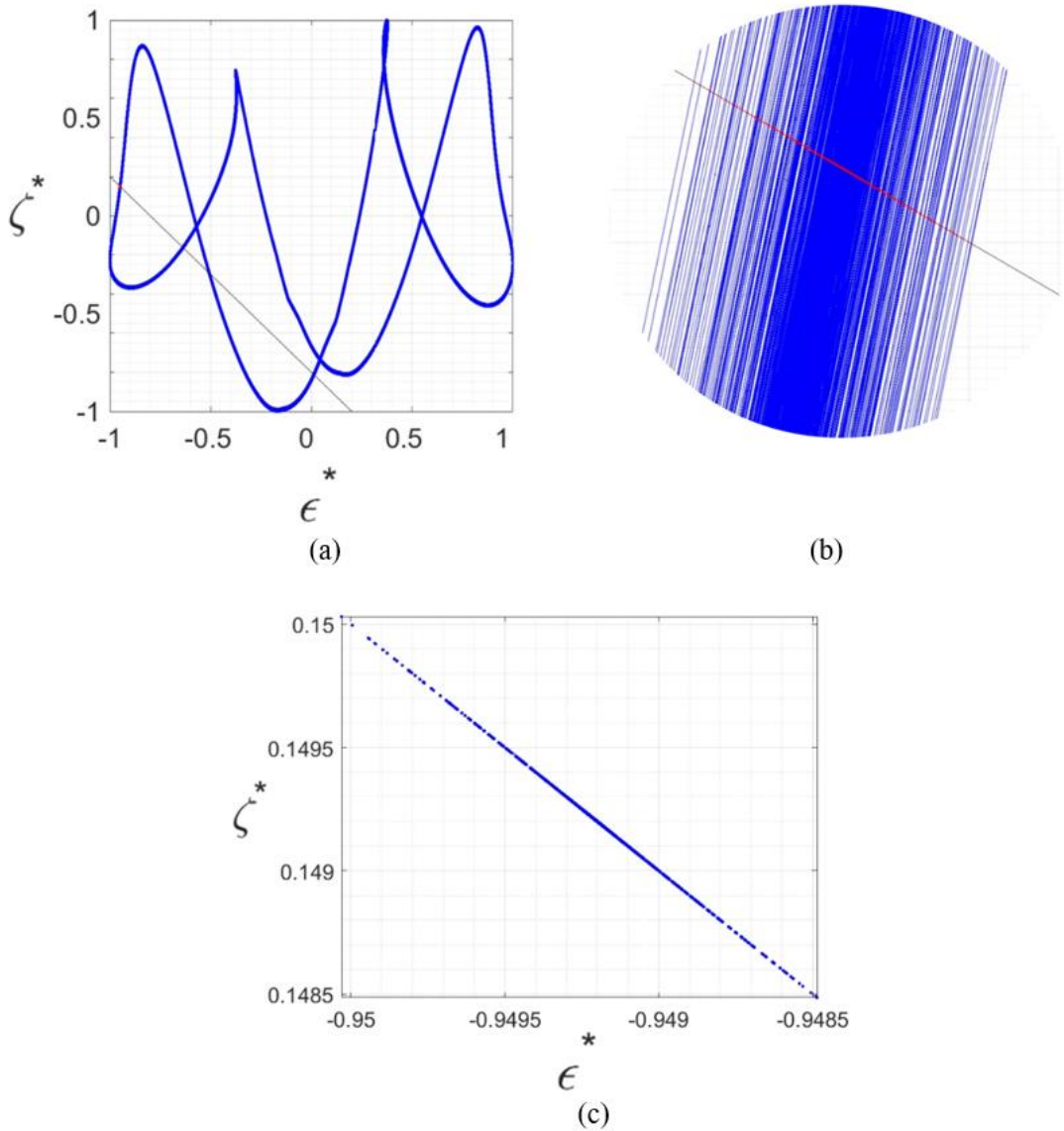


Figure IV.25 (a) Intersection between the line and the phase diagram of the normalized strain rate, ζ^* and vorticity, ϵ^* , in chamber C6 for $D/d = 6.65$ at $Re = 300$, during 114 s. (b) Close up of the intersection. (c) Poincaré section.

Three types of Poincaré maps were built, shown in the example of Figure IV.26, for $D/d = 6.65$. As the attractor is being built, the attractor is crossed by the intersection line several times. The relation between ϵ_i^* and ϵ_{i+1}^* of the intersection points corresponds to the first type of Poincaré map (Figure IV.26a). The relation between the iteration of the intersection points, i.e., the flow time at which a certain data point was added to the attractor, and the value of the vorticity is represented in Figure IV.26b and corresponds to the second type of Poincaré map. Although the plots of Figure IV.26a and Figure IV.26b are 2D, the discrete systems that they represent are 1D since only one variable of the initial system, the vorticity, is being used. From the analysis of Figure IV.26a and Figure IV.26b, it is possible to conclude that the maps are the top and front/side

views of a 3D structure, represented in Figure IV.26c, which corresponds to the third type of Poincaré map.

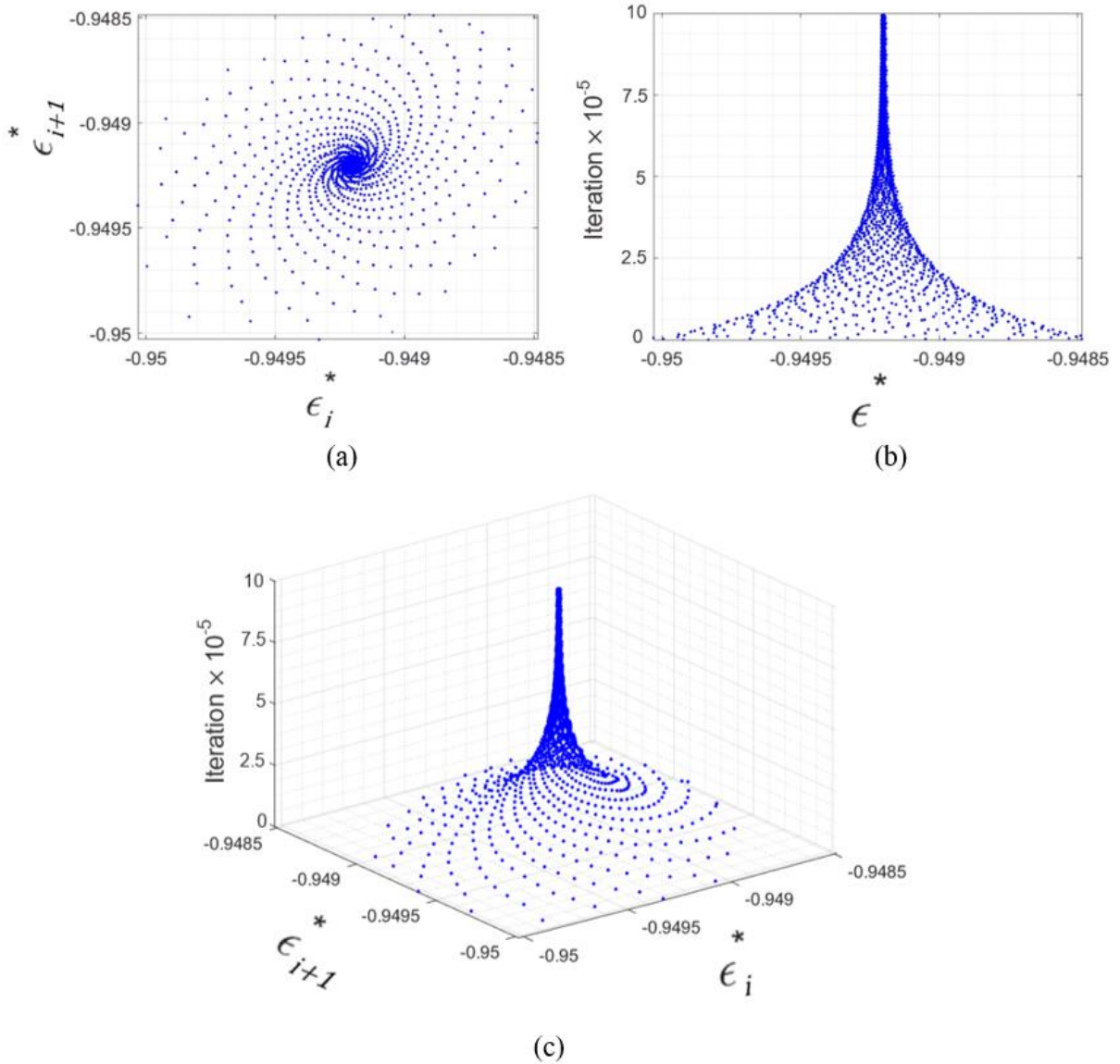


Figure IV.26 (a) Poincaré map ϵ_i^* vs ϵ_{i+1}^* . (b) Poincaré map ϵ^* vs iteration. (c) 3D Poincaré map.

To obtain the results shown in Figure IV.25 and in Figure IV.26, 10^6 data points (iterations) were used, corresponding to 114 s flow time (104τ) which is considered sufficient to have a full representation of the NETmix mixing dynamics.

For $D/d = 6.65$, Figure IV.25b shows that for a very large number of iterations there is a tendency of the attractor series to pass through the middle path. This behaviour is visible in Figure IV.26a and in Figure IV.26b. Figure IV.26a shows that a larger number of points is located in the centre of the map forming a *spinning spiral* shape. This behaviour is also visible in Figure IV.26b since a large number of points have a middle vorticity. In fact, for a larger number of iterations (last 10^4), the values of the vorticity are between -0.94919 and -0.94891, while for the first iterations

(10^4) the values vary between -0.95000 and -0.94850, as will be further discussed in this Section. All the points that were registered have different coordinates which shows that the NETmix system is not periodic, although the trajectories of the attractor have a similar path. As will be shown further in this work, the NETmix system is *quasi-periodic*.

If the Poincaré section is changed, the Poincaré maps are different, as shown in Figure IV.27. As the line that intersects the strange attractor moves up in the “arm”, the spiral of the Poincaré maps spins to the right.

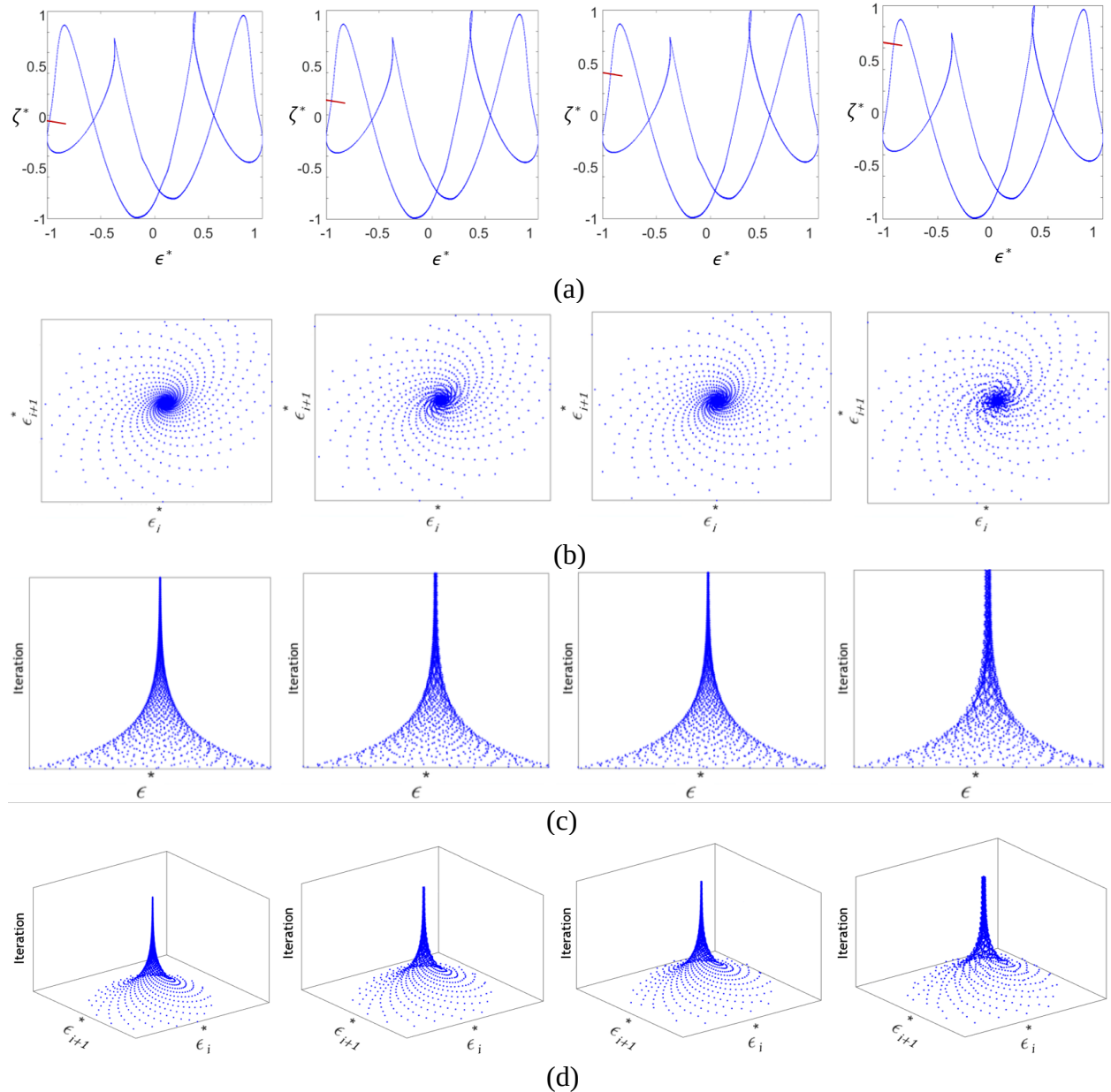


Figure IV.27 (a) Intersection between the line and the phase diagram of the normalized strain rate, ζ^* and vorticity, ϵ^* , in chamber C6 for $D/d = 6.65$ at $Re = 300$, during 114 s. (b) Poincaré map ϵ_i^* vs ϵ_{i+1}^* . (c) Poincaré map ϵ^* vs iteration. (d) 3D Poincaré map.

The variation of the Poincaré maps with the section is shown in the video, Poincare_6_65.mp4, of the folder *Controlled_Combustion_in_NETmix_videos*.

For $6.35 < D/d < 6.85$, with 10^6 points it is possible to distinguish the “arms” of the attractor. However, for $6.95 < D/d < 7.15$, the attractor is too thick, as shown in Figure IV.28. In this way, the Poincaré analysis needs to be done in 3D. For the lower values of D/d , a 3D analysis was also performed for comparison purposes. The 3D attractors that were used for the analysis are shown in Figure IV.29.

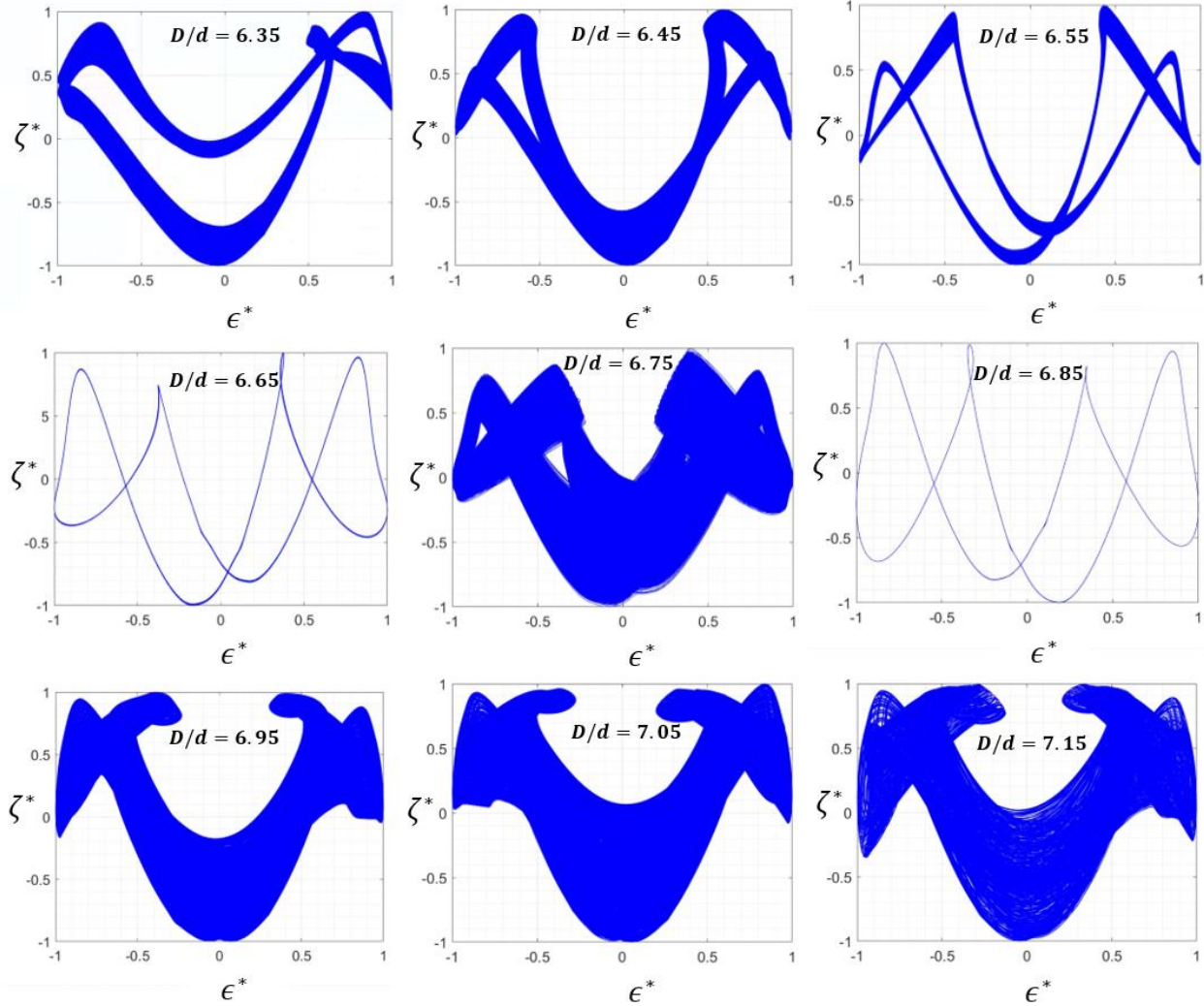


Figure IV.28 2D phase diagrams of the normalized strain rate, ζ^* , and vorticity, ϵ^* , in chamber C6, for $6.35 < D/d < 7.15$ at $Re = 300$ during 114 s.

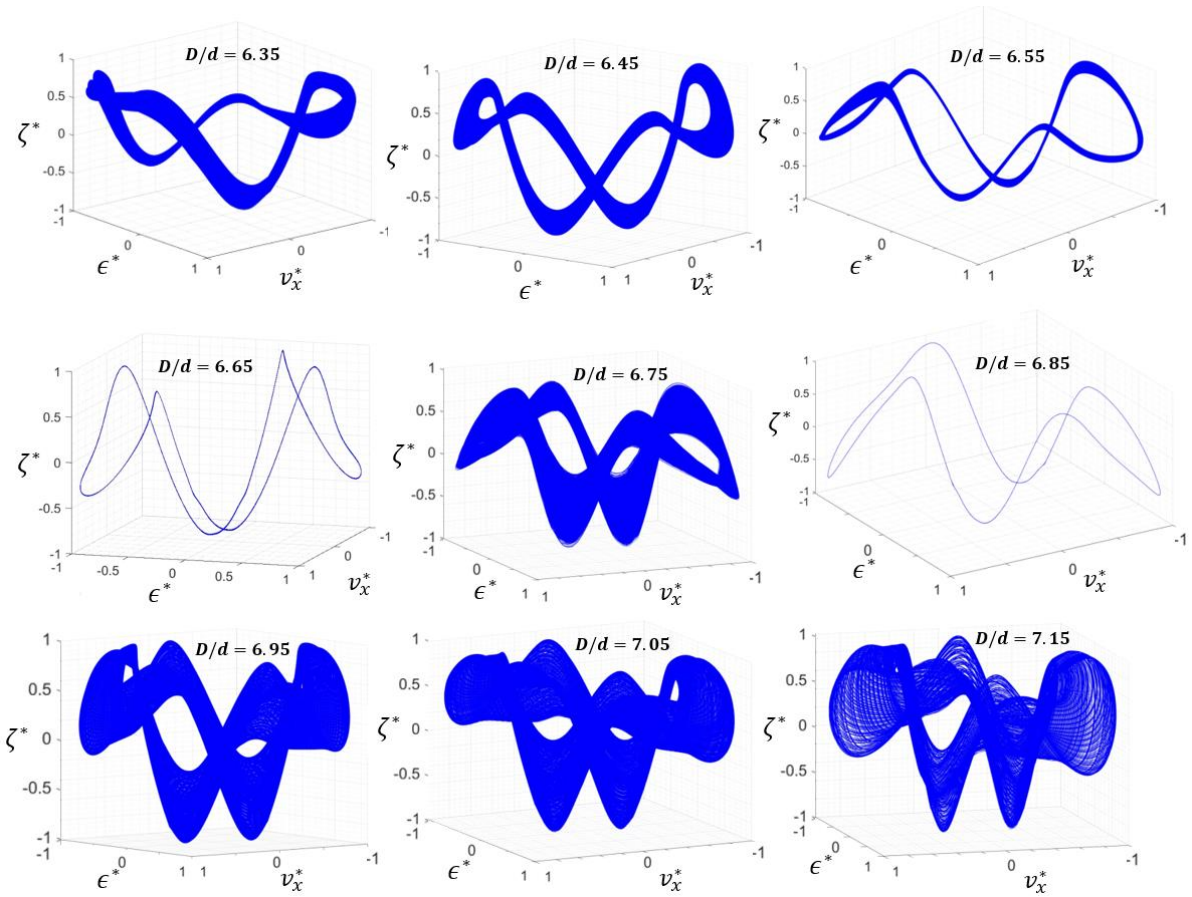


Figure IV.29 3D phase diagrams of the normalized strain rate, ζ^* , vorticity, ϵ^* , and x-velocity, v_x^* , in chamber C6, for $6.35 < D/d < 7.15$ at $Re = 300$ during 114 s.

As an example, the 3D analysis will be detailed for $D/d = 6.65$.

If the Poincaré map is made from the intersection of the attractor with a plane at $\zeta^* = 0$, it is possible to identify eight Poincaré sections, as shown in Figure IV.30. The sections are plotted in Figure IV.31, in which the changes in the attractor shape are visible. Moreover, it is possible to conclude that the 3D Poincaré sections, ϵ^* vs v_x^* , are similar to the 2D Poincaré maps, ϵ_i^* vs ϵ_{i+1}^* .

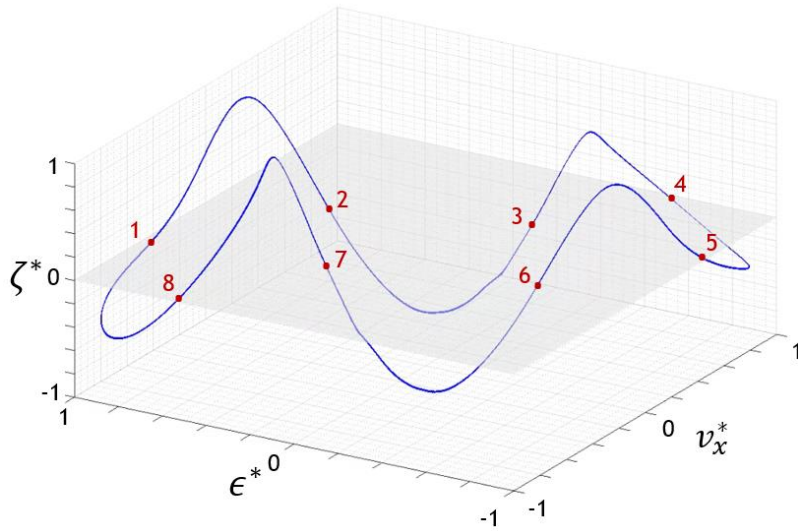


Figure IV.30 Intersection between $\zeta^* = 0$ and the 3D phase diagram of the normalized strain rate, ζ^* , vorticity, ϵ^* , and x-velocity, v_x^* , in chamber C6, for $D/d = 6.65$ at $Re = 300$ during 114 s.

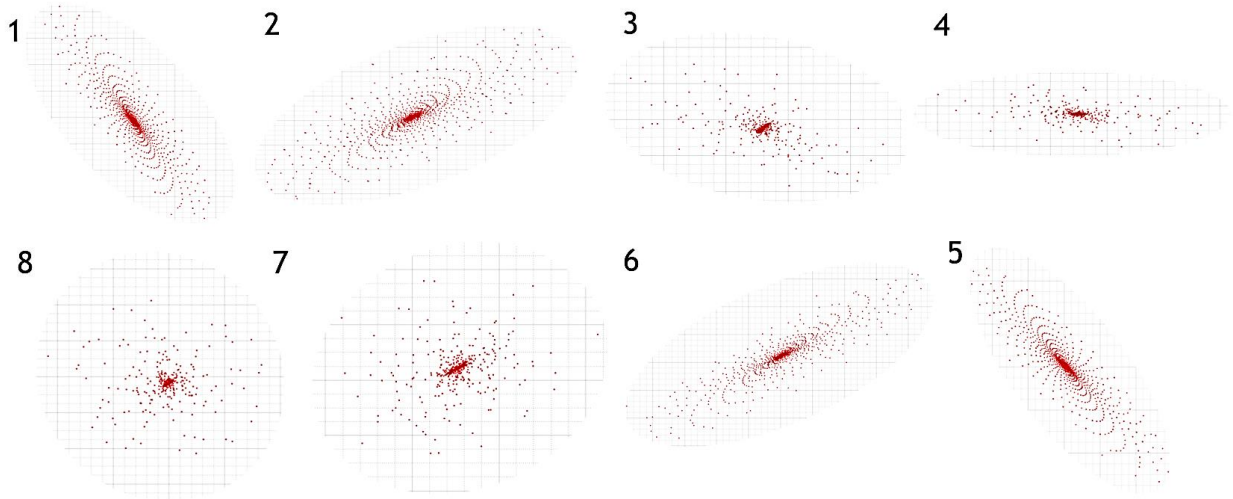


Figure IV.31 Poincaré sections of the 3D phase diagram of the normalized strain rate, ζ^* , vorticity, ϵ^* , and x-velocity, v_x^* , in chamber C6, for $D/d = 6.65$ at $Re = 300$ during 114 s.

In similarity to the 2D analysis, if the section plane is changed, the Poincaré maps are different, as shown in Figure IV.32. As the plane has a higher strain rate, the spiral spins to the right. As previously shown, the Poincaré sections change with the portion of the attractor that is intersected. Comparing Figure IV.32 with Figure IV.33, it is visible that the Poincaré maps are also different if the intersection is performed in a different “arm” of the phase diagram.

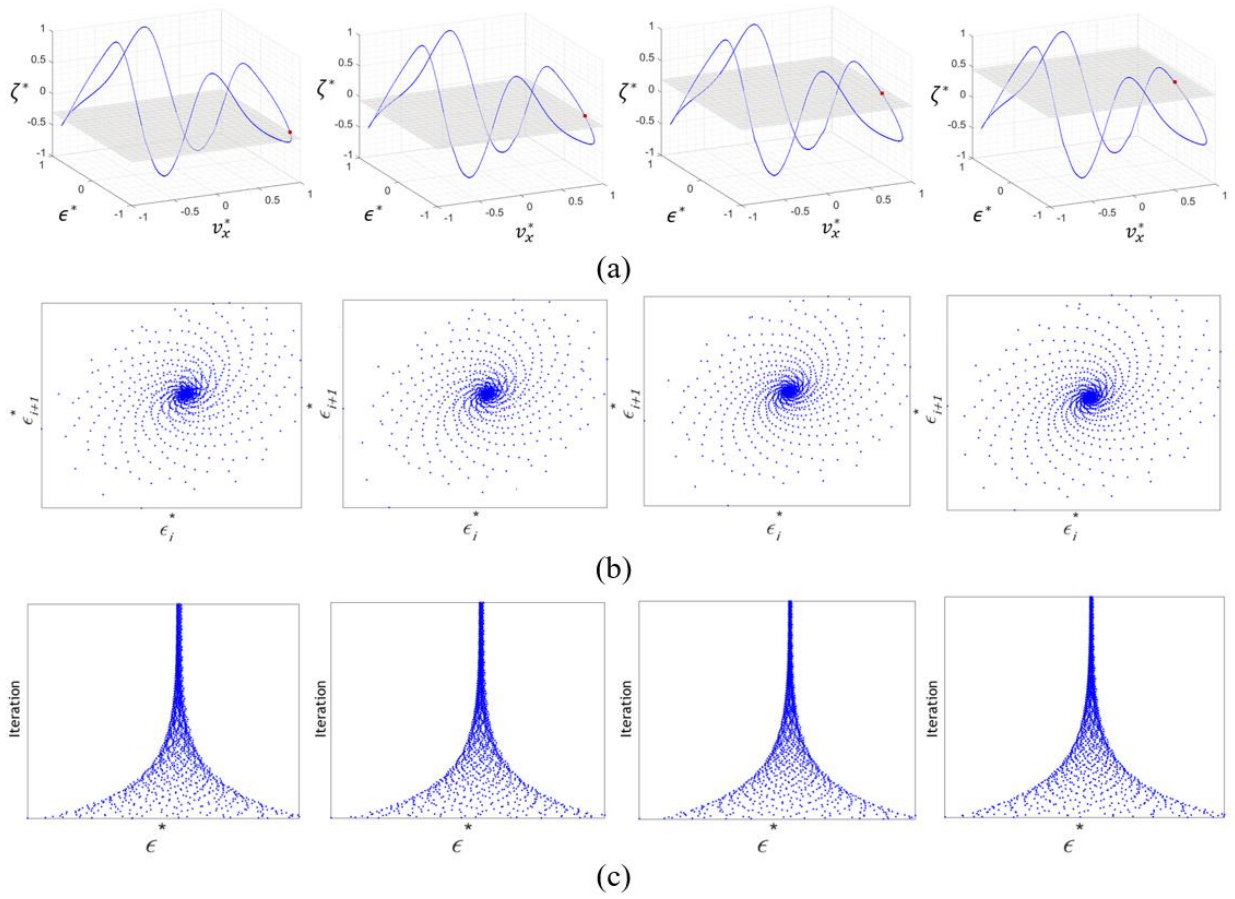


Figure IV.32 Intersection between the line and the phase diagram (right “arm”) of the normalized strain rate, ζ^* and vorticity, ϵ^* , in chamber C6, for $D/d = 6.65$ at $Re = 300$ during 114 s. (b) Poincaré map ϵ_i^* vs ϵ_{i+1}^* . (c) Poincaré map ϵ^* vs *iteration*.

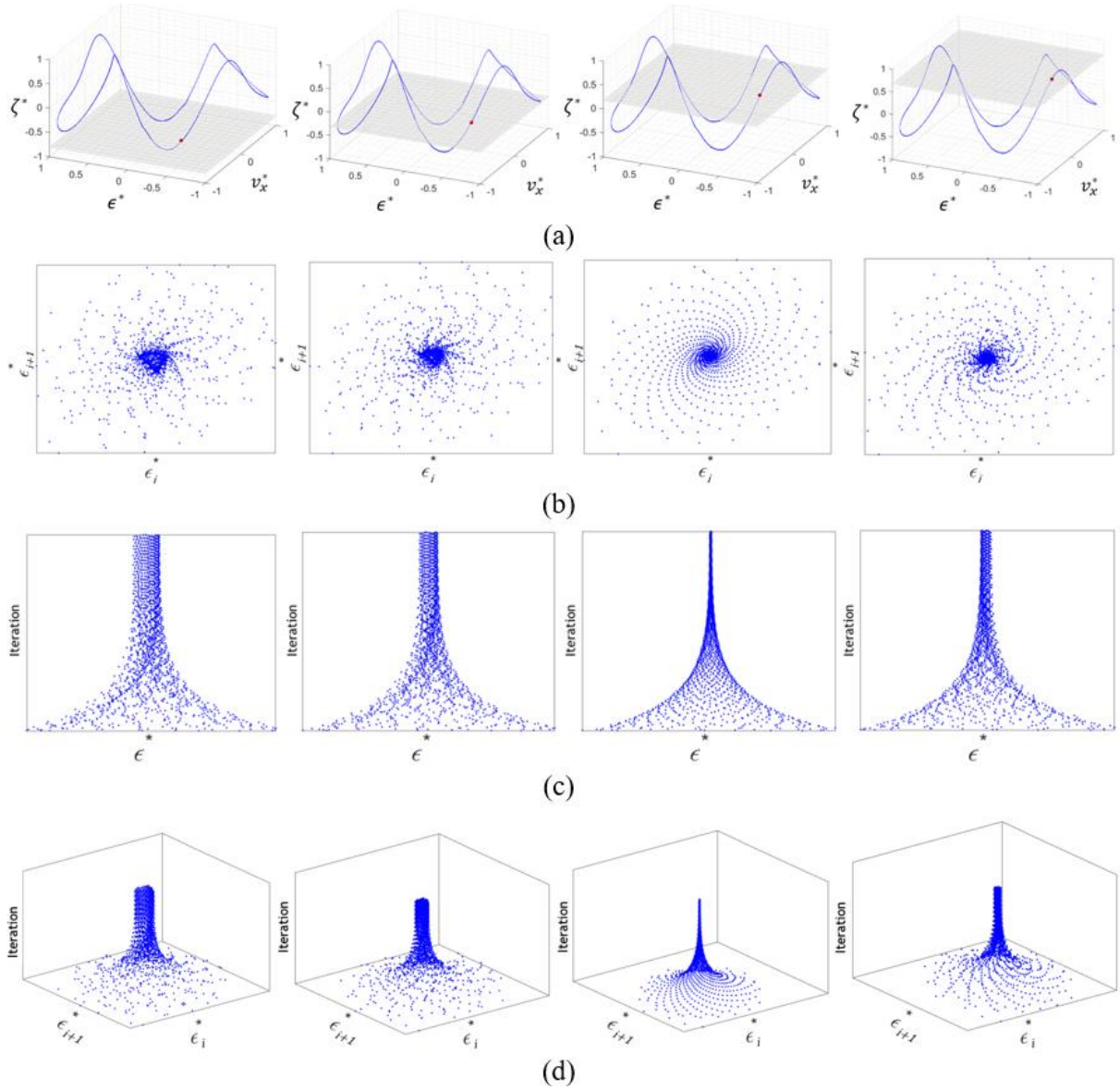
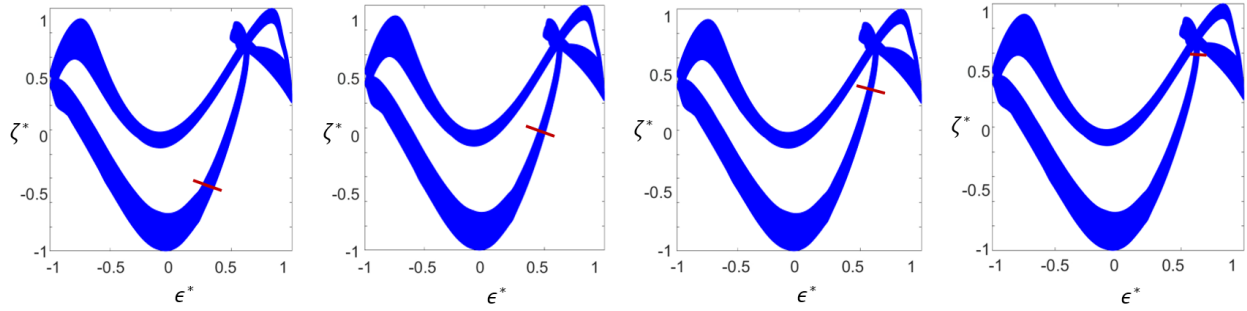
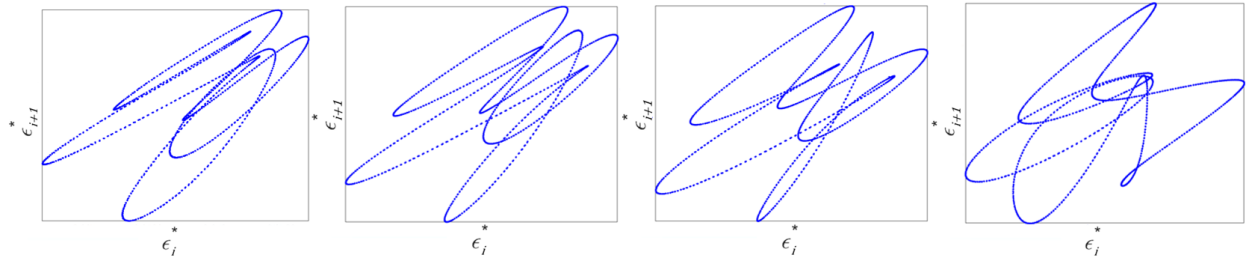
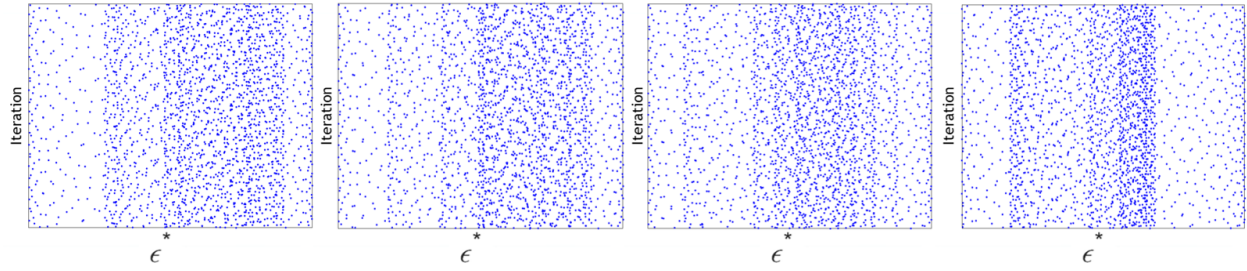


Figure IV.33 Intersection between the line and the phase diagram (left “arm”) of the normalized strain rate, ζ^* and vorticity, ϵ^* , in chamber C6, for $D/d = 6.65$ at $Re = 300$ during 114 s. (b) Poincaré map ϵ_i^* vs ϵ_{i+1}^* . (c) Poincaré map ϵ^* vs iteration. (d) 3D Poincaré map.

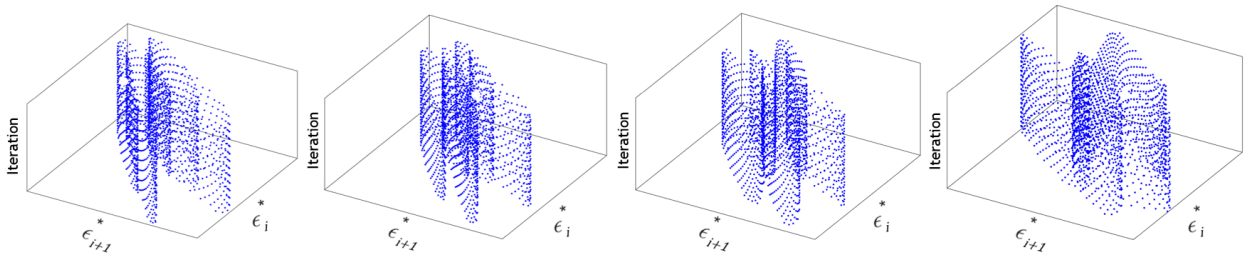
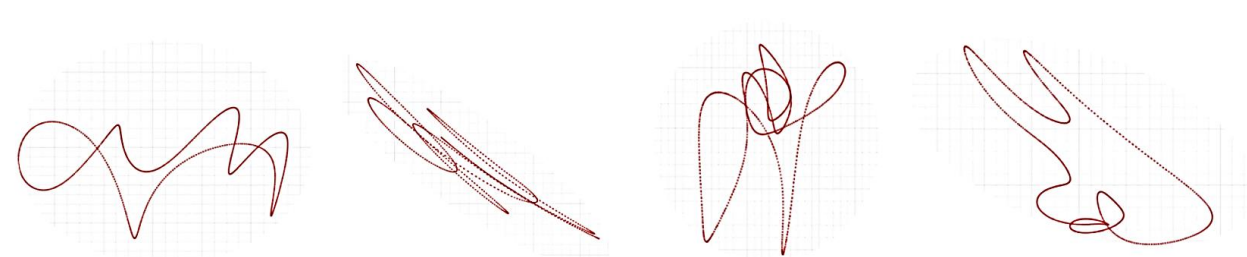
Comparing the Poincaré maps that were obtained from a 2D (Figure IV.27) or a 3D (Figure IV.32 and Figure IV.33) analysis, it is possible to conclude that the quasi-periodic behaviour of the NETmix reactor can be assessed from either of the studies. In this way, the attractors can be analysed in 2D or in 3D. The 2D and 3D Poincaré analysis is shown in Table IV.4 for the ratios $6.35 < D/d < 7.15$.

Table IV.4 2D and 3D Poincaré Analysis for $6.35 < D/d < 7.15$. **$D/d = 6.35$ – 2D Analysis**

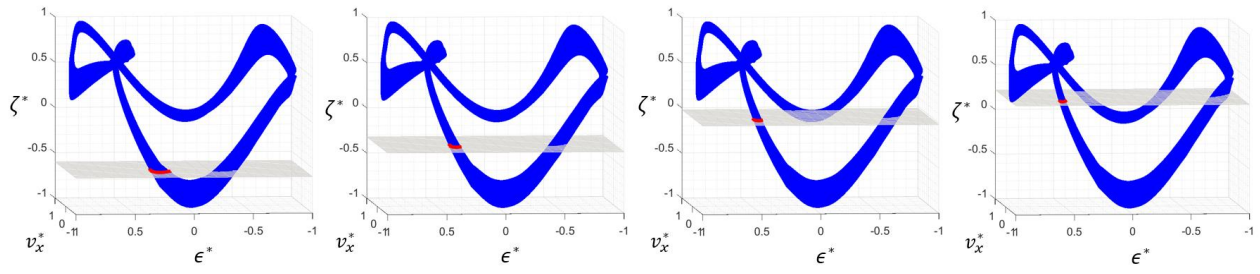
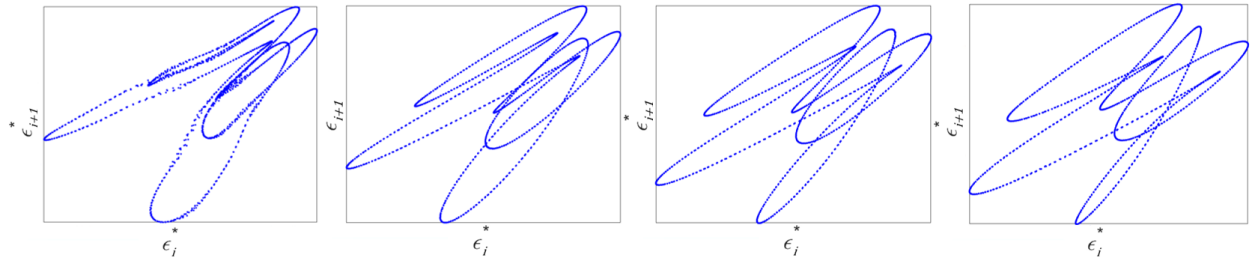
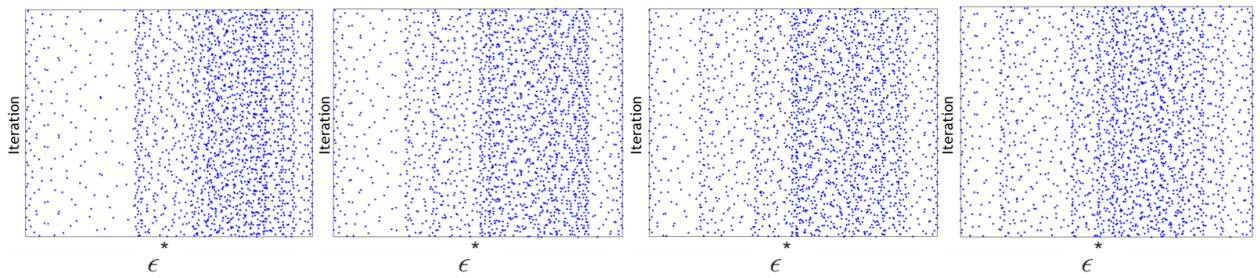
Attractor intersection with line

Poincaré map ϵ_i^* vs ϵ_{i+1}^* Poincaré map ϵ^* vs iteration

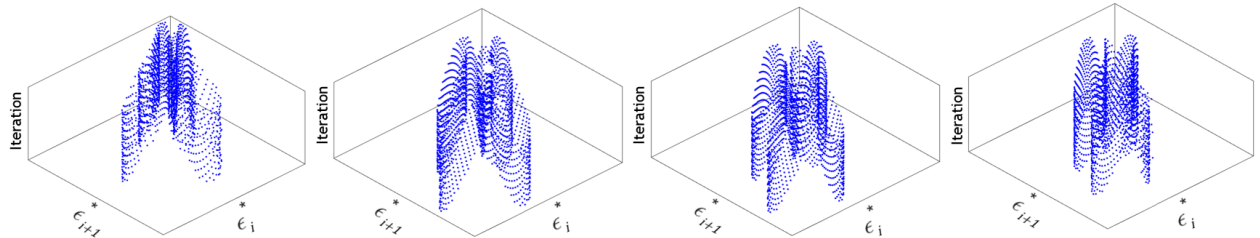
3D Poincaré map

 **$D/d = 6.35$ – 3D Analysis**Poincaré section (from intersection with plane $\zeta^* = 0$)

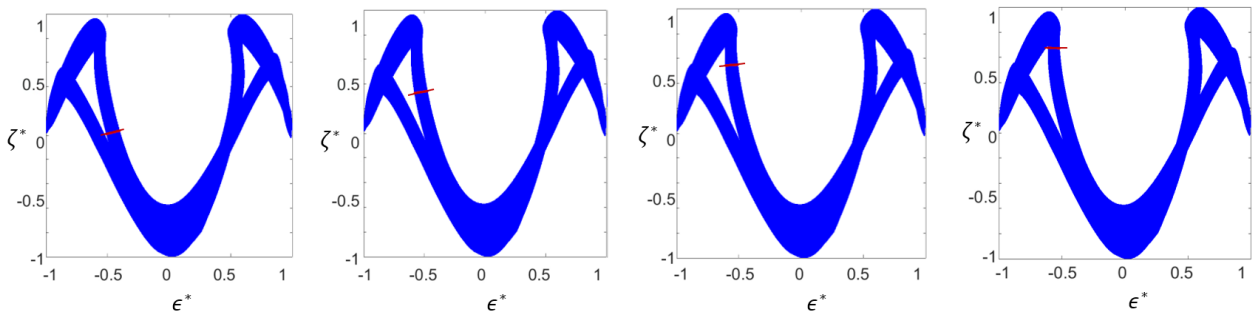
Attractor intersection with plane

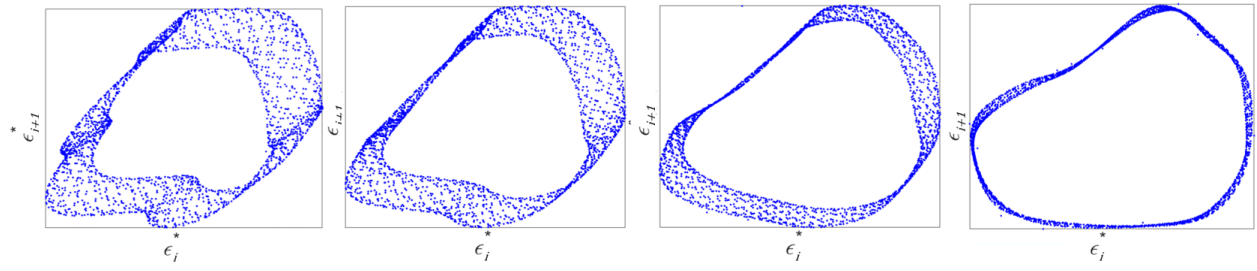
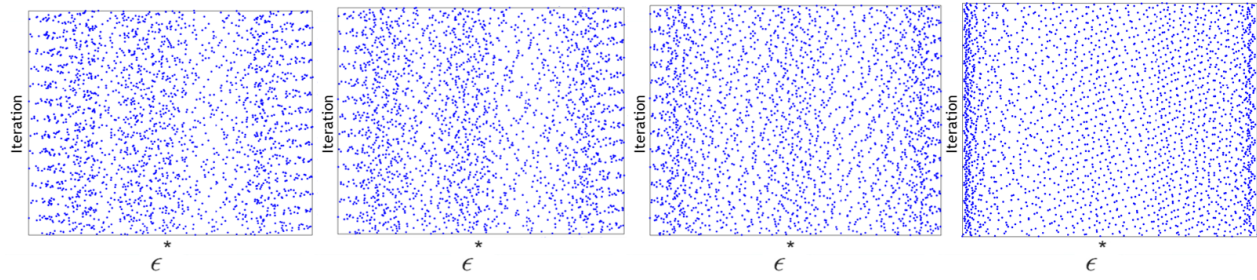

 Poincaré map ϵ_i^* vs ϵ_{i+1}^*

 Poincaré map ϵ^* vs iteration


3D Poincaré map

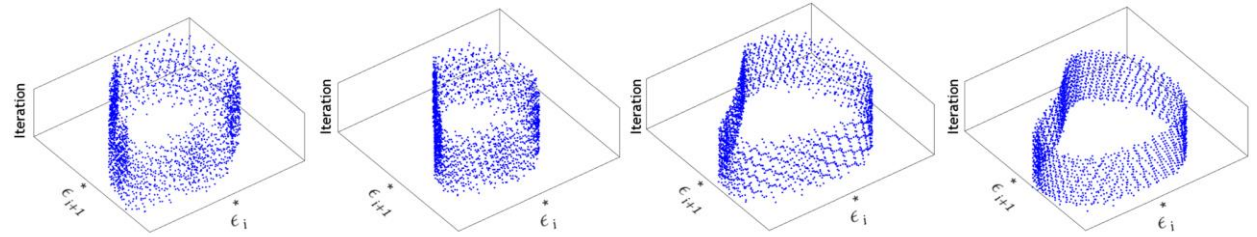

 $D/d = 6.45$ – 2D Analysis

Attractor intersection with line

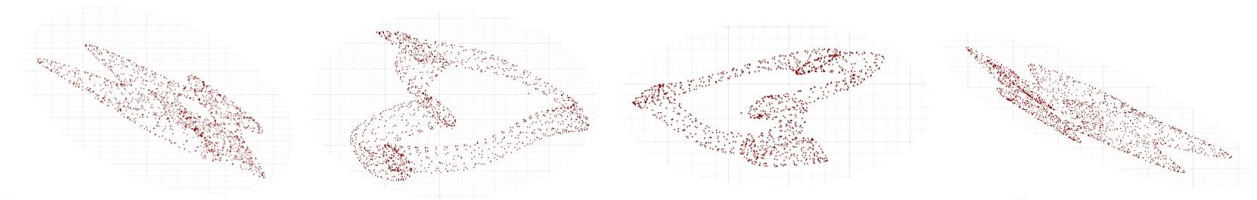


Poincaré map ϵ_i^* vs ϵ_{i+1}^*

 Poincaré map ϵ^* vs iteration


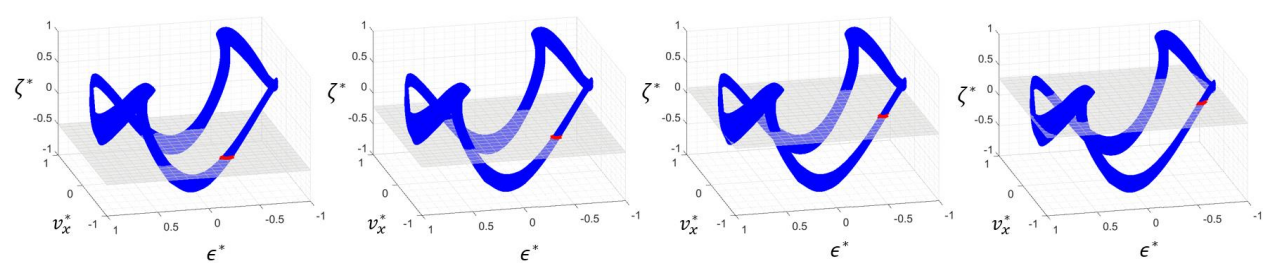
3D Poincaré map

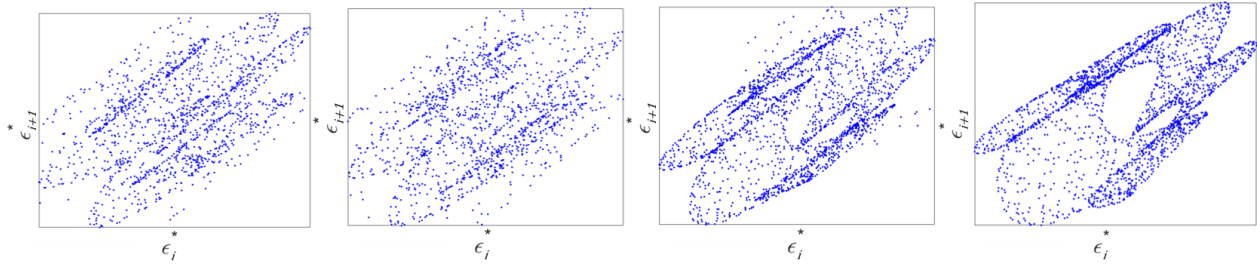
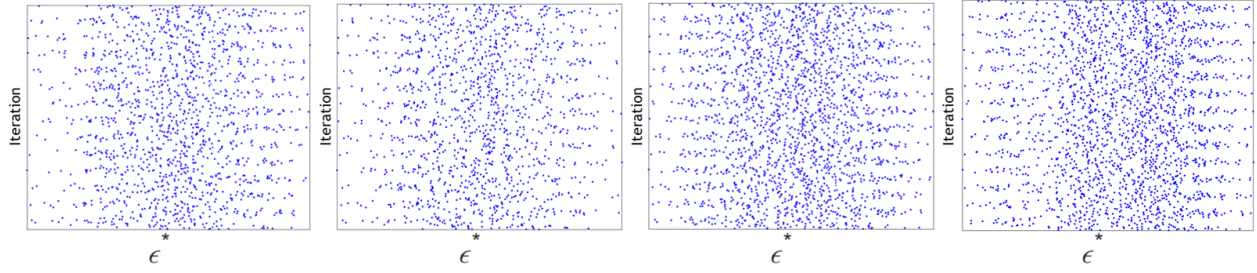


$D/d = 6.45$ – 3D Analysis

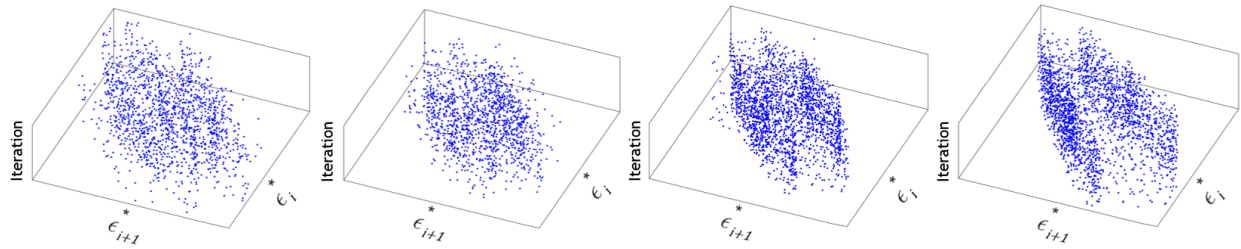
 Poincaré section (from intersection with plane $\zeta^* = 0$)


Attractor intersection with plane



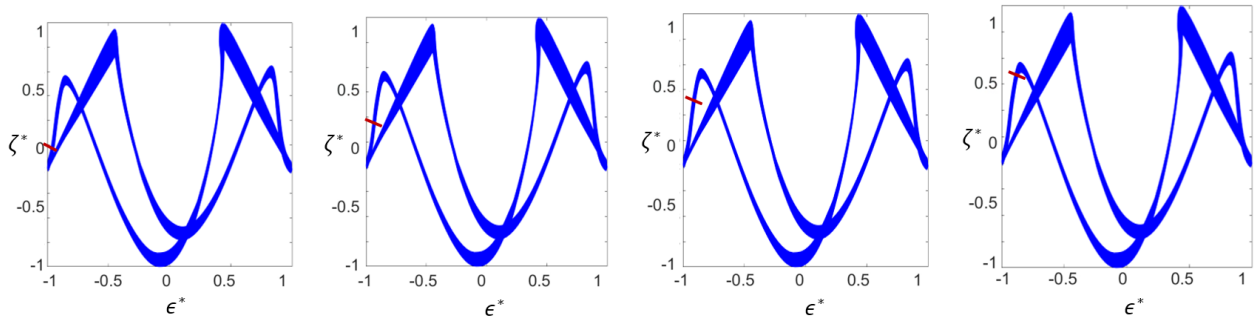
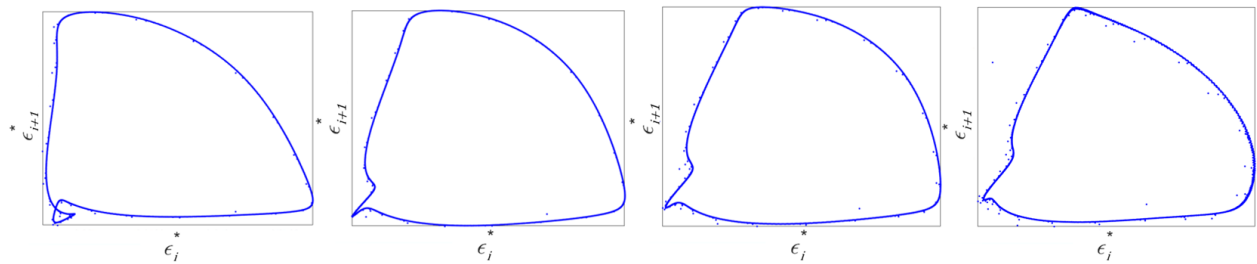
Poincaré map ϵ_i^* vs ϵ_{i+1}^*

 Poincaré map ϵ^* vs iteration


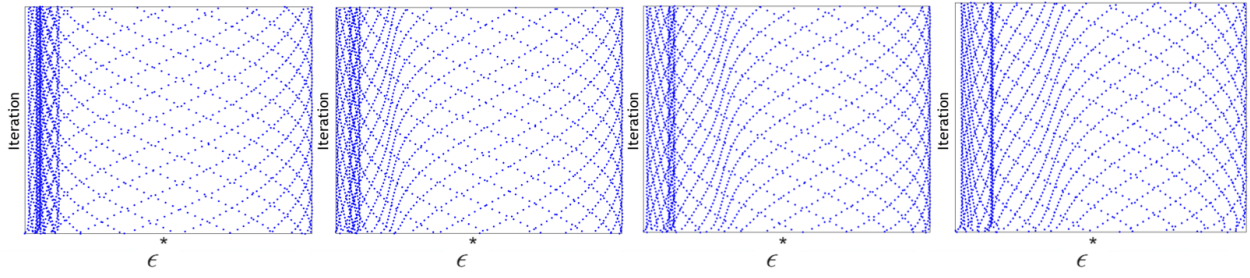
3D Poincaré map



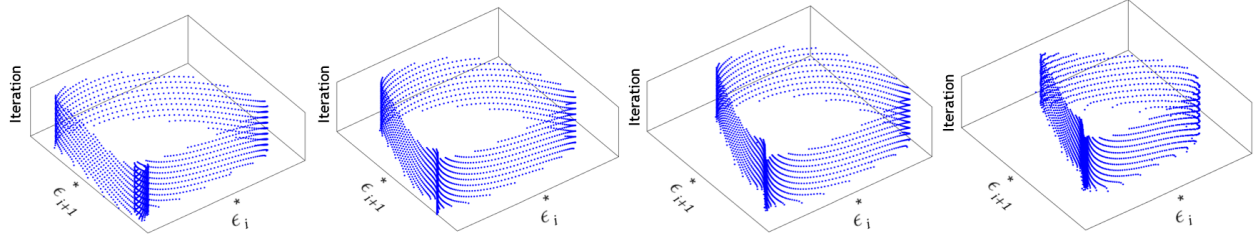
$D/d = 6.55$ – 2D Analysis

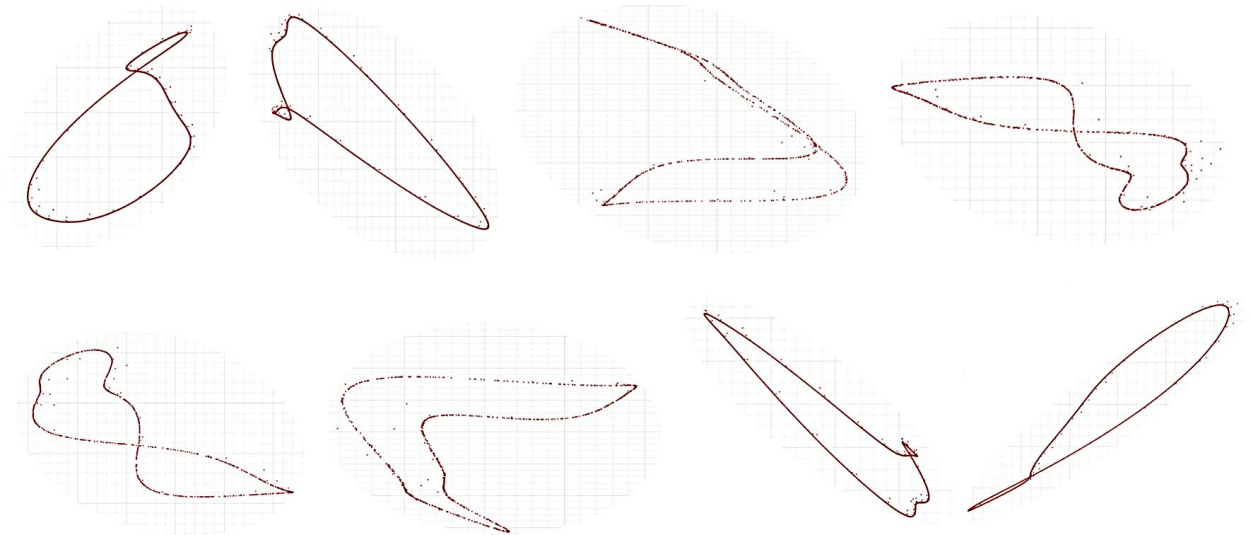
Attractor intersection with line


 Poincaré map ϵ_i^* vs ϵ_{i+1}^*


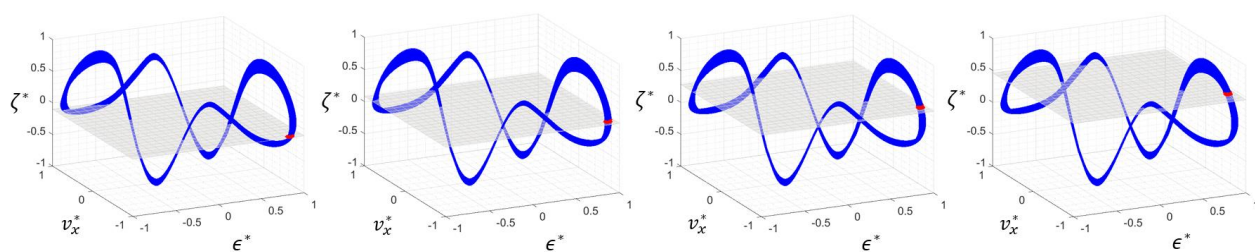
Poincaré map ϵ^* vs iteration


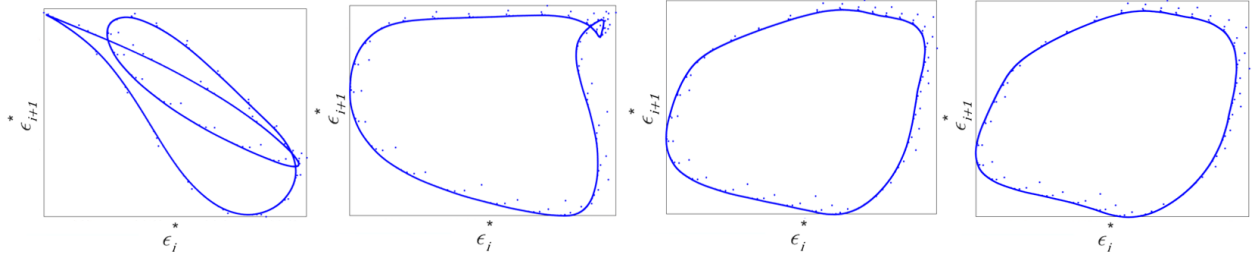
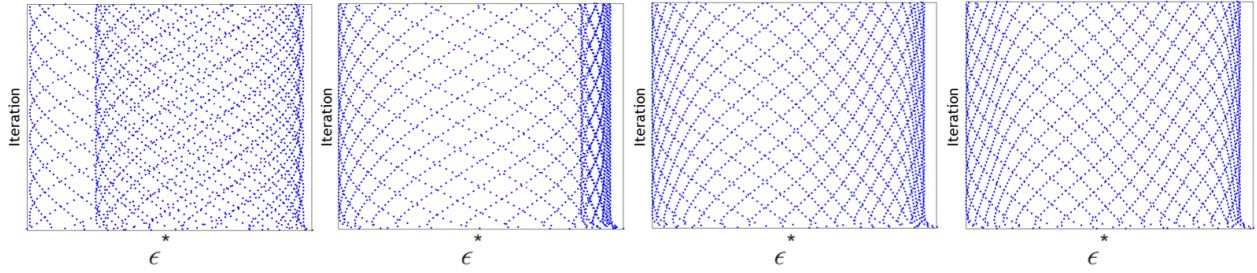
3D Poincaré map


 $D/d = 6.55$ – 3D Analysis

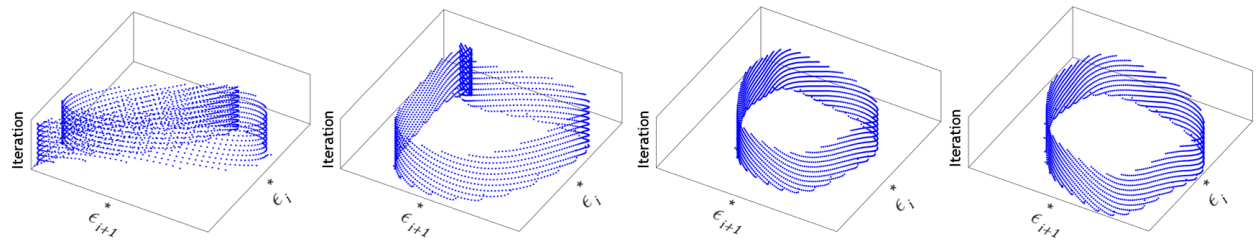
 Poincaré section (from intersection with plane $\zeta^* = 0$)


Attractor intersection with plane



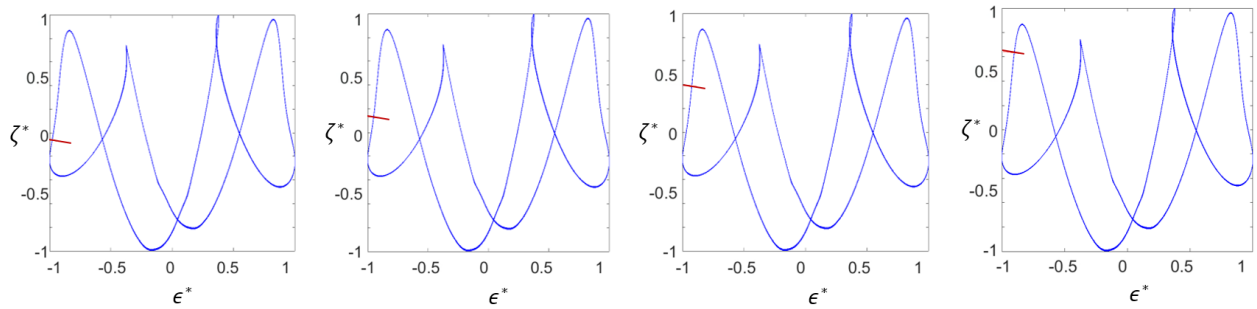
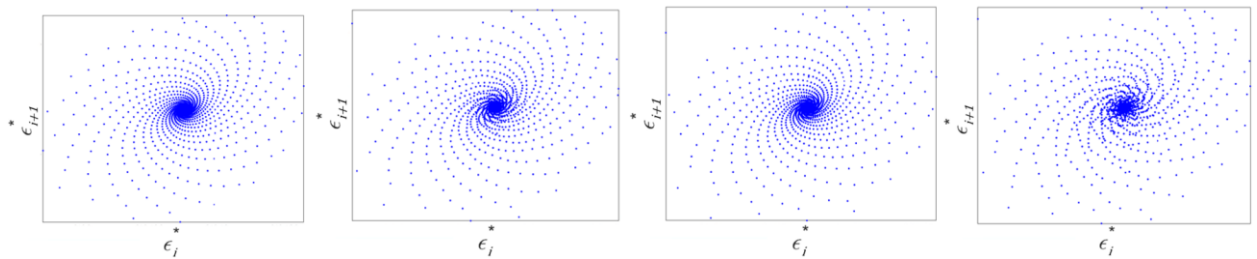
Poincaré map ϵ_i^* vs ϵ_{i+1}^*

 Poincaré map ϵ^* vs iteration


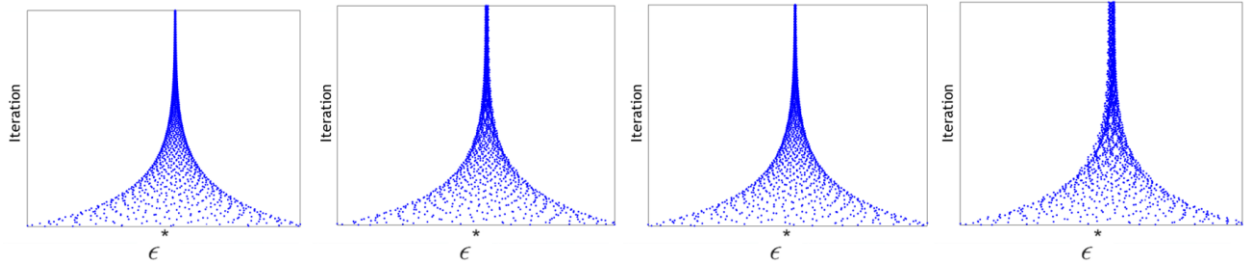
3D Poincaré map



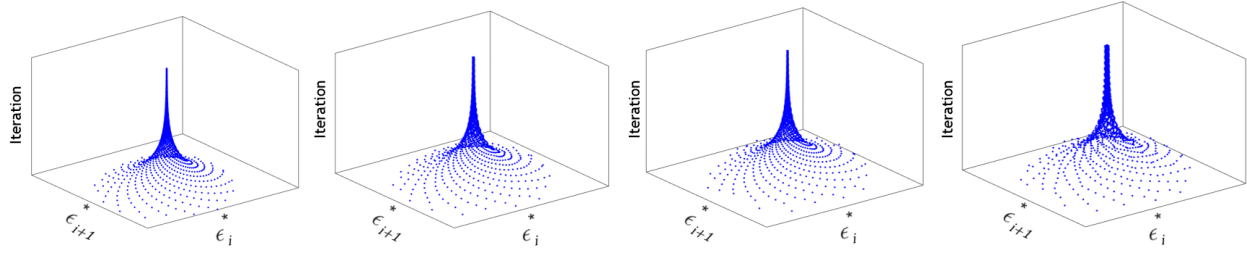
$D/d = 6.65$ – 2D Analysis

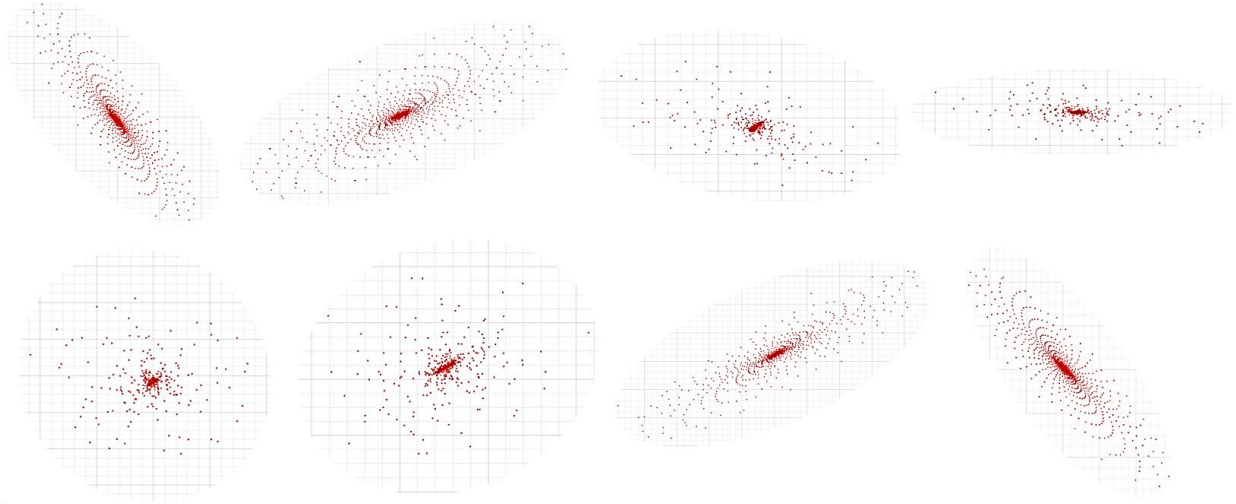
Attractor intersection with line


 Poincaré map ϵ_i^* vs ϵ_{i+1}^*


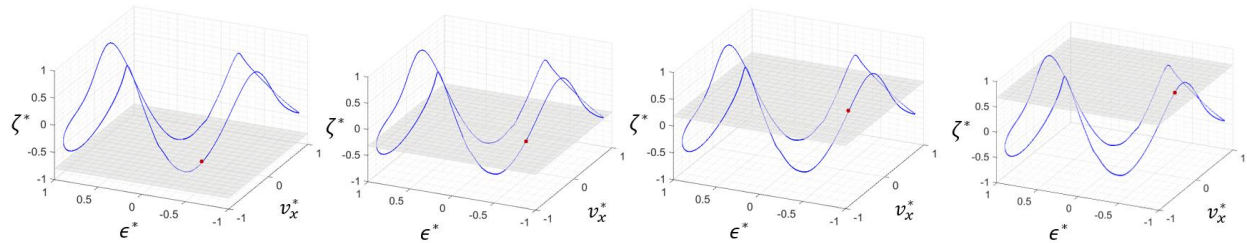
Poincaré map ϵ^* vs iteration


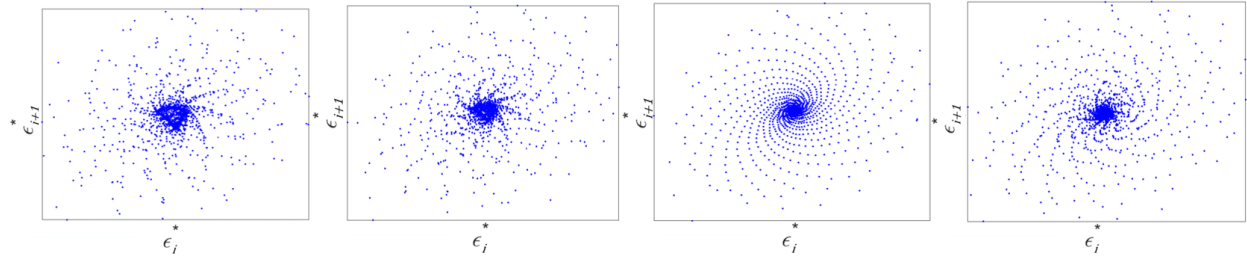
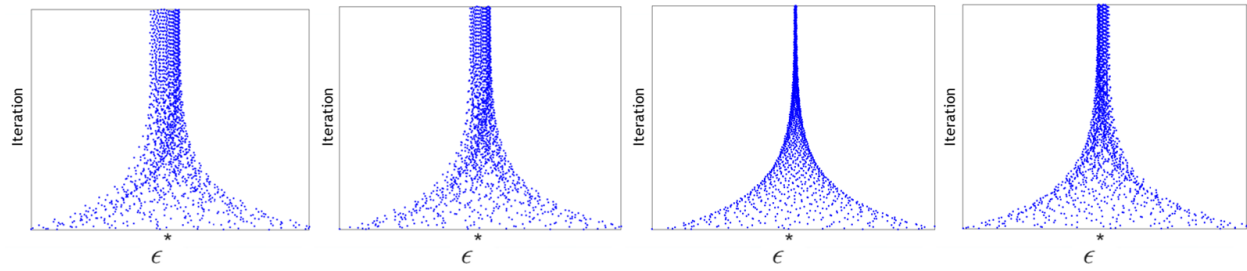
3D Poincaré map


 $D/d = 6.65$ – 3D Analysis

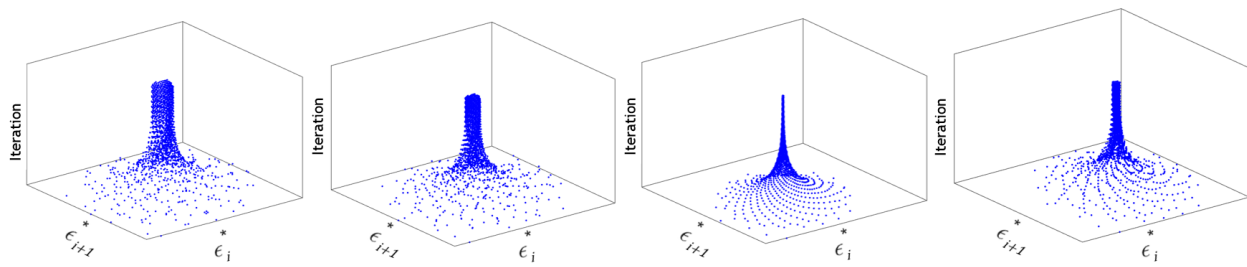
 Poincaré section (from intersection with plane $\zeta^* = 0$)


Attractor intersection with plane



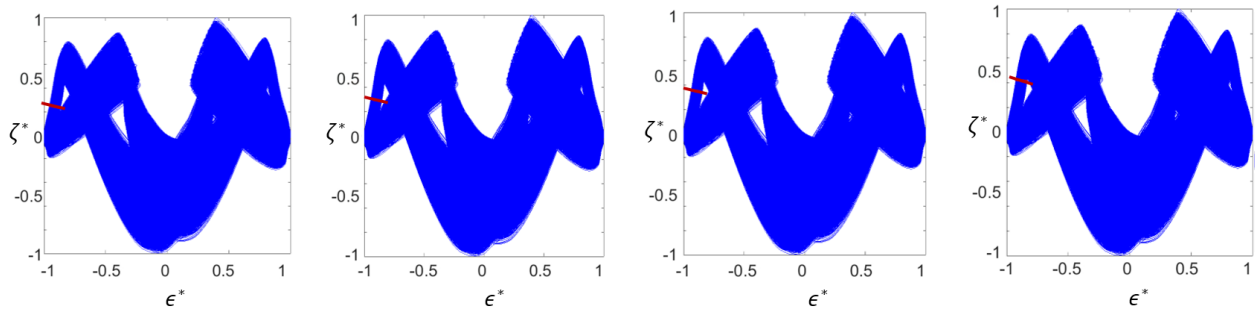
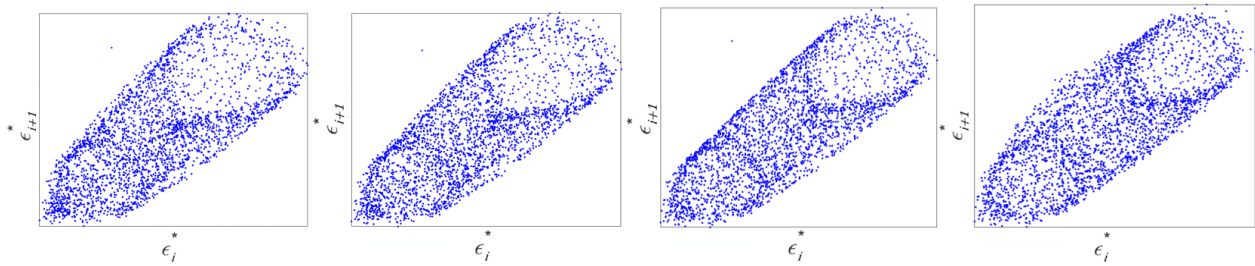
Poincaré map ϵ_i^* vs ϵ_{i+1}^*

 Poincaré map ϵ^* vs iteration


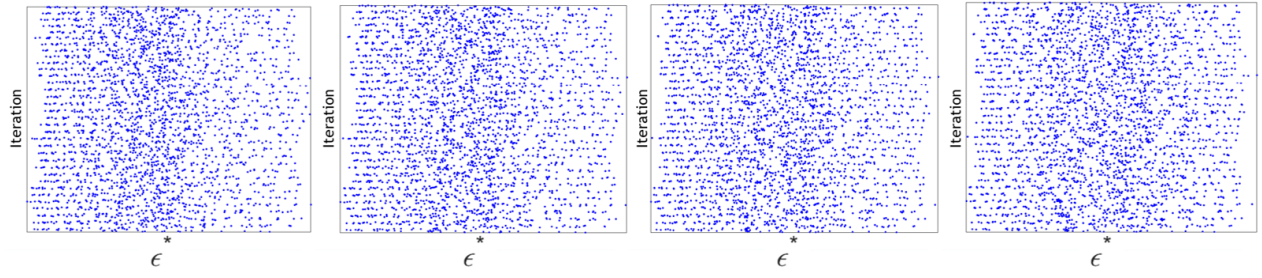
3D Poincaré map



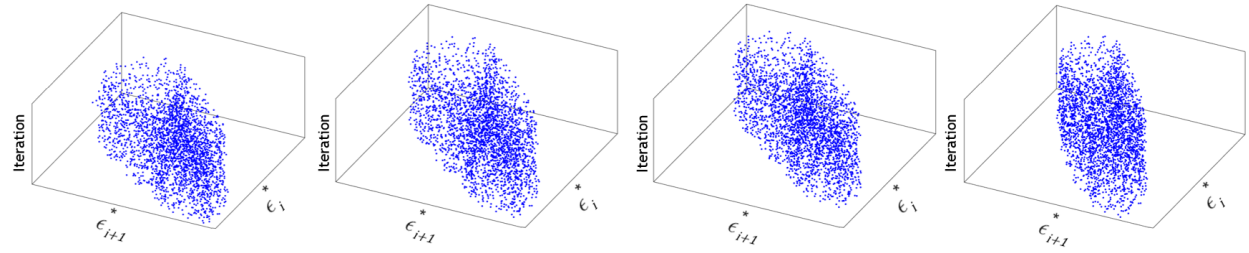
$D/d = 6.75$ – 2D Analysis

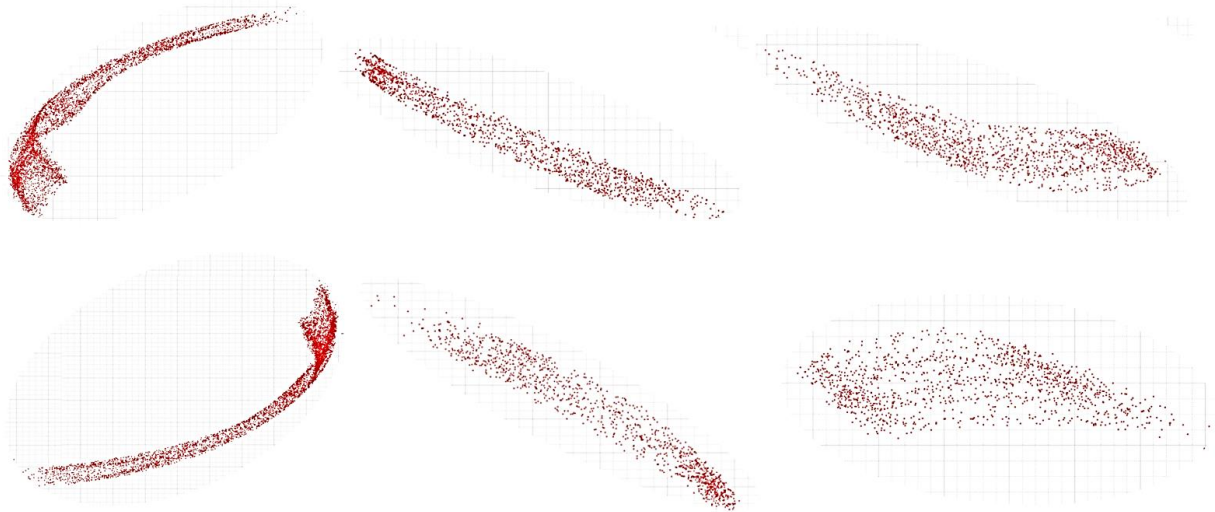
Attractor intersection with line


 Poincaré map ϵ_i^* vs ϵ_{i+1}^*


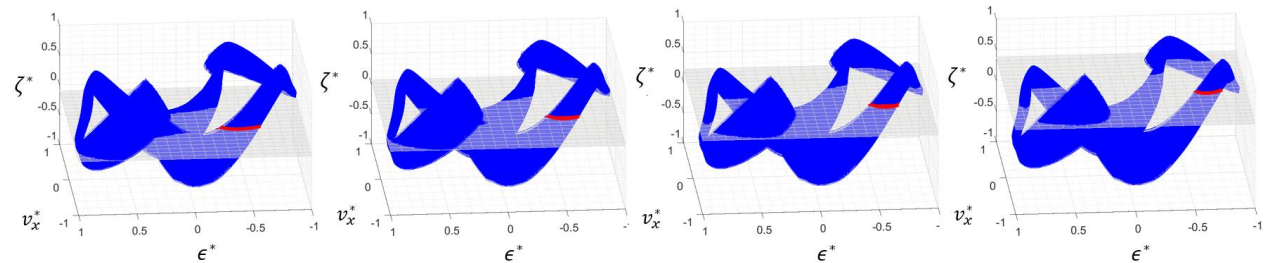
Poincaré map ϵ^* vs iteration


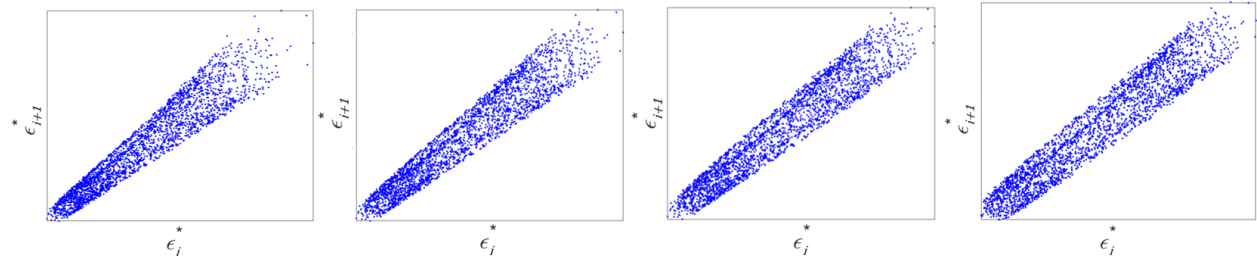
3D Poincaré map


 $D/d = 6.75$ – 3D Analysis

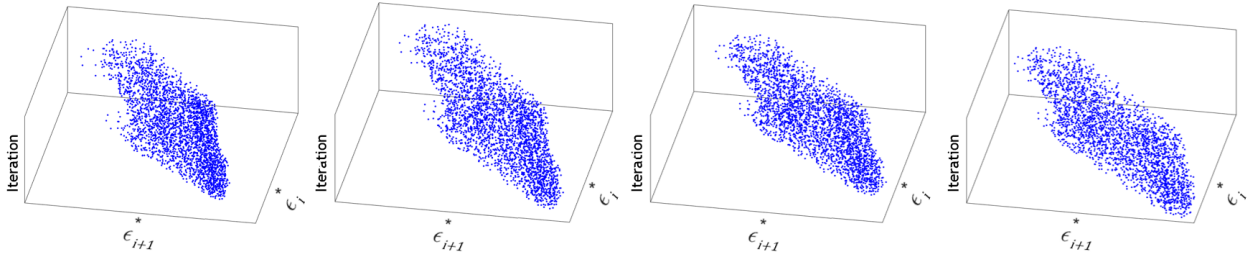
 Poincaré section (from intersection with plane $\zeta^* = 0$)


Attractor intersection with plane



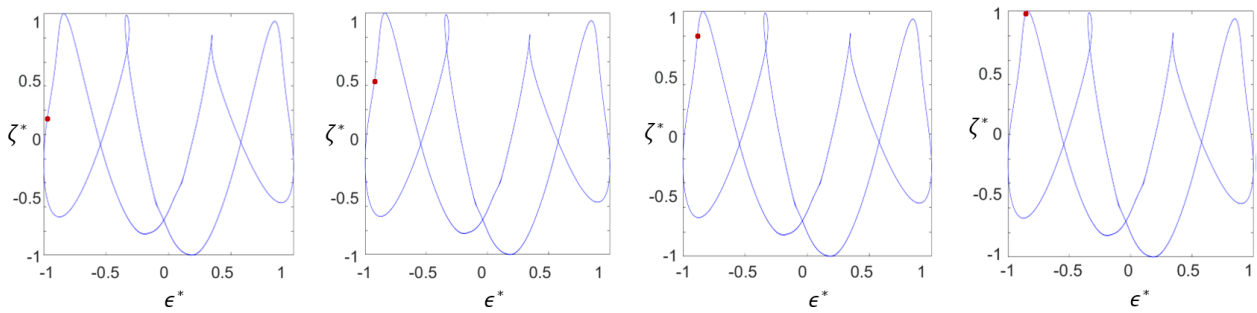
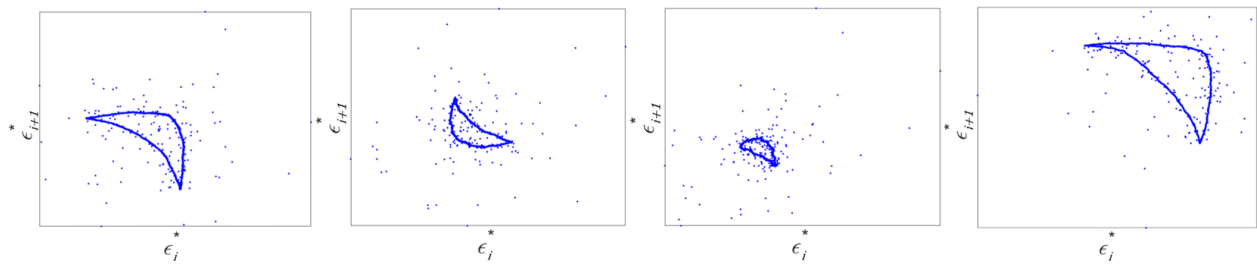
Poincaré map ϵ_i^* vs ϵ_{i+1}^*

 Poincaré map ϵ^* vs iteration

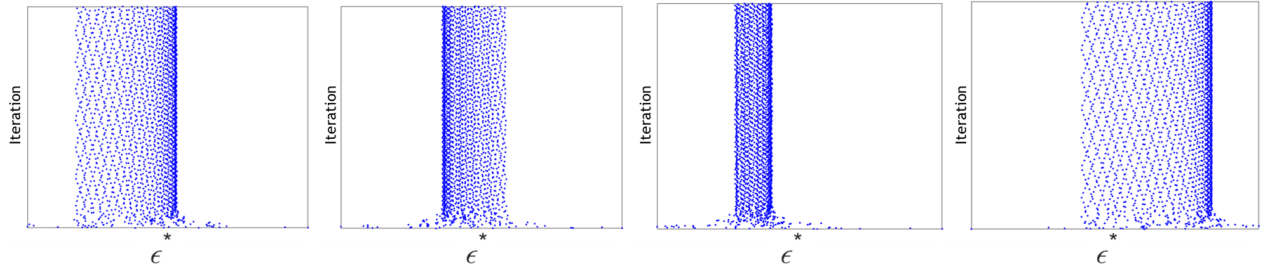

3D Poincaré map



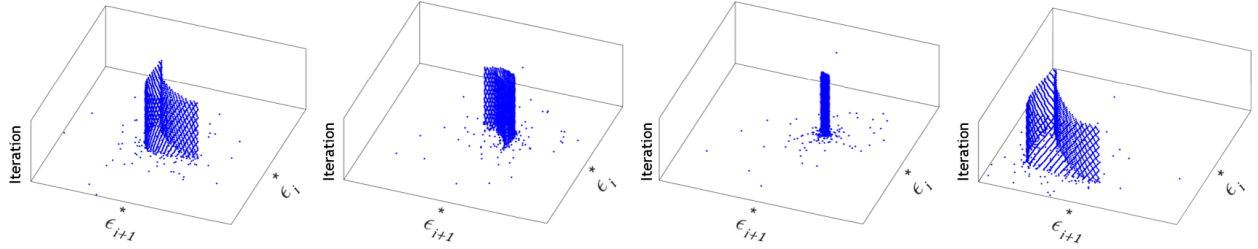
$D/d = 6.85$ – 2D Analysis

Attractor intersection with line

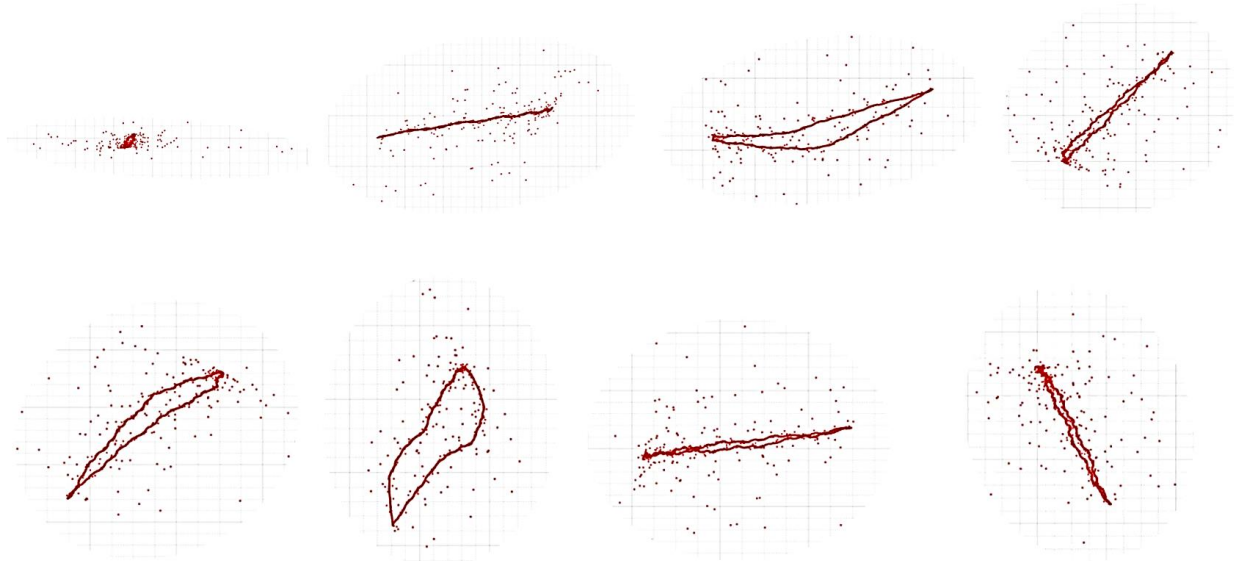

 Poincaré map ϵ_i^* vs ϵ_{i+1}^*


Poincaré map ϵ^* vs iteration


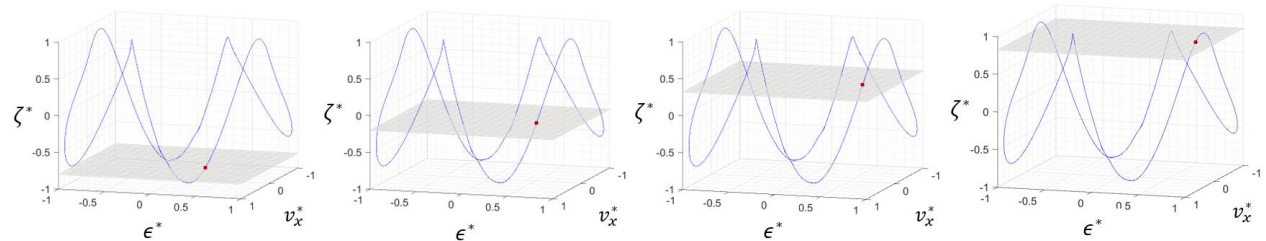
3D Poincaré map

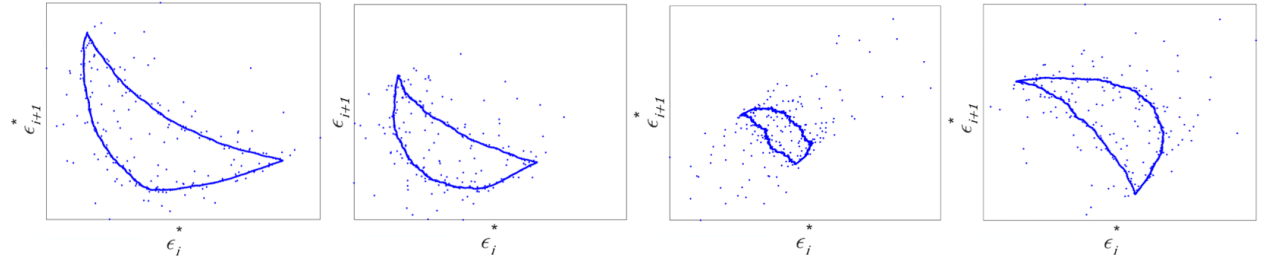
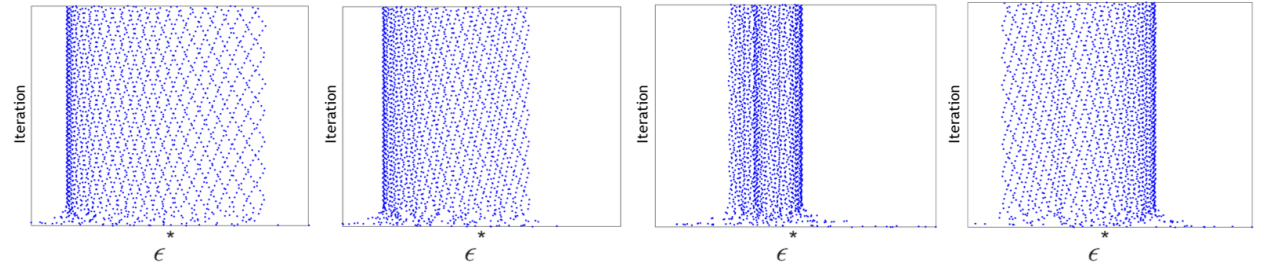


D/d = 6.85 – 3D Analysis

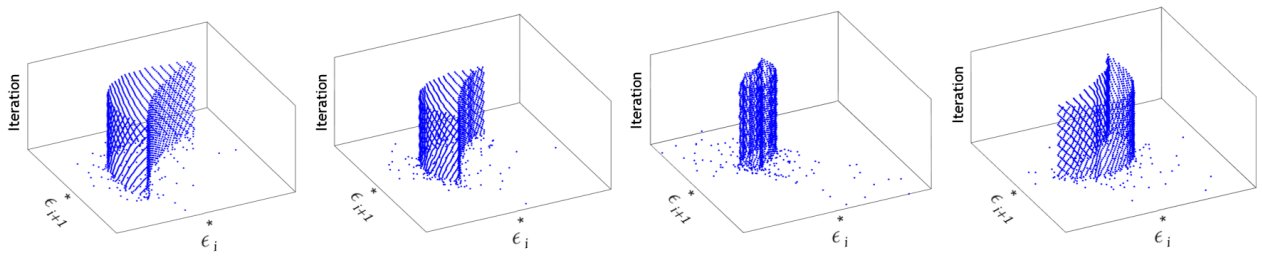
 Poincaré section (from intersection with plane $\zeta^* = 0$)


Attractor intersection with plane



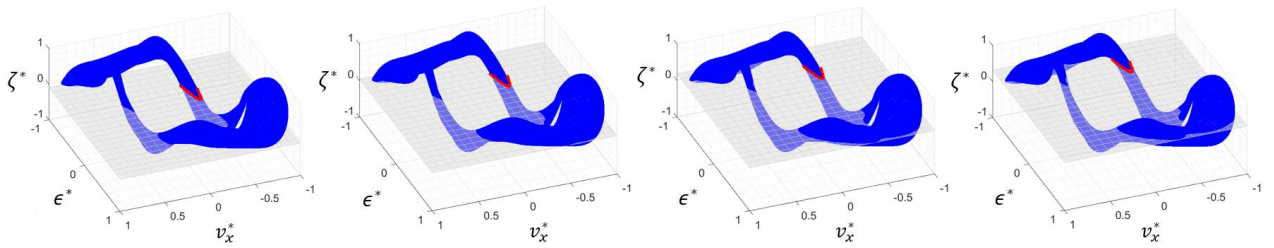
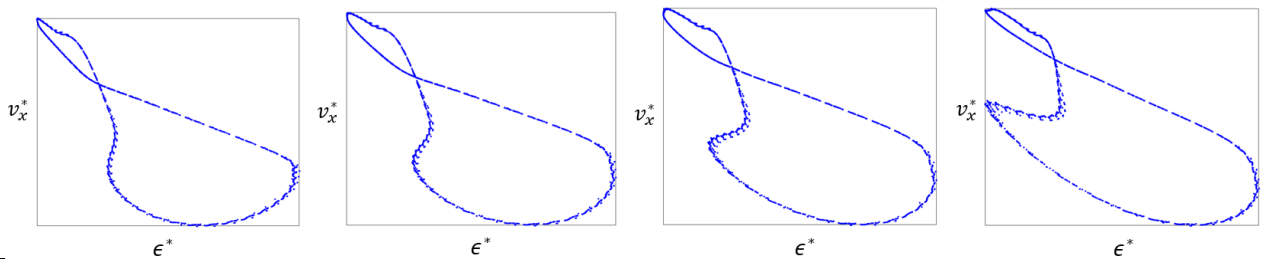
Poincaré map ϵ_i^* vs ϵ_{i+1}^*

 Poincaré map ϵ^* vs iteration


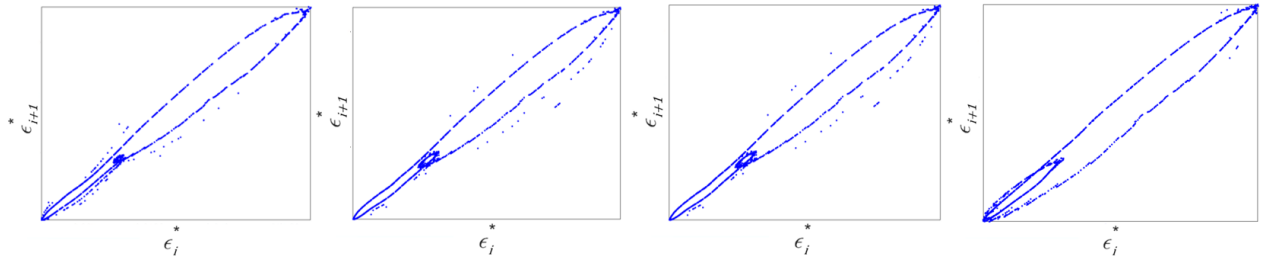
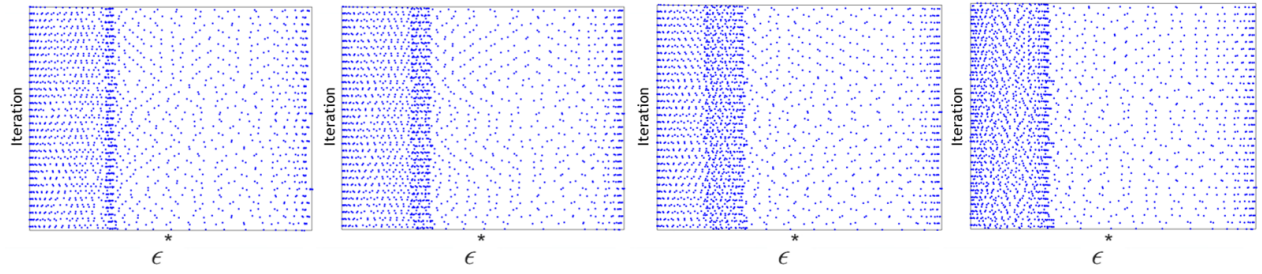
3D Poincaré map



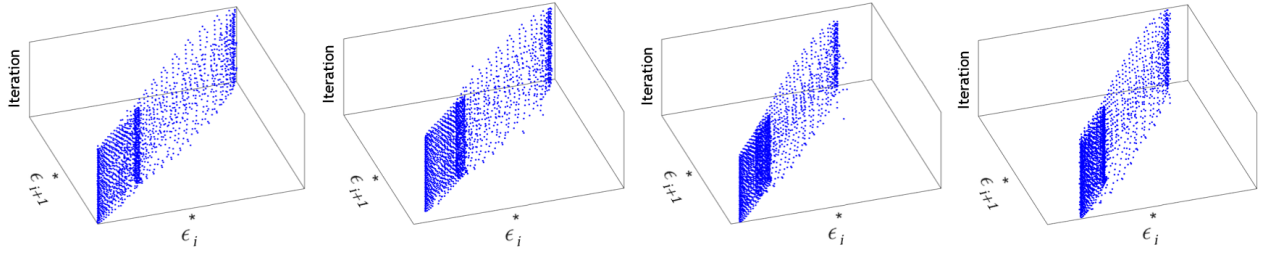
$D/d = 6.95$ – 3D Analysis

Attractor intersection with plane


 Poincaré section (ϵ^* vs v_x^*)


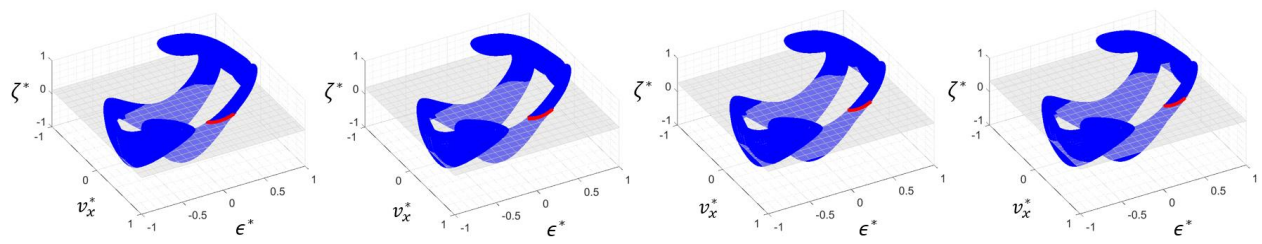
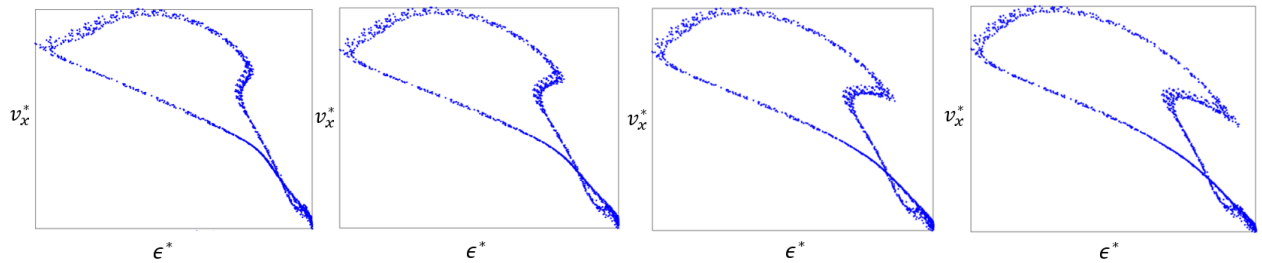
Poincaré map ϵ_i^* vs ϵ_{i+1}^*

 Poincaré map ϵ^* vs iteration


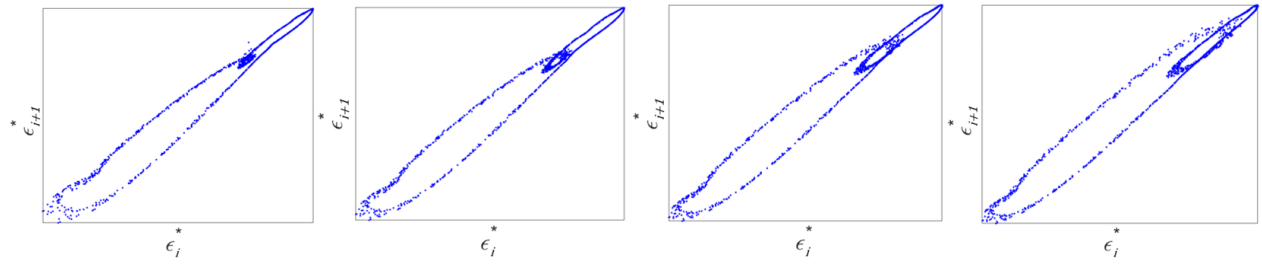
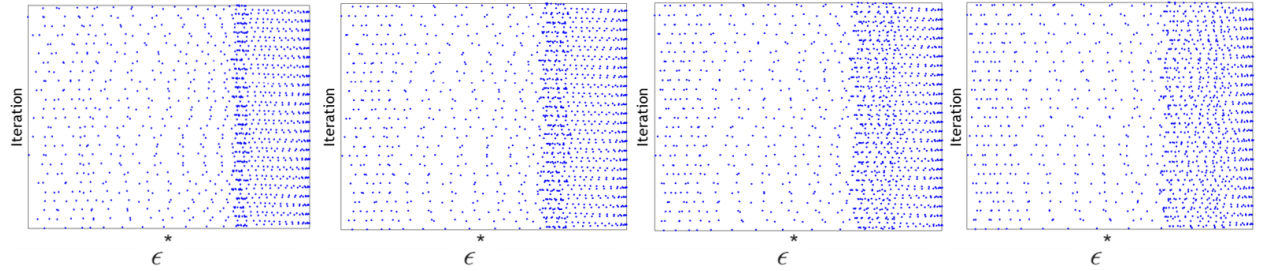
3D Poincaré map



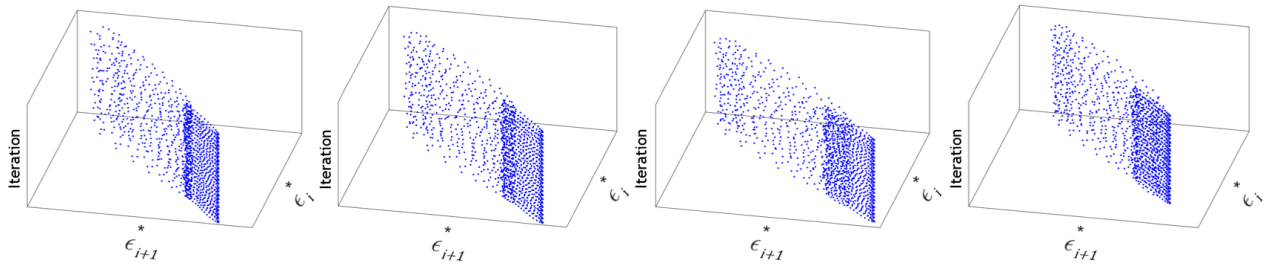
$D/d = 7.05$ – 3D Analysis

Attractor intersection with plane


 Poincaré section (ϵ^* vs v_x)


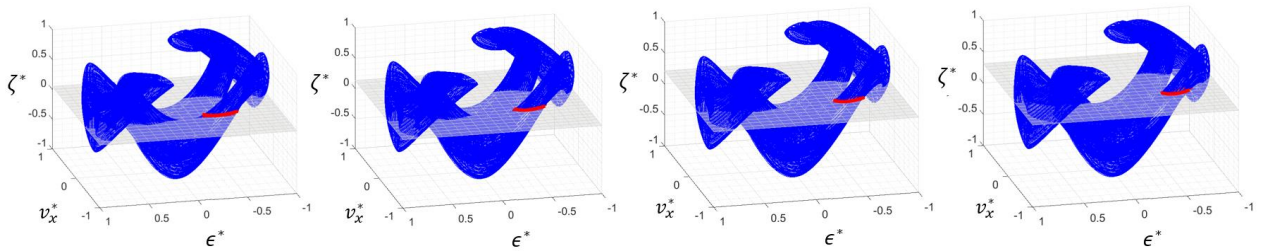
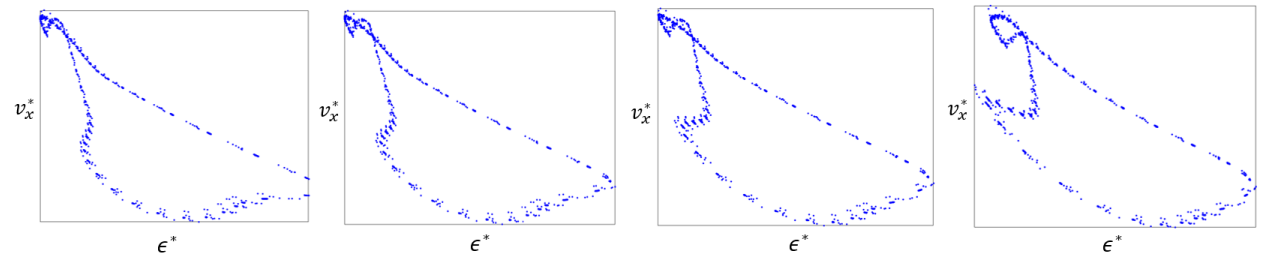
Poincaré map ϵ_i^* vs ϵ_{i+1}^*

 Poincaré map ϵ^* vs iteration


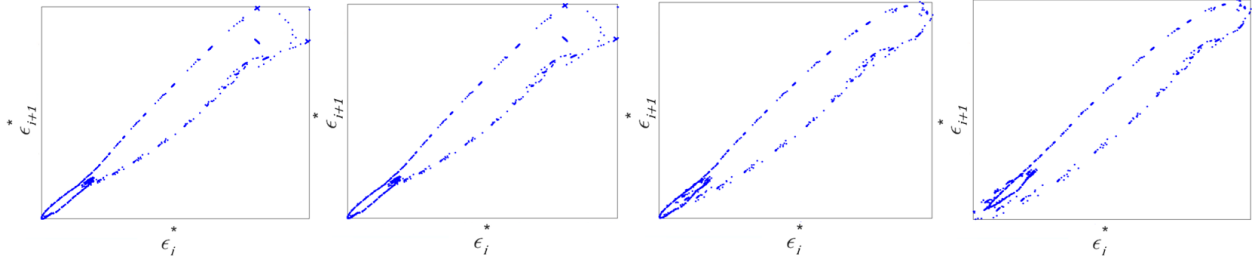
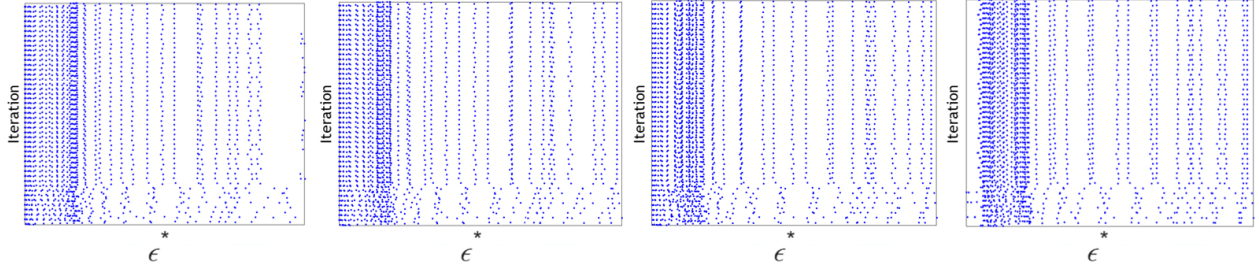
3D Poincaré map



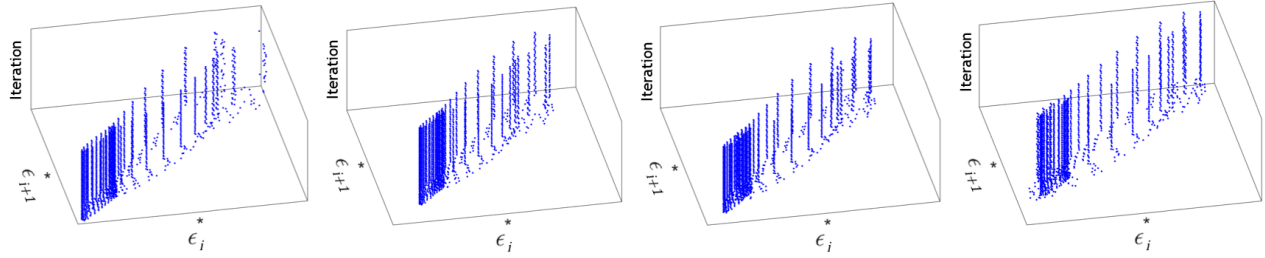
$D/d = 7.15$ – 3D Analysis

Attractor intersection with plane


 Poincaré section (ϵ^* vs v_x^*)


Poincaré map ϵ_i^* vs ϵ_{i+1}^* Poincaré map ϵ^* vs iteration

3D Poincaré map



In order to compare the ratios $6.35 < D/d < 7.15$, the Poincaré maps are shown in Figure IV.34 and in Figure IV.35. In Figure IV.36 are shown the 3D maps. In these figures, the axis scale was omitted since the vorticity values are different for each attractor. The maximum and minimum values as well as the amplitude of the vorticity are shown in Table IV.5 for the first 10^4 iterations, *it 1*, and for the last 10^4 iterations, *it N*.

Analysing Figure IV.35 it is visible that when the attractor starts to take shape at $D/d = 6.35$, the points of the Poincaré map have a tangled relation. As the attractor assumes a *parabola* shape between $D/d = 6.45$ and $D/d = 6.55$, the Poincaré points make a circular shape. For the best ratios, $D/d = 6.65$ and $D/d = 6.85$, where the attractor is *W* shaped, the points are concentrated, i.e., they have a smaller amplitude. The shape of the map for $D/d = 6.65$ is peculiar since it forms a spinning spiral, as already mentioned. For the larger ratios, $6.95 < D/d < 7.15$, as the attractor gets thicker and similar to a *net*, the Poincaré points have an elliptical relation.

For all the ratios except $D/d = 6.65$ and $D/d = 6.85$, the relation between the vorticity of the points of the Poincaré section is maintained since the data points are equally distributed as the number of iterations increases, as shown in Figure IV.34 and Table IV.5. For several ratios $D/d = 6.35$,

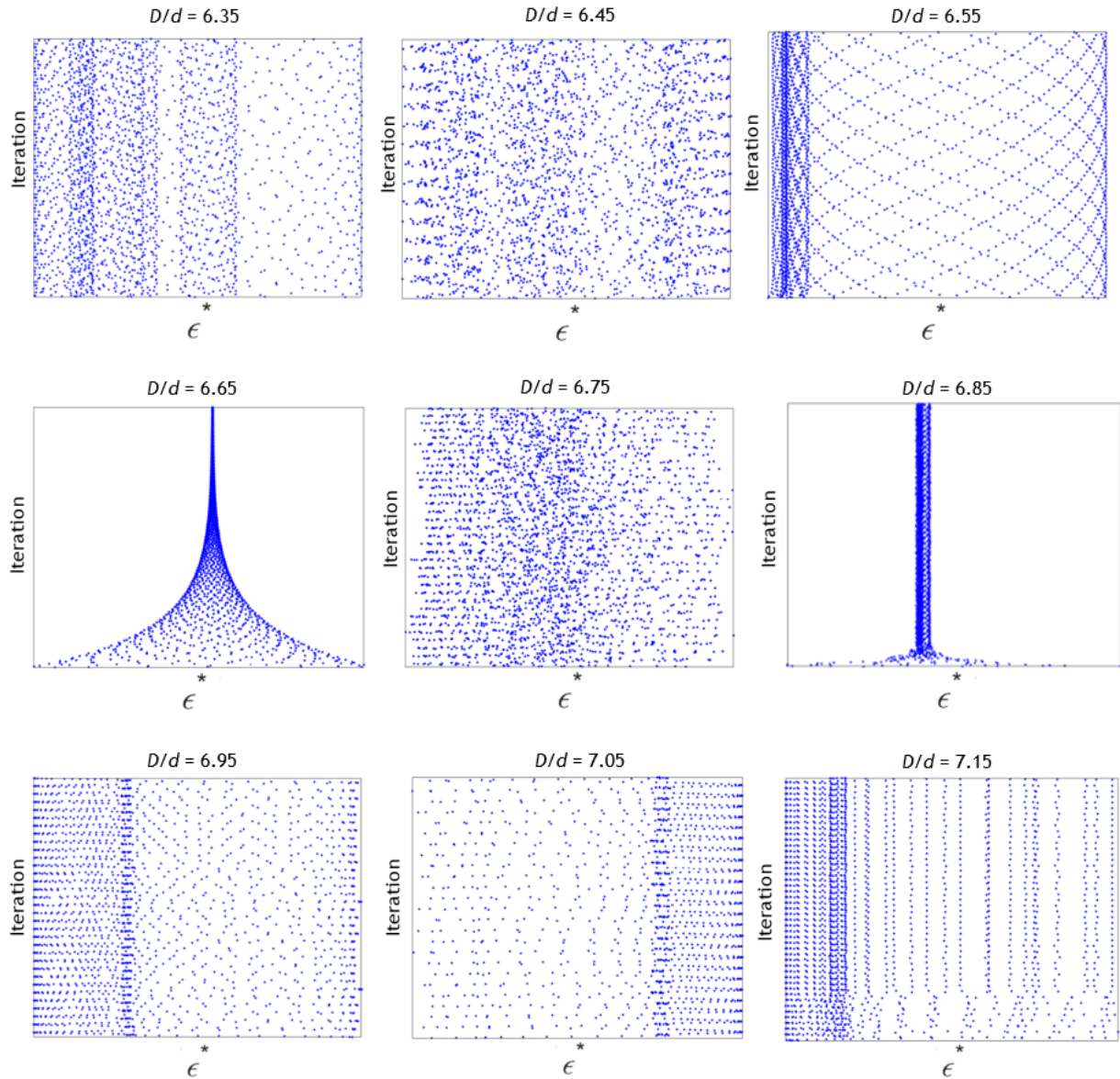
$D/d = 6.55$, $D/d = 6.85$, $D/d = 6.95$ and $D/d = 7.15$, the system tends to lower vorticities since there is a larger number of points at the left of the map. In contrast, $D/d = 7.05$ tends to higher vorticities since there is a larger number of points at the right of the map. The bias of the points is particularly visible in Figure IV.34 for $6.95 < D/d < 7.15$. For $D/d = 6.95$ and $D/d = 7.15$ which have a bias to the left, the maps have a lasso at the left bottom. For $D/d = 7.05$, Figure IV.35 shows a lasso at the top right.

In sections IV.2 and IV.3.1 it was shown that for $6.65 < D/d < 6.85$, the best ratio is $D/d = 6.65$ since the BLMS study showed that the exit conditional probabilities were closer to 0.5. Moreover, the measurements of the interfacial area generation have shown that a larger area, associated to better mixing, was obtained with $D/d = 6.65$.

From the Poincaré maps, it is possible to conclude that with $D/d = 6.65$ and $D/d = 6.85$, for a larger number of iterations, the amplitude of the vorticity is small, 2.79×10^{-4} with $D/d = 6.65$ and 3.39×10^{-6} with $D/d = 6.85$ (see Table IV.5). For these ratios, Table IV.5 shows that there is a decrease of an order of magnitude from $\Delta\epsilon^*(it\ 1)$ to $\Delta\epsilon^*(it\ N)$; for the other ratios, $\Delta\epsilon^*(it\ 1) = \Delta\epsilon^*(it\ N)$. Figure IV.34 shows that the attractor for $D/d = 6.85$ takes less iterations (flow time) to stabilize since the Poincaré map assumes a cylindrical shape with a biased base. In contrast, at $D/d = 6.65$, the biased base takes a larger number of iterations to “disappear”. Thus, the Poincaré map assumes a spinning spiral shape, instead of a cylindrical shape. The fact that the vorticity has a smaller amplitude for $D/d = 6.85$ (in the order of 10^{-6}) indicates that the behaviour of the NETmix system is nearly periodic. The Poincaré map shows that the points are biased to the left where a larger concentration of points is visible. Moreover, the structure is slightly displaced to the left. For $D/d = 6.65$, the data points are centred, and their distribution is uniform (there is no bias). These characteristics might explain the better mixing for $D/d = 6.65$. It is known that mixing is promoted by chaotic features, the fact that the amplitude of the vorticity is larger, in the order of 10^{-4} , possibly promotes mixing since the system is “less periodic” than with the ratio $D/d = 6.85$. In Table IV.4 is shown that the attractor changes its shape for $D/d = 6.85$ while for $D/d = 6.65$, the shape is maintained. Thus, it is possible to conclude that an attractor that holds its shape and is not biased in a quasi-periodic regime are the best conditions for mixing in the NETmix reactor.

Table IV.5 Maximum and minimum vorticity, ϵ^* , in chamber C6 for $6.35 < D/d < 7.15$, at $Re = 300$ during 114 s.

Vorticity Amplitude						
D/d	$\epsilon^*_{min} (it 1)$	$\epsilon^*_{max} (it 1)$	$\epsilon^*_{min} (it N)$	$\epsilon^*_{max} (it N)$	$\Delta\epsilon^* (it 1)$	$\Delta\epsilon^* (it N)$
6.35	0.90500	0.93600	0.93600	0.93600	3.10×10^{-2}	3.10×10^{-2}
6.45	-0.61500	-0.48000	-0.61500	-0.48000	1.35×10^{-1}	1.35×10^{-1}
6.55	-0.90850	-0.88550	-0.90850	-0.88550	2.30×10^{-2}	2.30×10^{-2}
6.65	-0.95000	-0.94850	-0.94919	-0.94891	1.50×10^{-3}	2.79×10^{-4}
6.75	-0.92600	-0.85600	-0.92600	-0.85600	7.00×10^{-2}	7.00×10^{-2}
6.85	-0.96596	-0.96593	-0.96595	-0.96594	3.00×10^{-5}	3.39×10^{-6}
6.95	-0.51520	-0.18550	-0.51520	-0.18550	3.30×10^{-1}	3.30×10^{-1}
7.05	0.14380	0.61040	0.14380	0.61040	4.67×10^{-1}	4.67×10^{-1}
7.15	-0.59160	-0.20420	-0.59160	-0.20420	3.87×10^{-1}	3.87×10^{-1}

Figure IV.34 Poincaré map ϵ^* vs iteration for $6.35 < D/d < 7.15$, during 114 s.

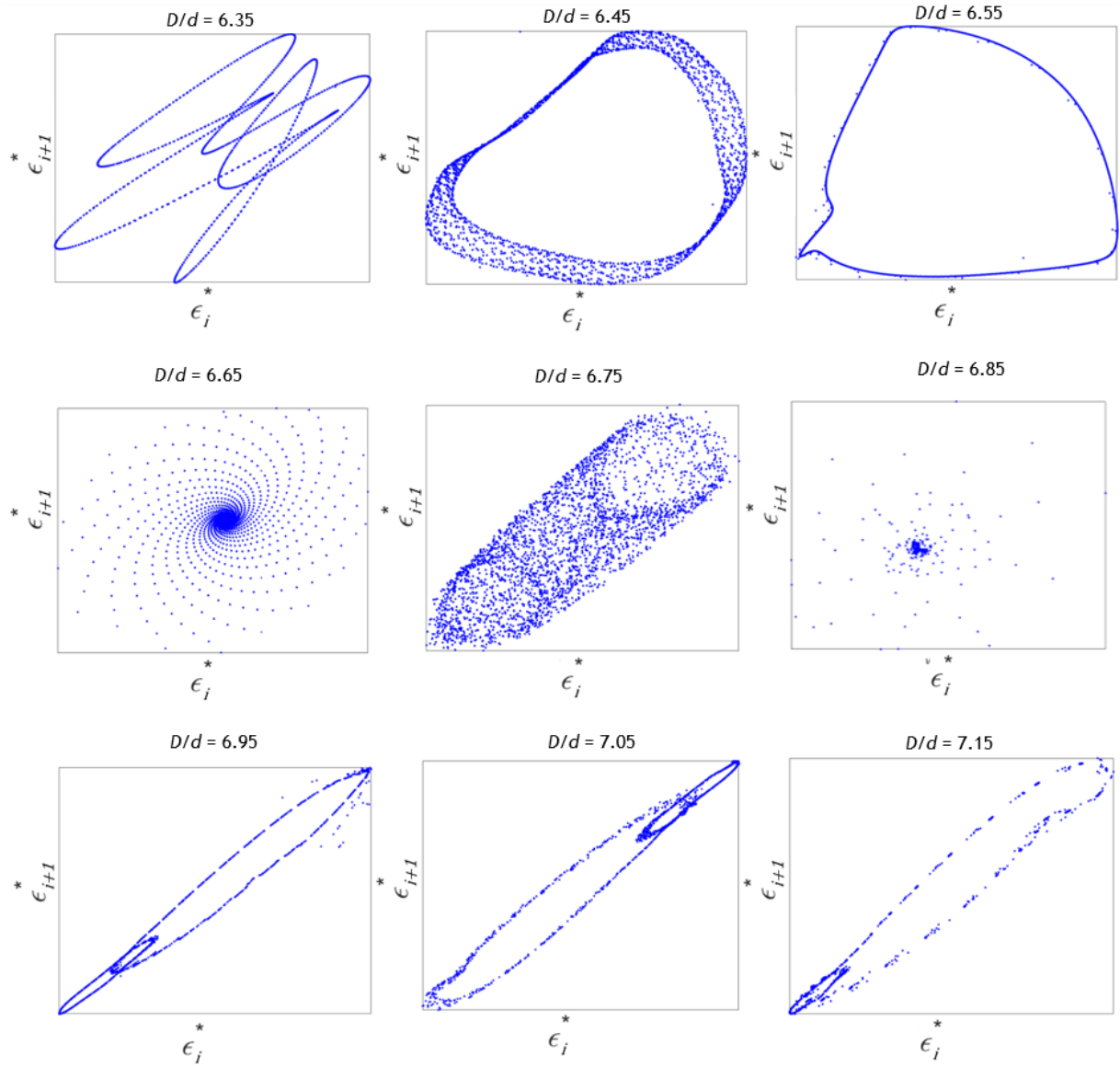


Figure IV.35 Poincaré map ϵ_i^* vs ϵ_{i+1}^* for $6.35 < D/d < 7.15$, during 114 s.

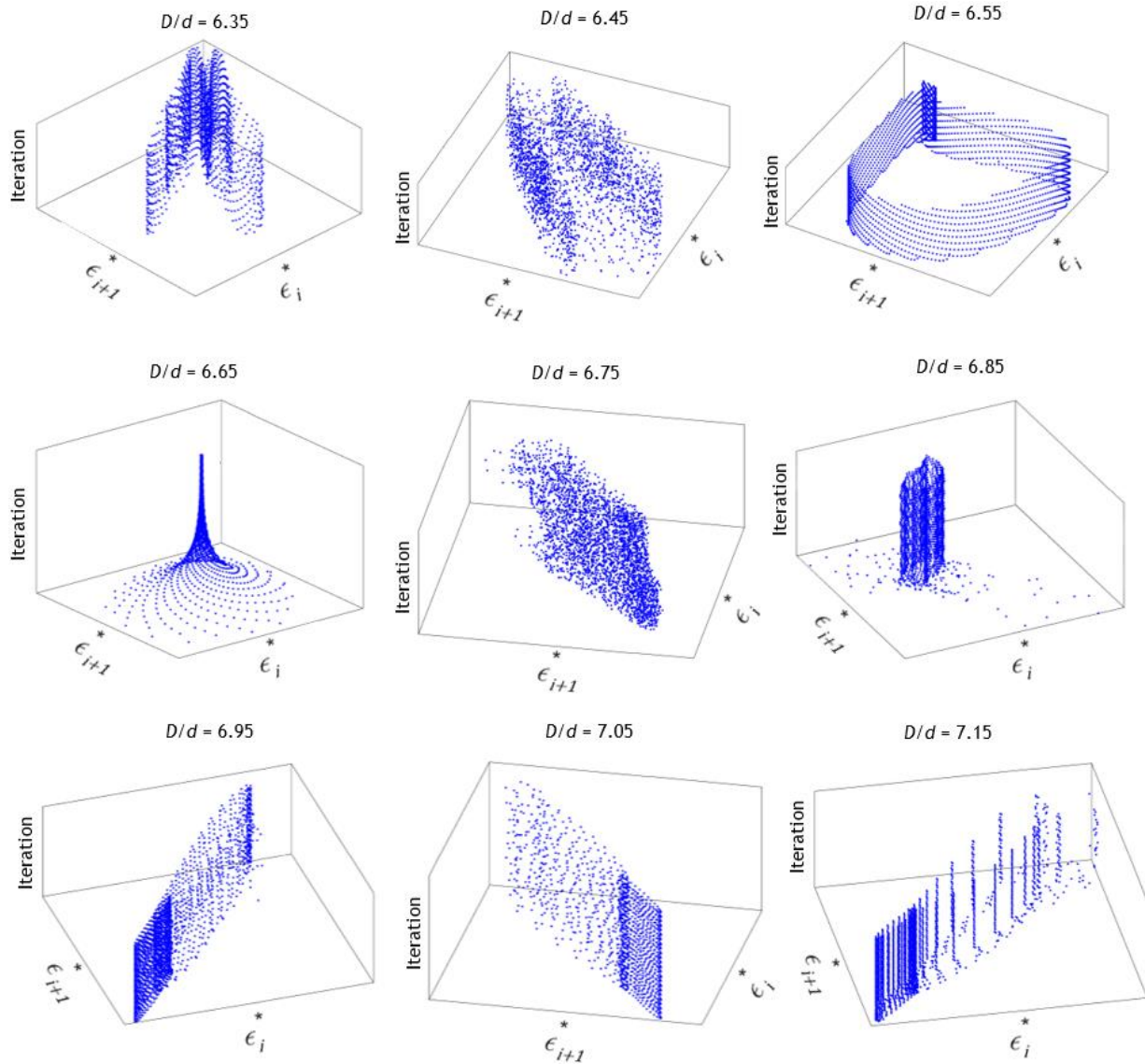


Figure IV.36 Poincaré maps 3D for $6.35 < D/d < 7.15$, during 114 s.

For all the ratios, the variation of the Poincaré maps with the intersection line is shown in the videos, *Poincare_maps.mp4*, *Poincare_maps_1.mp4* and *Poincare_maps_3D.mp4* of the folder *Mixing_and_Controlled_Combustion_in_NETmix_videos*.

The algorithms that were developed to perform the attractor intersection to obtain the Poincaré sections and maps for the 2D and 3D analysis are shown below.

Note that, as the attractor is built, each iteration (flow time) provides a new data pair of strain rate, ζ^* , and vorticity, ϵ^* (see Figure IV.24). Thus, the attractor is constructed through the increment of series of data points which form a *line* with a more or less repetitive trajectory, depending on the ratio D/d .

2D Poincaré Section Algorithm

1. Chose a line in the form $y = mx + b$ that crosses one of the “arms” of the attractor (ϵ^* vs ζ^*);
2. Select the portion of the attractor that is going to be intersected (maximum and minimum values of ϵ^* and ζ^* as well as their iterations, it);
3. Divide the attractor data points, i , into series, i.e., $it(i + 1) = it(i) + 1$;
4. For each series, draw the line $y = m_2x + b_2$ between two consecutive points, ϵ_i^* and ϵ_{i+1}^* ;
5. Intersect $m_2x + b_2 = mx + b$, and find the value of x ;
5. If $\epsilon_i^* < x < \epsilon_{i+1}^*$, the intersection for that series is found;
6. Repeat for all the series of the attractor;

The intersection is shown schematically in Figure IV.37.

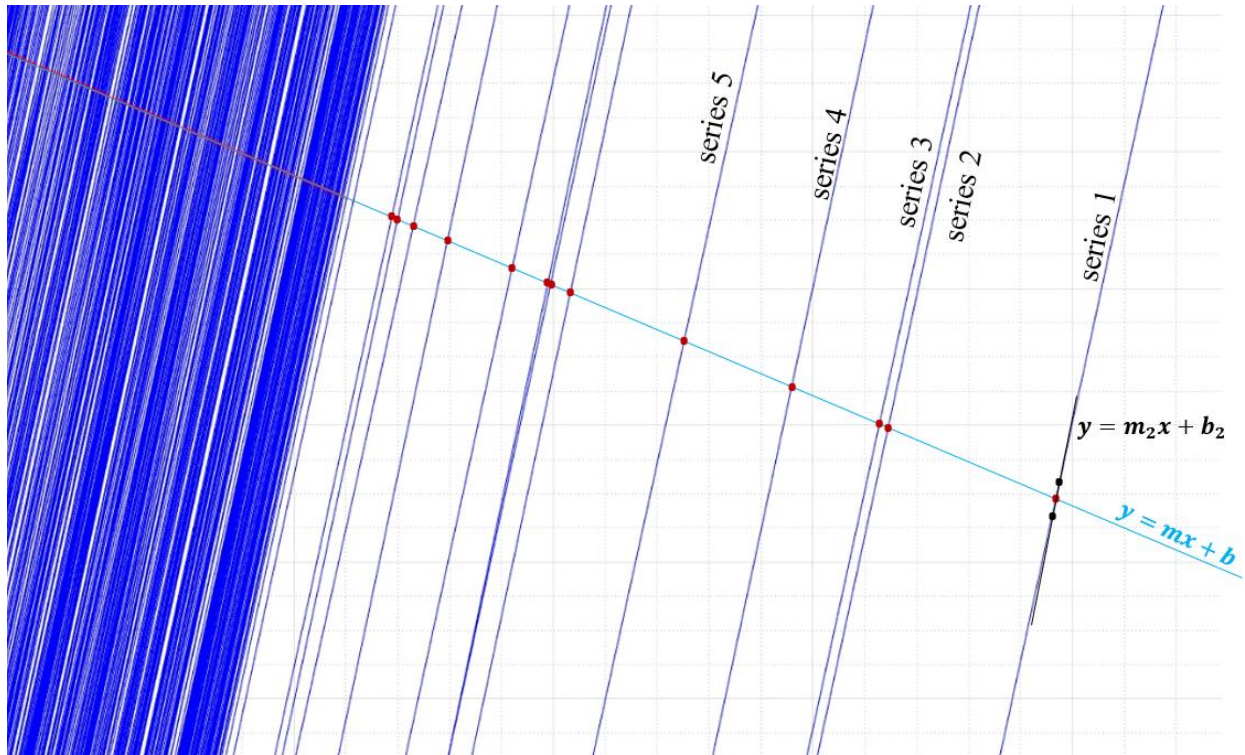


Figure IV.37 Intersection of the 2D strange attractor with a line to obtain the Poincaré section points.

3D Poincaré Section Algorithm

1. Chose a plane in the form $0(x - 0) + 0(y - 0) + 1(z - 0) = b$ that crosses one of the “arms” of the attractor (ϵ^* vs ζ^* vs v_x^*);
2. Select the portion of the attractor that is going to be intersected (maximum and minimum values of ϵ^* , ζ^* and v_x^* , as well as their iterations, it);

3. Divide the attractor data points, i , into series, i.e., $it(i + 1) = it(i) + 1$;
4. For each series, draw the 3D line in the parametric form between two consecutive points with ϵ_i^* and ϵ_{i+1}^* : $xp = \epsilon^*(i) + m(\epsilon^*(i + 1) - \epsilon^*(i))$, $yp = v_x^*(i) + m(v_x^*(i + 1) - v_x^*(i))$ and $zp = \zeta^*(i) + m(\zeta^*(i + 1) - \zeta^*(i))$;
5. Intersect the 3D line with the plane and find the value of m with MATLAB[®] function *solve*.
6. Calculate xp , yp and zp ;
7. If $\zeta_i^* < zp < \zeta_{i+1}^*$, the intersection for that series is found;
8. Repeat for all the series of the attractor.

IV.3.3.3 Bifurcation of the NETmix System

Chaotic systems are sensitive to “environmental” changes. In the previous sections it was shown that a change in a control parameter, in this case, the ratio D/d , promotes different behaviours in the NETmix system which are visible, for example, by the presence of different strange attractors. In the NETmix system, concerning the control parameter D/d , the attractor is maintained. In this way, a *global bifurcation* occurs (see Section IV.1). Moreover, since the attractor changes with D/d , the NETmix system has several bifurcations, i.e., transitions between two distinct responses of the system. To assess where these transitions occur, a spectral analysis was performed. The spectral analysis was made on the dynamic x -velocity, using the Fast Fourier Transform (FFT)

$$\gamma_x(f) = \frac{1}{\nabla t_k Npoints} \left| \sum_{k=1}^{Npoints-1} v_x^*(t_k) e^{-i2\pi f t_k} \right| \quad (IV.7)$$

where $v_x^*(t_k) = v_x(t_k) - \overline{v_x(t_k)}$, f is the frequency, t_k is the time and ∇t_k is the time step of the range of points that was used. The velocity data was provided from the CFD simulations presented previously.

Figure IV.38 shows the spectral analysis for $6.25 < D/d < 7.25$. For the lower and larger ratios $D/d = 6.25$ and $D/d = 7.25$, which have poor mixing and are represented by an undefined structure (see Figure IV.23), the frequencies are not discrete. For $D/d = 6.35$, where the attractor appears, the frequencies are discrete, it is possible to distinguish a principal frequency at 20 Hz and two harmonics at 40 Hz and 60 Hz. It is visible a large number of interferences, which decreases for the middle ratios. At $D/d = 6.65$ and $D/d = 6.85$, the principal frequency, 20 Hz, has a higher amplitude and only one harmonic is visible, at 60 Hz. For $D/d = 6.75$, two interferent frequencies

can be distinguished near 20 Hz, which explains the fact that this ratio is not as good as the ratios with a dilution factor closer to 2, $D/d = 6.65$ and $D/d = 6.85$. For $6.95 < D/d < 7.15$, the frequencies are less discrete, i.e., the peaks have a wider base, and a larger number of interferences with lower amplitudes can be distinguished. In all the cases that were shown, the number of frequencies is higher than two, confirming the quasi-periodic/chaotic behaviour of the NETmix system. Note that, the presence of more than two frequencies was already visible in the velocity histories (Figure IV.21), where it is possible to distinguish the unfolding of the waves in at least two zones with different period (the dark blue zones are the overlap of the different frequencies).

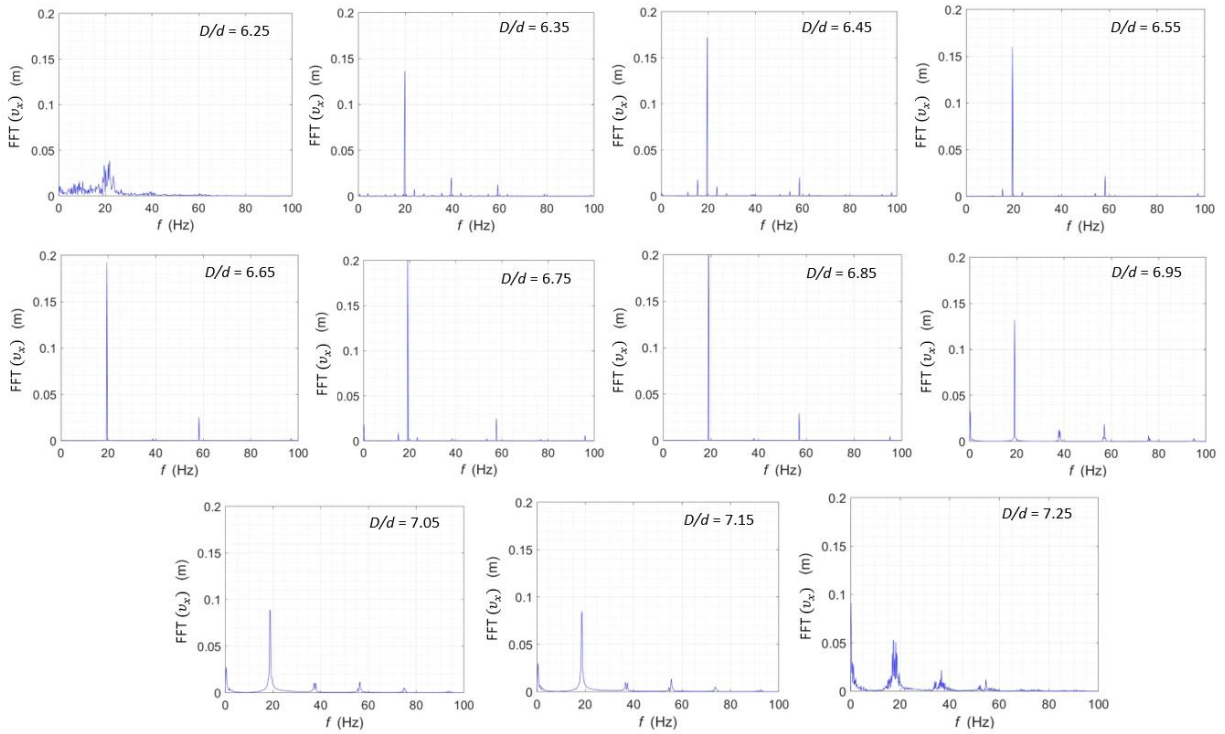


Figure IV.38 Spectral analysis in chamber C6 for $6.25 < D/d < 7.25$, at $Re = 300$ during 114 s.

From the analysis presented in Figure IV.38, it was possible to assess the oscillating frequencies of the NETmix system and to establish a relation between the attractors shape and the oscillations. To clearly understand the bifurcations of NETmix, the spectral analysis is presented in Figure IV.39, using a logarithmic scale in the y-axis. For $6.25 < D/d < 6.45$, the NETmix system is *strong-chaotic* (SC) due to the presence of a large number of interferences. At $D/d = 6.55$, the system is *weak-chaotic* (WC), in fact the number of interferent frequencies is clearly smaller. For $D/d = 6.65$ and $D/d = 6.85$, the system is *quasi-periodic* (QP), since nearly no interferent frequencies are visible. For $D/d = 6.75$, the system is already considered weak-chaotic since the number of interferent frequencies is low, but fairly noticeable. For $6.95 < D/d < 7.05$, the system is clearly weak-chaotic and becomes strong chaotic for $D/d = 7.15$ and $D/d = 7.25$ (Suzuki et al. 2016). It is then possible to establish the NETmix system pattern: SC-WC-QP-WC-QP-WC-SC

with 6 transitions. Since the chaotic behaviour is alternated with quasi-periodic behaviour, the bifurcation of the NETmix system is called *intermittent* (Hilborn 2001).

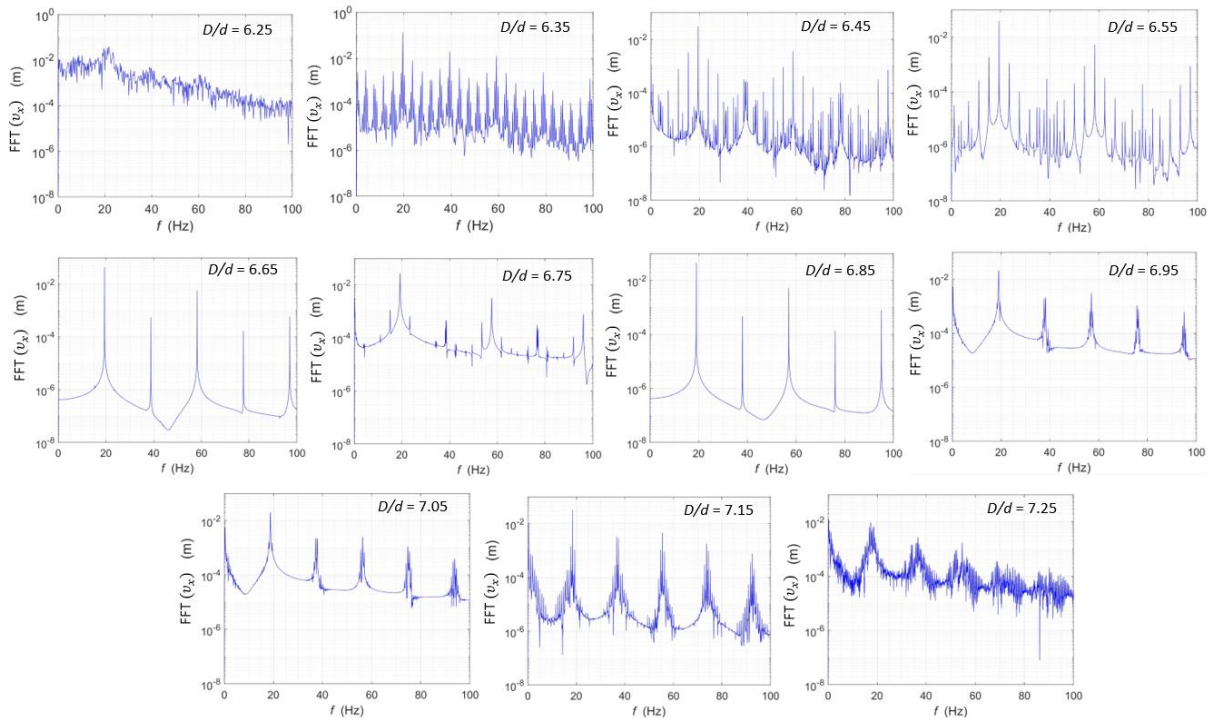


Figure IV.39 Spectral analysis in logarithmic scale in chamber C6 for $6.25 < D/d < 7.25$, at $Re = 300$ during 114 s.

Figure IV.40 shows an example of each behaviour, SC, WC and QP. It is possible to conclude that the quasi-periodic regime is associated to a regular behaviour of the system. The prevalence of a discrete strong oscillating frequency implies more regular oscillations, visible in the plot of the velocities. In consequence, a very thin strange attractor with trajectories that are very close to each other is obtained. In the weak-chaotic regime, the presence of interferent frequencies is visible, making the behaviour of the system less regular. The irregularity increases as the system enters in the strong-chaotic regime, where it is possible to observe a large number of interferent frequencies. The plot of the velocities presents an irregular behaviour, and the trajectories of the attractor are less similar to each other.

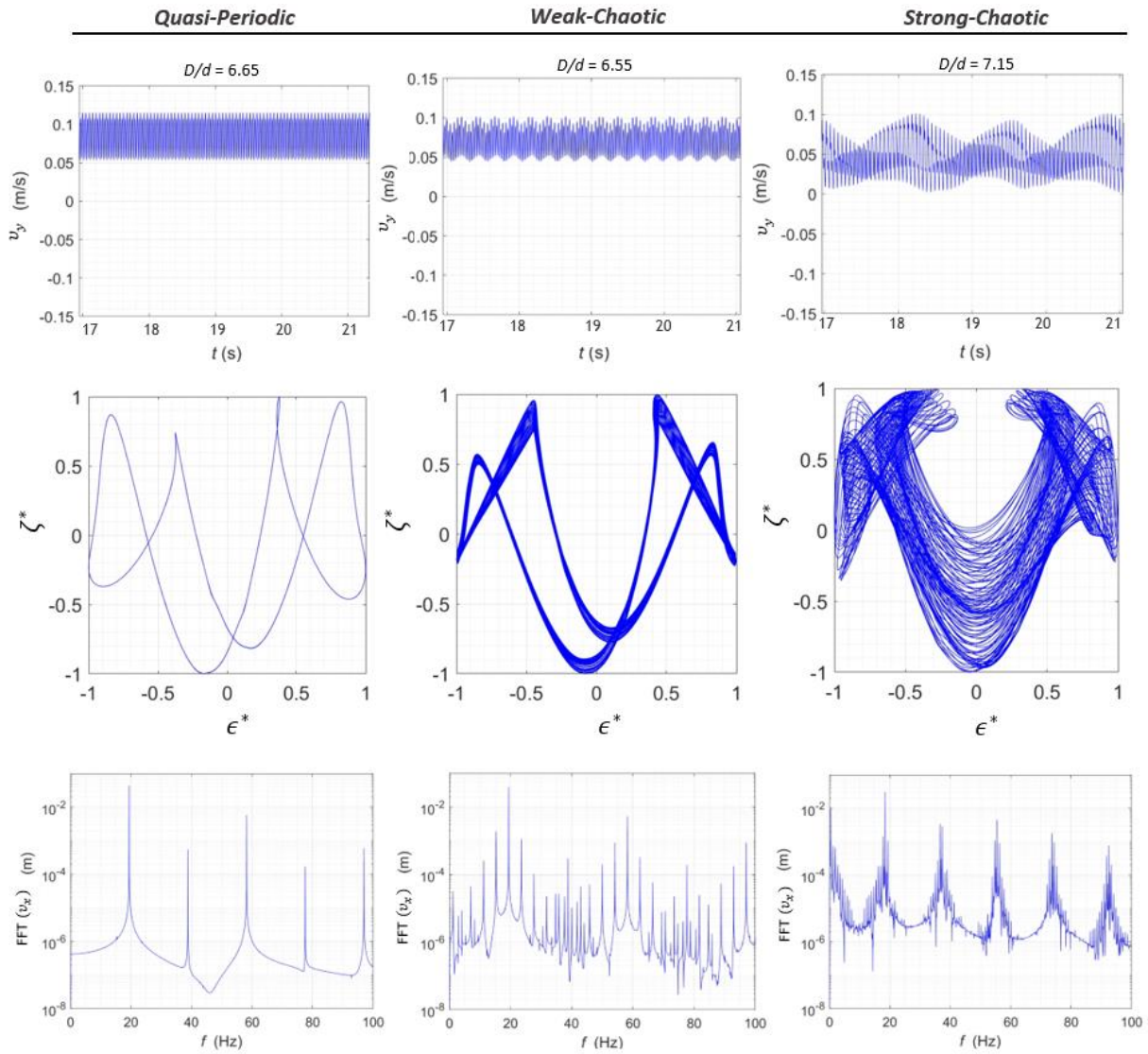


Figure IV.40 Three types of chaoticity in the NETmix reactor: QP ($D/d = 6.65$), WC ($D/d = 6.55$) and SC ($D/d = 7.15$).

IV.3.3.4 $D/d = 6.65$ Dynamic Behaviour

In the previous sections, it was shown that the ratio that leads to the best mixing in the NETmix reactor is $D/d = 6.65$. For this ratio, the dynamic behaviour of the NETmix system will be analysed in the centre of all the chambers (C2 to C8) and channels ($l1$ to $l9$ and $r1$ to $r9$) which are represented schematically at the left of Table IV.6.

The history of the y -velocity for $D/d = 6.65$ was previously shown in Figure IV.21 for chamber C6. The regular behaviour is maintained in the centre of all chambers and channels. However, the amplitude of the velocity changes from the first to the last row of the ExtendedNUB model, as shown in Figure IV.41, which can be related with the turbulence intensity, I_{v_x} , studies of Section II.3.3. In Chamber C2, v_y is negative and the oscillations have a smaller amplitude with the lowest

value of $I_{v_x} \cong 0.15$. In chambers C4 and C6, v_y is positive and its amplitude is approximately the triple of C2. The turbulence intensity is also higher, $I_{v_x} \cong 0.38$ and $I_{v_x} \cong 0.42$, respectively for C4 and C6. In fact, chambers C4 and C6 are less subjected to the inlet and outlet boundary conditions which exert an influence on the reactor dynamics. From chamber C2 to C4, the increase of amplitude of v_y is quite noticeable. In fact, the oscillation of the inlet jets is still being developed in chamber C2, while in chamber C4 the oscillating behaviour is already developed. From chamber C6 to chamber C8, the amplitude of v_y is slightly smaller ($I_{v_x} \cong 0.36$), due to the influence of the outlet which dampens the oscillations, as explained in previous chapters of this work.

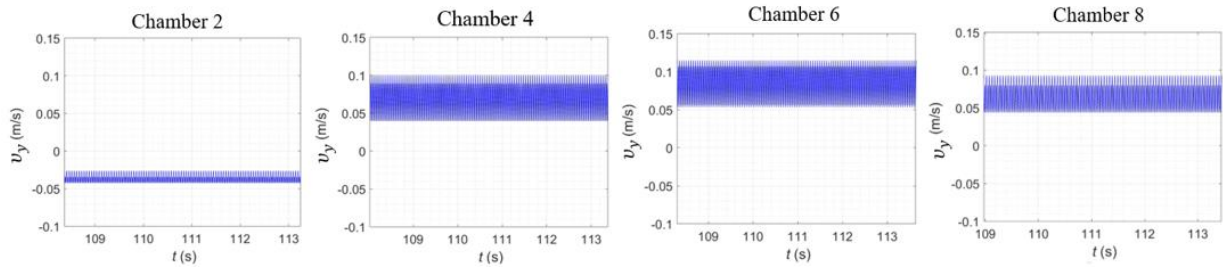


Figure IV.41 y -velocity in the centre of C2, C4, C6 and C8 of the ExtendedNUB model for $D/d = 6.65$.

In Table IV.6 are represented the maximum and minimum values for v_x (in white) and v_y (in cream) for the left channels (left side of the table), and for the right channels (right side of the table). The velocities at the centre of the chambers are shown in blue.

Table IV.6 y and x -velocities in the centre of chambers and channels.

<i>Left side</i>					<i>Right side</i>				
Channel/ chamber	$v_{x_{min}}$ (m/s)	$v_{x_{max}}$ (m/s)	$v_{y_{min}}$ (m/s)	$v_{y_{max}}$ (m/s)	$v_{y_{min}}$ (m/s)	$v_{y_{max}}$ (m/s)	$v_{x_{min}}$ (m/s)	$v_{x_{max}}$ (m/s)	Channel/ chamber
<i>l9</i>	0.155	0.220	0.153	0.194	0.143	0.180	-0.196	-0.158	<i>r9</i>
<i>l8</i>	-0.191	-0.141	0.158	0.197	0.153	0.194	0.130	0.180	<i>r8</i>
C8	-0.104	0.071	0.038	0.104	0.038	0.104	-0.104	0.071	C8
<i>l7</i>	0.144	0.206	0.160	0.206	0.160	0.206	-0.206	-0.144	<i>r7</i>
<i>l6</i>	-0.184	-0.135	0.154	0.194	0.156	0.197	0.136	0.185	<i>r6</i>
C6	-0.105	0.095	0.051	0.119	0.051	0.119	-0.105	0.095	C6
<i>l5</i>	0.158	0.209	0.159	0.208	0.159	0.208	-0.209	-0.158	<i>r5</i>
<i>l4</i>	-0.187	-0.136	0.156	0.188	0.158	0.193	0.138	0.184	<i>r4</i>
C4	-0.080	0.087	0.040	0.100	0.040	0.100	-0.08	0.087	C4
<i>l3</i>	0.145	0.198	0.152	0.195	0.152	0.195	-0.196	-0.145	<i>r3</i>
<i>l2</i>	-0.180	-0.138	0.151	0.176	0.150	0.175	0.138	0.181	<i>r2</i>
C2	-0.032	0.035	-0.042	-0.025	-0.042	-0.025	-0.032	0.035	C2
<i>l1</i>	0.140	0.163	0.147	0.160	0.147	0.160	-0.163	-0.140	<i>r1</i>

In the chambers and channels (except for C2), v_y is positive. Analysing v_x in the centre of the chambers, it is visible that, for all the chambers, $v_{x_{min}}$ is negative and $v_{x_{max}}$ is positive. In contrast, in the channels, v_x maximum and minimum is always positive or negative. At the left channels, v_x is positive in the odd rows, and negative in the even rows. At the right channels, v_x is negative in the odd rows, and positive in the even rows. It is also visible that the absolute values of $v_{x_{min}}$ and $v_{x_{max}}$ are nearly the same for the left and right channels. In the channels, the alternation of v_x between positive and negative values is visible in the phase diagrams of the normalized velocities, v_x^* vs v_y^* , shown in Figure IV.42 and in Figure IV.43. The phase diagrams of the left channels are shown in Figure IV.42. It is visible that the strange attractor is composed of a twisted loop which has an inclination to the right in odd rows (positive v_x), and an inclination to the left in even rows (negative v_x). In contrast, the attractors of the right channels (Figure IV.43) show an inclination to the left in odd rows (negative v_x), and an inclination to the right in even rows (positive v_x).

The average amplitude of v_x and v_y in the first two rows (*l1*, *l2*, *r1* and *r2*) is approximately a half of the average amplitude of the other rows. The phase diagrams (Figure IV.42 and Figure IV.43)

of the first rows show a loop with a rounder shape in comparison to the attractors of the upper rows, which are elongated. For several channels, *l4*, *l6*, *l8*, *l9*, *r4*, *r6* and *r8*, the attractor assumes a *heart* shape. From the first to the last row, the amplitude of v_x and v_y increases approximately three times.

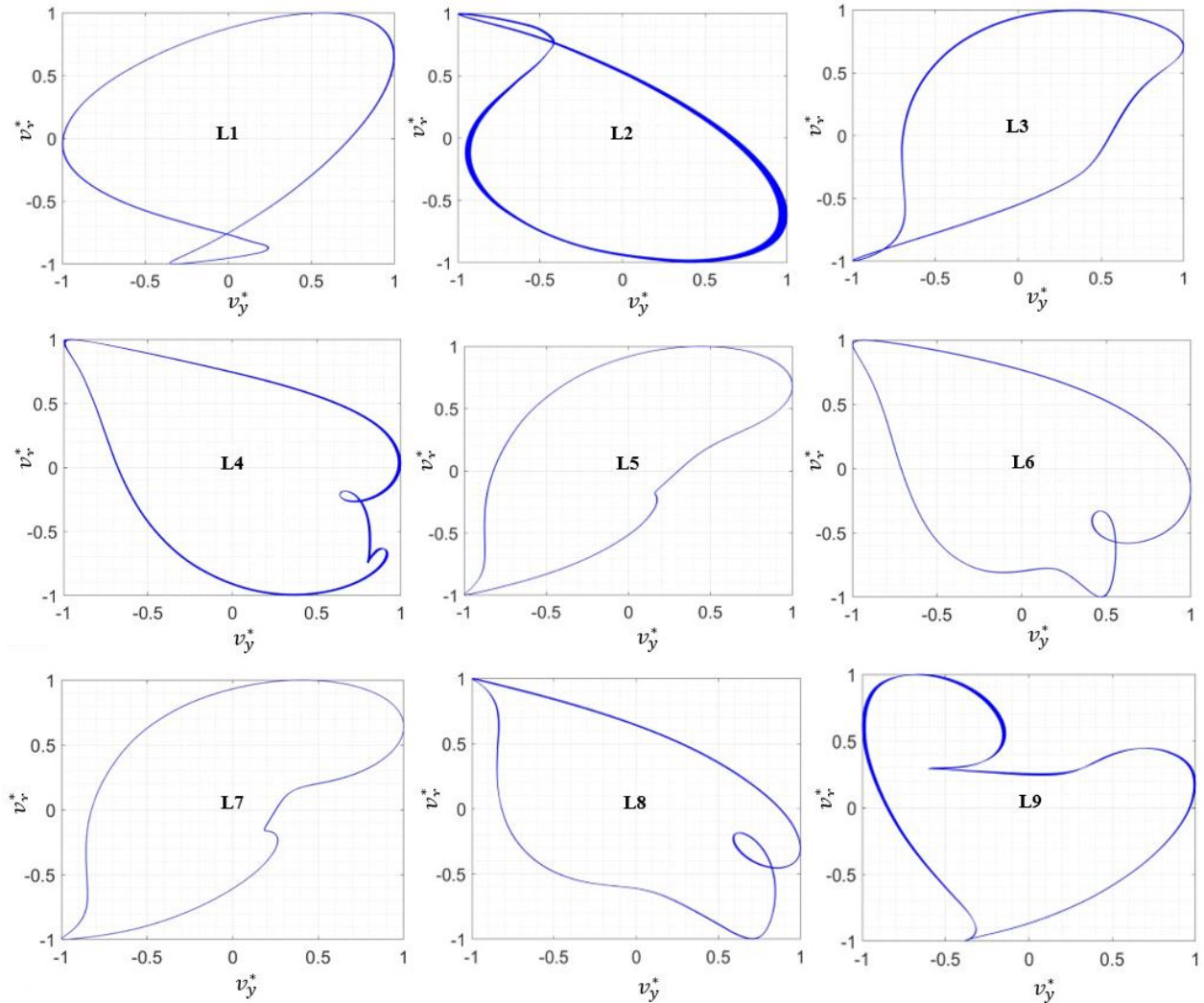


Figure IV.42 Phase diagrams of the normalized x-velocity, v_x^* , and y-velocity, v_y^* , in the centre of channels *l1* to *l9*, at $Re = 300$ during 4τ .

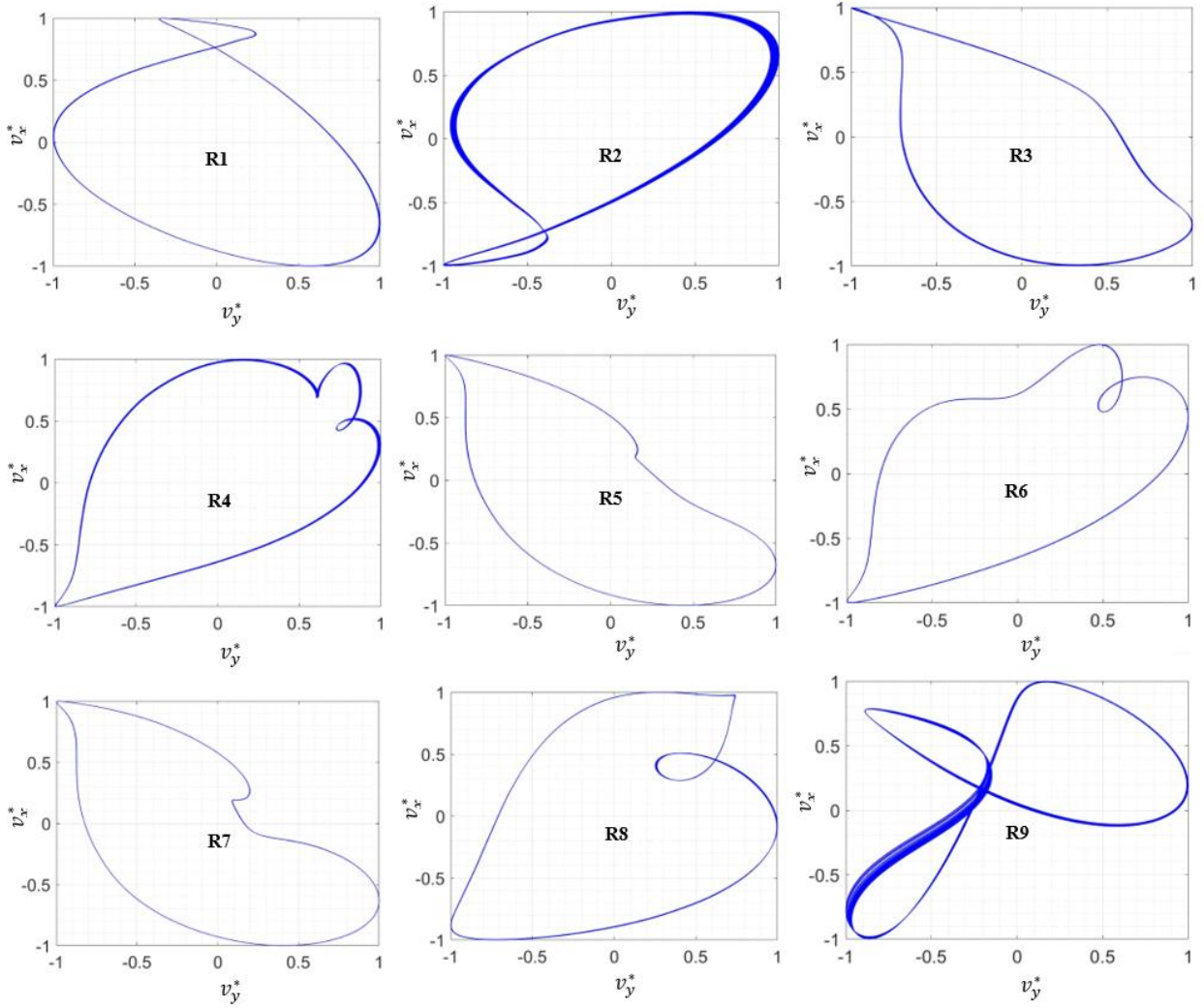


Figure IV.43 Phase diagrams of the normalized x -velocity, v_x^* , and y -velocity, v_y^* , in the centre of channels $r1$ to $r9$, at $Re = 300$ during 4τ .

As previously said, the maximum and minimum values of v_x in the centre of the chambers are positive and negative. In fact, Figure IV.44 shows that the strange attractor loop does not have an inclination to the left or to the right. The amplitude of v_x and v_y in C2 is approximately three times smaller than the amplitudes of the upper chambers (C4 to C8) since the oscillations are still being developed due to the proximity to the inlets. The loop is then thicker in C2 and then evolves to an 8 shaped thin strange attractor for the upper chambers. In C8, it is visible that the 8 shape starts to untwist due to the effect of the outlet boundary condition which dampens the oscillations (see section II.3.3).

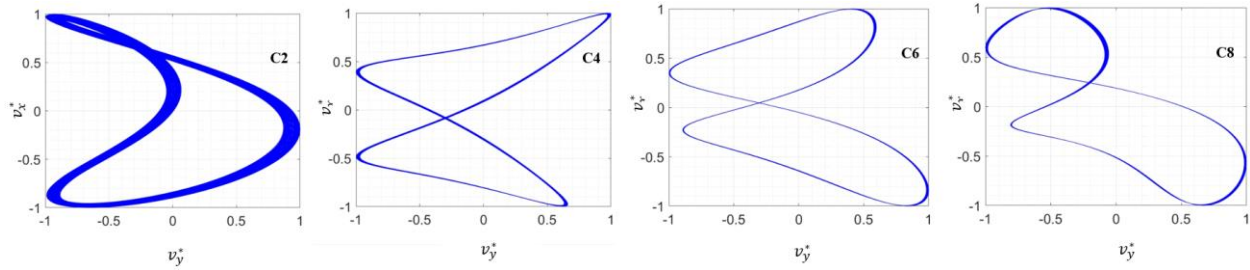


Figure IV.44 Phase diagrams of the normalized x -velocity, v_x^* , and y -velocity, v_y^* , in the centre of chambers C2 to C8, at $Re = 300$ during 4τ .

In Table IV.7 are shown the maximum and minimum values of vorticity and strain rate in the centre of chambers and channels. It is visible that the minimum of the vorticity is negative in the chambers and channels (except $r8$) and the maximum is positive (except $r9$). The strain rate is always positive.

Table IV.7 Strain rate and vorticity in the centre of chambers and channels.

<i>Left side</i>					<i>Right side</i>				
Channel/ chamber	ϵ_{min} (s^{-1})	ϵ_{max} (s^{-1})	ζ_{min} (s^{-1})	ζ_{max} (s^{-1})	ζ_{min} (s^{-1})	ζ_{max} (s^{-1})	ϵ_{min} (s^{-1})	ϵ_{max} (s^{-1})	Channel/ chamber
$l9$	-110	500	30	450	130	840	-880	-110	$r9$
$l8$	-150	130	20	200	0	300	10	450	$r8$
C8	-350	350	240	375	240	375	-350	350	C8
$l7$	-80	100	20	155	20	130	-100	70	$r7$
$l6$	-350	40	10	210	5	175	-100	170	$r6$
C6	-350	350	270	360	270	360	-350	350	C6
$l5$	-80	110	20	130	20	125	-110	80	$r5$
$l4$	-320	10	40	195	20	185	-100	120	$r4$
C4	-400	350	250	370	250	370	-400	350	C4
$l3$	-10	290	20	170	25	175	-280	10	$r3$
$l2$	-120	120	20	150	20	160	-120	110	$r2$
C2	-250	200	60	190	60	190	-250	200	C2
$l1$	-150	50	0	199	0	199	-50	150	$r1$

In the chambers, the amplitude of the vorticity in C2 is approximately a half of the vorticity of the other chambers, C4 to C8. Although the amplitude of the strain rate in C2 is close to the amplitude of the other chambers, the absolute values are smaller. As previously said, this is explained by the proximity to the inlets, since the oscillating behaviour promoted by the inlet jets is still being

developed. The phase diagrams of Figure IV.45 show that, in C2, the strange attractor is thicker and has a *bow-tie* shape. The attractor evolves to a *W* shape in C4 and C6 and starts to untwist in C8, due to the effect of the outlet boundary condition which dampens the oscillations (see section II.3.3).

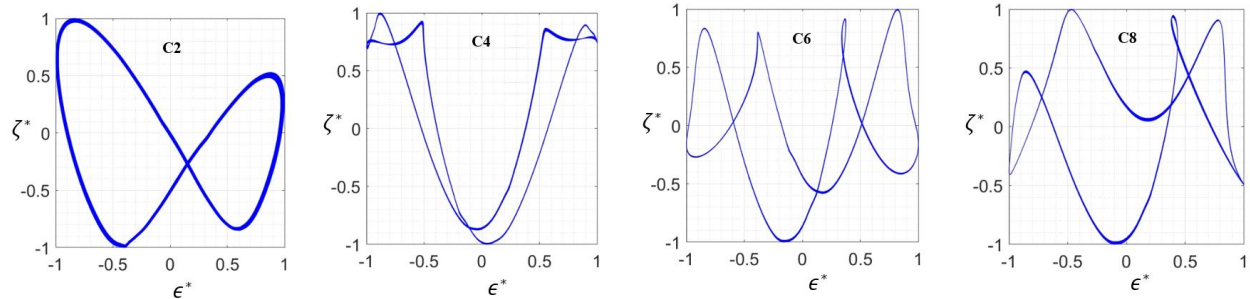


Figure IV.45 Phase diagrams of the normalized strain rate, ζ^* , and vorticity ϵ^* , in the centre of chambers C2 to C8, at $Re = 300$ during 4τ .

In the channels, the amplitude of the vorticity, as well as the absolute values, do not increase or decrease substantially, from the bottom to the top row. However, in the upper row (*r9* and *l9*) the amplitude is approximately three times higher than in the other rows. This behaviour is also verified for the strain rate. The phase diagrams of Figure IV.46 and Figure IV.47, which relate the strain rate with the vorticity, show a twisted loop without a particular shape or inclination. For *l9* and *r9*, in which the amplitudes of the vorticity and strain rate are larger, the attractors have a shape of an *elongated narrow loop*.

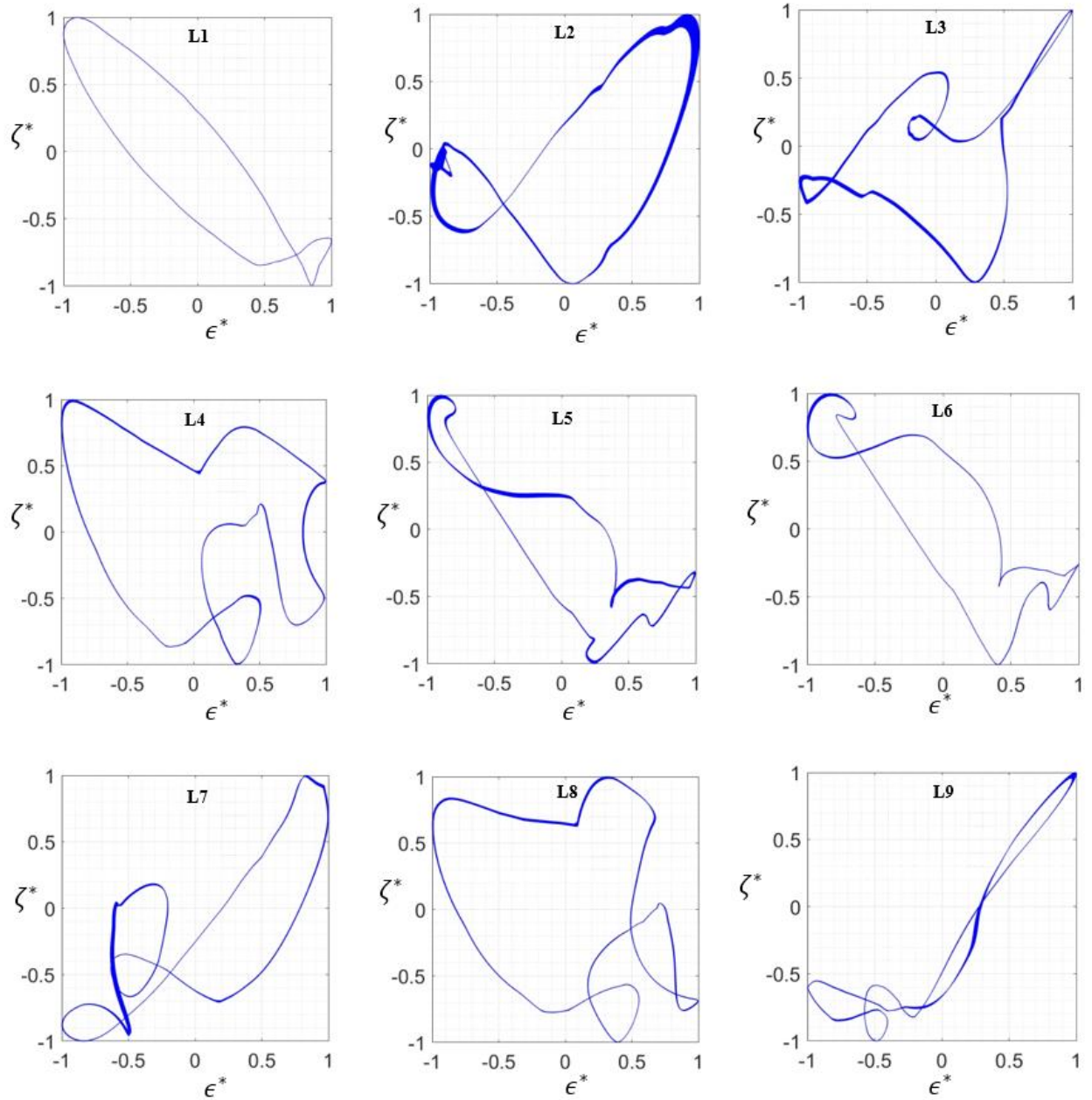


Figure IV.46 Phase diagrams of the normalized strain rate, ζ^* , and vorticity ϵ^* , in the centre of channels *L1* to *L9*, at $Re = 300$ during 4τ .

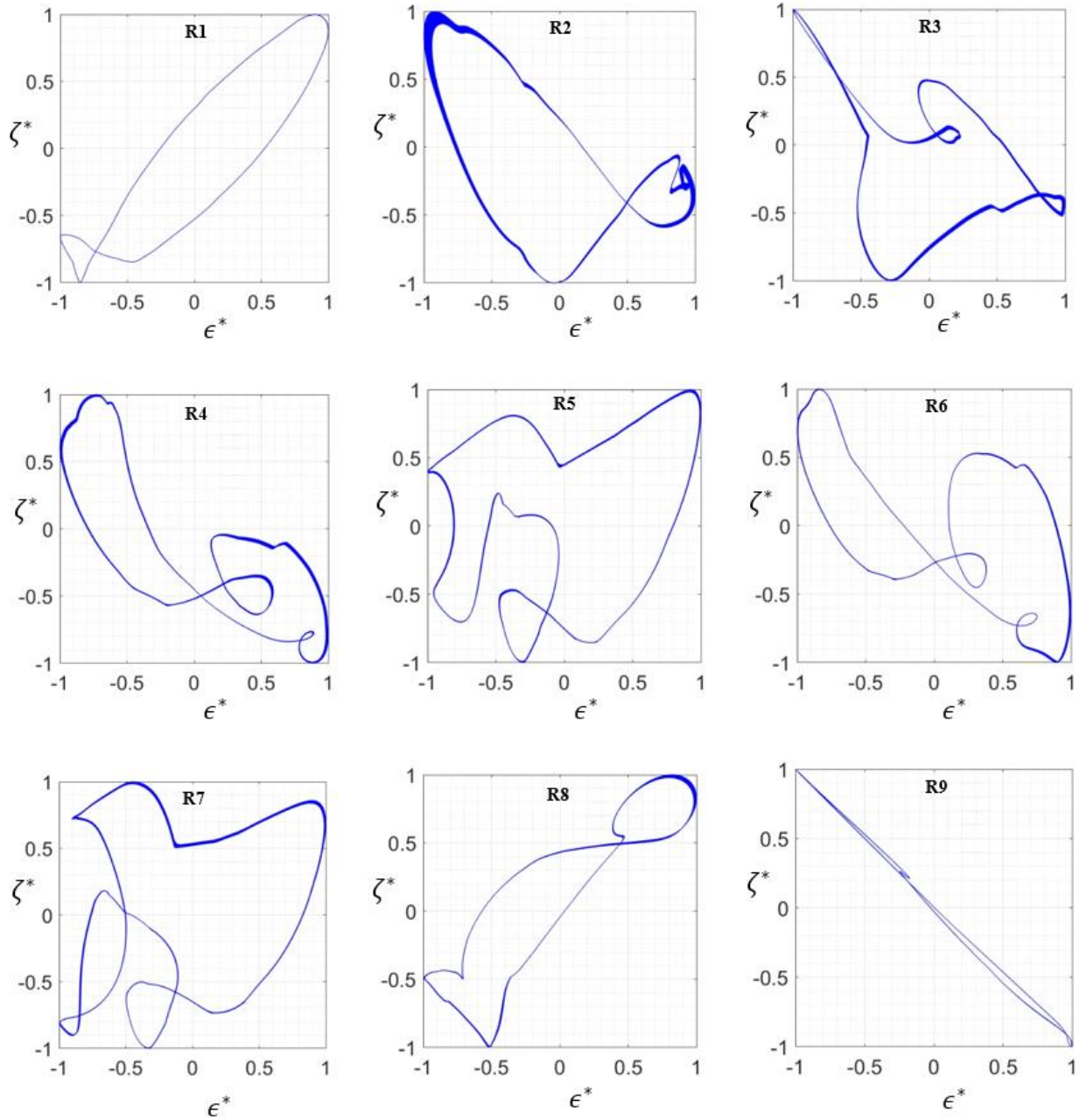


Figure IV.47 Phase diagrams of the normalized strain rate, ζ^* , and vorticity ϵ^* , in the centre of channels $r1$ to $r9$, at $Re = 300$ during 4τ .

In Figure IV.48 is represented the spectral analysis in the centre of the chambers. It is visible that the principal frequency is 20 Hz. In C2, where the amplitude of the x -velocity and vorticity are smaller due to the proximity to the inlets, the FFT value of the principal frequency is smaller, approximately 0.11 m. The FFT value triples in C4 and attains the maximum value in C6, approximately 0.30 m. In C8, the FFT value decreases slightly due to the effect of the outlet boundary condition which dampens the oscillations (see section II.3.3). From C4 to C8 it is possible to distinguish a second frequency at 60 Hz.

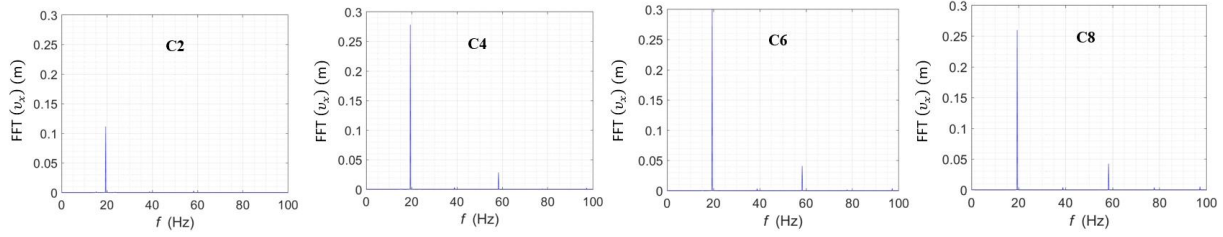


Figure IV.48 Spectral analysis in the centre of chambers C2 to C8, at $Re = 300$ during 4τ .

In Figure IV.49 and in Figure IV.50 are represented the spectral analysis in the centre of the channels. In similarity to the chambers, it is visible that the principal frequency is 20 Hz since this is the frequency with the highest value (amplitude) of FFT. In the first row of channels (*l1* and *r1*), which has a smaller amplitude of x -velocity and vorticity, the FFT has a small amplitude and it is only possible to distinguish one interfering frequency at 40 Hz. The amplitude of the principal frequency starts to increase in the second row of channels (*l2* and *r2*) and from the third to the last rows, several harmonics of the principle frequency are visible at 40 Hz, 60 Hz, 80 Hz and 100 Hz (for some cases). In the last row (*l9* and *r9*), the amplitude of the second frequency, 40 Hz, increases to a value that is close or higher than the principal frequency due to the outlet condition that is imposed in the CFD simulation, as explained previously. In general, the amplitude of the principal frequency in the channels is approximately three times lower than in the chambers.

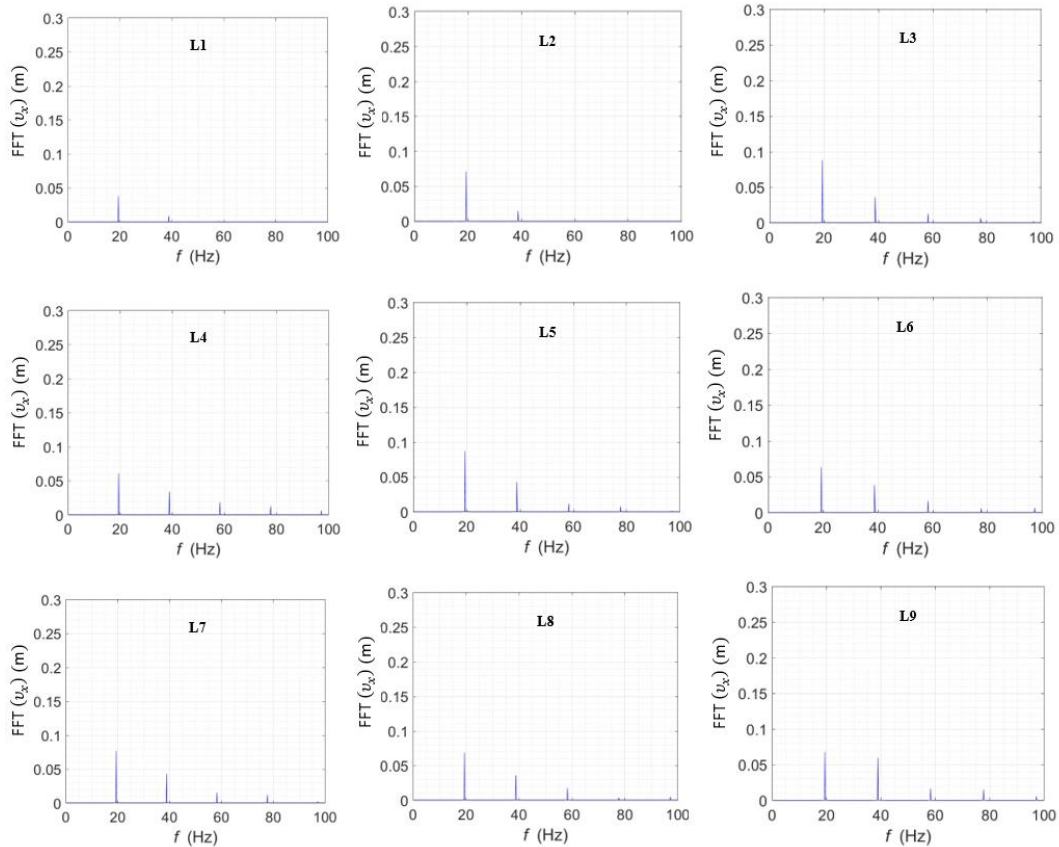


Figure IV.49 Spectral analysis in the centre of channels *l1* to *l9*, at $Re = 300$ during 4τ .

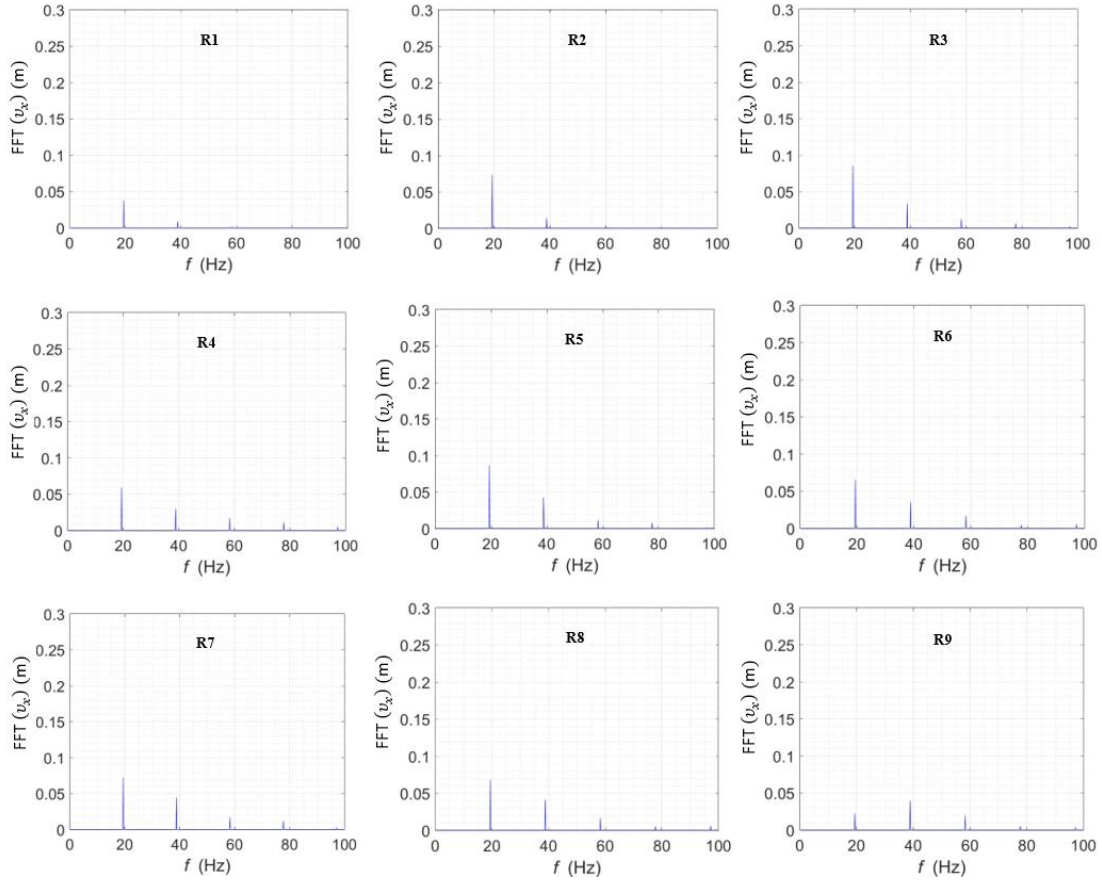


Figure IV.50 Spectral analysis in the centre of channels *r1* to *r9*, at $Re = 300$ during 4τ .

3D Analysis

A 3D mesh of ExtendedNUB with $D/d = 6.65$, shown in Figure IV.51, was built from the extrusion of the 2D mesh with depth $\omega = 3$ mm, using ANSYS® ICEM CFD™. The cell elements have an average edge length of $\Delta x = 1.7 \times 10^{-5}$ m and the complete mesh has 8.5×10^6 elements.

The CFD model was previously explained in Section II.3. For 3D geometries, $v_{inj} = \frac{\mu Re}{\rho D_h}$, with $D_h = \frac{4A_{channel}}{P_{channel}} = 1.5$, in which $A_{channel}$ and $P_{channel}$ are the area and perimeter of the inlet, respectively. The simulation was performed for $Re = 300$ with an inlet velocity, $v_{inj} = 0.20$ m/s, and time step, $\Delta t = 8.53 \times 10^{-5}$ s (Courant number, $C = 1$). The residence time in one NETmix chamber is given by $\tau_c = \frac{\pi D^2}{8v_{inj}d} = 0.087$ s, and the residence time of NETmix is $\tau = 0.78$ s.

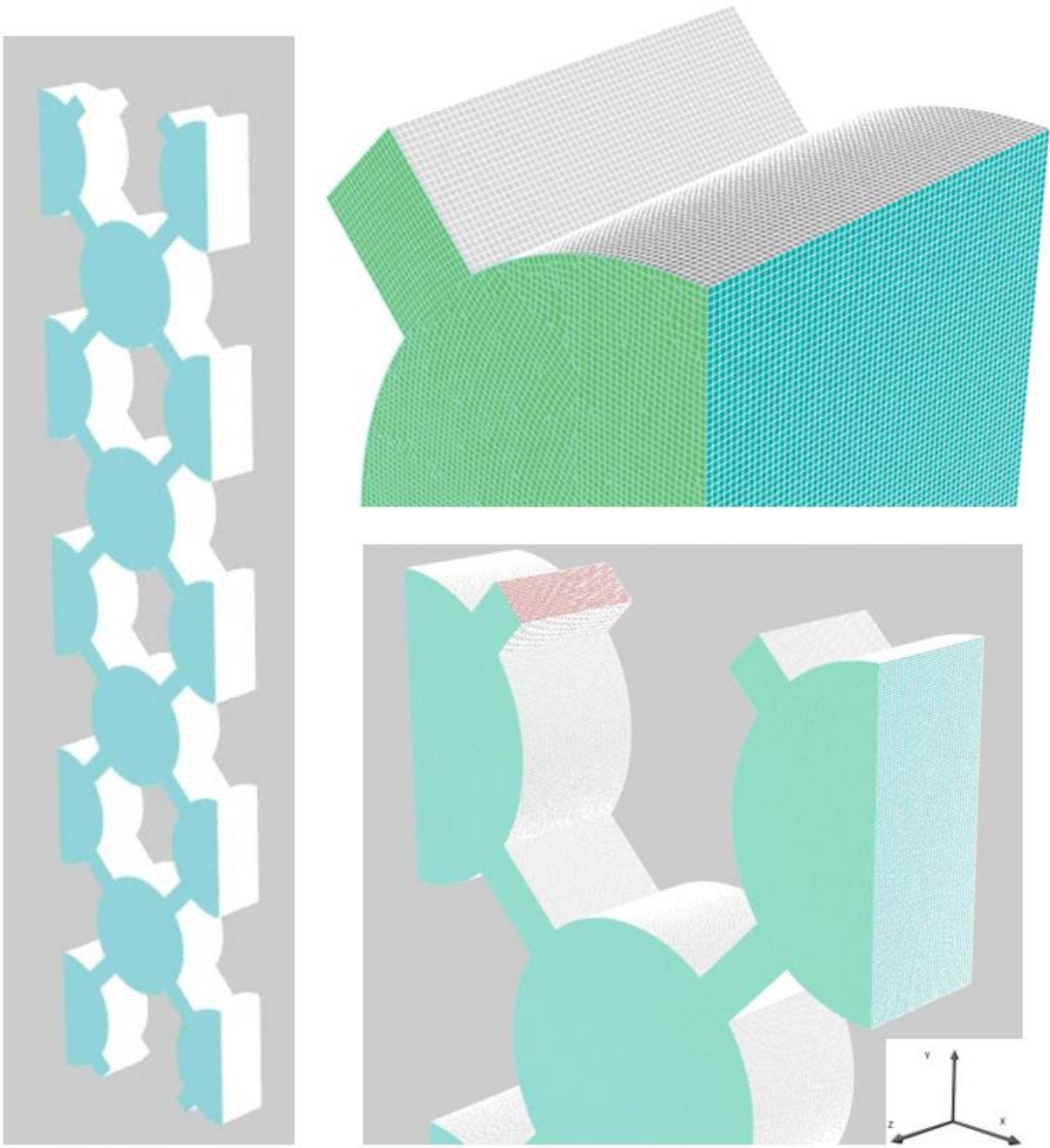


Figure IV.51 3D mesh of ExtendedNUB.

The velocity magnitude and z -component of vorticity maps in the xy plane at $\omega = 1.5$ mm are shown in Figure IV.52. It is visible that the oscillations, characterized by the formation of vortices at the top, bottom and sides of the mixing chambers, are similar to the 2D ExtendedNUB simulation, validating, once again, the 2D model to study the NETmix hydrodynamics. Note that, the vorticity varies between -100 s^{-1} and 100 s^{-1} , in similarity to the 2D result (see Section II.3.3).

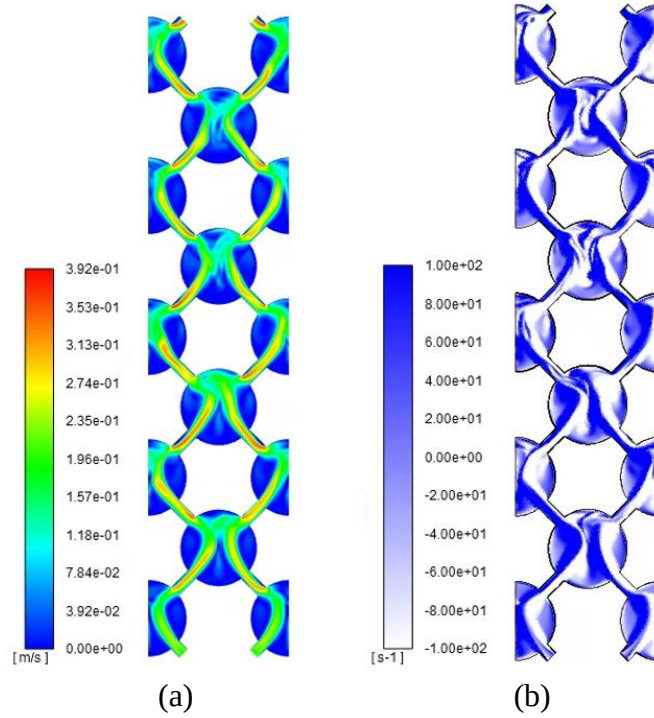


Figure IV.52 3D ExtendedNUB map of: (a) velocity magnitude, (b) z-component of vorticity.

The velocities, strain rate and vorticity were recorded in the centre of chambers C2, C4, C6 and C8. Figure IV.53 shows the x -velocity history in the centre of C6 where it is visible that the oscillations take approximately 8τ (6.5 s flow time) to stabilize, in similarity to the 2D result (see Section II.3.3. and IV.3.2).

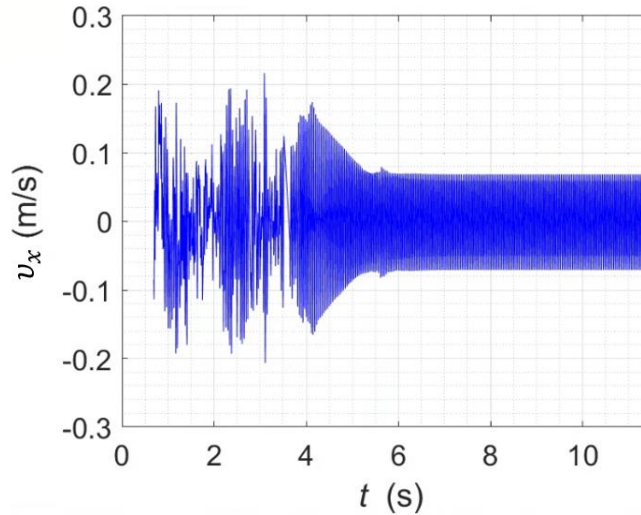


Figure IV.53 x -velocity history in the centre of C6 of the 3D ExtendedNUB model.

The history of v_y in the centre of C2, C4, C6 and C8 is shown in Figure IV.54. Comparing with the 2D model, the presence of more than two frequencies is more visible. As in the 2D simulation, the y -velocity has negative values in chamber C2, where the oscillations are being developed (see Figure IV.52). In chamber C6, which is less affected by the boundary conditions of the model, the y -velocity has the highest values, up to ca. 0.1 m/s, and then decreases in C8 due to the proximity to the outlet, as previously explained.

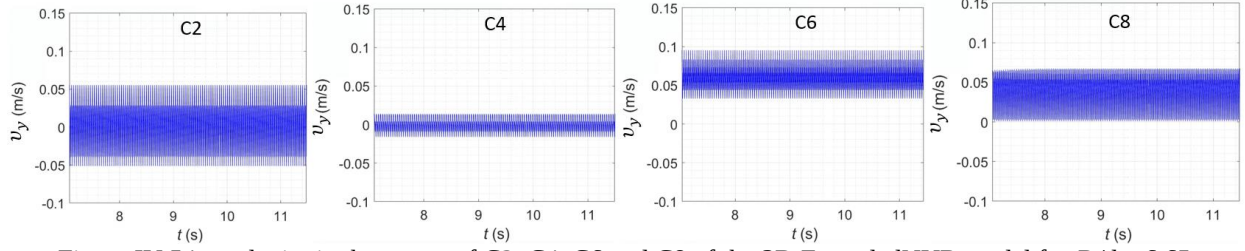


Figure IV.54 y -velocity in the centre of C2, C4, C6 and C8 of the 3D ExtendedNUB model for $D/d = 6.65$.

In similarity with the 2D model, the strange attractor of the strain rate and vorticity, shown in Figure IV.55, has a shape that starts to twist in the first chambers, C2 and C4, forming a tangled structure in C6 and C8.

As expected, the strange attractors from the 3D simulation are different from the 2D simulation since chaotic systems are sensitive to parameter changes, as previously shown for the D/d analysis. The sensitivity of the NETmix system to parameter changes will be analysed in the next Section of this work.

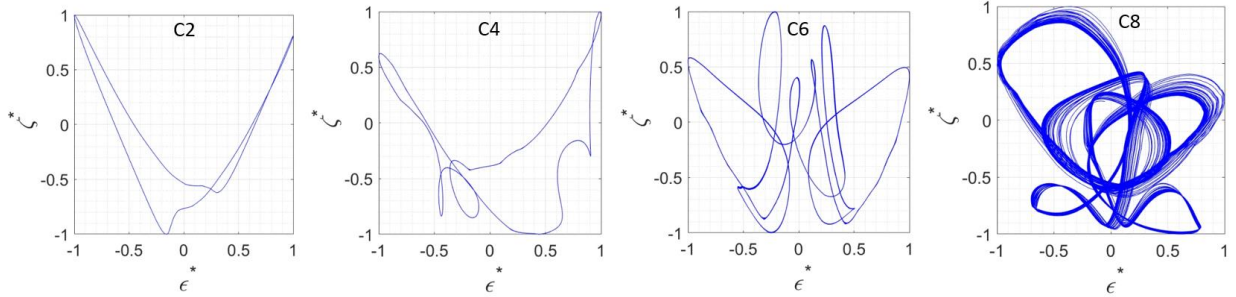


Figure IV.55 Strange attractor in the centre of C2, C4, C6 and C8 of the 3D ExtendedNUB model for $D/d = 6.65$.

The relation between the normalized velocities of the 3D simulation, v_x^* , v_y^* and v_z^* , is represented by the strange attractors of Figure IV.56.

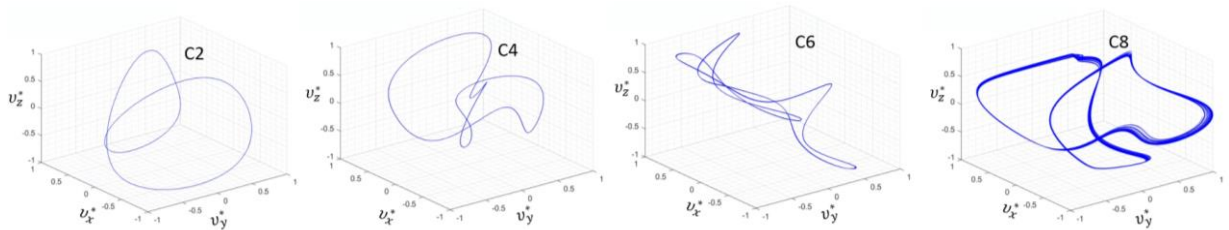


Figure IV.56 3D strange attractor in the centre of C2, C4, C6 and C8 of the 3D ExtendedNUB model for $D/d = 6.65$.

The principal frequency of oscillation in the 3D simulation is 25 Hz, while in 2D it was 20 Hz, as shown in Figure IV.57. The larger interferent frequency is close to 80 Hz, while in 2D it was approximately at 60 Hz. The amplitude of the principal frequency is larger at C6, as expected. Its value is ca. a half of the 2D result.

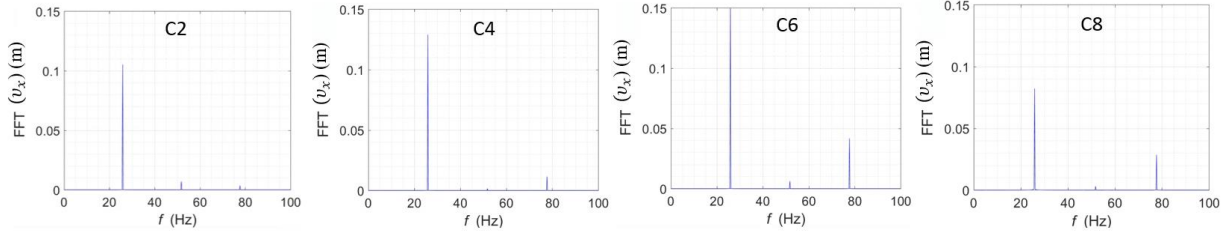


Figure IV.57 Spectral analysis in the centre of C2, C4, C6 and C8 of the 3D ExtendedNUB model for $D/d = 6.65$.

The fact that in 3D the number of interferent frequencies is larger at C6 and C8 is visible in the spectra with logarithmic scale, shown in Figure IV.58.

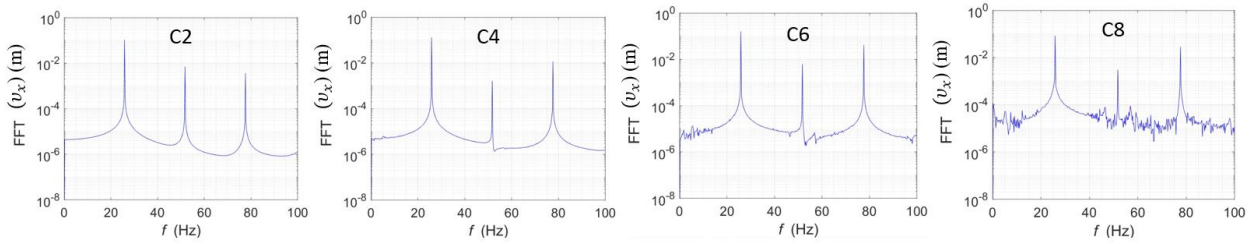


Figure IV.58 Spectral analysis with logarithmic scale in the centre of C2, C4, C6 and C8 of the 3D ExtendedNUB model for $D/d = 6.65$.

It is possible to conclude that the oscillations of NETmix are slightly more irregular in 3D, since the vortices are developed in 3 directions, x , y and z . In general, the chaotic behaviour of NETmix is similar to the 2D studies. In this way, as stated in previous chapters of this work, the main features of mixing occur in the plane xy . It is then possible to study NETmix using 2D simulations without compromising the accuracy of the results.

IV.3.3.5 Sensitivity Analysis of Chaos

As previously said, chaotic systems are sensitive to *environmental changes*. In the previous sections it was shown that changing the ratio D/d has a major impact in the behaviour of the NETmix system.

In this section, the influence of the mesh will be evaluated. In the previous chapters a symmetrical mesh in relation to the x and y axis was used (Matos et al. 2021). In this section, the 2D ExtendedNUB simulation was repeated for $D/d = 6.75$, at $Re = 300$, during 4τ , using different meshes. Figure IV.59 shows the four different meshes that were used: the symmetrical mesh already used, M1, and three asymmetrical meshes M2, M3 and M4 (the y -axis is shown in red). Meshes M1, M2 and M3 are quadrilateral based and M4 is triangular based.

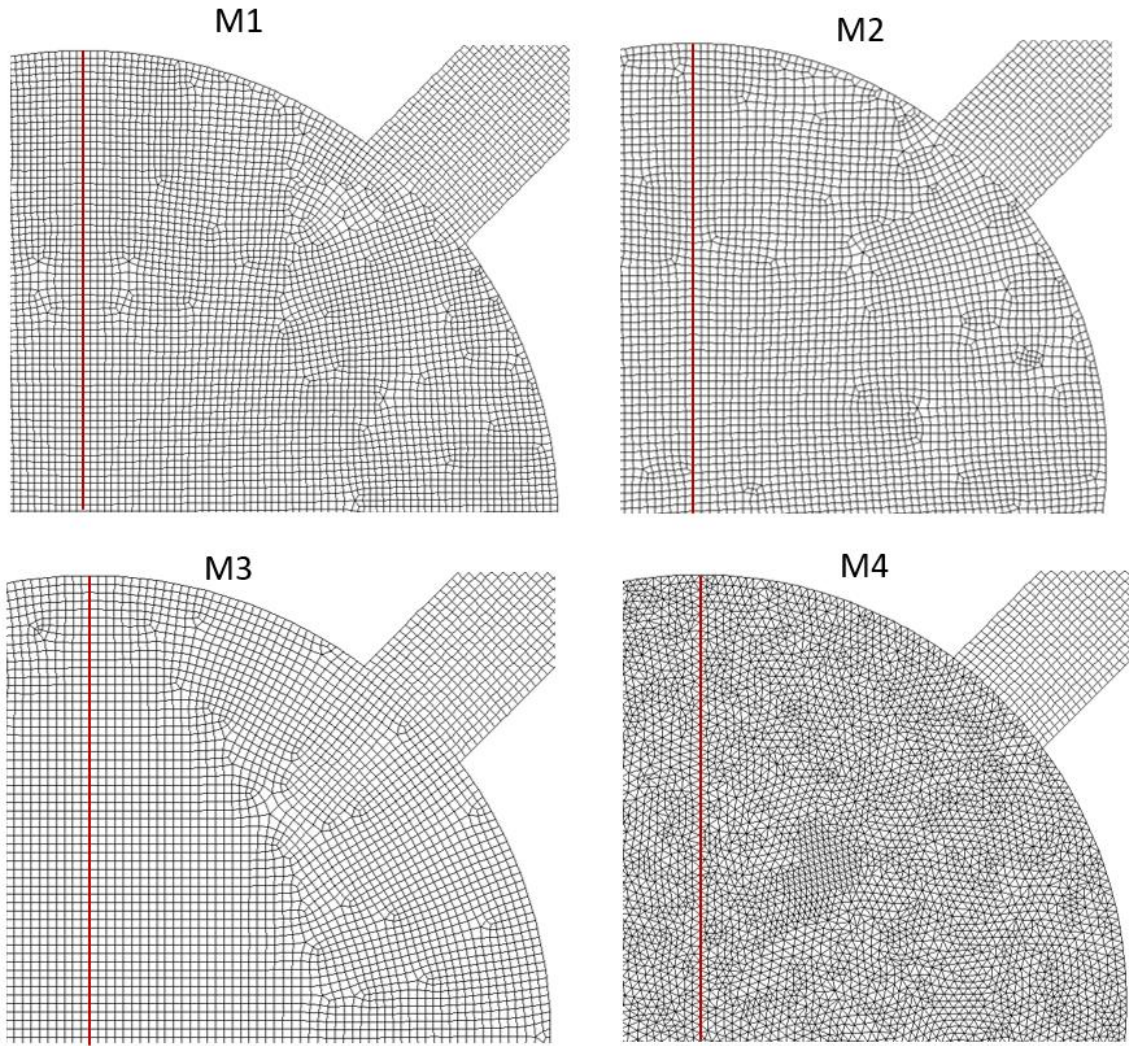
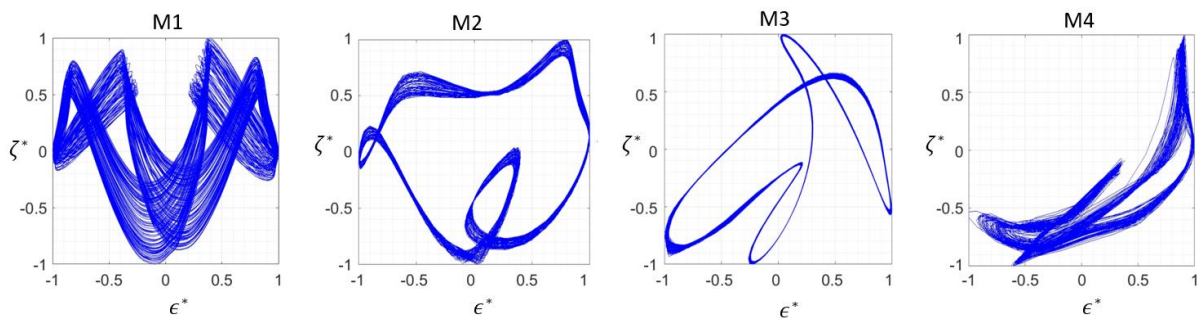


Figure IV.59 Meshing of the NETmix chamber.

In Figure IV.60 are shown the strange attractors that are obtained in the centre of chamber C6 for $D/d = 6.75$ with each mesh. As expected, the results show a different strange attractor for each mesh. Since chaotic systems are sensitive to all parameters, in this work, the symmetrical mesh, M1, was chosen to avoid numerical dispersion due to the presence of asymmetrical elements in the mesh. A detailed analysis of the sensitivity of chaos in NETmix is done in Appendix A, including other parameters.

Figure IV.60 Phase diagrams of the normalized strain rate, ζ^* and vorticity, ϵ^* , in chamber C6 for $D/d = 6.75$, at $Re = 300$ during 4τ , using M1, M2, M3 and M4.

IV.4 Computational Aspects

The CFD simulations of NETmix that provided the velocity fields for BLMS and LMS were run in 2 nodes of a computational cluster (FEUP) Intel® Xeon® with 16 cores at 2.1 GHz and 64 GB of RAM. A 2D ExtendedNUB simulation takes approximately 3 days to run 16τ , ca. 17 s flow time (1.5×10^5 time steps).

IV.4.1 BLMS Analysis

The data was saved from ANSYS® FLUENT™ in files with ASCII format. The data processing was made in MATLAB® R2018a. The conversion of the data in files .mat and their processing are shown in Appendix D.2.

BLMS was run in MATLAB® R2018a, using a x64-based processor Intel® Xeon® X5687 with 8 cores at 3.60 GHz and 24 GB of RAM. For the optimisation of the NETmix topology, 5000 injections were performed for each D/d , which took approximately 1 day. The MATLAB® code of BLMS as well as the code of the distribution of the particles over the inlet are shown in Appendix D.6.

IV.4.2 LMS Analysis

LMS was run in MATLAB® R2018a, using a x64-based processor Intel® Xeon® X5687 with 8 cores at 3.60 GHz and 24 GB of RAM. The MATLAB® code of LMS for NETmix is shown in Appendix D.4.2. To perform 3τ , corresponding to 446 iterations, LMS took approximately 1 day to run. In the last iterations, the total number of particles (red series and blue series) was 8.6×10^6 .

IV.4.3 Striation Thickness Analysis

The striation thickness algorithm was run in MATLAB® R2018a, using a x64-based processor Intel® Xeon® X5687 with 8 cores at 3.60 GHz and 24 GB of RAM. The MATLAB® code for the striation thickness computation is shown in Appendix D.7. The computation of the striation thickness for the particles at the eight locations (see Section IV.3.1.1) took approximately 1 day.

IV.4.4 CFD Tracer Simulation Analysis

The CFD simulation to perform the tracer analysis of ExtendedNUB was run in a x64-based processor Intel® Xeon® X5687 with 8 cores at 3.60 GHz and 24 GB of RAM. The simulation took approximately 6 days to perform 1.5×10^5 time steps (16τ flow time).

IV.4.5 Chaoticity Analysis

To perform the analysis of chaos in NETmix, the 2D CFD simulations mentioned in the beginning of this section were run for longer flow time, approximately 10^6 time steps in total. The simulations were run in 2 nodes of a computational cluster (FEUP) Intel® Xeon® with 16 cores at 2.1 GHz and 64 GB of RAM, and took approximately 2 months.

The 3D simulation of ExtendedNUB with $D/d = 6.65$ was run in a x64-based processor Intel® Xeon® Silver 4210 with 20 cores at 2.20 GHz and 128 GB of RAM, and took approximately 2 months to perform 1.5×10^5 time steps (16τ flow time).

The data was saved from ANSYS® FLUENT™ in text files .out. The conversion of the data in files .xlsx was made in VBA. The data processing was made in MATLAB® R2018a. The data conversion and processing are shown in Appendix D.3. The plot of strange attractors as well as the spectral analysis is shown Appendix D.8. The constructions of the 2D and 3D Poincaré maps is in Appendix D.9.

IV.5 Conclusions

A new version of LMS, the Batch Lagrangian Mixing Simulation (BLMS) algorithm, was developed to optimise the topology of NETmix. In this model, fixed particles are used to track the fluids inside the NETmix chambers.

The macromixing analysis of NETmix performed with BLMS (applied to chamber C6 of the ExtendedNUB model) has shown that nearly perfect mixing (dilution factor of 2, corresponding to an exit conditional probability of 0.5) can be obtained if the ratio between the chamber diameter and the channel width is within the range $6.65 < D/d < 6.85$.

A micromixing analysis of NETmix was performed to study the chaotic system of the reactor. The application of LMS to one NETmix chamber has shown a pattern similar to the mixing pattern from CFD, characterized by the presence of vortices, especially at the top, bottom and sides of the mixing chambers. Moreover, the interfacial area generation is exponential which is characteristic of chaotic flows. The striation thickness analysis has shown values below 10^{-6} m.

For the numerical validation of the BLMS results, a tracer simulation was performed. The study has shown that in chamber C6 of the ExtendedNUB model the molar fraction of the tracer is close to 0.5, as expected for nearly perfect mixing.

Phase diagrams of the vorticity vs the strain-rate (in chamber C6) were plotted for several ratios, $6.25 < D/d < 7.25$. It was shown that the NETmix chaotic behaviour is represented by a strange attractor which is sensitive to the topology of the reactor. For the best mixing ratios, $6.65 < D/d < 6.85$, the strange attractor has a thin *W* shape.

Since the strange attractors present an apparent periodic behaviour, Poincaré maps were used to perform a detailed analysis. It was shown that each data point has different coordinates, which agrees with the characteristics of a chaotic behaviour.

From velocity histories and frequency analysis, it was shown that within the range $6.25 < D/d < 7.25$, NETmix presents three different states of chaotic behaviour: *strong-chaotic* (SC), *weak-chaotic* (WC) and *quasi-periodic* (QP), with the scheme SC-WC-QP-WC-QP-WC-SC, which shows an *intermittent* bifurcation. The best mixing, between $6.65 < D/d < 6.85$, occurs at a quasi-periodic regime and has a discrete principal frequency at 20 Hz with a larger amplitude.

Chapter V – Combustion Modelling

The previous chapters were dedicated to hydrodynamics and mixing studies in the NETmix reactor, which enabled to obtain an optimised topology with nearly perfect mixing.

Here, combustion will be simulated using the optimised reduced-geometric model of NETmix. This chapter is dedicated to combustion modelling and simulation, using CFD and the Lamellar Micromixing Model. To perform combustion, three reactive schemes of the hydrogen combustion will be used: the global reaction scheme with and without the reverse rate, and the 19-reactions scheme.

The State of the Art of this chapter starts by emphasizing the importance of performing controlled combustion which is a means to reduce pollution and improve the environment. The reaction schemes of the hydrogen combustion will then be approached. After that, the State of the Art will focus on the review of methods to model combustion, especially the flamelet models, which will be described for premixed and non-premixed combustion. A model to simulate reactive flows, the Lamellar Micromixing Model will also be reviewed since it will be adapted for combustion in this work.

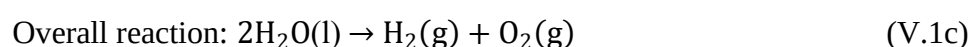
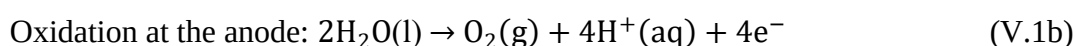
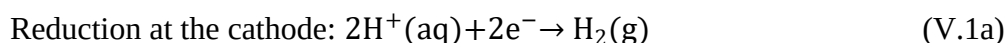
In the previous chapters, the hydrodynamics and mixing studies as well as the NETmix model optimisation were performed for liquids. After the State of the Art, this chapter starts by performing the numerical validation of the model, ExtendedNUB, for gases. The hydrogen combustion will then be studied for premixed and non-premixed reactive mixtures. This will enable to understand the influence of the composition of the reactive mixture in the outcome of the reaction in terms of products and temperature. Moreover, the influence of the mixture properties as well as the diffusion model will be assessed. Over this chapter, the comparison between the global reaction scheme, with and without the reverse rate, and the 19-reactions scheme will be made.

To end this chapter, the Lamellar Micromixing Model will be adapted for combustion in NETmix.

V.1 State of the Art

Combustion occurs when fuel is mixed with oxygen under certain conditions. The products of combustion include water vapor and other species (which depends on the fuel), including pollutants, as will be discussed further.

In general, air is used to provide oxygen for the combustion reactions. For specific cases where pure oxygen is required, separation processes are used. The most used method to obtain oxygen is by fractional distillation of liquefied air, in which O_2 is obtained as a liquid and N_2 as a vapor. Another via to obtain oxygen from the air is with the Pressure Swing Adsorption (PSA) method in which zeolites are used to absorb nitrogen, and oxygen is recovered in a gas stream with 90% to 93% of O_2 . Oxygen can also be obtained from the electrolysis of water (Emsley, 2001), given by



V.1.1 Pollutant Emissions from Combustion

Waste sent to the atmosphere by combustion processes are called *emissions* which are divided in gases and solid particles. This work will only focus on gaseous emissions.

From industrial processes to personal use devices, the sources of air pollution from combustion are divided in two main groups: *stationary* sources and *mobile* sources. Stationary sources include combustion in boilers, furnaces and gas turbines (see Chapter VI for a more detailed description of these devices), very common in manufactory industries and construction. The energy industry, which comprises heat energy, electricity production and petroleum refining, is also included in the stationary source. Mobile sources are related with emissions from means of transport which involve internal combustion engines (see Chapter VI for a more detailed description of these devices).

The main pollutants that result from combustion are CO_2 , CO , NO_x and SO_x . CO_2 is a natural component of the atmosphere and the main contributor for the *greenhouse effect*, which is responsible to maintain the surface temperature of the earth (Gaba and Iordache 2019). Nowadays, CO_2 is considered a pollutant due to the large amount of emissions to the atmosphere which leads to *global warming* effects, i.e., the raise of the surface temperature of the earth. CO is a combustion by-product of carbonate fuels. A way to avoid the formation of CO is to perform *complete combustion* in which oxygen is sufficient to burn all the fuel (Turns 2000). NO_x and SO_x are the main causes of acid rains. SO_x is only produced if the fuel contains sulfur, which is common in industrial fuels. In this work, SO_x will not be considered. NO_x is a precursor of the O_3 formation. The principal factors that influence the formation of NO_x compounds are the oxygen concentration and the temperature, as shown in Figure V.1. For temperatures higher than ca.

1300°C the formation of NO_x is higher. Recently, *lean combustion* has been gaining attention. In lean combustion, the reaction is performed with excess of oxygen, reducing the NO_x emissions (Rankin et al. 2008). Lean combustion has already been applied to internal combustion and diesel engines (Rankin et al. 2008, Choir et al. 2019).

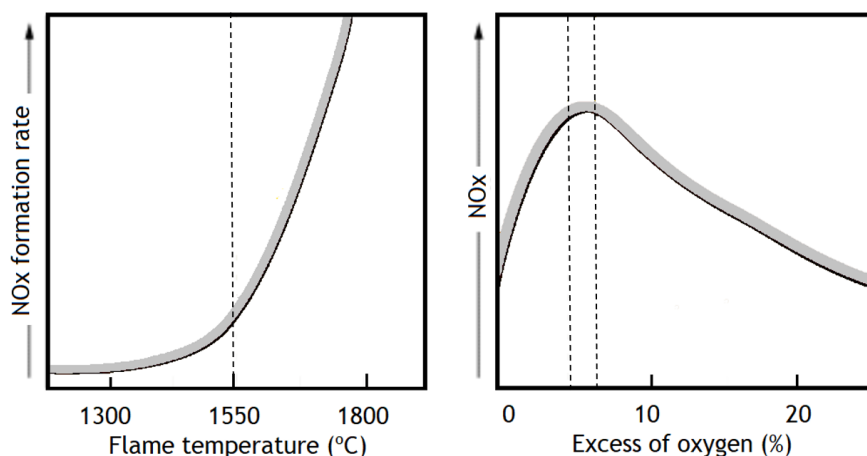


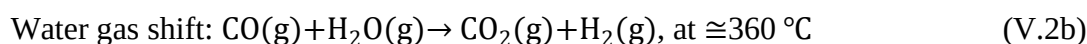
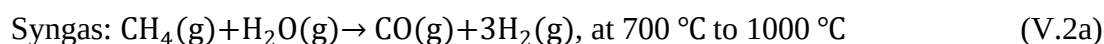
Figure V.1 NO_x formation (adapted from AlenTec 2011).

If the oxidation reaction occurs at temperatures below the autoignition, the system has a *cool* or *cold flame*. These flames have an oscillatory behaviour and are associated to slow combustion processes which are lean in heat, light and pollutants such as carbon dioxide. Cool flames are commonly associated to *engine knock*, in which low-octane fuels of the remaining unburnt Fuel-Air mixture ignites, causing a local heat release which produces a knocking sound and eventually damages the engine due to overheating or melting (Gray et al., 1994, Pearlman et al., 1999).

V.1.2 H₂ Combustion

Hydrogen is the simplest fuel to use in combustion reactions. In fact, the reactive system is only composed of H₂ and O₂. Thus, only a few elementary steps are needed to perform combustion (Williams 2008). One of the advantages of using hydrogen as a fuel is that no carbon compounds or ashes are emitted from the combustion reaction. Moreover, hydrogen has the highest heating value, 141.65 MJ/Kg, when compared to other fuels (Ali and Basit 1993). Hydrogen has been used in fuel cells and in internal combustion engines (Li et al. 2017).

Hydrogen is mainly obtained from natural gas (48%) by a steam reforming process, given by



Other methods in which hydrogen is produced from natural gas are the methane pyrolysis and partial oxidation. Hydrogen can also be obtained from oil (30%) and coal (18%) by coal gasification. A smaller amount of hydrogen (4%) is produced by water electrolysis, shown in Equation V.1 (Press et al., 2008, Dincer et al. 2015).

In industry, hydrogen is used in several processes, especially for the synthesis of ammonia in refineries and for methanol production (Hydrogen Europe 2019). Since the system Hydrogen-Air is extremely reactive, it is important to understand the conditions under which autoignition can occur which could compromise the safety of the industrial processes and its surrounding areas. In fact, *autoignition*, i.e., the mixture reacts without any source of heat, can occur with a lean concentration of fuel in the case of the Hydrogen-Air system, when comparing to other Fuel-Air systems. The auto-ignition of hydrogen occur at ca. 585 °C (Perry and Green 1997). For combustion to occur, the mixture hydrogen-oxygen needs to be in the *Flammable* or *Explosive Range*. The lower percentage of fuel by volume of air at which combustion occurs is the Lower Flammable or Explosive Limit (LFL or LEL), the higher percentage is the Upper Flammable or Explosive Limit (UFL or UEL). For hydrogen, the flammable limits are between 4% and 75% by volume of air, measured at 20 °C and 1 atm (Das 2016).

In this way, safety precautions have been a driving force to study the chemistry of the system Hydrogen-Air (Williams 2008, Fernández-Galisteo 2009) and several mechanisms have already been proposed as will be discussed in the next section.

The overall H_2 combustion in gaseous phase is given by $2H_2 + O_2 \rightarrow 2H_2O$, with an enthalpy of formation, $\Delta H_f^\circ = -241.8$ kJ/mol (Perry and Green 1997).

The adiabatic flame temperature of the system H_2 -Air varies with the composition of the mixture, which is commonly measured through the equivalence ratio, θ , i.e., the ratio between fuel/air and stoichiometric fuel/air, given by

$$\theta = \frac{m_{fuel}/m_{O_2}}{(m_{fuel}/m_{O_2})_{st}} = \frac{n_{fuel}/n_{O_2}}{(n_{fuel}/n_{O_2})_{st}} \quad (V.3)$$

in which m represents the mass, n the number of moles and st the stoichiometric conditions. For a mixture at stoichiometric conditions, $\theta = 1$.

For a classic experimental set with a Smithells burner (head with $D \cong 1$ cm), shown in Figure V.3, the adiabatic flame temperature is shown in Figure V.2. It is visible that the highest temperature, 2400 °C, is obtained at $\theta \cong 1.07$ (Drell et al., 1957).

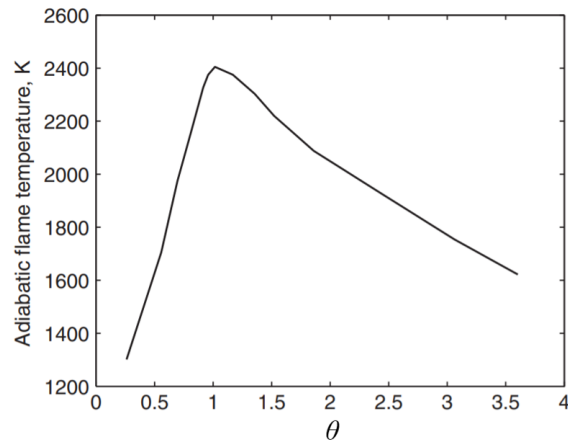


Figure V.2 Adiabatic flame temperature for the system H_2 -Air (adapted from White et al. 2006).

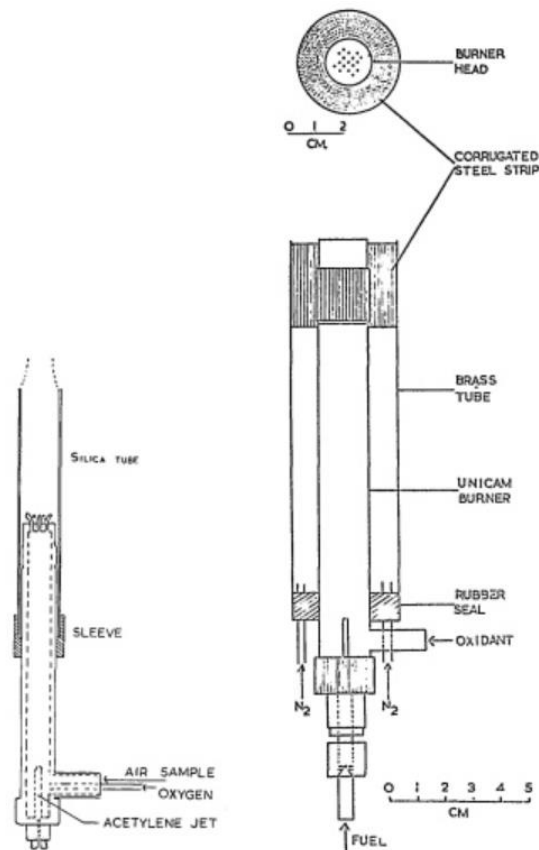


Figure V.3 Smithells burner scheme (adapted from Kirkbright and West 1968).

V.1.2.1 Reaction Mechanisms and Kinetics

The detailed mechanism for the Hydrogen-Air combustion was developed at the San Diego University and is composed of 268 reactions (Cerfacs 2019). As the complete mechanism is too demanding in terms of computational resources, in the last years, research has been done in order to reduce the mechanism (Saxena 2006). Nowadays, there are several models for the Hydrogen-Air system. In 1999, Mueller et al. proposed a 19-steps H - O mechanism which was later modified

by Li et al. (2004), who used updated chemical kinetics. A 19-steps mechanism was also presented by Conaire et al. (2004). Reduced mechanisms with 21 *H-O* reactions based on the original San Diego mechanism were proposed by Saxena (2006), Williams (2008) and Konnov (2008). In 2011, Boivin developed a 12-steps mechanism. A reduced mechanism which considers the interaction of the by-products with the nitrogen that is present in the air, the *H-O-N mechanism*, was proposed by Turns (2000).

A revised reduced mechanism with 19 reactions, including the kinetic parameters which will be presented next, is available in ANSYS Chemkin® (Conaire et al. 2004, Naik et al. 2009, Ansys 2021), shown in Table V.1. This scheme will be used further in this work.

Table V.1 19-reactions scheme for H₂ combustion (adapted from Ansys 2021).

19-Reactions Scheme of Hydrogen							
N°	Reaction	ΔH_f° (kJ/mol)	ΔS_f° (J/(mol K))	$\mathcal{A}$ (cm ³ , K, mol, s)	b	E_a (cal/mol)	d
H ₂ /O ₂ chain reactions							
1	H+O ₂ ↔ O+OH	70.00	25.20	3.55×10^{15}	-0.40	1.66×10^4	0
2	O+H ₂ ↔ H+OH	8.00	6.70	5.08×10^4	-2.70	6.29×10^3	0
3	H ₂ +OH ↔ H ₂ O+H	-62.80	-10.90	2.16×10^8	1.50	3.43×10^3	0
4	O+H ₂ O ↔ OH+OH	70.80	17.60	2.97×10^6	2.00	1.34×10^4	0
H ₂ /O ₂ dissociation/recombination reactions							
5	H ₂ +M ↔ H+H+M ^(a)	436.00	98.70	4.58×10^{19}	0.60	1.04×10^5	1
6	O+O+M ↔ O ₂ +M ^(a)	-498.00	-117.20	6.16×10^{15}	0	0	-1
7	O+H+M ↔ OH+M ^(a)	-428.00	-92.00	4.71×10^{18}	0	0	-1
8	H+OH+M ↔ H ₂ O+M ^(a)	-498.80	-109.60	3.80×10^{22}	0	0	-1
Formation and consumption of HO ₂							
9	H+O ₂ +M ↔ HO ₂ +M ^{(b),(c)} Troe, Low	-215.91	-90.50	1.48×10^{12} 6.37×10^{20}	0 -1.72	0 5.25×10^2	-1
10	HO ₂ +H ↔ H ₂ +O ₂	-220.09	-8.20	1.66×10^{13}	0	8.23×10^2	0
11	HO ₂ +H ↔ OH+OH	-142.09	23.70	7.08×10^{13}	0	2.95×10^2	0
12	HO ₂ +O ↔ O ₂ +OH	-212.09	-1.50	3.25×10^{13}	0	0	0
13	HO ₂ +OH ↔ H ₂ O+O ₂	-282.89	-19.10	2.89×10^{13}	0	-4.97×10^2	0
Formation and consumption of H ₂ O ₂							
14	H+HO ₂ ↔ OH+OH ^(e) H+HO ₂ ↔ OH+OH	-140.29 -140.29	-20.25 -20.25	4.20×10^{14} 1.30×10^{11}	0 0	1.20×10^4 -1.63×10^3	0 0
15	H ₂ O ₂ +M ↔ OH+OH+M ^{(a),(d)} Troe, Low	214.11	134.45	2.95×10^{14} 1.20×10^{17}	0 0	4.84×10^4 4.84×10^4	1
16	H ₂ O ₂ +H ↔ H ₂ O+OH	-284.69	24.85	2.41×10^{13}	0	3.97×10^3	0
17	H ₂ O ₂ +H ↔ HO ₂ +H ₂	-79.80	12.05	4.82×10^{13}	0	7.95×10^3	0
18	H ₂ O ₂ +O ↔ OH+HO ₂	-71.80	18.75	9.55×10^6	2	3.97×10^3	0
19	H ₂ O ₂ +OH ↔ HO ₂ +H ₂ O ^(e) H ₂ O ₂ +OH ↔ HO ₂ +H ₂ O	-142.60 -142.60	1.15 1.15	1.00×10^{12} 5.80×10^{14}	0 0	0 9.56×10^3	0 0

- (a) Third body efficiencies, $a_{H_2,k} = 2.5$, $a_{H_2O,k} = 12.0$
 (b) Third body efficiencies, $a_{H_2,k} = 2.0$, $a_{H_2O,k} = 11.0$, $a_{O_2,k} = 0.78$
 (c) Pressure dependent reaction
 (d) Pressure dependent reaction
 (e) Duplicate reaction

Another popular mechanism for the H_2 combustion is the San Diego mechanism which does not consider the reactions involving nitrogen. Considering only the reactions that involve H and O, the reduced San Diego mechanism is composed of 21 reactions (San Diego Mechanism Web Page 2016), listed in Table V.2.

Table V.2 21-reactions scheme for H_2 combustion (adapted from Williams 2008).

21-Reactions Scheme of Hydrogen							
N°	Reaction	ΔH_f° (kJ/mol)	ΔS_f° (J/(mol K))	A (cm ³ , K, mol, s)	b	E_a (kJ/mol)	d
H ₂ /O ₂ chain reactions							
1	$H+O_2 \leftrightarrow OH+O$	70.00	25.20	3.52×10^{16}	-0.70	71.4	0
2	$H_2+O \leftrightarrow OH+H$	8.00	6.70	5.06×10^4	2-70	26.3	0
3	$OH+H_2 \leftrightarrow H_2O+H$	-62.80	-10.90	1.17×10^9	1.30	15.2	0
4	$H_2O+O \leftrightarrow OH+OH$	70.80	17.60	7.60×10^0	3.80	53.4	0
H ₂ /O ₂ direct recombination reactions							
5	$H+M+H \leftrightarrow M+H_2^{(a)}$	-436.00	-98.70	1.30×10^{18}	-1.00	0	-1
6	$H+M+OH \leftrightarrow M+H_2O^{(a)}$	-498.80	-109.60	4.00×10^{22}	-2.00	0	-1
7	$O+O+M \leftrightarrow M+O_2^{(a)}$	-498.00	-117.20	6.17×10^{15}	-0.50	0	-1
8	$H+O+M \leftrightarrow M+OH^{(a)}$	-428.00	-92.00	4.71×10^{18}	-100	0	-1
9	$OH+O+M \leftrightarrow HO_2+M^{(a)}$	-285.91	-115.70	8.00×10^{15}	0	0	-1
Formation and consumption of HO ₂							
10	$H+O_2+M \leftrightarrow HO_2+M^{(b),(d)}$ Troe, high	-215.91	-90.50	5.75×10^{19} 4.65×10^{12}	-1.40 0.4	0 0	-1
11	$HO_2+H \leftrightarrow OH+OH$	-142.09	23.70	7.08×10^{13}	-0.50	1.2	0
12	$HO_2+H \leftrightarrow H_2+O_2$	-220.09	-8.20	1.66×10^{13}	0	3.4	0
13	$HO_2+H \leftrightarrow H_2O+O$	-212.89	6.10	3.10×10^{13}	0	7.2	0
14	$HO_2+O \leftrightarrow OH+O_2$	-212.09	-1.50	2.00×10^{13}	0	0	0
15	$HO_2+OH \leftrightarrow H_2O+O_2$	-282.89	-19.10	2.89×10^{13}	0	-2.1	0
Formation and consumption of H ₂ O ₂							
16	$OH+OH+M \leftrightarrow H_2O_2+M^{(c),(e)}$ Troe, high	-214.11	-134.45	2.30×10^{18} 7.40×10^{13}	-0.90 -0.40	-7.1 0	-1
17	$HO_2+HO_2 \leftrightarrow H_2O_2+O_2$	-140.29	-20.25	3.02×10^{12}	0	5.8	0
18	$H_2O_2+H \leftrightarrow HO_2+H_2$	-79.80	12.05	4.79×10^{13}	0	33.3	0
19	$H_2O_2+H \leftrightarrow H_2O+OH$	-284.69	24.85	1.00×10^{13}	0	15.0	0
20	$H_2O_2+OH \leftrightarrow HO_2+H_2O$	-142.60	1.15	7.08×10^{12}	0	6.0	0
21	$H_2O_2+O \leftrightarrow HO_2+OH$	-71.80	18.75	9.63×10^6	2.00	2.0	0

- (a) Third body efficiencies, $a_{H_2,k} = 2.5$, $a_{H_2O,k} = 12.0$
 (b) Third body efficiencies, $a_{H_2,k} = 2.5$, $a_{H_2O,k} = 16.0$
 (c) Third body efficiencies, $a_{H_2,k} = 2.0$, $a_{H_2O,k} = 6.0$
 (d) Pressure dependent reaction
 (e) Pressure dependent reaction

A reduced mechanism which considers the interaction of the by-products with the nitrogen that is present in the air, the *H-O-N mechanism* was proposed by Turns (2000), which considers 23 reactions, as shown in Table V.3.

Table V.3 23-reactions scheme for H_2 combustion (adapted from Turns 2000).

23-Reactions Scheme of Hydrogen							
N°	Reaction	ΔH_f° (kJ/mol)	ΔS_f° (J/(mol K))	$\mathcal{A}$ (cm ³ , K, mol, s)	b	E_a (cal/mol)	d
1	$H+O_2+M \leftrightarrow HO_2+M^{(a)}$	215.91	90.50	3.61×10^{17}	-0.72	0	-1
2	$H+H+M \leftrightarrow H_2+M$	436.00	98.70	1.00×10^{18}	-1.00	0	-1
3	$H+H+H_2 \leftrightarrow H_2+H_2$	436.00	98.70	9.20×10^{16}	-0.60	0	-1
4	$H+H+H_2O \leftrightarrow H_2+H_2O$	436.00	98.70	6.00×10^{19}	-1.25	0	-1
5	$H+M+OH \leftrightarrow M+H_2O^{(b)}$	498.8	109.6	1.60×10^{22}	-2.00	0	-1
6	$H+M+O \leftrightarrow M+OH^{(b)}$	428.00	92.00	6.20×10^{16}	-0.60	0	-1
7	$O+O+M \leftrightarrow M+O_2$	498.00	117.20	1.89×10^{17}	0	-1.788	-1
8	$H_2O_2+M \leftrightarrow M+OH+OH$	-214.11	-134.45	1.30×10^{17}	0	45.500	1
9	$H_2+O_2 \leftrightarrow OH+OH$	-78.00	-31.9	1.70×10^{13}	0	47.780	0
10	$H_2+OH \leftrightarrow H+H_2O$	62.80	10.90	1.17×10^9	1.30	3.626	0
11	$O+OH \leftrightarrow H+O_2$	70.00	25.2	3.61×10^{14}	-0.50	0	0
12	$H_2+O \leftrightarrow OH+H$	-8.00	-6.70	5.06×10^4	2.67	6.290	0
13	$OH+HO_2 \leftrightarrow H_2O+O_2$	282.89	19.10	7.50×10^{12}	0	0	0
14	$H+HO_2 \leftrightarrow OH+OH$	142.09	-23.70	1.40×10^{14}	0	1.073	0
15	$O+HO_2 \leftrightarrow OH+O_2$	212.09	1.50	1.40×10^{13}	0	1.073	0
16	$OH+OH \leftrightarrow O+H_2O$	70.80	17.60	6.00×10^8	1.30	0	0
17	$H+HO_2 \leftrightarrow H_2+O_2$	220.09	8.20	1.25×10^{13}	0	0	0
18	$HO_2+HO_2 \leftrightarrow H_2O_2+O_2$	140.29	20.25	2.0×10^{12}	0	0	0
19	$H_2O_2+H \leftrightarrow HO_2+H_2$	79.80	-12.05	1.6×10^{12}	0	3.800	0
20	$H_2O_2+OH \leftrightarrow HO_2+H_2O$	142.60	-1.15	1.00×10^{13}	0	1.800	0
21	$N_2+O \leftrightarrow NO+N$	268.97	11.33	1.40×10^{14}	0	75.800	0
22	$N+O_2 \leftrightarrow NO+O$	-88.39	13.58	6.40×10^9	1.00	6.280	0
23	$N+OH \leftrightarrow NO+H$	-158.39	-11.62	4.00×10^{13}	0	0	0

(a) Third body efficiencies, $a_{H_2,k} = 2.86$, $a_{H_2O,k} = 18.6$

(b) Third body efficiencies, $a_{H_2O,k} = 5.0$

The properties of the species that are present in the previous reaction schemes are listed in Table V.4 at the reference temperature, 25 °C (Ansys 2021, NIST 2018).

Table V.4 Properties of the H-O reactive system.

Properties of the system H-O-N					
	Species	ΔH_f° (kJ/mol)	ΔS_f° (J/(mol K))	ρ (kg/m ³)	μ (kg/(m s))
Atomic hydrogen	H	218.00	114.60	0.041	7.49×10^{-6}
Hydrogen	H ₂	0	130.50	0.082	8.41×10^{-6}
Water vapor	H ₂ O	-241.80	188.70	0.55	1.34×10^{-5}
Hydrogen peroxide	H ₂ O ₂	-136.11	232.95	1.38	9.83×10^{-5}
Hydroperoxyl	HO ₂	2.09	229.10	1.34	9.83×10^{-5}
Atomic Nitrogen	N	472.68	153.28	1.25	1.76×10^{-5}
Nitrogen	N ₂	0	191.61	1.25	1.76×10^{-5}
Nitrogen oxide	NO	90.29	210.76	1.17	1.47×10^{-5}
Atomic oxygen	O	249.00	161.10	0.65	1.87×10^{-5}
Oxygen	O ₂	0	205.00	1.30	1.92×10^{-5}
Hydroxyl	OH	39.00	183.70	0.69	1.97×10^{-5}

The forward, kf_k , and backward, kb_k , rate coefficients for each reaction k , are given by

$$kf = \mathcal{A} T^\delta e^{\frac{-E_a}{RT}} \quad (\text{V.4a})$$

$$kf = kb \left(\frac{p}{RT} \right)^d e^{\frac{-\Delta H_f^\circ + T \Delta S_f^\circ}{RT}} \quad (\text{V.4b})$$

in which T is the temperature, E_a is the activation energy, $\mathcal{A}$ is the pre-exponential factor, δ is the temperature exponent, p is the atmospheric pressure, R is the ideal gas constant, ΔH_f° is the enthalpy of formation of each reaction and ΔS_f° is the entropy of formation of each reaction. Parameter d is given by $\sum_{i=1}^n \nu_{i,k}$ in which $\nu_{i,k}$ are the stoichiometric coefficients of species i in reaction k .

The rate of each reaction is given by

$$r_k = kf_k \prod_{i=1}^n C_i^{\nu'_{i,k}} - kb_k \prod_{i=1}^n C_i^{\nu''_{i,k}} \quad (\text{V.5})$$

in which C_i is the concentration of species i , $\nu'_{i,k}$ are the stoichiometric coefficients of species i as reactants in reaction k and $\nu''_{i,k}$ are the stoichiometric coefficients of species i as products in reaction k .

In *duplicate* reactions, different Arrhenius parameters are used for the same reaction. In this case, the rate of the reaction is obtained from the sum of the two expressions.

If a *third body*, M, is present (see reactions (a) and (b) of Table V.2), the total concentration of the mixture is included in the rate expression which is given by

$$r_k = \left(\sum_{i=1}^n a_{i,k} C_i \right) \left(k f_i \prod_{i=1}^n C_i^{\nu'_{i,k}} - k b_i \prod_{i=1}^n C_i^{\nu''_{i,k}} \right) \quad (\text{V.6})$$

in which C_i is the concentration and $a_{i,k}$ are the third body efficiencies of species i in reaction k . If all the species of the mixture contribute equally as third bodies,

$$C_M = \sum_{i=1}^n C_i \quad (\text{V.7})$$

On gaseous combustion, the reactive molecules collide with other molecules, changing the speed and the result of the reaction. Due to the redistribution of energy and angular momentum produced by these collisions, it has been shown that certain reactions depend on the pressure of the engine (SND 2015). In order to have a better representation of the reaction kinetics, pressure-dependent reactions are included in the reactive schemes.

In *pressure-dependent* or *pressure fall-off* reactions, the rate expressions depend on the pressure and temperature, and the reaction occurs between the Arrhenius high-pressure and low-pressure limits. Three different approaches can be used to represent the rate expressions in pressure-dependent reactions: Lindemann (Lindemann, F. 1922), Troe (Gilbert et al. 1983) and SRI (Steward et al. 1989).

The net forward rate coefficient, $k f_{net}$, is given by

$$k f_{net} = k f_{high} \left(\frac{E}{1+E} \right) F \quad (\text{V.8})$$

with

$$E = \frac{k f_{low} C_M}{k f_{high}} \quad (\text{V.9a})$$

$$k f_{low} = \mathcal{A}_{low} T^{\beta_{low}} e^{\frac{-E_{a_{low}}}{RT}} \quad (\text{V.9b})$$

$$k f_{high} = \mathcal{A}_{high} T^{\beta_{high}} e^{\frac{-E_{a_{high}}}{RT}} \quad (\text{V.9c})$$

If the Lindemann approach is used, $F = 1$.

For the Troe approach, F is given by

$$\log(F) = \frac{\log(F_c)}{1 + \left(\frac{\log(E) + c_1}{c_2 - c_3(\log(E) + c_1)} \right)^2} \quad (\text{V.10})$$

in which $c1 = -0.4 - 0.67 \log(F_c)$, $c2 = 0.75 - 1.27 \log(F_c)$ and $c3 = 0.14$. F_c is obtained from

$$Fc = (1 - \alpha)e^{-T/T1} + \alpha e^{-T/T2} + e^{-T3/T} \quad (V.11)$$

in which α , $T1$, $T2$ and $T3$ are specified for each reaction.

For the SRI approach, F is given by

$$F = c4(c1e^{-c2/T} + e^{-T/c3})^G T^{c5} \quad (V.12)$$

in which $c1$, $c2$, $c3$, $c4$ and $c5$ are specified for each reaction. G is obtained from

$$G = \frac{1}{1+(\log(E))^2} \quad (V.13)$$

Global Mechanisms

Global mechanisms can be obtained if steady-state approximations are imposed to the detailed mechanism.

Several global mechanisms are shown in the work of Balakrishanan et al. (1995). They start from a 4-steps mechanism (derived from the 21-steps mechanism):

- (1) $H+O_2 \leftrightarrow OH+O$
- (2) $H_2+O+M \leftrightarrow OH+H+M$
- (3) $OH+H_2 \leftrightarrow H+H_2O$
- (4) $H+H+M \leftrightarrow M+H_2$

which is simplified, originating propositions for a 3-steps model and for a 2-steps model:

- (1) $3H_2+O_2 \leftrightarrow H_2O+2H$
- (2) $2H+M \leftrightarrow H_2+M$

In 1993, He and Clavin proposed models with the global reaction of hydrogen and with a 2-steps scheme:

- (1) $3H_2+O_2+H \leftrightarrow 2H_2O+3H$
- (2) $H+H+M \leftrightarrow H_2+M$

Another model with the global reaction was recently proposed by Fernández-Galisteo et al. (2008), who performed steady-state simplifications from a 7-steps scheme.

Further in this work, the global scheme with one reaction, $H_2 + 0.5O_2 \rightarrow H_2O$, provided by Ansys (2021) will be used.

Since the rate exponent is 1 for the reactants and products, the reaction rate is given by

$$r = kfC_{H_2}C_{O_2} \quad (V.14)$$

in which C is the molar concentration of the reactants. The Arrhenius parameters for the calculation of kf (Equation V.4a) are $A = 9.87 \times 10^8 \text{ m}^3/(\text{kmol s})$, $b = 0$ and $E_a = 3.10 \times 10^7 \text{ J/kmol}$.

If the backward reaction is included, $H_2 + 0.5O_2 \leftrightarrow H_2O$, the reaction rate is given by

$$r = kfC_{H_2}C_{O_2} - kbC_{H_2O} \quad (V.15)$$

in which the backward rate coefficient, kb , is calculated from Equation V.4b, with $d = 0.5$, $\Delta H_f^\circ = -241.8 \text{ kJ/mol}$ and $\Delta S_f^\circ = -44.3 \text{ J/(mol K)}$.

V.1.3 Combustion Modelling

If the combustible substance is in the gaseous phase, the burning process is called *homogeneous combustion*, which differs from the *heterogeneous combustion* where the combustible and the comburent have different phases. In homogeneous reactions, which is the case of this work, the reaction rate can be faster, of the same order, or slower than the rate of mixing, which leads to three types of reactions: *very rapid reactions*, *rapid reactions* and *slow reactions*, respectively.

The lowest temperature at which combustion occurs, for a given compound, is called *Ignition Temperature*. When oxygen is mixed with fuel under certain conditions that provide ignition, the temperature of the reaction zone rises, and a flame can be developed. In those cases, the reaction zone is called *flame front* and combustion is in the *flame mode*, in which the reaction occurs as the flame moves towards the unburnt gas. The temperature of the flame when the reaction heat is released is the *Adiabat flame temperature*.

When rapid oxidation occurs in the mixture oxygen-fuel, the combustion reactions are very fast, and the heat released is called *autoignition*, i.e., the mixture reacts without any source of heat. In those cases, the combustion occurs in a *non-flame mode*.

If combustion in flame mode occurs, there are two types of flames: *premixed* and *non-premixed* or *diffusion* flames. In *premixed flames*, the fuel is mixed with the oxygen, at a molecular level, before the start of the chemical reaction. In *non-premixed flames*, at start, the oxygen is not mixed with the fuel and the chemical reaction occurs in the interface between the reactants.

In order to model combustion in flame mode, which is the case of this work, two main methods have been used: Probability Density Functions (PDF) and Flamelet models.

In the PDF method, the equations of transport and species (mass fraction and enthalpy) are solved, considering a diffusion coefficient for the reactants (Vassilatos and Toor 1965, Pope 1985, Givi and McMurty 1988). Several works that used PDFs to model reactive flows were presented by Pope (1976) and O'Brien (1980), and more recent approaches are described in Pope (1991). The PDF method has already been applied, for example, to model non-premixed methane jets flames (Chen et al. 1989) and to study the NO formation in non-premixed Hydrogen-Air jet flames (Chen et al. 1992).

In this work, the flamelet models for non-premixed and premixed combustion will be described with more detail in the next sections since they will be used to adapt the Lamellar Micromixing Model (Section V.1.3.3), which will be applied to combustion for the first time.

V.1.3.1 Flamelet Models for Non-premixed or Diffusion Flames

The flamelet models are one of the most used approaches to study combustion. Several reactive schemes have already been modelled such as the system CO-H₂-N₂ in turbulent jets (Haworth et al. 1988), the formation of CO (Mauß et al. 1990), the formation and oxidation of soot in Diesel engines (Pitsch et al. 1995), the formation of NO_x (Peters 1995) and the formation of pollutants in gas-turbine combustors (Barths et al. 1998). More recently, the system Methane-Air was studied, using concentric tubes (Carbonell et al. 2009).

In PDF and CFD simulations, the chemistry of the reaction is simulated simultaneously with the flow equations. This is made by using the continuity (Equation II.5) and Navier-Stokes (Equation II.8) equations, presented in Chapter II, coupled with the advection-diffusion-reaction equation:

$$\frac{\partial C_i}{\partial t} + \mathbf{v} \cdot \nabla C_i = \mathcal{D} \nabla^2 C_i + r c_i \quad (\text{V.16})$$

in which C_i and $r c_i$ are the concentration and production rate of each species i of the mixture, $\mathbf{v}$ is the velocity vector and $\mathcal{D}$ is the diffusion coefficient (Santos 2012).

In contrast, the flamelet models consider the flow and mixing dynamics separately from the chemistry of the reaction.

Combustion occurs due to advection and diffusion, which are related with the flow and the mixing process, together with the chemical reaction. Advection and diffusion occur with similar timescales. However, the timescale of the reaction can have a different order of magnitude, which differs depending on the reaction (Peters 1984). In this way, in flamelet models, the mixing flow field is simulated separately from the chemistry of the reaction.

In fact, the laminar flame concept considers that the chemistry is fast enough (when compared to the flow dynamics) to enable the chemical reactions to occur in asymptotically thin layers, *flamelets*, embedded within the flow (see Figure V.4). To consider the flamelets one-dimensional and time dependent, the flamelet models introduce a new parameter, *Scalar dissipation rate*, of a conserved scalar, in general the mixture fraction, which represents the diffusion time scale that is compared with the chemical time scale (Peters 1984, Peters 1986).

To apply the flamelet models, the turbulent flames, shown in Figure V.4, are considered as an ensemble of stretched laminar flamelets. In this way, it is important to understand when the flames can be considered as an ensemble of laminar flamelets, which is related with the stretch of a flame.

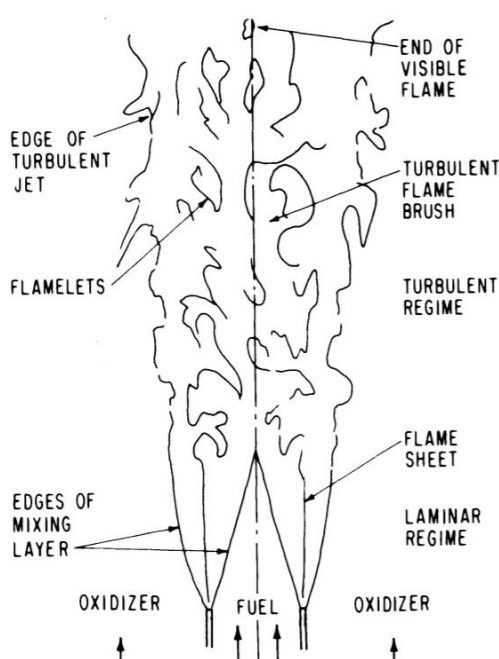


Figure V.4 Schematic representation of a turbulent diffusion flame (from Williams 1974).

Stretch of a Flame

In previous works (Klimov 1963, Williams 1974), it was shown that the stretch of a flame has a major impact on the flame structure. The stretch of a flame can occur in the flux direction or in its opposite direction which is called *flame compression*. The stretch of a flame can be interpreted as the strain rate of turbulent flows, in the order of ν/η^2 , in which ν is the kinematic viscosity and η is the Kolmogorov scale. Fuel blobs smaller than the Kolmogorov scale will be consumed before stretching and blobs larger than the Kolmogorov scale will be stretched before consumption. Since most blobs have an initial larger size when compared to the Kolmogorov scale, the flame stretch has a massive importance when flames are analysed (Williams 1974). In this way, the stretch has

a higher impact in the flame dynamics in comparison to the flame curvature, except near the extinction of the flame where its curvature becomes important (Williams 1974).

Flamelet Model Equations

The species and enthalpy balances (Peters 1984) can be generally written as

$$\rho \frac{\partial y_i}{\partial t} + \rho v \frac{\partial y_i}{\partial x} + \frac{\partial j_{ix}}{\partial x} = r c_i \quad (\text{V.17})$$

$$\rho \frac{\partial h}{\partial t} + \rho v \frac{\partial h}{\partial x} - \frac{\partial}{\partial x} \left(\frac{\lambda}{c_p} \frac{\partial h}{\partial x} \right) = - \frac{\partial}{\partial x} \sum_{i=1}^n h_i \left(\frac{\lambda}{c_p} \frac{\partial y_i}{\partial x} + j_{ix} \right) + \frac{\partial p}{\partial t} + q_R \quad (\text{V.18})$$

in which y_i is the molar fraction of each species i , h is the enthalpy, ρ , c_p and λ are the density, specific heat capacity and thermal conductivity of the mixture, respectively. v is the velocity and x represents the position in the flow field. h_i and $r c_i$ are the specific heat and production rate of each species i of the mixture, respectively. p is the pressure, which can be neglected if the process is non-confined, and q_R is the heat released by radiation which can also be neglected, depending on the system.

In the previous balances, the diffusion flux, j_{ix} , is given by Fick's law as

$$j_{i\alpha} = -\rho \mathcal{D} \frac{\partial y_i}{\partial x_\alpha} \quad (\text{V.19})$$

in which $\mathcal{D}$ is the diffusion coefficient which is assumed similar for all species and the Lewis number, which represents the relation between the thermal and mass diffusivities, is given by $\text{Le} = \frac{\lambda}{\rho \mathcal{D} c_p} = 1$, i.e., the thermal and mass layers have a similar behaviour.

A general combustion reaction can be expressed by $\nu_F F + \nu_O O_2 \rightarrow P$, where the fuel, F , reacts with oxygen, O_2 , producing a certain amount of products, P . ν_F and ν_O are the stoichiometric coefficients of fuel and oxygen, respectively. If the reaction occurs in non-premixed mode, the oxygen and the fuel come from different streams: stream1 for the fuel and stream2 for the oxidizer. In this case the conserved scalar, Z , is defined as

$$Z = \frac{Z_F}{Z_{F,1}} = 1 - \frac{Z_O}{Z_{O,2}} \quad (\text{V.20})$$

where Z_F is the mass fraction of the elements that came from the fuel stream at any point of the mixture, $Z_{F,1}$ is the mass fraction of fuel in the fuel stream (which might not be equal to one due

to the presence of inert compounds), Z_O is the mass fraction of oxygen that came from the oxidizer stream at any point of the mixture and $Z_{O,2}$ is the mass fraction of oxygen in the oxidizer stream.

For the previous reaction, the stoichiometric mixture fraction, Z_{st} is given by

$$\frac{Z_{F,st}}{\nu_F \mathcal{M}_F} = \frac{Z_{O,st}}{\nu_O \mathcal{M}_O} \quad (\text{V.21})$$

thus

$$Z_{st} = \left(1 + \frac{y_{F,1} \nu_O \mathcal{M}_O}{y_{O,2} \nu_F \mathcal{M}_F} \right)^{-1} \quad (\text{V.22})$$

where $y_{F,1}$ and $y_{O,2}$ are the molar fractions correspondent to $Z_{F,1}$ and $Z_{O,2}$, respectively. $\mathcal{M}_O$ and $\mathcal{M}_F$ are the molecular masses of oxygen and fuel, respectively.

Using the conserved scalar and neglecting the terms that are small comparing to the source terms of Equation V.23a and V.23b, the balances for the mixture fraction, Z , and for the temperature, T are given by

$$\rho \frac{\partial Z}{\partial t} + \rho v \frac{\partial Z}{\partial x} - \frac{\partial}{\partial x} \left(\rho \mathcal{D} \frac{\partial Z}{\partial x} \right) = r c_i \quad (\text{V.23a})$$

$$\rho \frac{\partial T}{\partial t} + \rho v \frac{\partial T}{\partial x} - \frac{\partial}{\partial x} \left(\rho \mathcal{D} \frac{\partial T}{\partial x} \right) = - \frac{1}{c_p} \sum_{i=1}^n h_i r c_i \quad (\text{V.23b})$$

in which ρ and c_p are the density and specific heat capacity of the mixture, respectively. v is the velocity and x represents the position coordinates of the flow field. h_i and $r c_i$ are the specific enthalpy and production rate of each element i of the mixture, respectively. $\mathcal{D}$ is the diffusion coefficient which is considered equal for all components i (Peters 1986).

In the flamelet model, a coordinate change from x to the mixture fraction, Z , enables to interpret the system as one-dimensional. After simplifications which are detailed in Peters (1984 and 1986), an equation that relates the species and the temperature balances can be written. To relate the chemical and the diffusion scales, the flamelet model introduces a new parameter, the scalar dissipation rate, χ . The dissipation rate varies through the laminar flame. However, in order to characterize each flamelet, a single value, usually at the stoichiometric mixture fraction, is chosen. The scalar dissipation rate, χ , at the stoichiometric mixture fraction is given by

$$\chi_{st} = 2 \mathcal{D}_{st} \left(\frac{\partial Z}{\partial x} \right)_{st}^2 \quad (\text{V.24})$$

The simplest flamelet model is the *Steady Flamelet Model* which is based on the counterflow diffusion flame for the calculation of the scalar dissipation. This model considers the timescales of the reaction much shorter than the advection and diffusion timescales. In the Steady Flamelet Model, the laminar flame structure is considered to remain in quasi-equilibrium with the local scalar dissipation rate, associated to the turbulent flow. Thus, the time derivatives can be omitted (Peters 1984, Peters 1986, Peters 2000).

The one-dimensional equation that relates the diffusion with the chemistry scales is then written as

$$\rho \frac{\chi_{st}}{2} \frac{\partial^2 T}{\partial Z^2} = \frac{1}{c_p} \sum_{i=1}^n h_i r c_i \quad (\text{V.25})$$

$$\rho \frac{\chi_{st}}{2Le_i} \frac{\partial^2 y_i}{\partial Z^2} = -r c_i \quad (\text{V.26})$$

in which the Lewis number, Le , is in general equal to one, in the case of fully turbulent regimes, and the diffusivities are considered equal for all species.

In the cases where the laminar flame thickness is larger than the smallest turbulence mixing scales, the flow has an influence on the stretching of the flames which affects their structure (Peters 1986). Moreover, in slow reactions, for example the formation of NO, the Steady Flamelet Model does not have an accurate prediction (Pitsch et al. 1998). In those cases, the time derivative needs to be conserved and the *Unsteady Flamelet Model* should be used. In the Unsteady Flamelet Model, the scalar dissipation changes rapidly, differing from the Steady Flamelet Model where the scalar dissipation has a slow variation (Peters 1984, Peters 2000). The flamelet equations are written as

$$\rho \frac{\partial T}{\partial t} - \rho \frac{\chi_{st}}{2} \frac{\partial^2 T}{\partial Z^2} = -\frac{1}{c_p} \sum_{i=1}^n h_i r c_i \quad (\text{V.27})$$

$$\rho \frac{\partial y_i}{\partial t} - \rho \frac{\chi_{st}}{2Le_i} \frac{\partial^2 y_i}{\partial Z^2} = r c_i \quad (\text{V.28})$$

Non-premixed Flamelet Model Variations

Variants of the classical steady and unsteady flamelet models for non-premixed combustion have already been developed, as will be reviewed next.

In 1998, Barths developed the *Multiple-Flamelets Model* to study of the NO_x and soot formation. This model uses a Lagrangian approach, considering each flamelet as a particle. The turbulent flow and mixing fields are computed through a CFD simulation. The flamelet equations are then used to model the chemistry of the process by the use of tracer particles.

Marracino and Lentini (1997) developed a model which incorporates the effects of radiation in non-premixed turbulent flames. The model was used to improve the studies on Methane-Air flames. Moreover, they extended the model for flames with non-unity Lewis numbers.

More recently, Pierce and Moin (2004) developed the *progress-variable* method which can be used to have a better prediction of extinction and reignition which are not well represented in the original flamelet models. The model uses a mapping approach, comprising two variables: the mixture fraction and the progress variable, which track the mixing of the fluids and the chemistry of the reaction, respectively. The flow is simulated with the large-eddy simulation (LES) technique. For the chemistry, a new model based on the steady flamelet model was developed. This approach was applied to the methane-fuelled coaxial jet combustor.

V.1.3.2 Flamelet Models for Premixed Flames

In similarity to non-premixed combustion, the flamelet model for premixed combustion considers the simulation of the flow and mixing separately from the chemistry of the reaction. The principal difference is on the interaction between the flame and the mixing and flow fields. In non-premixed combustion, the flamelets behaviour depends mostly on the mixing field. In premixed combustion, as the fuel is already mixed with the oxygen, the flamelets are more influenced by the interaction between the flame and the flow field, having a very small dependency on the mixing field. Since the length-scale of chemical reactions is much faster than the flow length-scale, the process is mainly controlled by turbulence. The spread of the flame that moves towards the unburnt gas originates two concepts related with flames in premixed regimes: the *flame speed* and the *flame thickness*. The flame speed represents the characteristic velocity scale of the flame propagation. The flame thickness is the characteristic length scale of the flame. Both quantities should be related with the flow time and length scales to characterize the flame in premixed combustion and find out whether the flamelet regime is applicable or not (Peters 2000). The flamelet model, which is applied in the flamelet regime, considers the smallest scale of the turbulent flow larger than the flame thickness. Thus, the laminar structure of the flamelets cannot be “destroyed”.

The flamelet model in premixed combustion has already been applied to study several systems, such as internal combustion engines (Wirth and Peters 1992) and Methane-Air jets (Muller et al. 1994).

Flamelet Regimes in Premixed Combustion

Considering the flame planar and the flow one-dimensional, the flame thickness, ℓ_F , is defined as

$$\ell_F = \frac{\lambda/c_p}{(\rho s_L)_u} \quad (\text{V.29})$$

where ρs_L is calculated in the unburnt gas. $s_L = \sqrt{\frac{\lambda}{\rho c_p} r c_i \frac{T_b - T_i}{T_i - T_u}}$ is the laminar burning velocity, in which, λ is the thermal conductivity, c_p is the specific heat and ρ is the density. b represents the burnt gas, u the unburnt gas and i the ignition (Peters, 2000)

The flame speed, $\mathcal{U}_F$, is defined as

$$\mathcal{U}_F = \frac{\lambda/c_p}{(\rho s_L^2)_u} \quad (\text{V.30})$$

and can be related with the flame thickness by $\mathcal{U}_F \ell_F = \nu$, and with the flame time by $t_F = \ell_F / \mathcal{U}_F$, in which ν is the kinematic viscosity.

Figure V.5 shows the division between several regimes in premixed turbulent combustion.

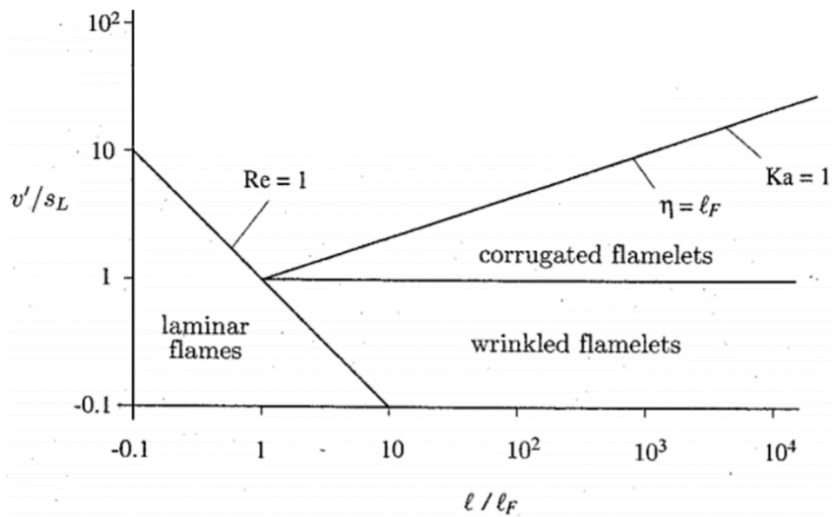


Figure V.5 Regimes in premixed turbulent combustion (adapted from Peters 2000).

In the previous diagram, ℓ is the turbulent length scale and $v' = \sqrt{2k/3}$ is the turbulence intensity, with $k = \frac{\overline{v^* v^*}}{2} = \frac{3\overline{v^{*2}}}{2}$, in which v^* is the fluctuation of the velocity. The flamelet regime is delimited by the Reynolds, Re, and Karlovitz, Ka, numbers.

The turbulent Re is defined as

$$\text{Re} = \frac{v' \ell}{s_L \ell_F} \quad (\text{V.31})$$

and the turbulent Ka is defined as

$$\text{Ka} = \frac{t_F}{t_\eta} = \frac{\ell_F^2}{\eta^2} \quad (\text{V.32})$$

where η represents the Kolmogorov scale which is the smallest scale in the turbulent regime. The Karlovitz number represents the relation between the chemical (flame) length scale and the Kolmogorov scale.

The flamelet regime, where the flamelet model can be applied, exists if $\text{Re} > 1$ and $\text{Ka} < 1$. In the flamelet regime, the length-scale of the turbulent regime is larger than the length-scale of the flame front. In this way, the flame front is deformed by the turbulent flow, maintaining its laminar structure. Two categories can be distinguished: *corrugated flamelets* and *wrinkled flamelets*. In the corrugated zone, the turbulence intensity is larger than the flame speed, which can lead to fractures of the flame front. In the wrinkled zone, the turbulence intensity is smaller than the flame speed. Thus, the flame front is mostly stretched or eventually wrinkled. Other regimes can be found for $\frac{v'}{s_L} > 10$, such as the *thin reaction zones regime* and the *broken reaction zones* (Peters 1986, Peters 2000).

Flamelet Equations

The *flame front* is considered as a surface, G , represented in Figure V.6. A reference point of the surface, G_0 is defined to determine whether a certain point of the flame front is in the burnt or unburnt side.

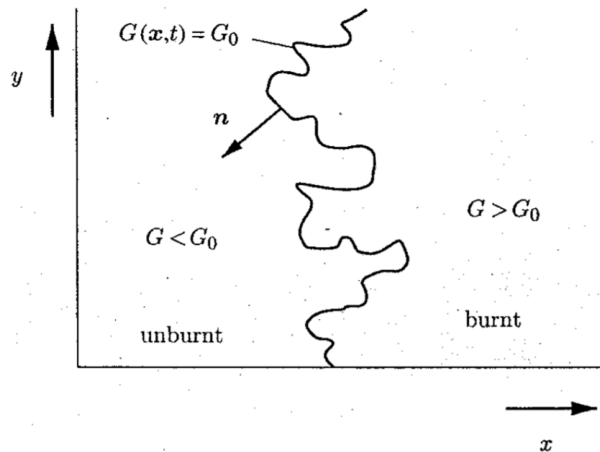


Figure V.6 Schematic representation of a flame front as an iso-scalar surface, G (adapted from Peters 2000).

The equation that describes the three-dimensional field, known as G -equation, is written as

$$\frac{\partial G}{\partial t} + v \cdot \nabla G = s_L |\nabla G| \quad (\text{V.33})$$

where v is the flow velocity and s_L is the laminar burning velocity.

This equation differs from the mixture fraction, Z , equation that was used in non-premixed flames since G is only defined at the flame surface, while the mixture fraction is well defined in the entire flow.

In similarity with Equation V.17, the mass balance can be written as

$$\rho \frac{\partial y_i}{\partial t} + \nabla \cdot (\rho v y_i) + \nabla \cdot (\rho \mathcal{D}_i \nabla y_i) = r c_i \quad (\text{V.34})$$

Using G with the assumptions fully described in Peters (2000), the flamelet equation can be obtained

$$\rho \frac{\partial T}{\partial t} + \rho S_L j \frac{\partial T}{\partial G} - \frac{\partial}{\partial G} \left(\rho \chi \frac{\partial T}{\partial G} \right) = - \frac{1}{c_p} \sum_{i=1}^n h_i r c_i \quad (\text{V.35a})$$

$$\rho \frac{\partial y_i}{\partial t} + \rho S_L j \frac{\partial y_i}{\partial G} - \frac{\partial}{\partial G} \left(\frac{\rho \chi}{\text{Le}_i} \frac{\partial y_i}{\partial G} \right) = r c_i \quad (\text{V.35b})$$

where $j = |\nabla G|$, at $G = G_0$. The scalar dissipation rate is $\chi = 2Dj^2$. Note that the number of Lewis, Le , tends to one in the corrugate regime.

The unsteady flamelet equations for premixed combustion are also valid for the *thin reaction zones* regime in which the time derivative is important. In the flamelet regime, it is possible to omit that term and use the steady model.

V.1.3.3 Lamellar Micromixing Model

In order to simulate a reactional process, the model needs to account for the fluid mechanics, diffusion and chemical reaction (Ottino 1980). One of the strategies is based on a statistical approach which uses Fick's law to describe the relation between the chemical reaction and diffusion (Murthy, 1975)

$$\frac{\partial C_i}{\partial t} + \frac{\partial (v C_i)}{\partial x} = \mathcal{D}_i \frac{\partial^2 C_i}{\partial x^2} + r c_i \quad (\text{V.36})$$

in which C_i is the concentration, $\mathcal{D}_i$ is the diffusion coefficient, $r c_i$ is the rate of production of species i and v is the velocity.

Another strategy is the Residence Time Distribution (RTD), a concept introduced by Danckwartz (1953), which measures the fraction of tracer at the outlet of the reactor.

Although these two approaches have been widely used (Ottino et al. 1979, Ottino 1980) none of them considers the close relation between mixing, reaction and diffusion.

The Lamellar Micromixing Model establishes a relation between the three variables through a stretching function.

As previously said in Chapter III, during the mixing process, the material is stretched and folded into laminae of fluid, leading to an increase of the interfacial area between the fluids, and decreasing the striation thickness. Considering a Lagrangian approach, introducing a stretching function, $\psi(\mathbf{x}, t)$, it is possible to have a local relation between mixing, diffusion and reaction, through the equation:

$$\frac{\partial C_i}{\partial t} + \psi x \frac{\partial C_i}{\partial x} = \mathcal{D}_i \frac{\partial^2 C_i}{\partial x^2} + r_{C_i} \quad (\text{V.37})$$

in which C_i is the concentration, $\mathcal{D}_i$ is the diffusion coefficient and r_{C_i} is the rate of production of species i (Ranz 1979).

As in the flamelet models, the Lamellar Micromixing Model considers fast chemical reactions, when compared to the diffusion scale. In this way, it is possible to consider a fluid filament, *lamina* (see Section III.1), as a Lagrangian reference to represent the flow and reduce the system to a one-dimensional problem. As shown in Figure V.7, if a lamina of fluid is selected, it is possible to simulate the evolution of the concentration of species, A (reactant) and B (product).

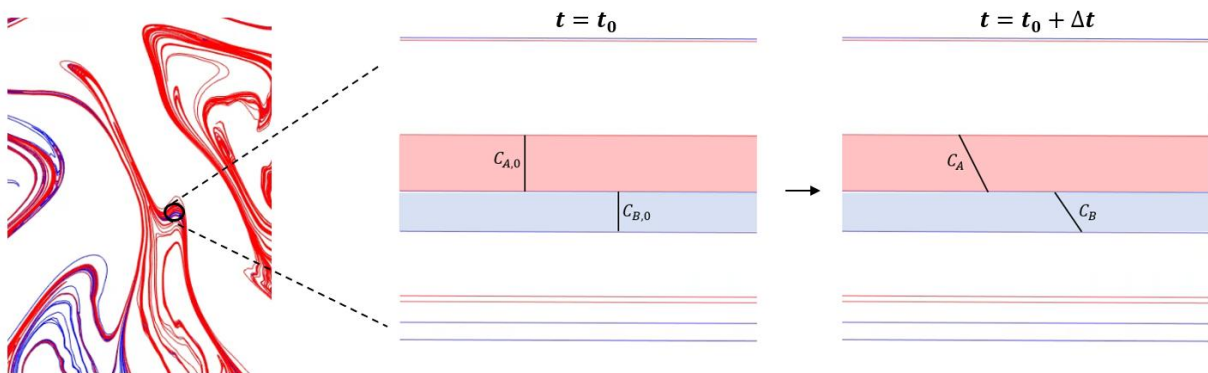


Figure V.7 Evolution of the concentration profile in a lamina of fluid.

The Lamellar Micromixing Model has recently been used to simulate chemical reactions in the Confined Impinging Jets (CIJ) reactor, considering the striation thickness as a measure of the stretching of the flow. The results were compared with experimental data, showing that the Lamellar Micromixing Model gives a good prediction of the evolution of the concentration of the species (Brito et al. 2020).

In this work, the striation thickness results that were presented in Chapter III will be used in the Lamellar Micromixing Model to simulate combustion reactions in the NETmix chambers. As shown in Sections V.1.3.1 and V.1.3.2, the stretch of a flame is, in general, more important than the curvature, which makes possible to implement the Lamellar Micromixing Model if the flame is in the flamelet regime.

V.2 Numerical Validation of ExtendedNUB for Gases

In the previous chapters, the NETmix reactor was studied and optimised using water. For the numerical validation of the hydrodynamics behaviour in NETmix with gases, a CFD simulation was performed with air, $\rho = 1.225 \text{ kg/m}^3$ and $\mu = 1.789 \times 10^{-5} \text{ kg/(m s)}$, considering the equations of Section II.3.2. The Coupled scheme was used with PRESTO! for the pressure-velocity coupling and with Third-Order MUSCL for the spatial discretization. The convergence criterion for the maximum residuals of continuity and momentum is 10^{-5} . The ExtendedNUB model, shown in Figure II.12 (Section II.3.1), was used with the best ratio, $D/d = 6.65$, at $\text{Re} = 300$. To keep the Courant number, $C = 1$, the inlet velocity was 2.2 m/s and the time step size was $\Delta t = 7.82 \times 10^{-6} \text{ s}$. The residence time in one NETmix chamber is $\tau_c = \frac{\pi D^2}{8v_{inj}d} = 0.0079 \text{ s}$, and the residence time of the ExtendedNUB model is $\tau = 0.071 \text{ s}$.

Figure V.8 shows the maps of the z -component of the vorticity and velocity magnitude for water and air at 16τ . It is visible that the dynamic behaviour is similar for water and air since the oscillations inside the chambers, which are promoted by the jets, are nearly the same. Moreover, the mixing features, such as vortices, present the same behaviour. The vorticity and velocity of air are a factor of 10 higher in comparison to water, due to the difference in the physical properties. In this way, for water the z -component of the vorticity varies between -100 s^{-1} and 100 s^{-1} , and for air varies between -1000 s^{-1} and 1000 s^{-1} .

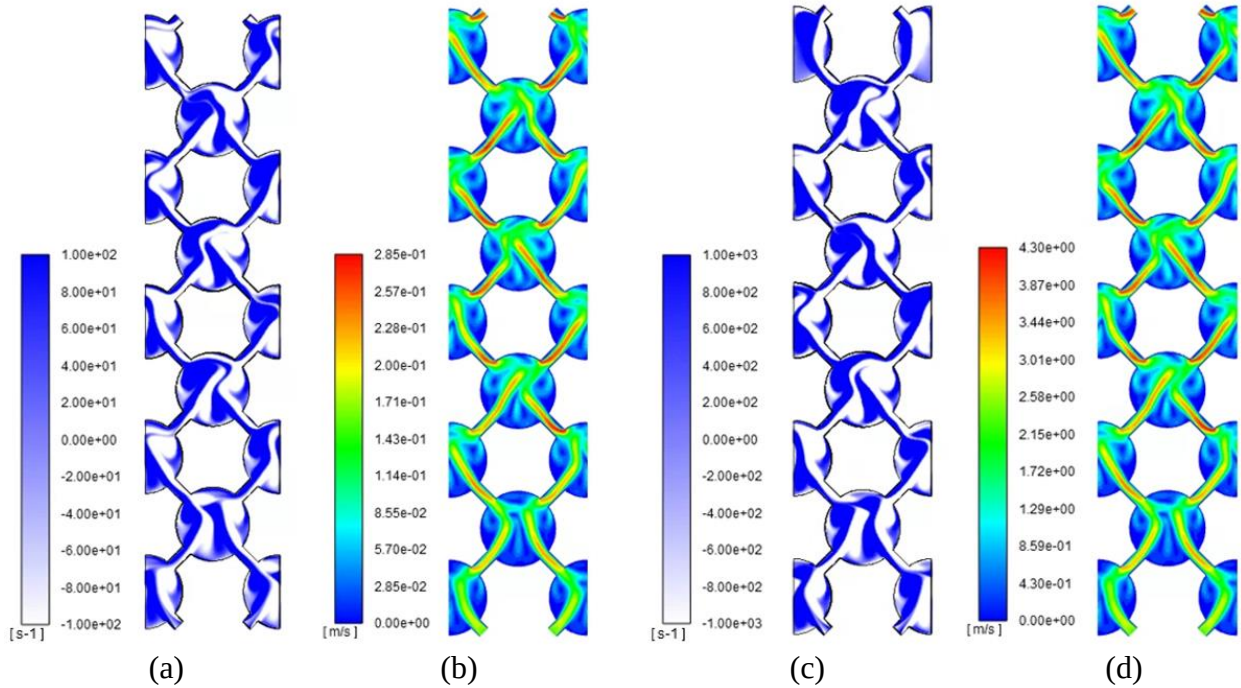


Figure V.8 Water maps of (a) the z -component of the vorticity and (b) velocity magnitude at 16τ . Air maps of (c) the z -component of the vorticity and (d) velocity magnitude at 16τ .

Hydrodynamics studies were performed in the centre of each chamber of ExtendedNUB for air and water, during 5τ . As expected, the velocities differ by a factor of 10. Figure V.9 shows that the behaviour of v_y is similar for water and air. In Chamber C2, v_y is negative and the oscillations have a lower amplitude. In chambers C4 and C6, v_y is positive and its amplitude is approximately the triple of C2. In fact, chambers C4 and C6 are less subjected to the inlet and outlet boundary conditions which exert an influence on the reactor dynamics. From chamber C2 to C4, the increase of the amplitude of v_y is quite noticeable. In fact, the oscillation of the inlet jets is still being developed in chamber C2, while in chamber C4 the oscillating behaviour is already developed. From chamber C6 to chamber C8, Figure V.9 shows that the amplitude of v_y is slightly smaller due to the influence of the outlet which dampens the oscillations, as explained in previous chapters of this work.

Comparing water with air, it is possible to conclude that the overall behaviour is similar, validating the model ExtendedNUB for liquids and gases.

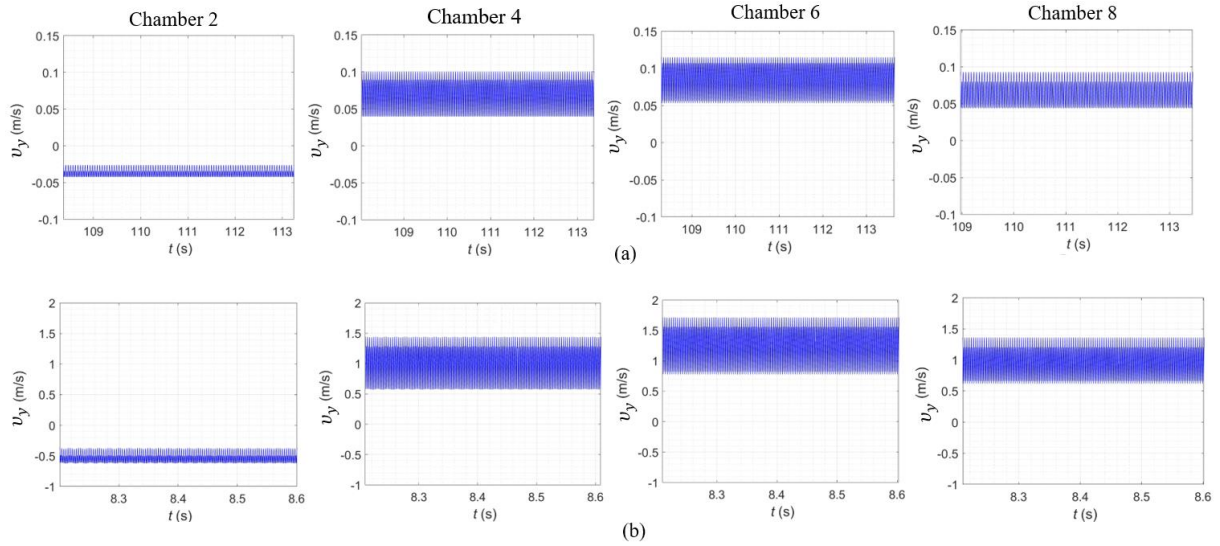


Figure V.9 v_y histories in the centre of chambers C2, C4, C6 and C8 of the ExtendedNUB geometry with $D/d = 6.65$, at $Re = 300$ during 5τ for: (a) water and (b) air.

Analysing in detail, it is visible that the NETmix oscillations are slightly more irregular with air, i.e., the amplitude of the oscillations is larger. In Figure V.9b it is possible to distinguish “waves”, especially in chambers C2 and C4, while in Figure V.9a the velocity histories are regular. This difference is also noticeable on the phase diagrams of the normalized strain rate, ζ^* , vs vorticity, ϵ^* , shown in Figure V.10. As explained in Section IV.3.3.1, more irregular oscillations are represented by thicker strange attractors, as visible in Figure V.10 which shows that the NETmix strange attractors are slightly thicker if air is used. Nevertheless, the shape of the attractors is similar, confirming the numerical validation of ExtendedNUB for gases.

The influence of the inlets and outlets, which was discussed in the numerical validation of the ExtendedNUB model in Section II.3.3 and shown in Figure V.9, is visible on the phase diagrams of Figure V.10. In chamber C2, which has a small value of intensity of turbulence, $I_{v_x} \cong 0.15$, since the oscillating behaviour of the NETmix jets is being developed, the strange attractor has a *bow-tie* shape. As the oscillations develop in chamber C4, I_{v_x} increases to approximately 0.38, and the attractor presents a parabolic structure with the vertex close to $\epsilon^* = 0$. Chamber C6 is less affected by the inlets and outlets. Thus, the highest value of $I_{v_x} \cong 0.42$ is attained and the strange attractor presents the already known *W* shape. In chamber C8, the intensity of turbulence decreases to approximately 0.36 due to the influence the outlet boundary condition which dampens the oscillations; the *W* shape starts to untangle.

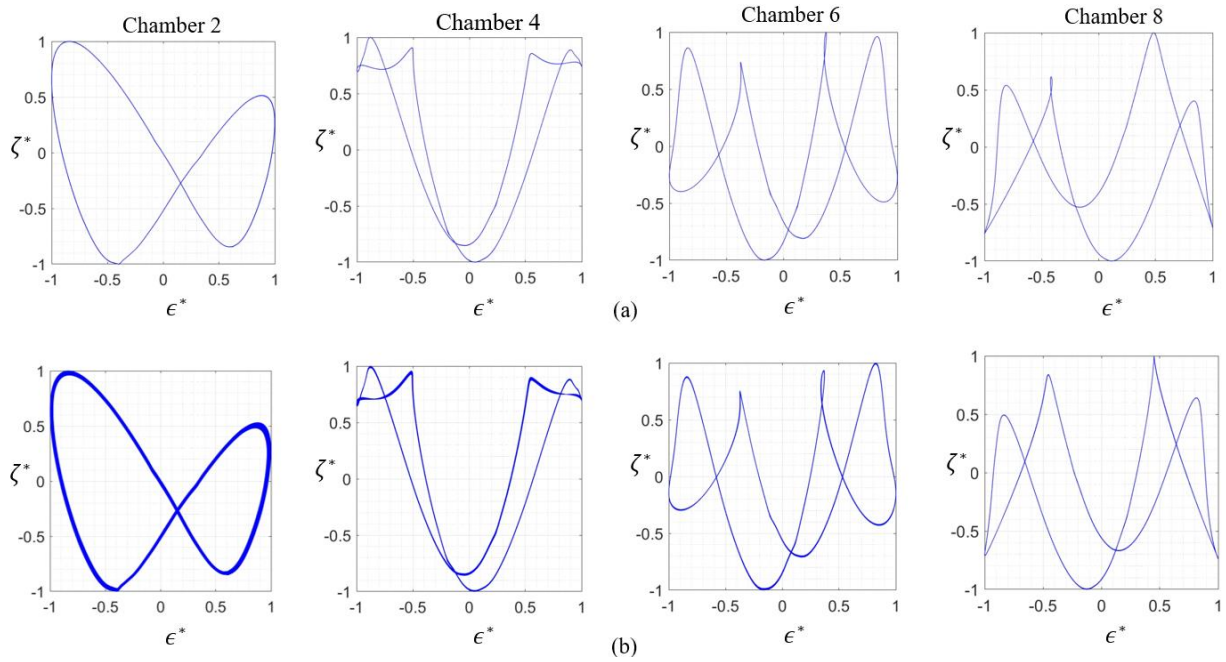


Figure V.10 Phase diagrams of ζ^* vs ϵ^* in the centre of chambers C2, C4, C6 and C8 of the ExtendedNUB geometry with $D/d = 6.65$, at $Re = 300$ during 5τ for: (a) water and (b) air.

Figure V.11 and Figure V.12 show the oscillating frequencies (Equation IV.7) in chamber C6 of ExtendedNUB for water and air, during 5τ . It is visible that the frequencies are discrete and have the same amplitude for both cases. Figure V.12 shows that the value of the principal oscillation frequency is 20 Hz for water (see Section IV.3.3.3) and approximately 250 Hz for air. As expected, the value of the principal frequency differs by a factor of 10 between water and air. For both cases, it is visible that the amplitude of the principal frequency is higher in chamber C6 which has the highest intensity of turbulence.

The slight difference between air and water, which was previously mentioned, can be evaluated from the spectrum analysis. In fact, Figure V.11b shows that the number of interferent frequencies is higher with air, which is associated with the larger irregularity of the oscillations, shown in Figure V.9b.

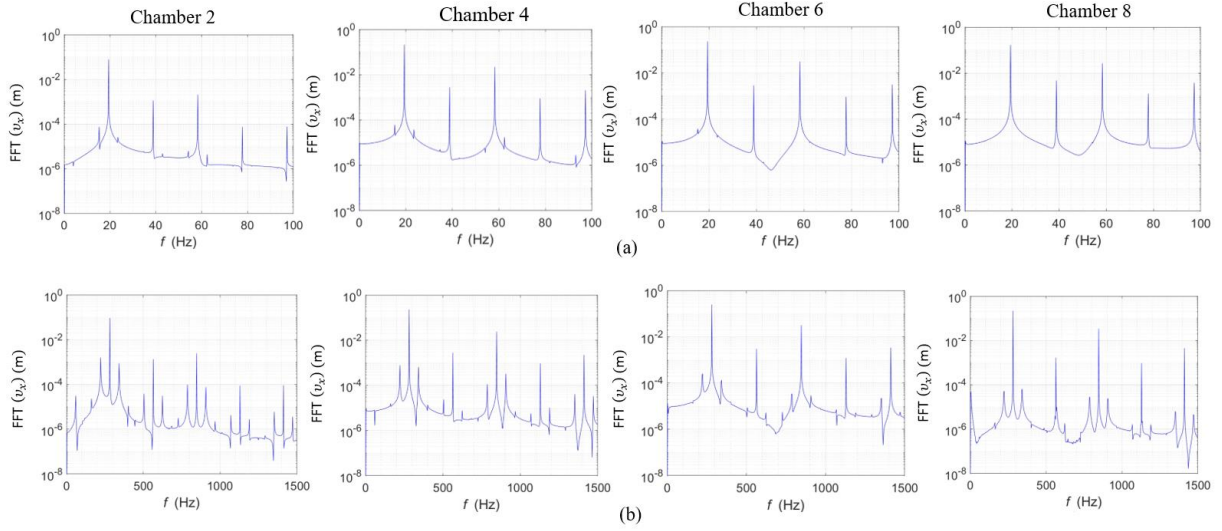


Figure V.11 FFT of v_x in logarithmic scale in the centre of chambers C2, C4, C6 and C8 of the ExtendedNUB geometry with $D/d = 6.65$, at $Re = 300$ during 5τ for: (a) water and (b) air.

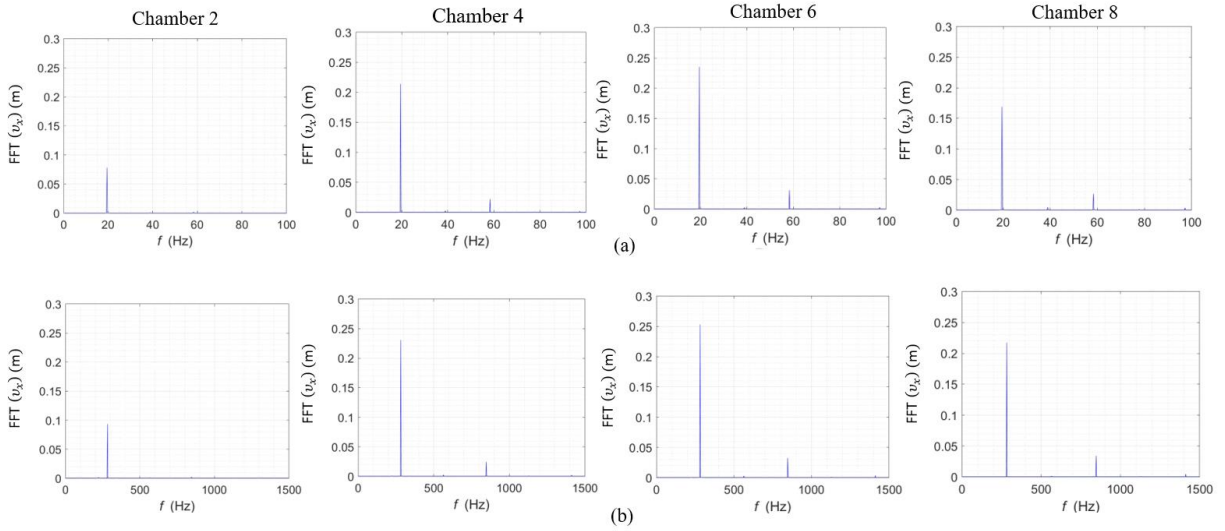


Figure V.12 FFT of v_x in the centre of chambers C2, C4, C6 and C8 of the ExtendedNUB geometry with $D/d = 6.65$, at $Re = 300$ during 5τ for: (a) water and (b) air.

The results that were previously presented in terms of hydrodynamics and spectral analysis have shown that the chaotic behaviour of the NETmix system as well as the oscillating behaviour that is responsible for mixing inside the chambers were maintained, validating the previous studies and the optimised model, ExtendedNUB, for gases.

V.2.1 Interfacial Area Generation in the NETmix Chambers for Air

To evaluate the interfacial area generation when air is being used in the NETmix reactor, LMS was applied to chamber C6. The particles were positioned over the CFD velocity field described in Section V.2. To implement the algorithm, 18 particles were injected at each inlet and the LMS equation, $\mathbf{X}_{i,j} = \mathbf{X}_{i-1,j} + \mathbf{v}_{i-1,j} \Delta t_{LMS}$ (Equation IV.3 of Section IV.3.1) was used for the tracking,

during 3τ . The interfacial area generation was computed from $\alpha = \frac{\sum_{i=1}^{np} |\mathbf{x}l_{i,j} - \mathbf{x}l_{i,j+1}| + \sum_{i=1}^{np} |\mathbf{x}r_{i,j} - \mathbf{x}r_{i,j+1}|}{s_0}$ (Equation IV.4).

As said in previous sections, for chaotic flows, the interfacial area generation is exponential and can be represented by the fitting $\alpha = ae^{bt}$. For air, the interfacial area generation in chamber C6 is given by $\alpha = 66e^{295t}$ ($R^2 = 0.99$). The results are shown in Figure V.13. and compared with a liquid mixture (see Section IV.3.1.1).

The value of parameter a is related to the early evolution of the interfacial area in the beginning of the particle tracking with LMS. As visible in Figure V.13, the value of a is similar for both cases which explains the similarity of the shape of the exponential curves. The specific generation of interfacial area is given by $b = \frac{1}{\alpha} \frac{d\alpha}{dt}$, which differs by a factor of 10 between water and air, as expected, due to the difference in the time step size. In this way, the rate of interfacial area generation is the same for water and air, and the Lagrangian analysis that was previously presented for liquids is valid for gases.

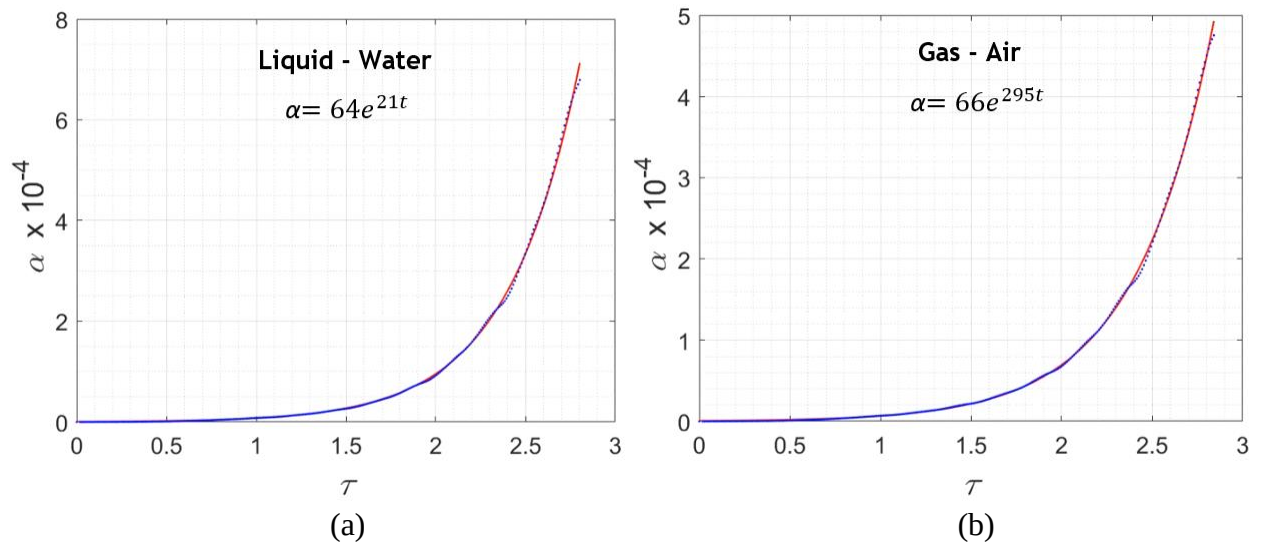


Figure V.13 Interfacial area generation in chamber C6 during 3τ for: (a) liquid and (b) gas.

V.3 CFD Simulation of H_2 Combustion in the ExtendedNUB Model

V.3.1 CFD Model

The ExtendedNUB model with $D/d = 6.65$ was used to perform combustion simulations, considering the discretization described in Section II.3.2.

The commercial finite volume CFD software ANSYS® FLUENT™ was used to solve the mass and momentum conservation equations, respectively defined as

$$\nabla \cdot \mathbf{v} = 0 \quad (\text{V.38a})$$

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + \mu \nabla^2 \mathbf{v} \quad (\text{V.38b})$$

where $\mathbf{v}$ is the velocity vector, p is the pressure, ρ and μ are the density and viscosity of the fluid, respectively.

The species transport equation is defined as

$$\frac{\partial}{\partial t} (Y_i \rho) + \nabla \cdot (\mathbf{v} Y_i \rho) = -\nabla \cdot \mathbf{J}_i + R_i \quad (\text{V.39})$$

in which Y_i is the mass fraction of each species, i , R_i is the rate of production of species i and $\mathbf{J}_i$ is the diffusion flux vector. The mass diffusion coefficients of $\mathbf{J}_i$ can be calculated by Fick diffusion or by Full multicomponent diffusion as will be discussed in the next subsection.

The rate of production of species i is given by

$$R_i = \mathcal{M}_i \sum_{j=1}^{nr} r_{i,j} \quad (\text{V.40})$$

in which $\mathcal{M}_i$ is the molecular weight of species i , and $r_{i,j}$ is the Arrhenius molar rate of consumption/production of species i in reaction j .

The energy equation is given by

$$\frac{\partial}{\partial t} (\rho E) + \nabla \cdot (\mathbf{v} (\rho E + p)) = \nabla \cdot (\sigma_{eff} \nabla T) - \sum_{i=1}^n h_i \mathbf{J}_i + \gamma_{eff} \cdot \mathbf{v} + Sh \quad (\text{V.41})$$

in which E is the energy, p is the pressure, σ_{eff} is the effective conductivity, h_i is the enthalpy of species i , γ_{eff} is the effective viscous dissipation and Sh includes the heat of chemical reaction and other volumetric heat sources. Note that the first term of the right side of the equation represents the energy transfer due to conduction, species diffusion and viscous dissipation, respectively.

The energy, E , is defined as

$$E = h - \frac{p}{\rho} + \frac{v^2}{2} \quad (\text{V.42})$$

where $\frac{v^2}{2}$ is the specific kinetic energy, in which v is the velocity. h is the enthalpy defined as

$$h = \sum_{i=1}^n h_i Y_i \quad (\text{V.43})$$

in which the enthalpy of each species i is calculated by

$$h_i = \int_{T_{ref}}^T c_{p,i} dT \quad (V.44)$$

where $c_{p,i}$ is the heat capacity of species i , and $T_{ref} = 298.15$ K.

V.3.1.1 Diffusion Models

In this work, three models of diffusion will be used: Fick's diffusion, Full Multicomponent diffusion and Thickened Flame Model.

Fickian Diffusion

If the Fick law is applied, the diffusive flux is defined as

$$\mathbf{J}_i = -\rho \mathcal{D}_i \nabla Y_i - \rho D_{T,i} \frac{\nabla T}{T} \quad (V.45)$$

in which Y_i is the mass fraction, $\mathcal{D}_i$ is the mass diffusion coefficient and $D_{T,i}$ is the thermal diffusion coefficient (if thermal diffusion is enabled) of species i in the mixture, and T is the temperature (Ansys 2021).

Full Multicomponent Diffusion

To calculate the flux vector, using the full multicomponent theory, the Maxwell-Stefan equation is applied,

$$\sum_{\substack{j=1 \\ j \neq i}}^N \frac{y_i y_j}{\mathcal{D}_{ij}} (\mathbf{v}_j - \mathbf{v}_i) = \mathbf{d}_i - \frac{\nabla T}{T} \sum_{\substack{j=1 \\ j \neq i}}^N \frac{y_i y_j}{\mathcal{D}_{ij}} \left(\frac{D_{T,j}}{\rho_j} - \frac{D_{T,i}}{\rho_i} \right) \quad (V.46)$$

in which y is the mole fraction, $\mathbf{v}$ is the diffusion velocity vector, $\mathcal{D}_{ij}$ is the binary mass diffusion coefficient and D_T is the thermal diffusion coefficient (if thermal diffusion is enabled) of species i and j in the mixture (Ansys 2021).

For ideal gases, the Maxwell diffusion coefficients are equal to the binary diffusion coefficients. If the external forces are the same for all species and pressure diffusion is negligible, $\mathbf{d}_i = \nabla y_i$.

If the mass diffusive flux, $\mathbf{J}_i = \rho_i \mathbf{v}_i$ is used in the Maxwell equation

$$\sum_{j=1, j \neq i}^N \frac{y_i y_j}{\mathcal{D}_{ij}} \left(\frac{\mathbf{J}_j}{\rho_j} - \frac{\mathbf{J}_i}{\rho_i} \right) = \nabla Y_i - \frac{\nabla T}{T} \sum_{j=1, j \neq i}^N \frac{y_i y_j}{\mathcal{D}_{ij}} \left(\frac{D_{T,j}}{\rho_j} - \frac{D_{T,i}}{\rho_i} \right) \quad (\text{V.47})$$

the diffusive flux can be obtained by

$$\mathbf{J}_i = - \sum_{j=1}^{N-1} \rho \mathcal{D}_{ij} \nabla Y_j - D_{T,i} \frac{\nabla T}{T} \quad (\text{V.48})$$

where Y_j is the mass fraction of species j (Ansys 2021).

Thickened Flame Model

As explained in Section V.1.3, the flames are influenced by the flame speed and the flame stretch. In ANSYS® FLUENT™, the Zimont turbulent flame speed, U_t , model is used for the prediction of premixed flames in the wrinkled or thickened (corrugated) flame regimes, according to

$$U_t = A(\sqrt{\bar{v}^2})^{3/4} \mathcal{U}_F^{1/2} D_t^{-1/4} \ell^{1/4} \quad (\text{V.49})$$

in which $\mathcal{U}_F$ is the laminar flame speed, $A = 0.52$ (default) is a constant of the model, $\bar{v}$ is the mean velocity, $D_t = \lambda/\rho c_p$ is the thermal diffusivity (molecular heat transfer coefficient of the unburnt mixture) and ℓ is the turbulence length scale. λ is the thermal conductivity, ρ and c_p are the density and heat capacity of the mixture, respectively.

The turbulence length scale is calculated from

$$\ell = C(\sqrt{\bar{v}^2})^3/\varepsilon \quad (\text{V.50})$$

in which $C = 0.37$ (default) is a constant and $\varepsilon = \frac{\mu}{\rho} \frac{\partial \bar{v}_i}{\partial x} \frac{\partial \bar{v}_j}{\partial x}$ is the turbulence dissipation rate (Ansys 2021).

V.3.1.2 Mixture Properties Models

To predict the mixture properties, laws based on the ideal gas equation were mainly used. In general, for systems with low pressures, high temperatures and low densities, the real gases can be considered to behave as ideal gases since the molecular size and intermolecular forces are not strongly affected (Çengel and Boles 2001, Tuckerman 2010).

In this work, the density, ρ , will be computed from the incompressible-ideal-gas model. The specific heat, c_p , will be predicted from the mixing-law model. For the thermal conductivity, λ ,

and viscosity, μ , the ideal-gas-mixing-law will be used. The mass diffusivity, $\mathcal{D}$, will be computed from the kinetic-theory model.

Incompressible Ideal Gas Law

The computation of the mixture density, ρ , from the incompressible ideal gas law is made according to

$$\rho = \frac{p}{\frac{R}{\mathcal{M}}T} \quad (\text{V.51})$$

in which p is the pressure, $R = 8314 \text{ J/(kmolK)}$ is the ideal gas constant, $\mathcal{M}$ is the molecular weight and T is the temperature (Ansys 2021).

Mixing Law

The prediction of the mixture specific heat capacity, c_p , from the mixing law is given by

$$c_p = \sum_i^n Y_i c_{p_i} \quad (\text{V.52})$$

in which Y_i is the mass fraction of species i and c_p is the specific heat capacity of the pure compounds (Ansys 2021).

Ideal Gas Mixing Law

The mixture thermal conductivity, λ , and viscosity, μ , are computed from

$$\lambda = \sum_i^n \frac{y_i \lambda_i}{\sum_j y_j \phi_{ij}} \quad (\text{V.53a})$$

$$\mu = \sum_i^n \frac{y_i \mu_i}{\sum_j y_j \phi_{ij}} \quad (\text{V.53b})$$

where

$$\phi_{ij} = \frac{\left(1 + \left(\frac{\mu_i}{\mu_j}\right)^{1/2} \left(\frac{\mathcal{M}_j}{\mathcal{M}_i}\right)^{1/4}\right)^2}{\left(8 \left(1 + \frac{\mathcal{M}_i}{\mathcal{M}_j}\right)\right)^{1/2}} \quad (\text{V.54})$$

in which y_i is the molar fraction of species i (Ansys 2021).

Kinetic Theory

The mass diffusivity, $\mathcal{D}$, is computed from

$$\mathcal{D}_{ij} = 0.00188 \frac{\left(T^3 \left(\frac{1}{\mathcal{M}_i} + \frac{1}{\mathcal{M}_j}\right)\right)^{1/2}}{p\sigma_{ij}^2\Omega_D} \quad (\text{V.55})$$

where Ω_D is the diffusion collision integral, which is a measure of the interaction of the molecules of the system, and

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (\text{V.56})$$

in which σ_i are the Lennard-Jones parameters for each species i (Ansys 2021).

V.3.1.3 Boundary and Initial Conditions

At the inlets, a constant velocity is imposed, v_{inj} , which is obtained from the Reynolds number, according to

$$v_{inj} = \frac{\mu_M \text{Re}}{\rho_M D_h} \quad (\text{V.57})$$

where $D_h = 2d$ is the hydraulic diameter for the 2D geometry (considering an infinite depth of the equivalent 3D geometry, $\omega \rightarrow \infty$), μ_M and ρ_M are the viscosity and density of the mixture, respectively, given by

$$\mu_M = \sum_{i=1}^n \mu_i y_i \quad (\text{V.58a})$$

$$\rho_M = \sum_{i=1}^n \rho_i y_i \quad (\text{V.58b})$$

in which y_i is the molar fraction, μ_i and ρ_i are the viscosity and density of species i , respectively.

The time step size, Δt , was calculated to maintain the Courant number, $C = \frac{v_{inj}\Delta t}{\Delta x} = 1$.

At the outlets, a constant and uniform pressure profile is used. A periodic boundary condition is set at each pair of half lateral chambers to reproduce the NETmix behaviour with only one column of chambers. The x and y components of the velocity are set to zero at the walls. The heat flux on the walls is equal to zero.

To perform the transient CFD simulation, the initial solution was obtained by setting all variables to zero. The molar fraction of the species is $y_i = 0$, except for N_2 , $y_{N_2} = 1$.

V.3.2 Global Reaction Scheme Simulation

In this section, the global reaction scheme of hydrogen, $H_2 + 0.5O_2 \rightarrow H_2O$ (see Section V.1.2.1), is going to be used to simulate combustion in ExtendedNUB.

The equivalence ratio is given by

$$\theta = \sum_{j=1}^{n_j} \frac{F_j y_{H_2,j}}{2F_j y_{O_2,j}} \quad (V.59)$$

in which F is the molar flow rate of inlet j and y is the molar fraction of H_2 or O_2 .

The Damköhler number relates the reaction rate with the mass transfer (diffusion). If $Da < 1$, diffusion occurs faster than the chemical reaction and the process is not limited by diffusion. For the combustion of H_2 , the Da number is given by

$$Da = \overline{C}_{H_2}^{in,0.5} \overline{C}_{O_2}^{in,0.5} \tau Kf \quad (V.60)$$

in which the passage time is $\tau = \frac{\pi D^2}{8d\overline{v}_{in,j}}$ and $\overline{v}_{in,j}$ is the average of the inlet velocity of the two inlet channels. Kf is the forward reaction rate coefficient. The Damköhler number is related with the Karlovitz number (see Section V.1.3) by $Ka = 1/Da$.

The conversions of H_2 or O_2 are given by

$$X_i = \frac{\sum_{j=1}^{n_j} F_j y_{i,j} - \sum_{k=1}^{n_k} F_k y_{i,k}}{\sum_{j=1}^{n_j} F_j y_{i,j}} \quad (V.61)$$

in which i is H_2 or O_2 , j represents the inlet channels and k the outlet channels.

As mentioned in the beginning of this chapter, combustion can be premixed, if the reactants are mixed before entering the reactor, or non-premixed if the reactants are not mixed until they enter the reactor. In the case of the ExtendedNUB model, combustion is premixed if the fuel and the oxygen enter the reactor from the same inlet. If the oxygen and the fuel enter the ExtendedNUB reactor from different inlets, combustion is non-premixed. The ExtendedNUB model with $D/d = 6.65$ was used to simulate combustion in the NETmix reactor.

In the cases that will be presented in the next sections, the reactants enter at 25 °C and 1 bar (constant) at both inlets. The inlet velocities will be varied to have a Re number at the inlet of 300.

The simulations will be run during 16τ (ca. 1.1 s flow time). Most of the reactive mixtures that will be simulated have $Ka < 1$ and $Da < 2$. Thus, the flamelet regime can be applied (see Section V.1.3) and the reactions are not significantly limited by diffusion.

V.3.2.1 Combustion Dynamic Flow Analysis

The properties of the mixture change during the reaction of combustion, as will be shown in Section V.3.2.2). In this way, if combustion occurs, the NETmix flow oscillating behaviour, characterized by the vortex formation especially at the top and bottom of the mixing chambers, is not as regular as shown in Section V.2 for non-reactive flows.

In this section, the dynamic behaviour of NETmix with combustion will be analysed.

The CFD model and reaction kinetics were previously described. For the transient simulations of this Section the species transport was computed using the Fickian diffusion. The transient calculations were performed with the First Order Implicit method. For the pressure-velocity coupling, the SIMPLEC method was used. The spatial discretization was performed with the Least Squares Cell Based algorithm for the gradient, PRESTO! for the pressure, Third-Order MUSCL for the momentum and Second Order Upwind for the energy and species. The convergence criterion for the maximum residuals of continuity and momentum is 10^{-5} , for the energy is 10^{-6} and for the species is 10^{-3} .

To analyse the dynamic flow in combustion, the reactive mixture *S7p* will be used (see Section V.3.2.2). In this case, premixed combustion occurs with the inlet composition, $y_{H_2} = 0.1$, $y_{O_2} = 0.2$ and $y_{N_2} = 0.7$. For an injection $Re = 300$, $v_{inj} = 2.30$ m/s and $\Delta t = 7.26 \times 10^{-6}$ s. The residence time of one NETmix chamber is $\tau_c = \frac{\pi D^2}{8 v_{inj} d} = 0.0076$ s, and the residence time of ExtendedNUB is $\tau = 0.068$ s.

Figure V.14a shows the vorticity maps of case *S7p* where is visible that the oscillations do not have the same behaviour of the flow without the combustion reaction (Figure V.14a). Moreover, the vorticity has a larger magnitude if combustion occurs. In fact, the vorticity varies in a range from -2000 s^{-1} to 2000 s^{-1} , while for air the range is between -1000 s^{-1} and 1000 s^{-1} (Figure V.14c). In Figure V.14b, the velocity map shows that the oscillations inside the NETmix chambers do not have a behaviour as regular as the flow without combustion (Figure V.14d). It is also visible that, if combustion occurs, the velocity is one order of magnitude higher.

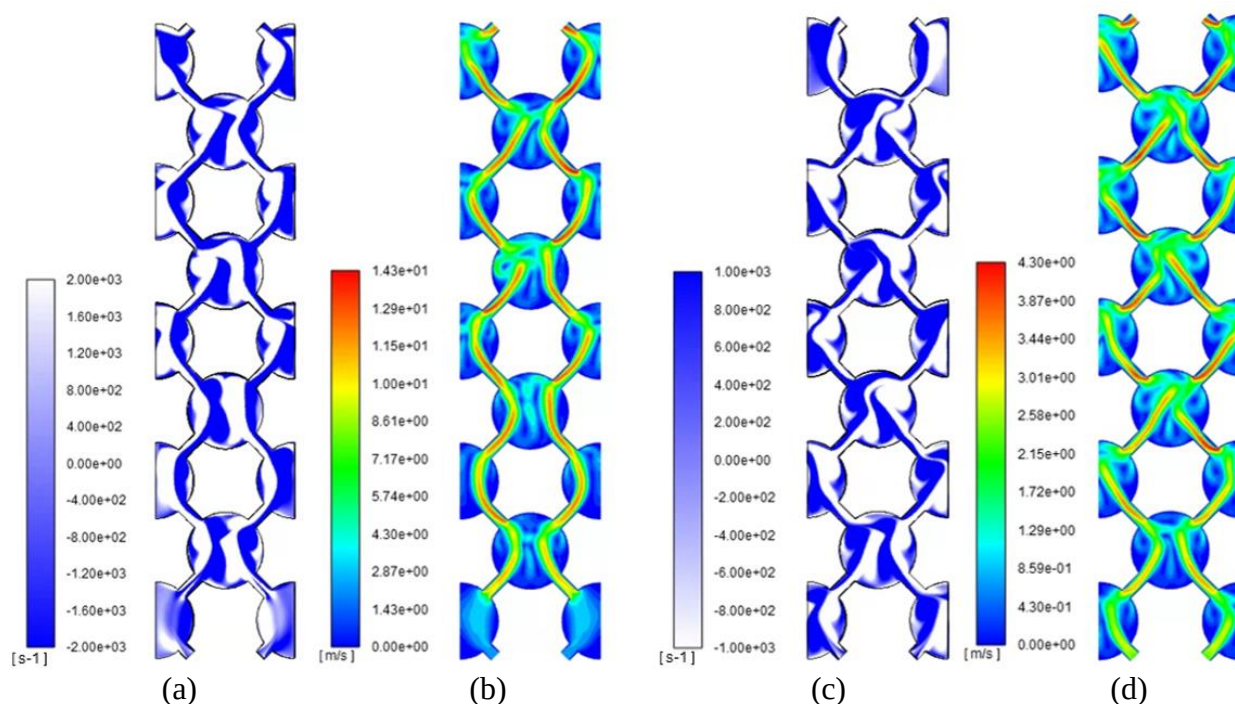


Figure V.14 *S7p* maps of: (a) *z*-component of the vorticity and (b) velocity magnitude. Non-reactive flow maps of (c) *z*-component of the vorticity and (d) velocity magnitude.

The oscillations inside chamber C6 are shown in the velocity maps of Figure V.15 for the hydrogen combustion, *S7p*, and for a non-reactive flow with air (see Section V.2), during 3.79τ . It is visible that for a non-reactive flow, the direction of the jets alternates between the left and the right, promoting a nearly periodic oscillating pattern. In contrast, if combustion occurs, the oscillations do not obey to a pattern. A video of the oscillations, *Combustion_vs_Air_Flow.mp4*, is shown in the folder *Mixing_and_Controlled_Combustion_in_NETmix_videos*.

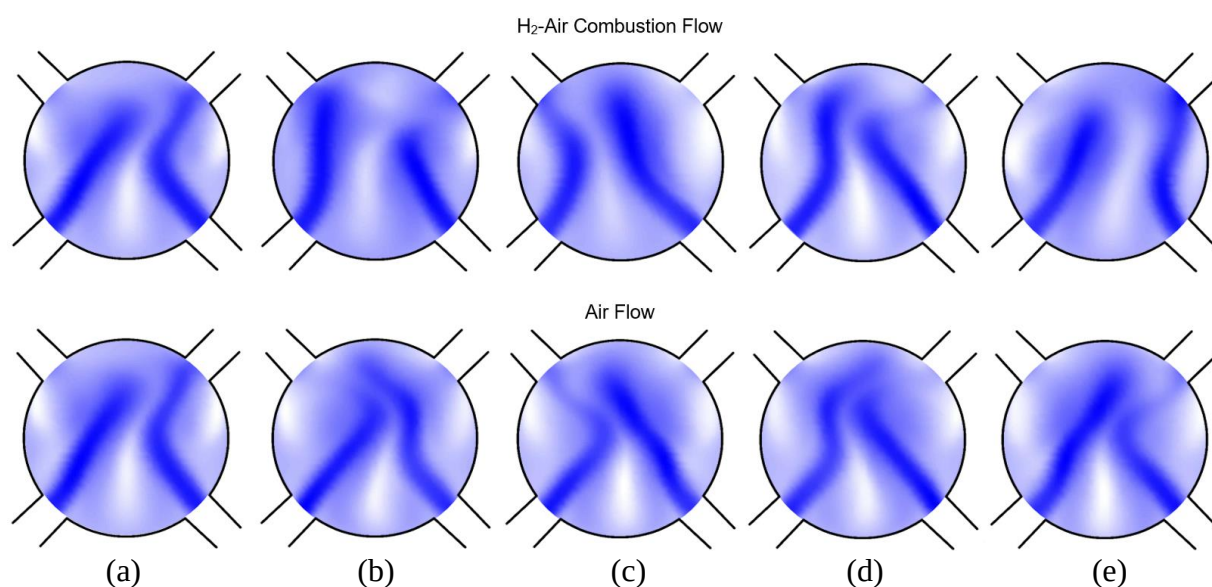


Figure V.15 NETmix oscillations at: (a) 0.76τ , (b) 1.52τ , (c) 2.27τ , (d) 3.00τ and (e) 3.79τ .

The y -velocity histories in the centre of the chambers of the ExtendedNUB model, presented in Figure V.16, show that the oscillations take approximately 0.05 s to stabilize. However, as previously said, they do not have a regular behaviour as shown in Section V.2. In fact, with a non-reactive flow, the amplitude of the oscillations is ca. 1 m/s (see Figure V.9) and with combustion the amplitude attains approximately 10 m/s, as shown in Figure V.16.

The amplitude of v_y is smaller in chamber C2 due to the proximity of the inlet. The amplitude of v_y increases, then, in C4, C6 and C8, where the oscillations inside the NETmix chambers are already developed. Differently from the studies that were performed with water and air (see Section V.2), if combustion occurs, the outlet condition imposed by the CFD model does not have a major impact in the amplitude of the velocity.

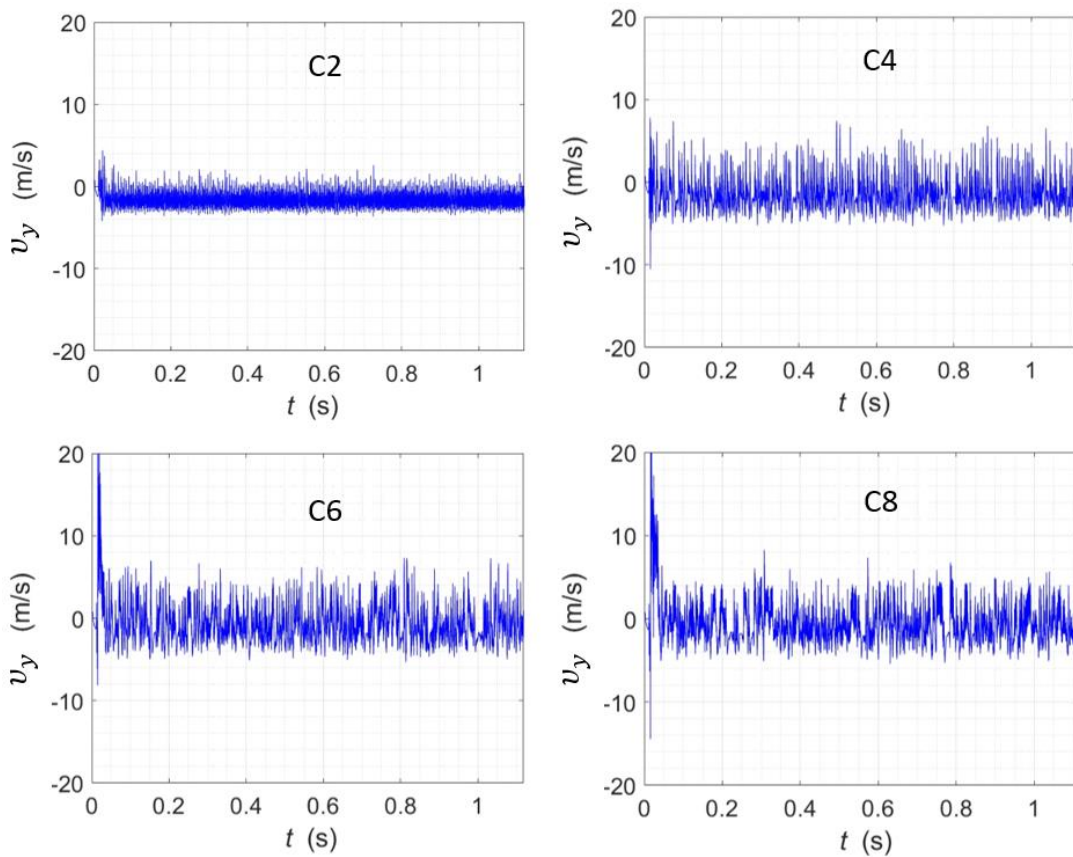


Figure V.16 $S7p$ y -velocity histories in the centre of chambers C2, C4, C6 and C8 of 2D ExtendedNUB.

In $S7p$, the temperature increases in the first chamber, forming a hotspot which reaches 2060 °C, as shown in the temperature map at 1.1 s (see Figure V.17a). The history of the temperature in the centre of chambers C2 to C8 is shown in Figure V.17b where it is visible that the temperature stabilizes after 0.05 s. In all chambers, the temperature attains a first plateau and at approximately 0.5 s decreases slightly. It is possible to conclude that the reaction starts in the first row of chambers where the maximum temperature is reached.

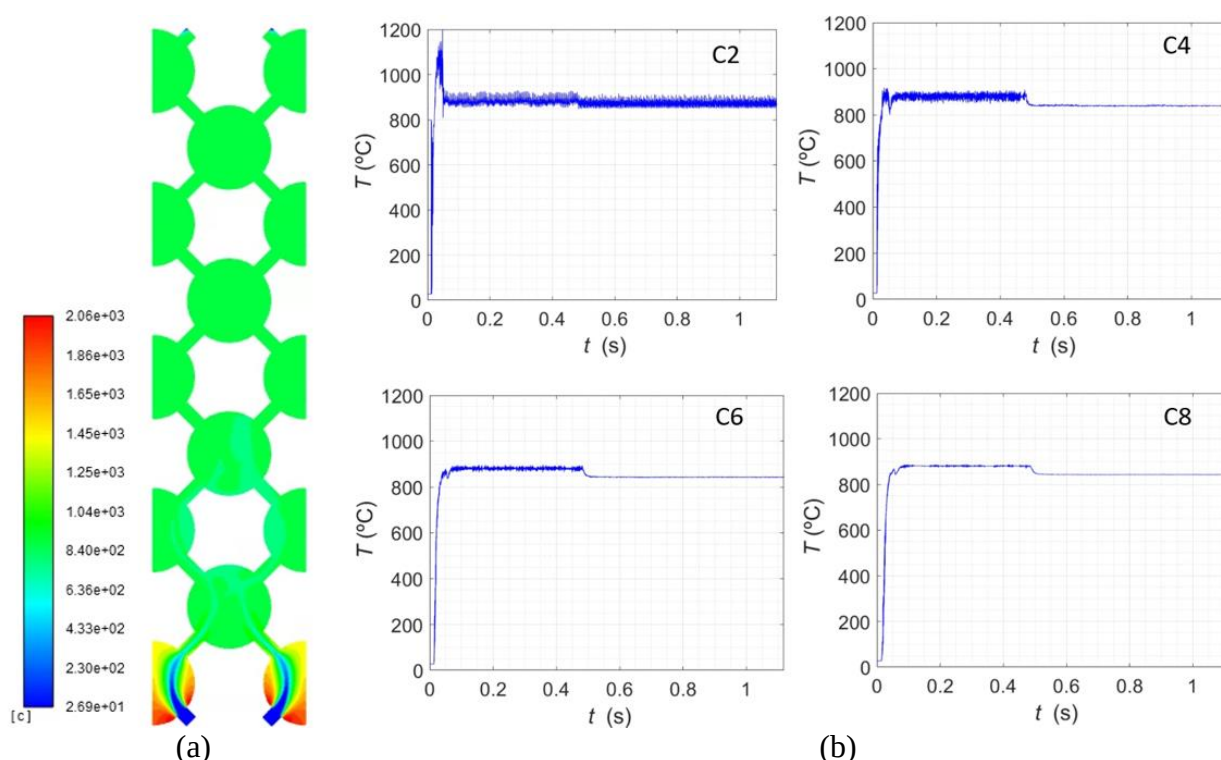


Figure V.17 S7p (a) temperature map at 1.1 s and (b) temperature history in the centre of C2 to C8.

Figure V.18a shows a reaction front in the first half of the first row of chambers. In the reaction front, the hydrogen and oxygen are consumed, as visible in Figure V.18b and in Figure V.18c, respectively. While the fuel is completely consumed in the reaction front, the oxygen decreases on the sides of the reaction front, where the temperature attains its maximum. The larger production of water occurs at the hotspot, as shown in Figure V.18d.

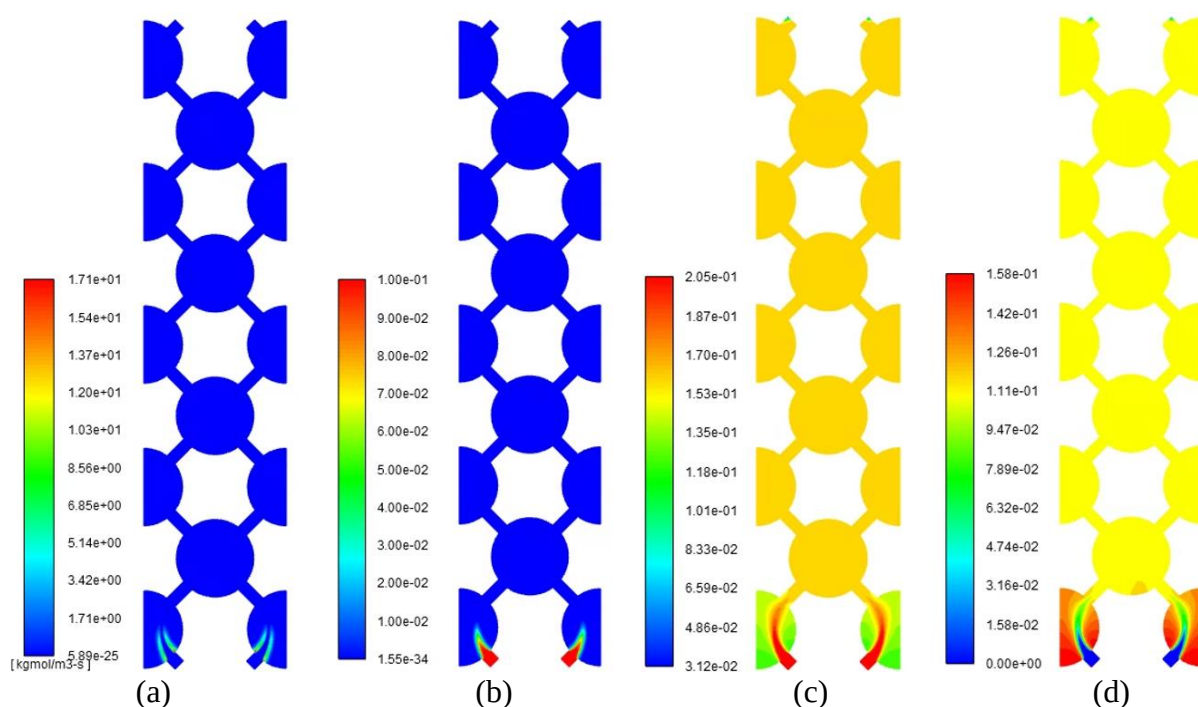


Figure V.18 S7p maps at 1.1 s of (a) reaction rate, (b) mole fraction of H₂, (c) mole fraction of O₂ and (d) mole fraction of H₂O.

A video, combustion.mp4, of the evolution of the velocity and temperature of $S7p$ is shown in the folder *Mixing_and_Controlled_Combustion_in_NETmix_videos*.

Depending on the reactive mixture, the NETmix flow with combustion assumes different behaviours. For the simulations that will be presented further in this work, the vorticity and velocity maps, as well as the maps of the molar fraction of the reactants and products are shown in Appendix C.

Interfacial Area Generation of Combustion in NETmix

To evaluate the interfacial area generation with combustion in the NETmix chambers, DLMS was applied to chamber C6 of the ExtendedNUB model, in similarity to what was done in Sections IV.3.1.1 and V.2.1. The velocity fields were recorded from the CFD $S7p$ case. The parameters of DLMS were previously described in Sections III.5 and III.6. The particle tracking in chamber C6 with DLMS is presented in Figure V.19. A video of the tracking, DLMS_Combustion.mp4, is shown in the folder *Mixing_and_Controlled_Combustion_in_NETmix_videos*.

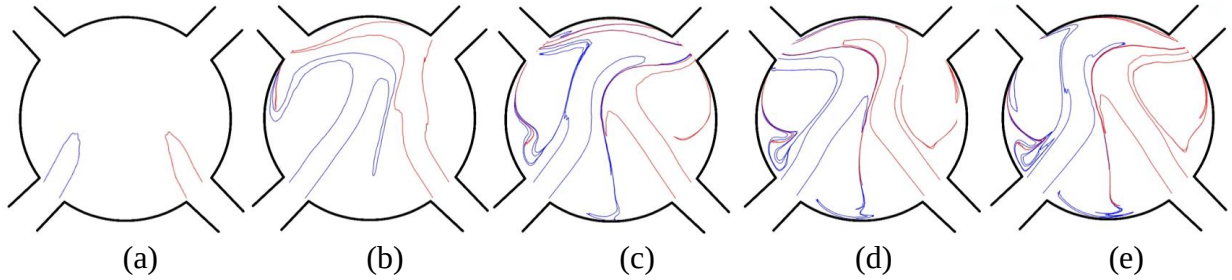


Figure V.19 Particle tracking with DLMS in C6 at: (a) 0.01τ , (b) 0.13τ , (c) 0.26τ , (d) 0.38τ and (e) 0.49τ .

The interfacial area generation equation, $\alpha = \frac{\sum_{i=1}^{np} |\mathbf{x}l_{i,j} - \mathbf{x}l_{i,j+1}| + \sum_{i=1}^{np} |\mathbf{x}r_{i,j} - \mathbf{x}r_{i,j+1}|}{s_0}$ (Equation IV.4.)

was used and an exponential fitting was applied to the data. The expression that represents the growth of interfacial area of combustion in NETmix is $\alpha = 1.1 \times 10^{-3} e^{5562t}$ ($R^2 = 0.99$). The results are shown in Figure V.20a and compared with air flow without combustion (Figure V.20b).

The value of parameter a is related to the early evolution of the interfacial area in the beginning of the particle tracking of DLMS. As visible in Figure V.20, the value of a is four orders of magnitude smaller if combustion occurs, which explains the flat curve until 0.35τ . The exponential curve of combustion is then sharper.

The specific generation of interfacial area is given by $b = \frac{1}{\alpha} \frac{d\alpha}{dt}$, which can be used to compare the interfacial area generation. Comparing the exponential fittings, it is visible that the value of b for

combustion is approximately 20 times the value for air. In fact, the interfacial area at the DLMS final time is ca. 2 orders of magnitude higher for combustion.

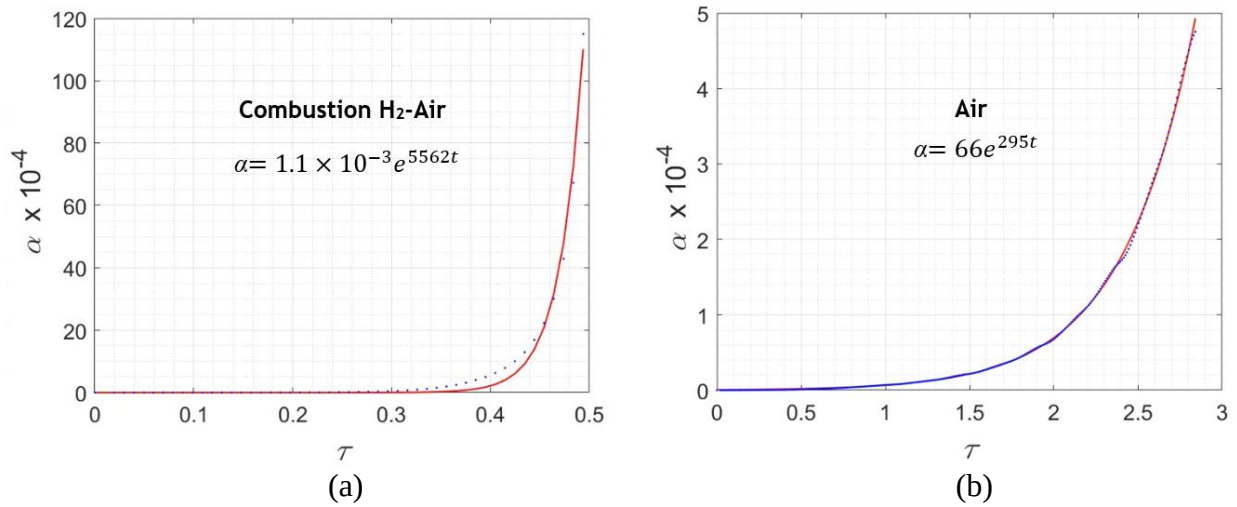


Figure V.20 Interfacial area generation in chamber C6 for: (a) H₂-Air combustion and (b) non-reactive Air flow.

V.3.2.2 Inlet Reynolds Study

To evaluate the influence of the inlet Reynolds number, the case that was previously presented, *S7p*, will be simulated at different Re: 100, 300 and 600. To change the inlet Re, the velocity of each inlet is calculated from Equation V.31, considering the properties of the mixture at the inlet temperature, 25 °C, listed in Table V.4. The time step is calculated to maintain the Courant number, $C = 1$. For the inlet reactive mixture of *S7p*, $y_{H_2} = 0.1$, $y_{O_2} = 0.2$ and $y_{N_2} = 0.7$, the inlet velocity and time step size for each Re are shown in Table V.5.

Table V.5 Inlet parameters for different Re.

Inlet Parameters		
Re	v_{inj} (m/s)	Δt (s)
100	0.77	2.24×10^{-5}
300	2.30	7.46×10^{-6}
600	4.60	3.73×10^{-6}

In Table V.6, are shown the results with different inlet Reynolds for *S7p*. The cases will be compared from the average molar fraction of each component at the outlet, $\overline{y_{out}}$, the maximum temperature, T_{max} , and the temperature in the centre of chamber C8, T_{C8} (upper full chamber of the ExtendedNUB geometry).

It is visible that as the inlet Re increases, the maximum temperature increases ca. 34% between Re = 100 and 300, and ca. 20% between Re = 300 and Re = 600. The temperature at C8 is close for the three cases.

Table V.6 Influence of the inlet Re for case *S7p*.

Inlet Re Study								
	Species	$y_{in,left}$	$y_{in,right}$	$\overline{y_{out}}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{c8}(^{\circ}C)$
<i>S7p</i> Re = 100	H ₂	0.1	0.1	0	1	0.26	1360	843
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
<i>S7p</i> Re = 300	H ₂	0.1	0.1	0	1	0.26	2060	843
	O ₂	0.2	0.2	0.14				
	N ₂	0.7	0.7	0.77				
	H ₂ O	0	0	0.093				
<i>S7p</i> Re = 600	H ₂	0.1	0.1	0	1	0.26	2580	858
	O ₂	0.2	0.2	0.11				
	N ₂	0.7	0.7	0.81				
	H ₂ O	0	0	0.080				

Figure V.21 shows the velocity maps for the three cases. It is visible that, at $Re = 100$, below the critical value (ca. $Re = 120$), the flow is steady and nearly symmetrical without vortices in the chambers. For Reynolds numbers above the critical value, $Re = 300$ and $Re = 600$, the flow is chaotic and the oscillating behaviour, characteristic of the NETmix reactor, is present (see Section II.3.3). For the highest value, $Re = 600$, it is visible that the vortices are larger and evolve from a lower row of chambers. As the Reynolds number increases from 100 to 600, the maximum velocity increases ca. one order of magnitude.

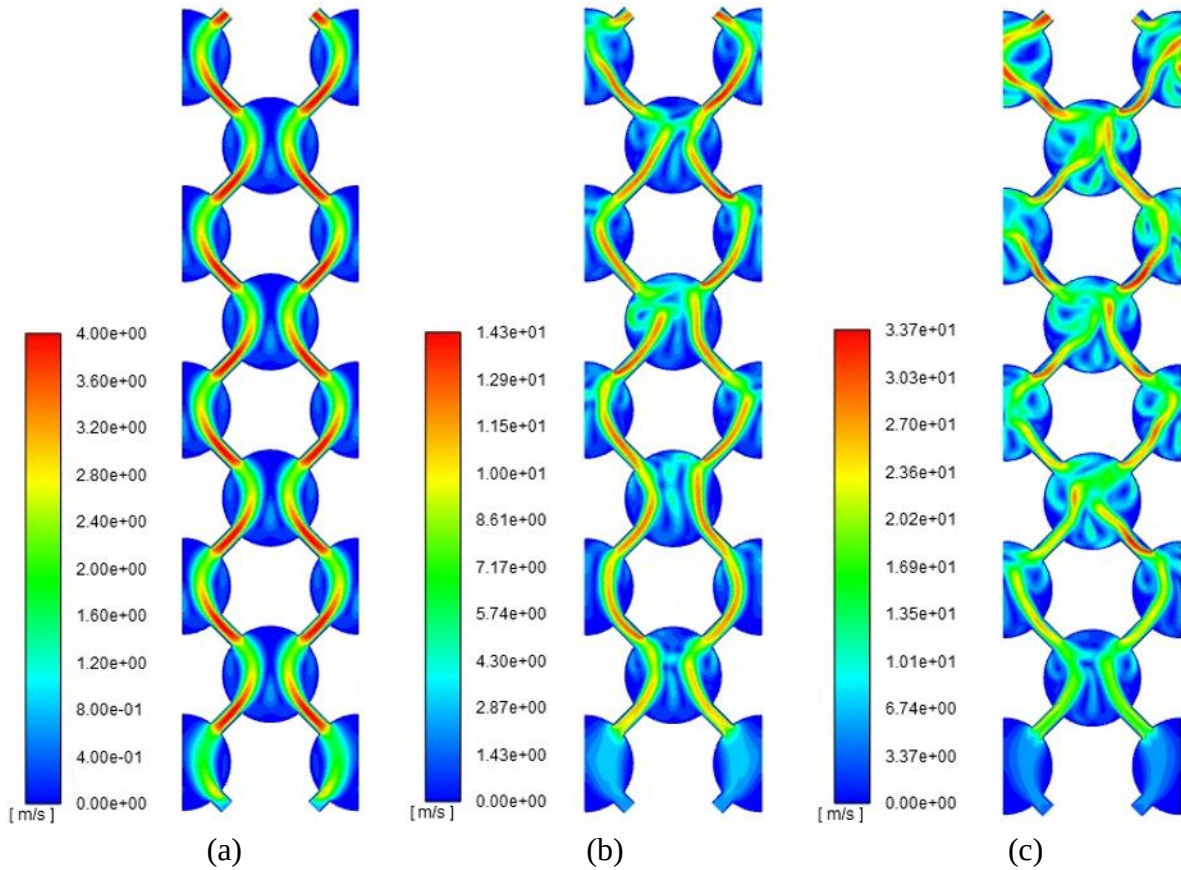


Figure V.21 Velocity maps of *S7p* at: (a) $Re = 100$, (b) $Re = 300$ and (c) $Re = 600$.

As the inlet Re number increases, the reaction is prolonged further in the reactor. As shown in Figure V.22, for $Re = 100$, the reaction front occurs in the end of the inlet channels. For $Re = 300$, the reaction front is extended to the first half of the reactor. If the inlet Re continues to increase to 600, the reaction front is present through the length, D , of the first row of chambers.

The highest maximum reaction rate is obtained at $Re = 600$ which is ca. 20% higher in comparison to $Re = 300$, which has the lowest value. The difference in the maximum rate between $Re = 100$ and $Re = 300$ is ca. 5%.

As shown in the previous section, the maximum temperature is attained on the sides of the reaction front, as visible in Figure V.23. For a lower inlet Reynolds, $Re = 100$, one hotspots is formed in each side of the chamber. For $Re = 300$ and $Re = 600$ three hotspots are formed, at the centre and on the sides of the chamber.

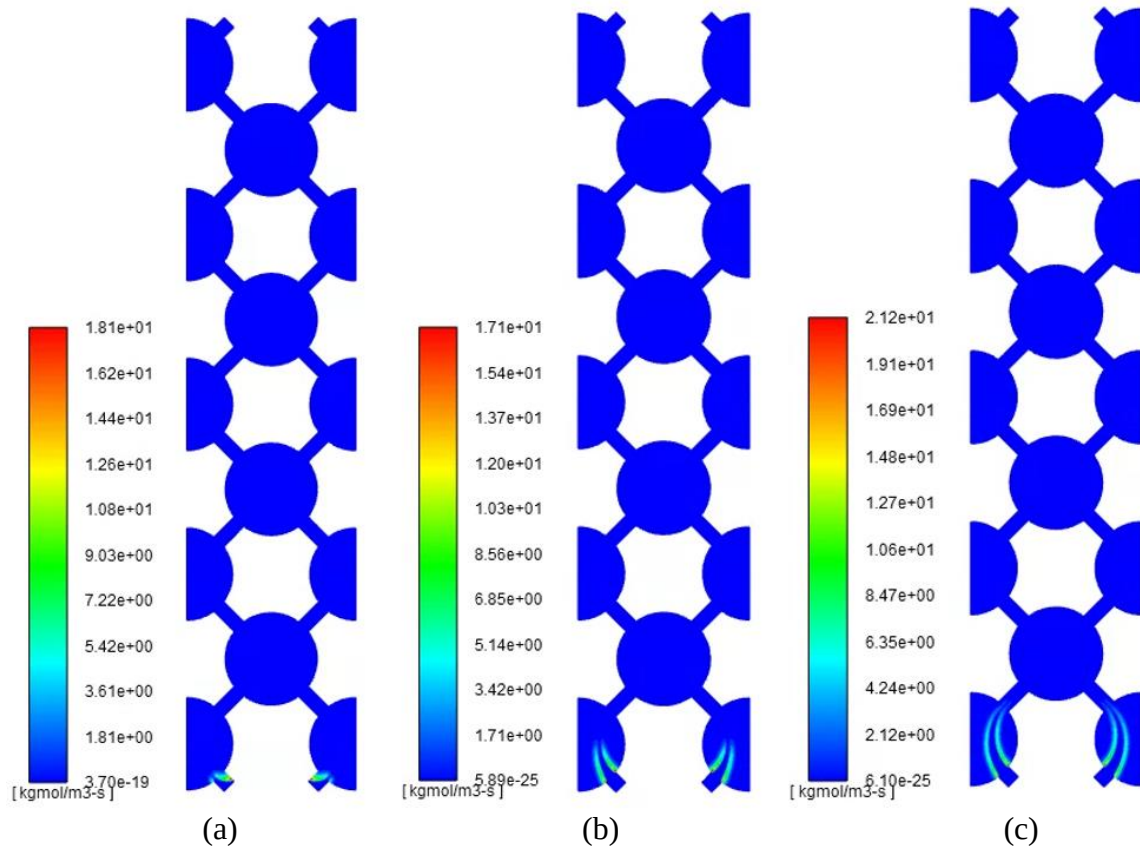


Figure V.22 Reaction rate maps of S7p at: (a) Re = 100, (b) Re = 300 and (c) Re = 600.

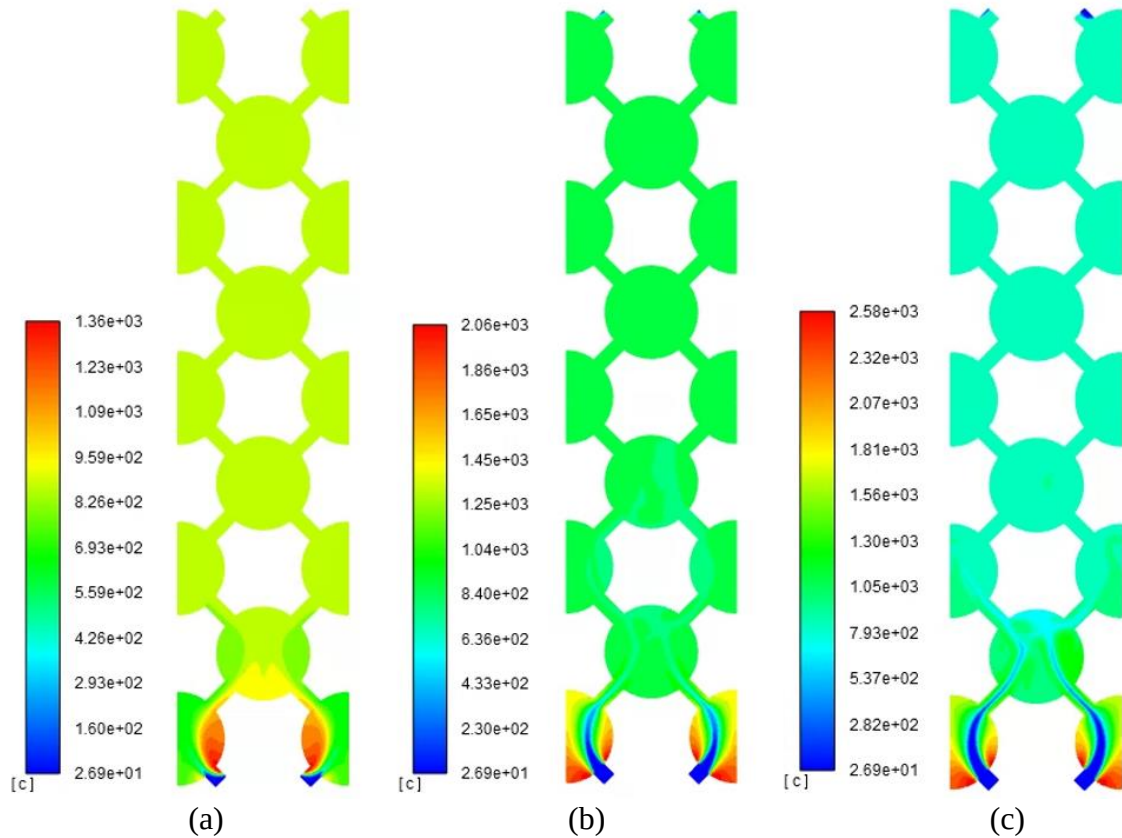


Figure V.23 Temperature maps of S7p at: (a) Re = 100, (b) Re = 300 and (c) Re = 600.

V.3.2.3 Premixed Combustion

From this section to the end of this work, the inlet Reynolds is set to 300. In order to set the inlet Reynolds number to $Re = 300$, the velocity of each inlet is calculated from Equation V.31, considering the properties of the mixture at the inlet temperature, 25 °C, listed in Table V.4.

The CFD model and kinetics were previously described. For the transient simulations in this Section, the species transport was computed using the Fickian diffusion. The transient calculations were performed with the First Order Implicit method. For the pressure-velocity coupling, the SIMPLEC method was used. The spatial discretization was performed with the Least Squares Cell Based algorithm for the gradient, PRESTO! for the pressure, Third-Order MUSCL for the momentum and Second Order Upwind for the energy and species. The convergence criterion for the maximum residuals of continuity and momentum is 10^{-5} , for the energy is 10^{-6} and for the species is 10^{-3} . To calculate the properties of the mixture, the incompressible-ideal-gas law was used for the density, ρ , and the mixing-law for the specific heat, c_p . The viscosity, thermal conductivity and mass diffusivity were constant (by default in ANSYS® FLUENT™), equal to $\mu = 1.72 \times 10^{-5}$ kg/(m s), $\lambda = 0.0454$ W/(m K) and $\mathcal{D} = 2.88 \times 10^{-5}$ m²/s, respectively.

In Table V.7, premixed cases of combustion which do not have an inert in the initial mixture are shown. As in the previous section, the cases are compared from the average molar fraction of each component at the outlet, $\overline{y_{out}}$, the maximum temperature, T_{max} , and the temperature in the centre of chamber C8, T_{C8} .

Table V.7 Premixed combustion without N₂ in ExtendedNUB, at $Re = 300$.

Premixed Combustion without N ₂								
	Species	$y_{in,left}$	$y_{in,right}$	$\overline{y_{out}}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{C8}(^{\circ}C)$
S1 $\theta = 2$ Da = 0.51 Ka = 1.98	H ₂	0.8	0.8	0.5	0.50	1	3090	3008
	O ₂	0.2	0.2	0				
	N ₂	0	0	0				
	H ₂ O	0	0	0.5				
S2 $\theta = 0.5$ Da = 3.75 Ka = 0.27	H ₂	0.5	0.5	0	6	0.50	3690	3584
	O ₂	0.5	0.5	0.33				
	N ₂	0	0	0				
	H ₂ O	0	0	0.67				
S3 $\theta = 0.125$ Da = 3.78 Ka = 0.27	H ₂	0.2	0.2	0	1	0.13	1630	1545
	O ₂	0.8	0.8	0.78				
	N ₂	0	0	0				
	H ₂ O	0	0	0.22				

S1 to S3 – premixed mixtures without N₂, simulated with constant properties

From *S1* to *S3*, the initial molar fraction of H_2 decreases. In *S1*, the initial quantity of H_2 is four times the quantity of O_2 , $\theta = 2$. Table V.7 shows that half of the products are H_2 since there is not enough oxygen to burn the fuel ($X_{H_2} = 0.50$, $X_{O_2} = 1$). In *S2*, the initial amount of hydrogen is the same as the initial amount of oxygen and θ is lower, $\theta = 0.5$. Since $X_{H_2} = 1$, there is enough oxygen to consume completely the fuel. The temperature of *S2* is then higher than *S1* since the fuel is consumed completely. In *S3*, $\theta = 0.125$, the amount of oxygen is too large in comparison to the amount of fuel. Since the oxygen is in excess, lean combustion occurs. In fact, the conversion of oxygen is small, $X_{O_2} = 0.13$, and all the fuel is consumed, $X_{H_2} = 1$. The production of H_2O is lower, as well as the temperature of combustion.

Comparing the results *S1* to *S3* it is possible to conclude that *S2* and *S3* are cases of lean combustion, i.e., the oxygen is in excess in comparison with the fuel. Even for lean combustion with a small θ , i.e., low quantity of fuel in relation to oxygen, the temperature reaches values larger than 1500 °C which is not desirable since the production of pollutants increases above 1000 °C.

In order to decrease the temperature, N_2 is going to be used to dilute the mixture H_2/O_2 . Table V.8 shows the reactive systems that were used. From *S4* to *S9*, the oxygen is in excess and lean combustion occurs.

In *S4*, the temperature is still higher than 1500 °C which indicates that the amount of N_2 is not enough to dilute the mixture. In *S5*, the amount of N_2 was doubled. However, since $\theta = 0.5$ is higher than in *S4* ($\theta = 0.2$), the decrease in the temperature is low, approximately 2%. In *S6*, the initial amount of fuel is lower, $\theta = 0.167$, which enables to decrease the temperature below 1000 °C. In *S7*, the amount of oxygen is lower, $\theta = 0.2$, and the temperature increases approximately 2%, as shown in Table V.8. In contrast, in *S8*, if the quantity of oxygen is increased, $\theta = 0.125$, the temperature decreases slightly, less than 1%. With an initial low amount of fuel and θ smaller than 0.1, $\theta = 0.071$, in *S9*, the temperature decreases to cold combustion values ($T < 585$ °C). Since the temperature is lower than the ignition of hydrogen, combustion without flame (or with cold flames) occurs by the oxidization of hydrogen.

In general, it is possible to conclude that the temperature of combustion decreases as the equivalence ratio, θ , decreases, i.e., the fuel in the reactive mixture is diluted by N_2 or O_2 .

Table V.8 Premixed combustion with N₂ in ExtendedNUB, at Re = 300.

Premixed Combustion with N ₂								
	Species	$y_{in,left}$	$y_{in,right}$	$\overline{y_{out}}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{c8}(^{\circ}C)$
S4 $\theta = 0.2$ Da = 3 Ka = 0.33	H ₂	0.2	0.2	0	1	0.20	1670	1549
	O ₂	0.5	0.5	0.44				
	N ₂	0.3	0.3	0.33				
	H ₂ O	0	0	0.22				
S5 $\theta = 0.5$ Da = 3.77 Ka = 0.27	H ₂	0.2	0.2	0	1	0.50	1630	1545
	O ₂	0.2	0.2	0.11				
	N ₂	0.6	0.6	0.67				
	H ₂ O	0	0	0.22				
S6 $\theta = 0.167$ Da = 1.74 Ka = 0.58	H ₂	0.1	0.1	0	1	0.17	897	832
	O ₂	0.3	0.3	0.26				
	N ₂	0.6	0.6	0.63				
	H ₂ O	0	0	0.11				
S7 $\theta = 0.25$ Da = 1.42 Ka = 0.70	H ₂	0.1	0.1	0	1	0.25	918	864
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
S8 $\theta = 0.125$ Da = 2 Ka = 0.50	H ₂	0.1	0.1	0	1	0.13	889	823
	O ₂	0.4	0.4	0.37				
	N ₂	0.5	0.5	0.53				
	H ₂ O	0	0	0.11				
S9 $\theta = 0.071$ Da = 1.36 Ka = 0.74	H ₂	0.05	0.05	0	1	0.071	503	482
	O ₂	0.35	0.35	0.33				
	N ₂	0.6	0.6	0.62				
	H ₂ O	0	0	0.051				

S4 to S9 – premixed mixtures with N₂, simulated with constant properties

In premixed combustion, since the reactants are already mixed, the reaction occurs close to the inlet channels. If no N₂ is used, the reaction front is in the beginning of the inlet channels, as shown in Figure V.25a. For S1, the maximum reaction rate, 559 kmol/(m³s), is the highest between the four cases (Figure V.24a). As θ decreases from 2 to 0.071 in cases S4 to S9, respectively, the reaction front occurs further in the reactor. In S4, the reaction occurs in the end of the inlet channels, attaining 227 kmol/(m³s) (Figure V.24b) which is approximately 41% lower than S1. In S7 and S9, the reaction occurs inside the first chamber, at the entrance of the chamber in S7 and in the first half of the chamber in S9. The maximum reaction rate continues to decrease to 23.4 kmol/(m³s) and 7.18 kmol/(m³s), respectively (Figure V.24c and Figure V.24bd). Comparing S9 to S1, the maximum reaction rate is two orders of magnitude lower.

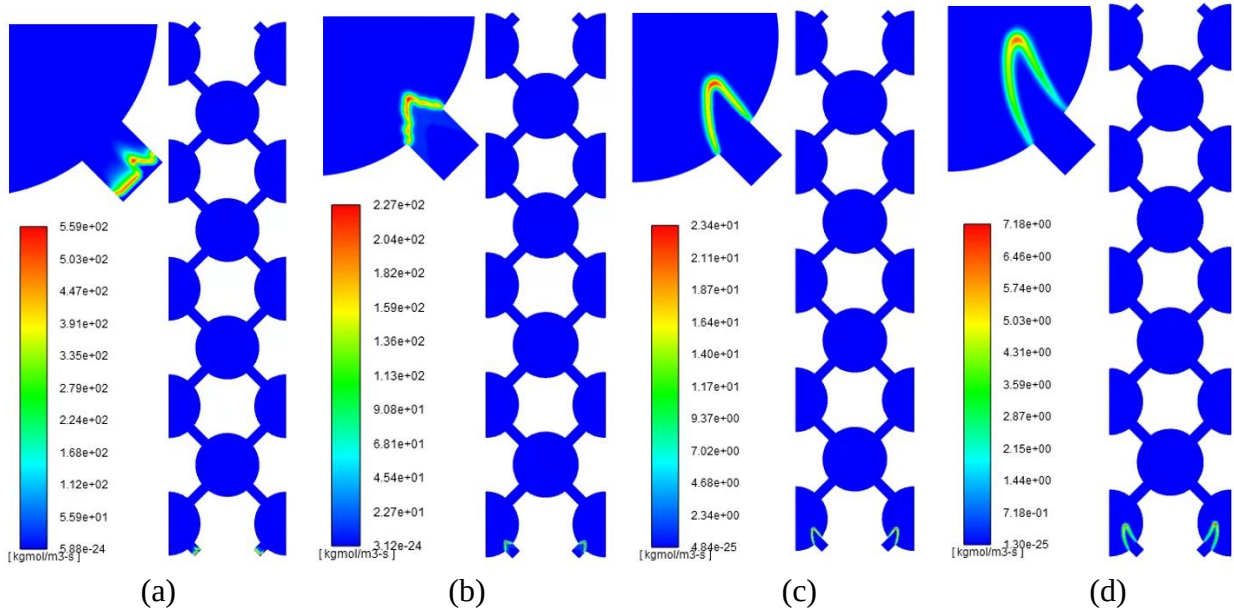


Figure V.24 Reaction rate maps of premixed combustion in ExtendedNUB of: (a) *S1*, (b) *S4*, (c) *S7* and (c) *S9*.

As shown in Figure V.25, in premixed combustion the temperature rises after the reaction front. Without N_2 , in *S1*, the maximum temperature is immediately attained and maintained in the entire reactor (less than 3% difference between T_{max} and T_{C8}), as shown in Figure V.25a. As the initial amount of fuel and θ decrease, the temperature reaches its maximum further in the reactor. In *S9*, Figure V.25d shows that the temperature starts to increase after the reaction front, but the maximum temperature is reached in chamber C4. From *S1* to *S9*, the maximum difference between T_{max} and T_{C8} is ca. 6% in *S4*.

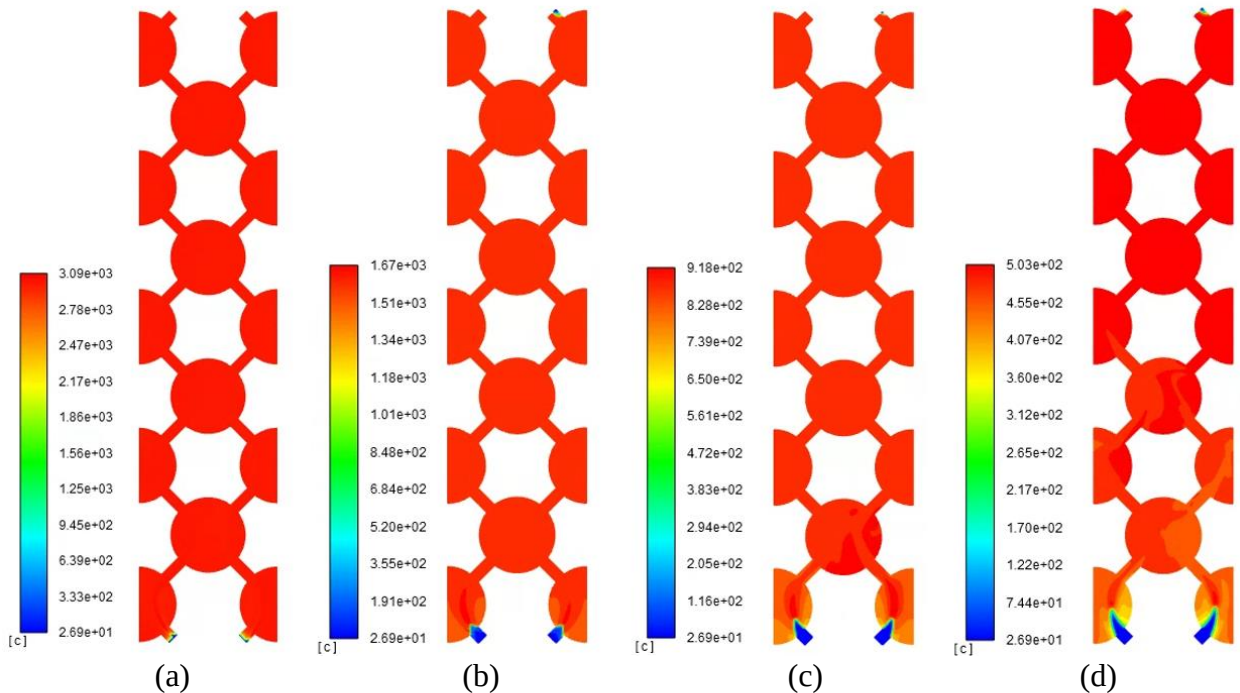


Figure V.25 Temperature maps of premixed combustion in ExtendedNUB of: (a) *S1*, (b) *S4*, (c) *S7* and (c) *S9*.

Gaseous Mixture Properties Effect

In the previous subsection the default conditions provided by ANSYS® FLUENT™ were used for the mixture properties. The viscosity, thermal conductivity and mass diffusivity were constant, $\mu = 1.72 \times 10^{-5}$ kg/(m s), $\lambda = 0.0454$ W/(m K) and $\mathcal{D} = 2.88 \times 10^{-5}$ m²/s, respectively. The density, ρ , and specific heat, c_p , were variable, computed from the incompressible-ideal-gas and mixing-law models, respectively. As stated in V.3.2.1., the properties of the gaseous mixture suffer changes as combustion occurs, exerting a major influence in the system. In this subsection, all the properties will be computed from models, which enables to consider the temperature influence in the properties. For that, the thermal conductivity and viscosity were computed from the ideal-gas-mixing-law, and the mass diffusivity from the kinetic-theory model (see Section V.3.1.2).

The effect of the properties will be analysed for premixed combustion with N₂. Two cases were chosen, case S4 which has the highest temperature, 1670 °C, and case S9 which has the lowest temperature, 503 °C (see Table V.8).

Table V.9 shows that if these cases are simulated with variable properties, S4p and S9p, the maximum temperatures are higher, 2440 °C and 1140 °C, respectively. In contrast, the temperatures at C8 are lower. In fact, considering the changes in all the properties, it is possible to predict hotspots in the reactor, as shown in Figure V.26. The maximum temperature is then attained in a small portion of the reactor and then decreases towards the outlet. In this way, the difference between T_{max} and T_{C8} is pronounced in comparison to the results of Table V.8.

As the temperature increases, the density decreases 88% for S4p and 59% for S9p in relation to the initial value (see Figure V.26c and Figure V.26d). In terms of viscosity, the temperature raise has a smaller effect, in fact the decrease is less than 5% and 2% in relation to the initial value for S4p and S9p, respectively (see Figure V.27a and Figure V.27b). The initial thermal conductivity is different for both cases, 4.25×10^{-2} W/(m K) for S4p and 2.85×10^{-2} W/(m K) for S9p. However, the values at C8 are close, 2.47×10^{-2} W/(m K) for S4p and 2.44×10^{-2} W/(m K) for S9p, showing that a reaction with higher temperatures causes a larger decrease of thermal conductivity (see Figure V.27c and Figure V.27d), 42% for S4p and 14% for S9p.

Differently from the previous properties which decrease as the temperature increases, i.e., the higher value of the property coincides with the inlet value which is at the lowest temperature of 25 °C, the heat capacity has a higher value for higher temperatures and then decreases towards the outlet, as shown in Figure V.28c and in Figure V.28d. The specific heat is higher for S4p which has higher temperatures. A similar behaviour occurs in the mass diffusion coefficients which have

a lower value at the inlets, increase at the hotspot, and then decrease towards the outlet. As an example, this effect is visible for the H_2 coefficient in Figure V.28a and in Figure V.28b. The difference between the initial and the maximum values of the coefficients for all compounds is at least one order of magnitude, two orders in some cases, as shown in Table V.9.

The variation of the properties as combustion occurs is also due to the formation of water which affects the mixture.

Table V.9 Mixture properties of $S4p$ and $S9p$.

Mixture Properties						
	$S4p$			$S9p$		
	Inlet average value	Maximum value	Value in C8	Inlet average value	Maximum value	Value in C8
$T(^{\circ}C)$	25	2440	1543	25	1140	465
$\rho(kg/m^3)$	1.00	1.00	0.12	1.15	1.15	0.47
$\mu(kg/(ms))$	1.81×10^{-5}	1.81×10^{-5}	1.72×10^{-5}	1.76×10^{-5}	1.76×10^{-5}	1.73×10^{-5}
$\lambda(W/(m K))$	4.25×10^{-2}	4.25×10^{-2}	2.47×10^{-2}	2.85×10^{-2}	2.85×10^{-2}	2.44×10^{-2}
$c_p(J/(Kg K))$	1150	1560	1417	1020	1270	1117
$\mathcal{D}_{H_2}(m^2/s)$	8.19×10^{-5}	3.31×10^{-3}	1.60×10^{-3}	8.05×10^{-5}	1.09×10^{-3}	3.74×10^{-4}
$\mathcal{D}_{O_2}(m^2/s)$	3.03×10^{-5}	9.80×10^{-4}	4.67×10^{-4}	2.23×10^{-5}	3.06×10^{-4}	1.03×10^{-4}
$\mathcal{D}_{H_2O}(m^2/s)$	2.78×10^{-5}	1.17×10^{-3}	5.59×10^{-4}	2.42×10^{-5}	3.90×10^{-4}	1.28×10^{-4}
$\mathcal{D}_{N_2}(m^2/s)$	2.70×10^{-5}	5.75×10^{-4}	4.57×10^{-4}	2.29×10^{-5}	3.13×10^{-4}	1.05×10^{-4}

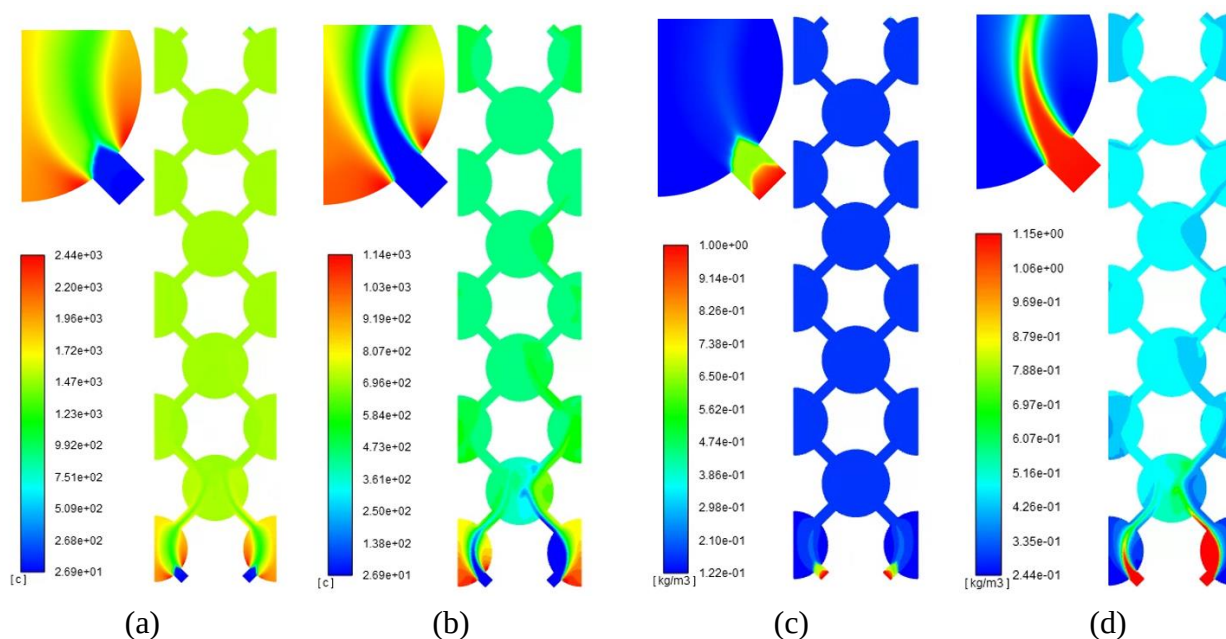


Figure V.26 Temperature map of: (a) $S4p$ and (b) $S9p$. Density map of: (c) $S4p$ and (d) $S9p$, at 1.1 s.

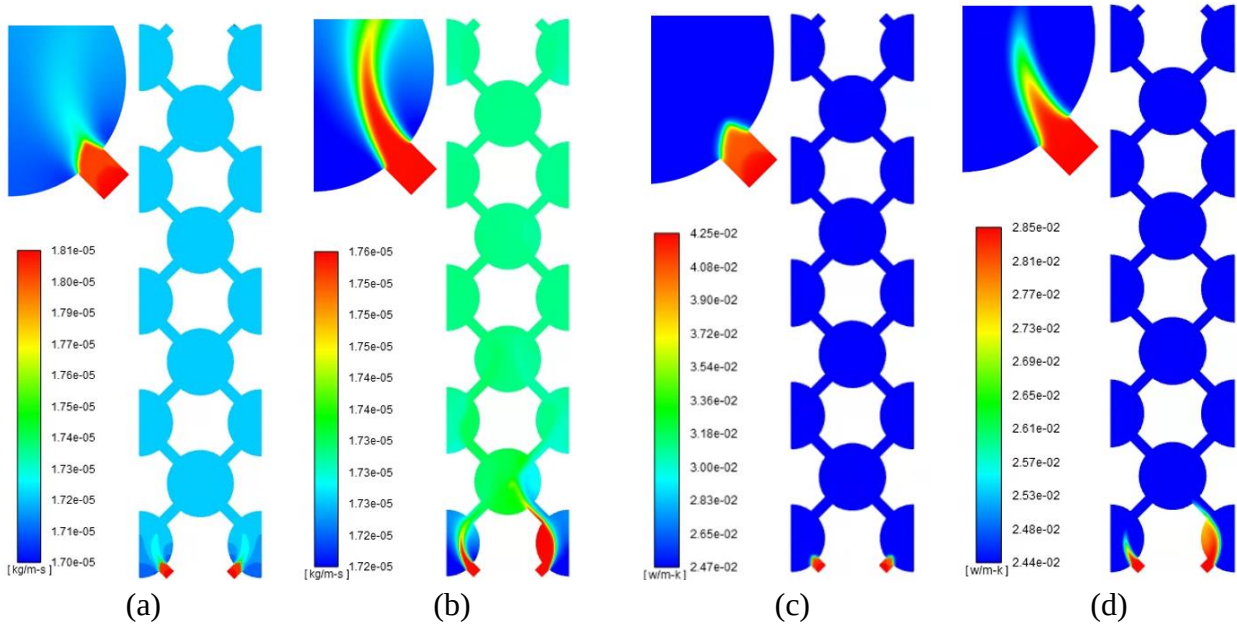


Figure V.27 Viscosity map of: (a) *S4p* and (b) *S9p*. Thermal conductivity map of: (c) *S4p* and (d) *S9p*, at 1.1 s.

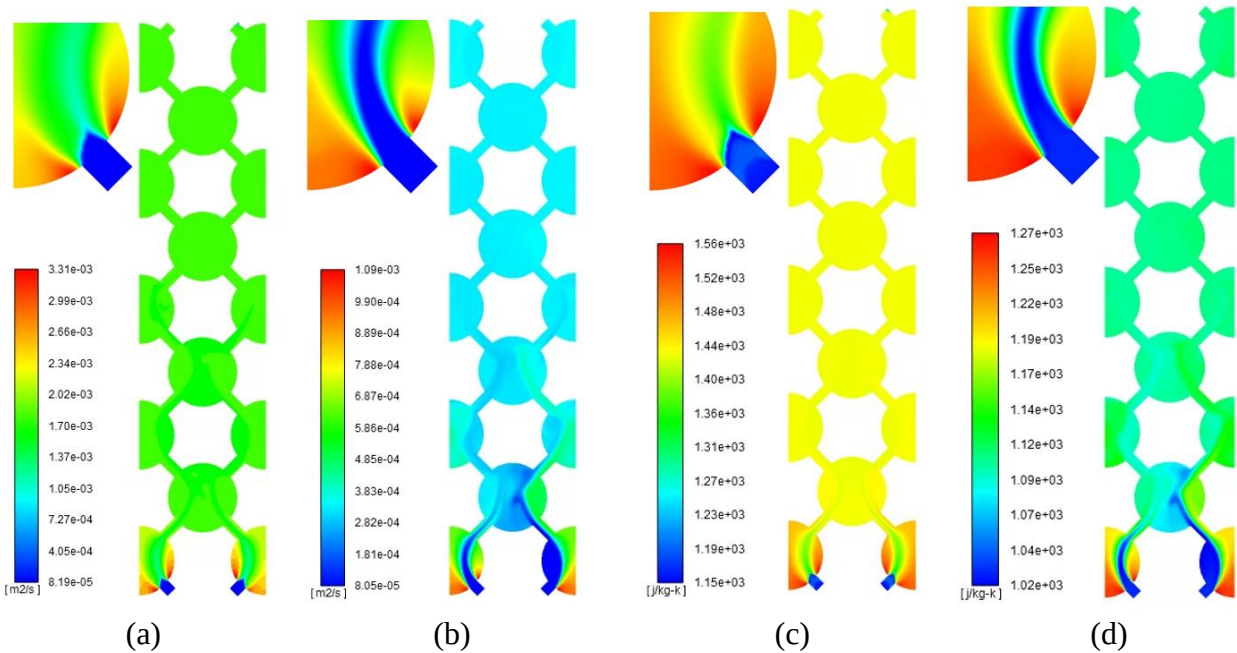


Figure V.28 H_2 laminar diffusion coefficient map of: (a) *S4p* and (b) *S9p*. Specific heat map of: (c) *S4p* and (d) *S9p*, at 1.1 s.

As previously shown, the temperature exerts a major influence in the mixture properties, which should be variable in order to obtain an accurate result of the simulation of combustion. The cases that were presented in the previous subsection, *S4* to *S9* were simulated with models to predict all the properties.

The results are shown in Table V.10 in which is visible that the relation between θ and T is maintained. In fact, with variable properties, the temperature of combustion decreases as the equivalence ratio, θ , decreases, i.e., the fuel in the reactive mixture is diluted by N_2 or O_2 .

From *S4p* to *S5p*, the amount of N_2 is doubled, however θ is more than the double (0.2 to 0.5), which explains a higher temperature at the hotspot, approximately 27%. The maximum temperature and the temperature at C8 are higher than 1500 °C. In *S6p*, the amount of fuel is lower, $\theta = 0.167$, and it is possible to decrease the maximum temperature more than 1000 °C in relation to *S5p*. The temperature at C8 is lower than 1000 °C. In *S7p*, if θ is increased by lowering the amount of O_2 , the maximum temperature increases ca. 4%. In contrast, if the initial amount of oxygen increases and θ decreases, in *S8p*, the maximum temperature decreases approximately 8% in relation to *S6p*. In *S9p*, a maximum temperature below 1500 °C is possible to achieve due to the low amount of fuel, $y_{H_2} = 0.05$, and $\theta < 0.1$, $\theta = 0.071$. In this case, the temperature at C8 is lower than 585 °C.

If models for the properties are used, the maximum temperatures are nearly 50% higher for most cases (except *S4p* which differs ca. 28% of *S4*), than the results that were previously reported in which several properties were constant. In Table V.8 was shown that only *S4* and *S5* had the maximum temperature above 1500 °C, and for the other cases the maximum temperature was below 1000 °C. In Table V.10 is visible that most cases have the maximum temperature above 2000 °C, including a case, *S5p*, with a maximum temperature above 3000 °C. *S9p* is the only case which has a maximum temperature below 1500 °C, which corresponds to *S9* which had a maximum temperature of 503 °C if several properties were constant. In terms of the temperature at C8, the difference between the two approaches is smaller with a maximum of ca. 2% difference. In most cases, T_{C8} is lower if laws are considered for all properties.

It is possible to conclude that if all properties are variable, the highest temperatures are localized in hotspots and the decrease of temperature inside the reactor is pronounced. In fact, the difference between T_{max} and T_{C8} (see Table V.10) is more than 50% for all cases (51%, 58%, 59%, 55% and 59%, respectively), except in *S4p*, in which the difference is ca. 37%.

Table V.10 Premixed combustion with N_2 and variable properties in ExtendedNUB, at $Re = 300$.

Premixed Combustion with N_2 (variable properties)								
	Species	$y_{in,left}$	$y_{in,right}$	$\overline{y_{out}}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{C8}(^{\circ}C)$
S4 $\theta = 0.2$ $Da = 3$ $Ka = 0.33$	H_2	0.2	0.2	0	1	0.20	2440	1543
	O_2	0.5	0.5	0.44				
	N_2	0.3	0.3	0.33				
	H_2O	0	0	0.22				
S5 $\theta = 0.5$ $Da = 3.77$ $Ka = 0.27$	H_2	0.2	0.2	0	1	0.50	3170	1561
	O_2	0.2	0.2	0.11				
	N_2	0.6	0.6	0.67				
	H_2O	0	0	0.22				

S6 $\theta = 0.167$ $Da = 1.74$ $Ka = 0.58$	H ₂	0.1	0.1	0	1	0.17	1980	823
	O ₂	0.3	0.3	0.26				
	N ₂	0.6	0.6	0.63				
	H ₂ O	0	0	0.11				
S7 $\theta = 0.25$ $Da = 1.42$ $Ka = 0.70$	H ₂	0.1	0.1	0	1	0.25	2060	843
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
S8 $\theta = 0.125$ $Da = 2$ $Ka = 0.50$	H ₂	0.1	0.1	0	1	0.13	1800	817
	O ₂	0.4	0.4	0.37				
	N ₂	0.5	0.5	0.53				
	H ₂ O	0	0	0.11				
S9 $\theta = 0.071$ $Da = 1.36$ $Ka = 0.74$	H ₂	0.05	0.05	0	1	0.07	1140	465
	O ₂	0.35	0.35	0.33				
	N ₂	0.6	0.6	0.62				
	H ₂ O	0	0	0.051				

S4p to S9p – premixed mixtures with N₂, simulated with variable properties

With several constant properties, it was shown, in Figure V.24, that the reaction front occurred in the end of the inlet channel for *S4* and in the beginning of the first chamber for *S7* and *S9*. If variable properties are used, the reaction front of *S4p* is in the end of the inlet channels. The reaction front of *S7p* is prolonged to half of the 1st row chambers. The reaction front of *S9p* is extended through the entire first chamber, as shown in Figure V.29. The maximum reaction rate is one order of magnitude higher for *S4p* in relation to *S7p* and *S9p*, in similarity to the previous results. The maximum reaction rates of *S4p* and *S7p* are approximately 48% and 30% lower than *S4* and *S7*, respectively. For *S9p*, the maximum reaction rate is ca. 34% higher than *S9*.

Although the front of the reaction is similar for both studies, with and without variable properties, the temperature raise is different. In Figure V.25, it was shown that the temperature raised immediately after the reaction front and was maintained nearly constant after the first chamber. If all the properties are variable, the maximum temperature occurs on the sides of the reaction front and then decreases towards the outlet of the reactor, as shown in Figure V.30.

In general, it is possible to conclude that the properties exert a major influence in the combustion process and should be considered. In further studies of this work, all the properties will be predicted by models.

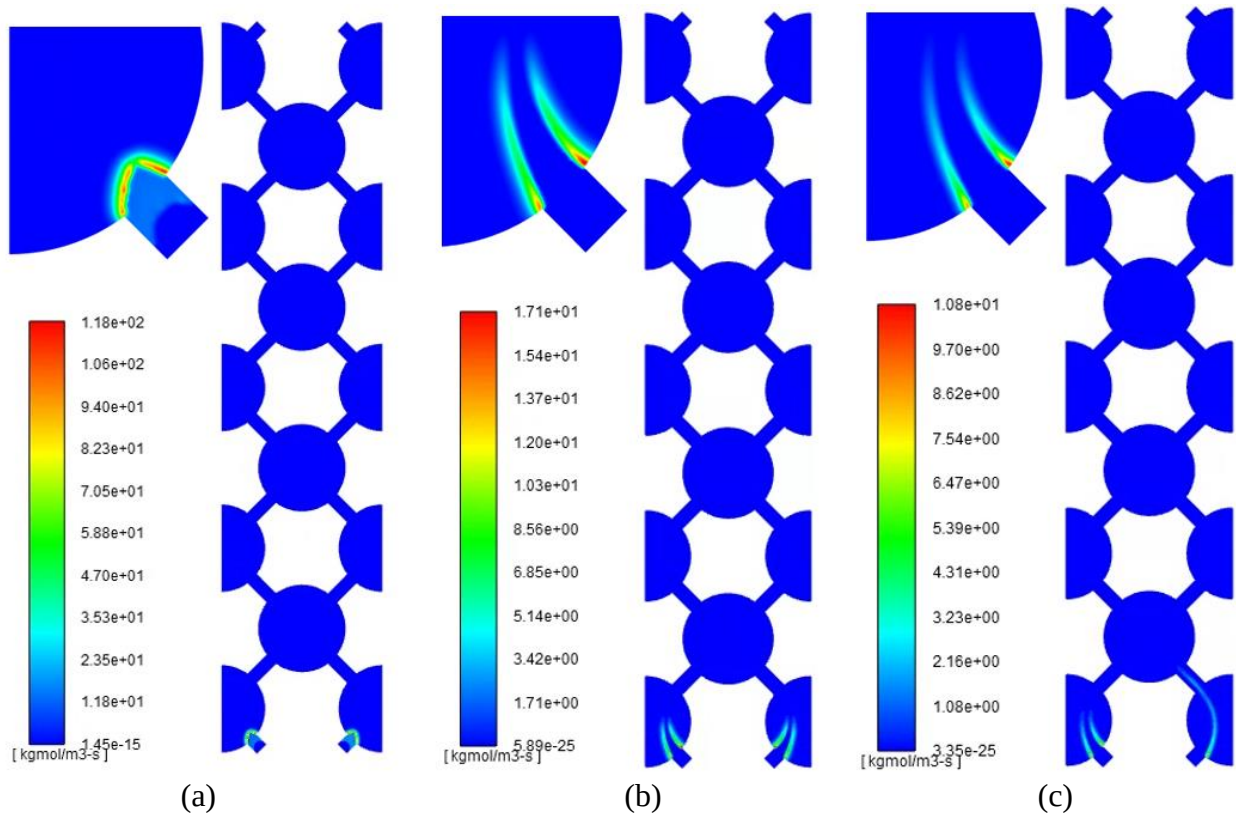


Figure V.29 Reaction rate maps of premixed combustion in ExtendedNUB of: (a) *S4p*, (b) *S7p* and (c) *S9p*, at 1.1 s.

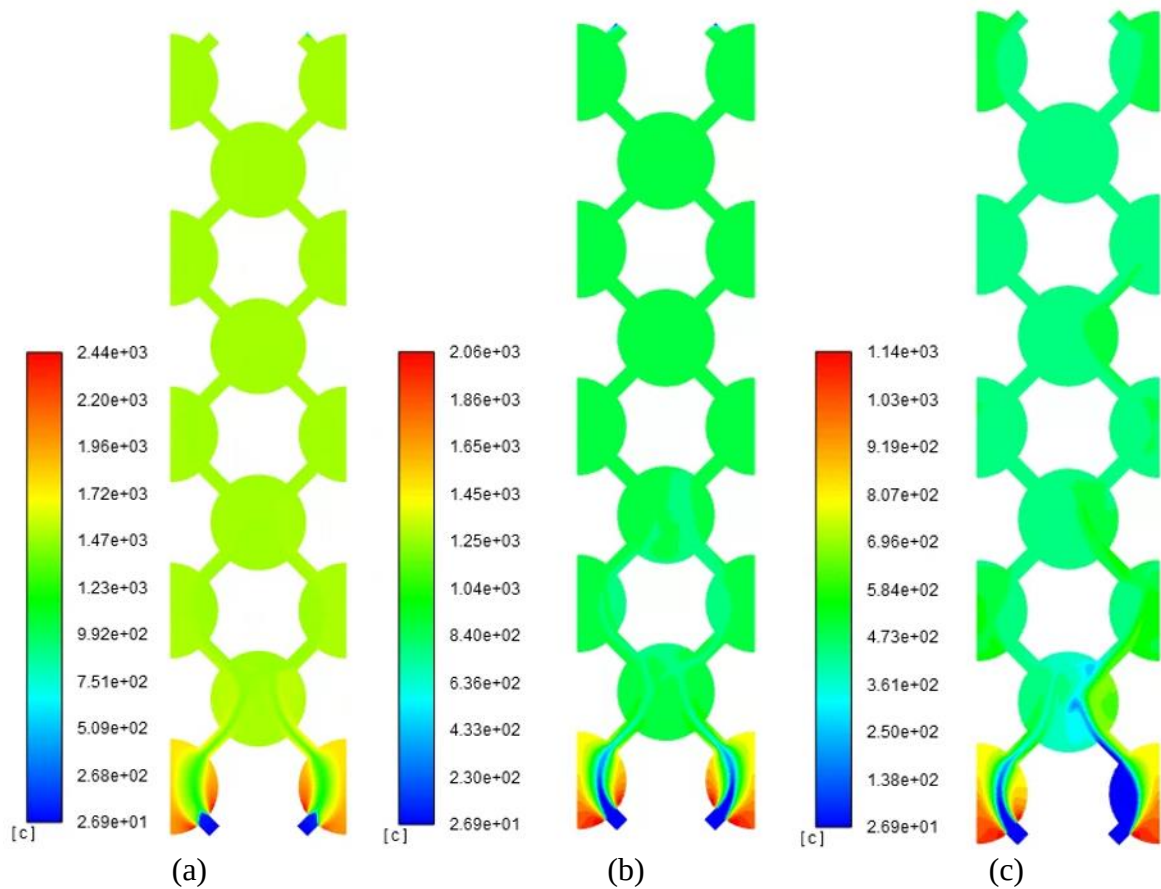


Figure V.30 Temperature maps of premixed combustion in ExtendedNUB of: (a) *S4p*, (b) *S7p* and (c) *S9p*, at 1.1 s.

V.3.2.4 Non-premixed Combustion

In this section, non-premixed combustion will be analysed. For that, the fuel/inert mixture was injected at the left outlet and air (20% oxygen, 80% nitrogen) was injected at the right.

Table V.11 lists the reactive mixtures that were simulated. In *S10p*, the fuel mixture is poor in fuel, $\theta = 0.27$, which is completely consumed, $X_{H_2} = 1$. Since the oxygen is in excess, lean combustion occurs. This is the premixed case with the lowest maximum temperature, as expected. In *S11p*, the amount of fuel is increased, $\theta = 2.14$, and all the oxygen is consumed. In this case, combustion is not lean and the maximum temperature approximately doubles in relation to *S10p*. If the amount of fuel continues to be increased in *S12p*, $\theta = 8.99$, the conversion of hydrogen is lower than in *S11p* since the amount of fuel is higher and exhausts the oxygen. However, the maximum temperature is the same as *S11p*.

Comparing with the premixed cases, the maximum temperatures are higher in non-premixed combustion. In fact, as the fuel stream is mixed with the oxygen stream, the heat production accumulates in the space and the reactor overheats. The difference of temperature between T_{max} and T_{C8} is larger. Thus, the decrease of temperature inside the reactor is more pronounced.

Table V.11 Non-premixed combustion in ExtendedNUB, at $Re = 300$.

Non-premixed Combustion								
	Species	$y_{in,left}$	$y_{in,right}$	$\overline{y_{out}}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{C8}(^{\circ}C)$
S10p $\theta = 0.27$ $Da = 0.73$ $Ka = 1.38$	H ₂	0.1	0	0	1	0.26	2380	563
	O ₂	0	0.2	0.075				
	N ₂	0.9	0.8	0.87				
	H ₂ O	0	0	0.053				
S11p $\theta = 2.14$ $Da = 1.38$ $Ka = 0.73$	H ₂	0.5	0	0.14	0.57	1	4730	1349
	O ₂	0	0.2	0				
	N ₂	0.5	0.8	0.68				
	H ₂ O	0	0	0.18				
S12p $\theta = 8.99$ $Da = 1.02$ $Ka = 0.98$	H ₂	0.9	0	0.63	0.13	1	4730	775
	O ₂	0	0.2	0				
	N ₂	0.1	0.8	0.27				
	H ₂ O	0	0	0.095				

S10p to *S12p* – non-premixed mixtures with N₂, simulated with variable properties

As shown in Figure V.32.a, in *S10p*, the reaction front is in the 3rd line of chambers since the mixture is poor in fuel. For higher θ , in *S11p*, the reaction front is extended to four lines of chambers, attaining the maximum reaction rate at the oxygen side (Figure V.31b). For larger $\theta = 8.99$, in *S12p*, the oxygen is exhausted faster, and the reaction is only extended to the first two

rows of chambers, as visible in Figure V.31c. The maximum reaction rate increases as the amount of fuel in the reactive mixture increases. Between $S10p$ and $S12p$, the maximum reaction rate nearly triples, as shown in Figure V.31.

As previously stated for premixed cases, hotspots tend to be formed on the sides of the reaction front. In non-premixed combustion a similar behaviour is observed, as visible in Figure V.32. With a lower amount of fuel ($S10p$), only one hotspot is formed (Figure V.32a). In $S11p$, θ is higher as well as the conversions of fuel and oxygen, and two hotspots are formed, as visible in Figure V.32b. If θ is increased, in $S12p$, the oxygen is consumed faster and only one hotspot is formed in the first chamber as shown in Figure V.32c.

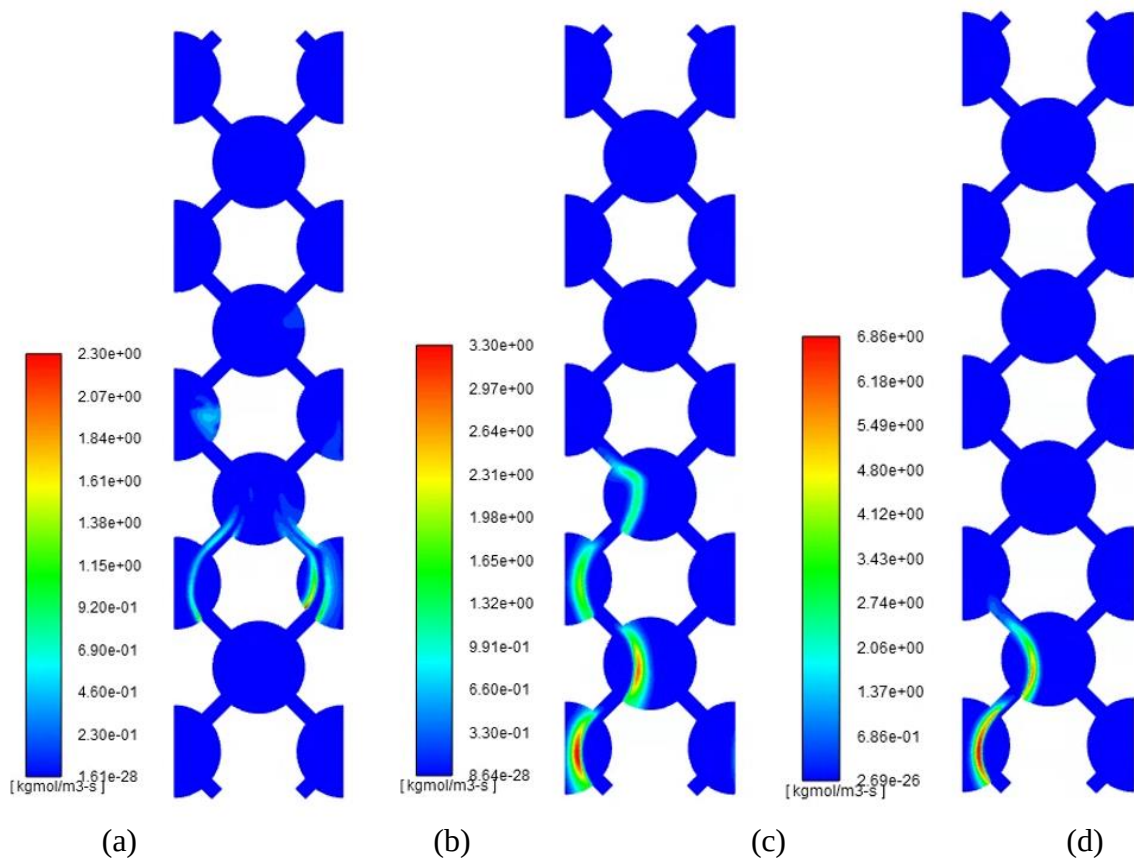


Figure V.31 Reaction rate of non-premixed combustion in ExtendedNUB of: (a) $S10p$, (b) $S11p$ and (c) $S12p$, at 1.1s.

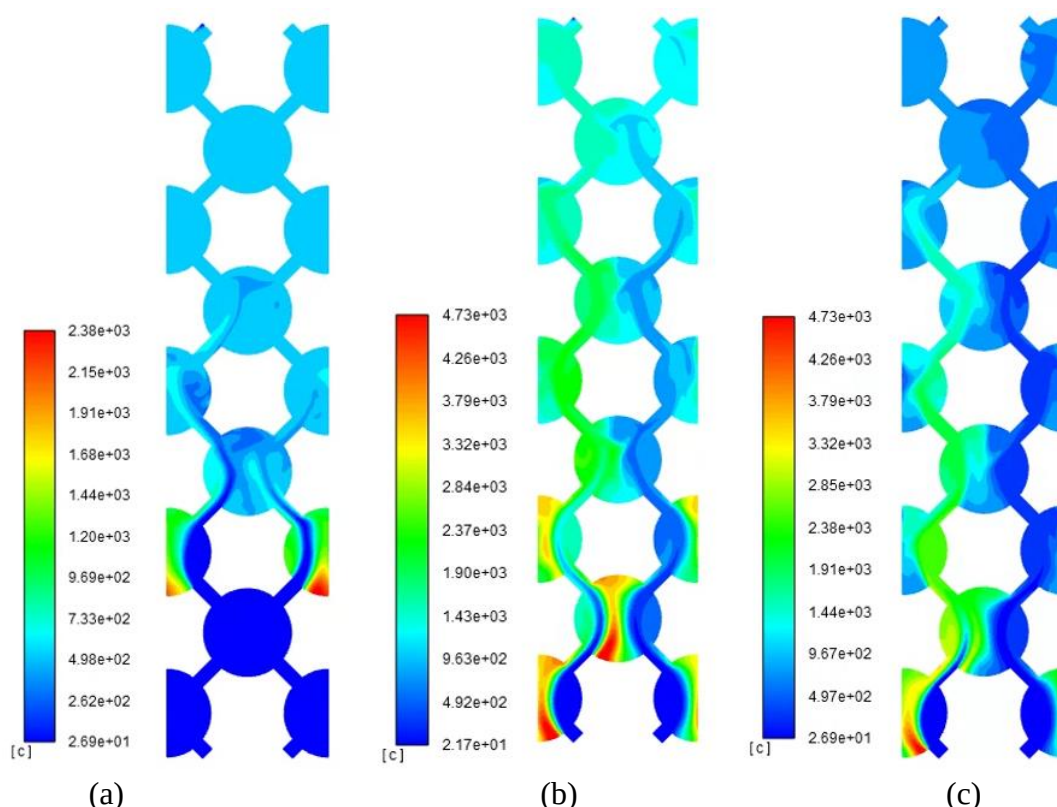


Figure V.32 Temperature maps of non-premixed combustion in ExtendedNUB of: (a) *S10p*, (b) *S11p* and (c) *S12p*, at 1.1s.

V.3.2.5 Diffusion and Thickened Flame Models

In the previous sections, the Fickian diffusion was used to simulate the species transport in the CFD model. In this section, the Fickian diffusion will be compared with the full multicomponent diffusion and with the thickened flame model (see Section V.3.1.1). To perform this comparison, premixed cases, *S1p*, *S7p*, *S9p*, and non-premixed cases, *S10p*, *S11p* and *S12p*, are shown in Table V.12.

For premixed combustion, the prediction of the maximum temperature by the three models differs less than 2%, as well as the prediction of the temperature at C8, except for *F3* which differs ca. 7% from *S9p*. In non-premixed combustion, the difference in the prediction of the maximum temperature between the models is less than 2%. However, for *S10p* and *S12p*, one of the models presents a larger difference from the others: *F4* differs ca. 31% from *M4* and *S10p*; and *S12p* differs ca. 23% from *M6* and *F6*. The difference in the prediction of T_{C8} is less than 4% between the three models, except between *F4* and *S10p* which differ ca. 15%. The temperature and reaction rate maps of the simulations with the multicomponent and thickened flame models are similar to the maps that were previously presented for the Fick model (see Appendix C).

In general, it is possible to conclude that the three models have a similar temperature prediction.

For the next sections of this work, the maxwell model will be applied since its predictions agree to at least one of the other models for all premixed and non-premixed cases that were presented.

Table V.12 Comparison between Fick, Maxwell and Thickened Flame models.

Models Comparison – Premixed Combustion								
	Species	$y_{in,left}$	$y_{in,right}$	$\bar{y}_{out}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{C8}(^{\circ}C)$
M1 (Maxwell) $\theta = 2$	H ₂	0.8	0.8	0.50	0.50	1	3230	3016
	O ₂	0.2	0.2	0				
	N ₂	0	0	0				
	H ₂ O	0	0	0.5				
F1 (Flame) $\theta = 2$	H ₂	0.8	0.8	0.50	0.50	1	3230	3027
	O ₂	0.2	0.2	0				
	N ₂	0	0	0				
	H ₂ O	0	0	0.50				
S1p (Fick) $\theta = 2$	H ₂	0.8	0.8	0.5	0.50	1	3260	3016
	O ₂	0.2	0.2	0				
	N ₂	0	0	0				
	H ₂ O	0	0	0.5				
M2 (Maxwell) $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	2030	851
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
F2 (Flame) $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	2020	867
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
S7p (Fick) $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	2060	843
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
M3 (Maxwell) $\theta = 0.071$	H ₂	0.05	0.05	0	1	0.070	1150	471
	O ₂	0.35	0.35	0.33				
	N ₂	0.6	0.6	0.62				
	H ₂ O	0	0	0.051				
F3 (Flame) $\theta = 0.071$	H ₂	0.05	0.05	0	1	0.070	1150	519
	O ₂	0.35	0.35	0.33				
	N ₂	0.6	0.6	0.62				
	H ₂ O	0	0	0.051				
S9p (Fick) $\theta = 0.071$	H ₂	0.05	0.05	0	1	0.070	1140	465
	O ₂	0.35	0.35	0.33				
	N ₂	0.6	0.6	0.62				
	H ₂ O	0	0	0.051				

Models Comparison – Non-premixed Combustion								
M4 (Maxwell) $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	2320	550
	O ₂	0	0.2	0.066				
	N ₂	0.9	0.8	0.87				
	H ₂ O	0	0	0.064				
F4 (Flame) $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	3480	434
	O ₂	0	0.2	0.070				
	N ₂	0.9	0.8	0.88				
	H ₂ O	0	0	0.053				
S10p (Fick) $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	2380	563
	O ₂	0	0.2	0.066				
	N ₂	0.9	0.8	0.87				
	H ₂ O	0	0	0.064				
M5 (Maxwell) $\theta = 2.14$	H ₂	0.5	0	0.14	0.57	1	4730	1341
	O ₂	0	0.2	0				
	N ₂	0.5	0.8	0.68				
	H ₂ O	0	0	0.18				
F5 (Flame) $\theta = 2.14$	H ₂	0.5	0	0.14	0.57	1	4730	1324
	O ₂	0	0.2	0				
	N ₂	0.5	0.8	0.68				
	H ₂ O	0	0	0.18				
S11p (Fick) $\theta = 2.14$	H ₂	0.5	0	0.14	0.57	1	4730	1349
	O ₂	0	0.2	0				
	N ₂	0.5	0.8	0.68				
	H ₂ O	0	0	0.18				
M6 (Maxwell) $\theta = 8.99$	H ₂	0.9	0	0.63	0.13	1	3610	802
	O ₂	0	0.2	0				
	N ₂	0.1	0.8	0.27				
	H ₂ O	0	0	0.095				
F6 (Flame) $\theta = 8.99$	H ₂	0.9	0	0.63	0.13	1	3580	818
	O ₂	0	0.2	0				
	N ₂	0.1	0.8	0.27				
	H ₂ O	0	0	0.095				
S12p (Fick) $\theta = 8.99$	H ₂	0.9	0	0.63	0.13	1	4730	775
	O ₂	0	0.2	0				
	N ₂	0.1	0.8	0.27				
	H ₂ O	0	0	0.095				

M1 to M6 – Mixtures simulated with Maxwell and variable properties

F1 to F6 – Mixtures simulated with Flame Thickened Model and variable properties

S1p to S10p – Mixtures simulated with Fick and variable properties

Flame Speed UDF

In the previous section, the Thickened Flame Model was applied considering 0.2 m/s for the Laminar Flame Speed (default value provided by the software ANSYS® FLUENT™). In this section, a User Defined Function (UDF) was developed to predict the laminar flame speed.

The H₂-O₂ flame speed, $\mathcal{U}_F$, can be related with the equivalence ratio, θ (starting at 298 K and 1 atm), according to Figure V.33 (Lee, J.H.S., 2006).

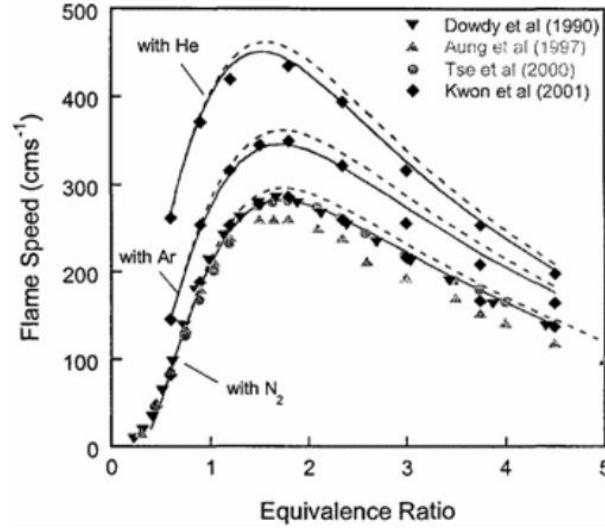


Figure V.33 Evolution of the flame speed with the equivalence ratio (from Lee, J.H.S. 2006).

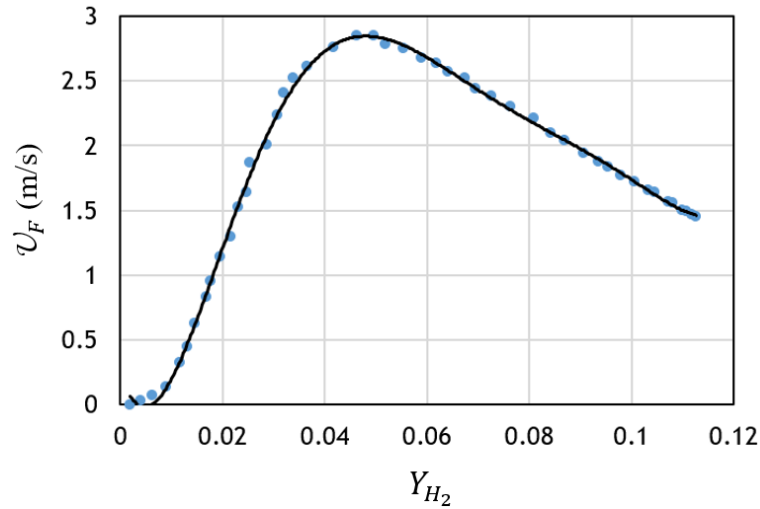
The relation between the equivalence ratio, θ , and the unburnt H₂ mass fraction, Y_{H_2} , is given by

$$\theta = \frac{Y_{H_2}}{1 - Y_{H_2}} \frac{1 - Y_{H_2,st}}{Y_{H_2,st}} \quad (V.62)$$

in which $Y_{H_2,st} = 0.02818$ is the stoichiometric value for the H₂ combustion in air (Göttgens, J. et al., 1992).

Data points with coordinates $(\theta, \mathcal{U}_F)$ were extracted from the N₂ curve of Figure V.33 and transformed into $(Y_{H_2}, \mathcal{U}_F)$, through Equation V.56. A polynomial fitting was then applied to the new data points, and a curve Y_{H_2} vs $\mathcal{U}_F$ ($R^2 = 0.998$) was obtained. The evolution of $\mathcal{U}_F$ with Y_{H_2} is shown in Figure V.34, where the data points are represented in blue and the fitting in black. The expression that relates $\mathcal{U}_F$ with Y_{H_2} is given by

$$\begin{aligned} \mathcal{U}_F = & 93921460Y_{H_2}^6 - 38372450Y_{H_2}^5 + 6080096Y_{H_2}^4 \\ & - 457737.4Y_{H_2}^3 + 15269.28Y_{H_2}^2 - 116.6239Y_{H_2} + 0.2387034 \end{aligned} \quad (V.63)$$

Figure V.34 Evolution of U_F with Y_{H_2} .

The cases that were presented in the previous section with the thickened flame model, *F2* and *F4*, were simulated using the UDF. The comparison of the results, with or without UDF, is shown in Table V.13. The difference in the prediction of the maximum temperature is less than 1% and the difference in the prediction of T_{c8} is less than 6%. The temperature and reaction rate maps of *F2* and *F4* are similar, with or without UDF (see Figure V.29 and Figure V.30 and Appendix C).

Table V.13 Flame speed UDF influence.

Flame Speed UDF Influence								
	Species	$y_{in,left}$	$y_{in,right}$	$\bar{y}_{out}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{c8}(^{\circ}C)$
<i>F2u (Flame UDF)</i> $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	2000	826
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
<i>F2 (Flame)</i> $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	2020	867
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
<i>F4u (Flame UDF)</i> $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	3450	475
	O ₂	0	0.2	0.070				
	N ₂	0.9	0.8	0.88				
	H ₂ O	0	0	0.053				
<i>F4 (Flame)</i> $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	3480	434
	O ₂	0	0.2	0.070				
	N ₂	0.9	0.8	0.88				
	H ₂ O	0	0	0.053				

F2u to *F4u* – Mixtures simulated with Thickened Model, using UDF for the flame speed

F2 to *F4* – Mixtures simulated with Thickened Model, using constant flame speed

The evolution of the flame speed is shown in Figure V.35a and in Figure V.35b. It is visible that, for all cases, the maximum flame speed is 2.39×10^{-1} m/s which corresponds to a hydrogen mass fraction of ca. 8.00×10^{-3} , as shown in Figure V.35c and in Figure V.35d. As the fuel is consumed and its fraction in the mixture decreases, the flame speed increases. The overall aspect of the flame speed maps is similar to the reaction rate maps.

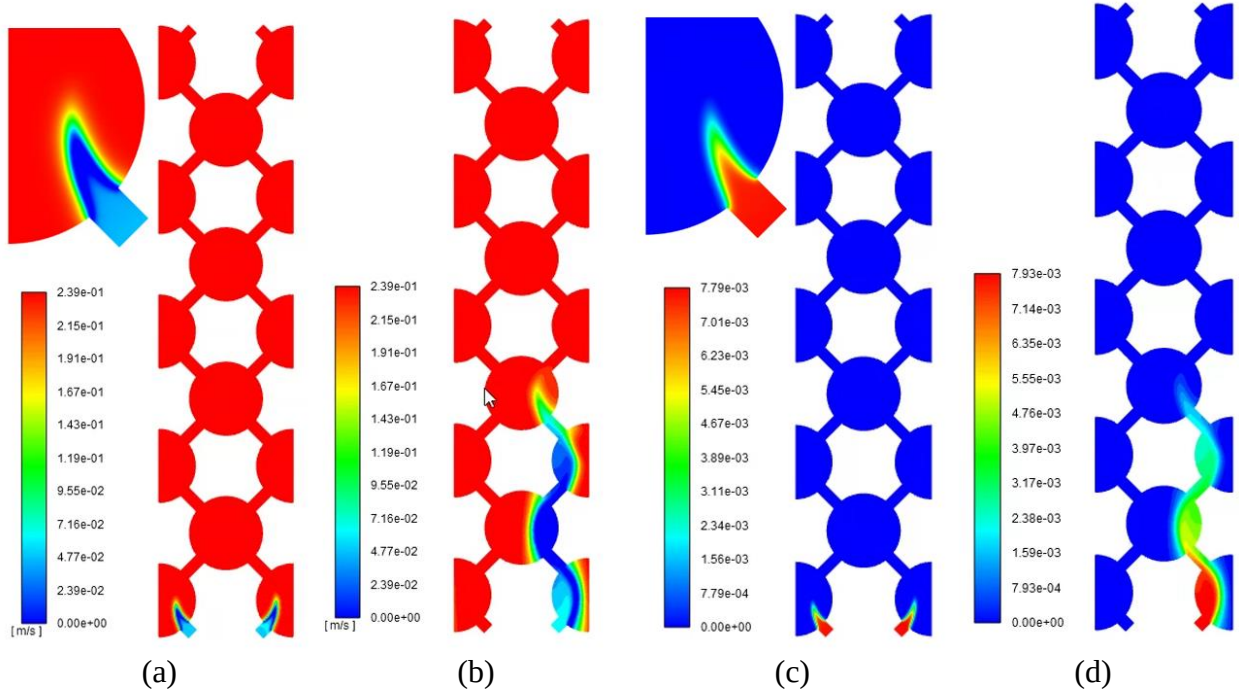


Figure V.35 Flame speed of: (a) F2u and (b) F4u. H₂ mass fraction of: (c) F2u and (d) F4u.

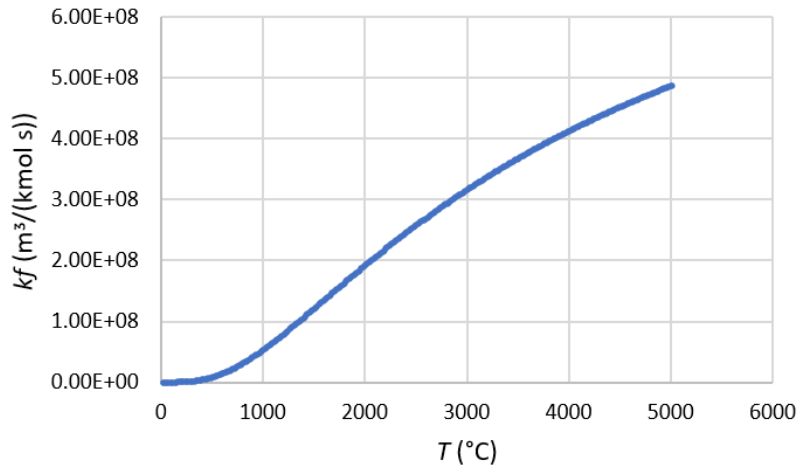
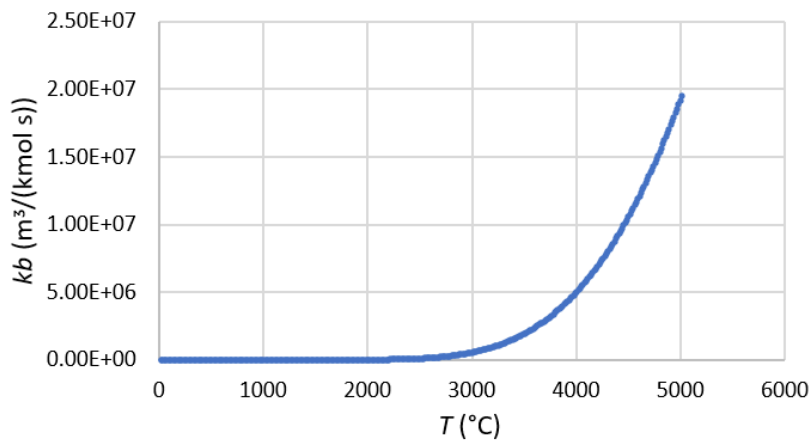
V.3.2.6 Backward Reaction Influence

In this section, the global reaction of the hydrogen combustion will be used, considering the backward rate. For that, kb was calculated in function of kf , according to $kf =$

$$kb \left(\frac{p}{RT} \right)^d e^{\frac{-\Delta H_f^\circ + T \Delta S_f^\circ}{RT}} \quad (\text{Equation V.4b}).$$

The plot of $kf = \mathcal{A} T^b e^{\frac{-E_a}{RT}}$ ($\mathcal{A} = 9.87 \times 10^8$ m³/(kmols), $b = 0$ and $E_a = 3.10 \times 10^7$ J/kmol) is shown in Figure V.36. The graphic shows a concave curve with $kf = 5.34 \times 10^7$ m³/(kmols) at 1000 °C.

In contrast, the plot of kb has a convex curve, as visible in Figure V.37. It is also noticeable that kb has low values for a larger range of temperature. In fact, at 1000 °C, $kb = 0.14$ m³/(kmols). The same order of magnitude of kf , 10^7 , is only attained for temperatures higher than 4000 °C. Since kb is always smaller than kf , the forward rate has a larger influence in the combustion process.

Figure V.36 k_f evolution from 25 °C to 5000 °C.Figure V.37 k_b evolution from 25 °C to 5000 °C.

The initial reactive mixtures that were previously presented will be simulated with the Multicomponent Diffusion Model and with the reverse rate (k_f and k_b), cases *B1* to *B12*, which correspond to the previous cases, *S1* to *S12*. For comparison purposes, three premixed cases, *B1*, *B7* and *B9* will be compared with the corresponding reactive mixture, simulated without k_b and with Multicomponent Diffusion, *M1*, *M2* and *M3*, respectively. A similar analysis will be done to three non-premixed cases, *B10*, *B11* and *B12* which will be compared with *M4*, *M5* and *M6* (see Appendix C).

The results are shown in Table V.14 where is visible that the maximum temperature is lower if the reverse reaction is considered.

For premixed combustion, as the amount of fuel in the reactive mixture decreases from *M1* to *M3*, the prediction of the temperature with the reverse reaction becomes closer to the result without the reverse rate. In fact, for lower temperatures, k_b has a low value as previously shown, and its influence is less visible.

The difference in the maximum temperature between *B1* and *M1* is ca. 27%. In *B7*, the difference to *M2* decreases to approximately 11% and *B9* has the same prediction as *M3*.

In the first case, *B1*, the temperature at C8 is ca. 22% lower than *M1*. In *B7* and *B9*, the prediction of the temperature at C8 has less than 1% difference when compared to *M2* and *M3*, respectively.

In the first case, *B1*, which has a larger amount of fuel, if the reverse reaction is considered, the conversion of fuel is not total, which explains the larger difference of temperature between *B1* and *M1*. In the other premixed cases, the influence of the reverse rate is not enough to prevent complete consumption of one of the reactants. The difference of temperature for those cases is then less pronounced. For non-premixed combustion, the prediction of the maximum temperature considering the reverse reaction is lower, having a difference of ca. 25%, 53% and 40% between *B10*, *B11*, *B12*, and *M4*, *M5*, *M6*, respectively.

The temperatures at C8 are closer for both approaches, having a maximum difference of approximately 12% between *B11* and *M5* and less than 1% difference for the other two cases. It is also visible that the decrease of temperature between T_{max} and T_{C8} is smaller if the reverse reaction is considered.

Table V.14 Hydrogen combustion with and without reverse reaction.

Premixed Combustion								
	Species	$y_{in,left}$	$y_{in,right}$	$\overline{y_{out}}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{C8}(^{\circ}C)$
B1 $\theta = 2$	H ₂	0.8	0.8	0.59	0.37	0.75	2300	2277
	O ₂	0.2	0.2	0.059				
	N ₂	0	0	0				
	H ₂ O	0	0	0.35				
M1 $\theta = 2$	H ₂	0.8	0.8	0.50	0.50	1	3230	3016
	O ₂	0.2	0.2	0				
	N ₂	0	0	0				
	H ₂ O	0	0	0.5				
B7 $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	1760	851
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
M2 $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	2030	851
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
B9 $\theta = 0.071$	H ₂	0.05	0.05	0	1	0.07	1150	473
	O ₂	0.35	0.35	0.33				
	N ₂	0.6	0.6	0.62				
	H ₂ O	0	0	0.051				

M3 $\theta = 0.071$	H ₂	0.05	0.05	0	1	0.070	1150	471
	O ₂	0.35	0.35	0.33				
	N ₂	0.6	0.6	0.62				
	H ₂ O	0	0	0.051				
Non-premixed Combustion								
B10 $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	1670	560
	O ₂	0	0.2	0.071				
	N ₂	0.9	0.8	0.86				
	H ₂ O	0	0	0.066				
M4 $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	2320	550
	O ₂	0	0.2	0.066				
	N ₂	0.9	0.8	0.87				
	H ₂ O	0	0	0.064				
B11 $\theta = 2.14$	H ₂	0.5	0	0.13	0.57	1	2070	1536
	O ₂	0	0.2	0				
	N ₂	0.5	0.8	0.68				
	H ₂ O	0	0	0.19				
M5 $\theta = 2.14$	H ₂	0.5	0	0.14	0.57	1	4730	1341
	O ₂	0	0.2	0				
	N ₂	0.5	0.8	0.68				
	H ₂ O	0	0	0.18				
B12 $\theta = 8.99$	H ₂	0.9	0	0.63	0.13	1	2040	805
	O ₂	0	0.2	0				
	N ₂	0.1	0.8	0.27				
	H ₂ O	0	0	0.095				
M6 $\theta = 8.99$	H ₂	0.9	0	0.63	0.13	1	3610	802
	O ₂	0	0.2	0				
	N ₂	0.1	0.8	0.27				
	H ₂ O	0	0	0.095				

B1 to *B12* – Mixtures simulated with Maxwell, including the reverse rate

M1 to *M6* – Mixtures simulated with Maxwell, only with the forward rate

Although the maximum temperature of *B1* is considerably lower than *M1*, the reaction rate and the temperature maps have a similar behaviour. As shown in Figure V.38, the reaction front is in the inlet channels, and the temperature rises after the reaction front. Since the reverse reaction is considered, negative values of reaction rate are visible in the reaction rate map of Figure V.38b. However, the reaction rate is close to zero in most of the reactor, as in *M1* without the reverse rate. The maximum reaction rate of *B1* is ca. 4% higher than *M1*.

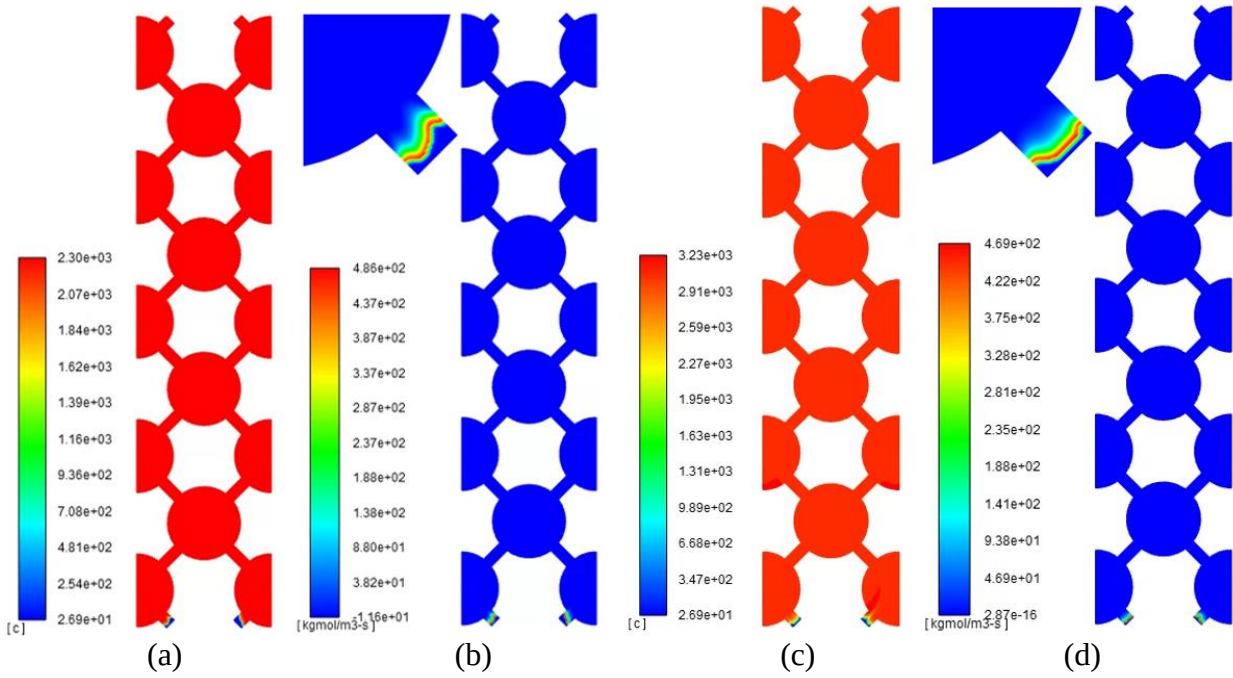


Figure V.38 *B1* maps of: (a) temperature and (b) reaction rate. *M1* maps of: (c) temperature and (d) reaction rate.

Comparing *B7* to *M2*, a similar pattern of the temperature and reaction rate maps is observed in Figure V.39. It is possible to notice that the hotspot is larger if the reverse reaction is considered. While in *M2* the hotspot is localized at the bottom of the first chamber, in *B7* the hotspot is extended to every zone of the first chamber around the inlet jets.

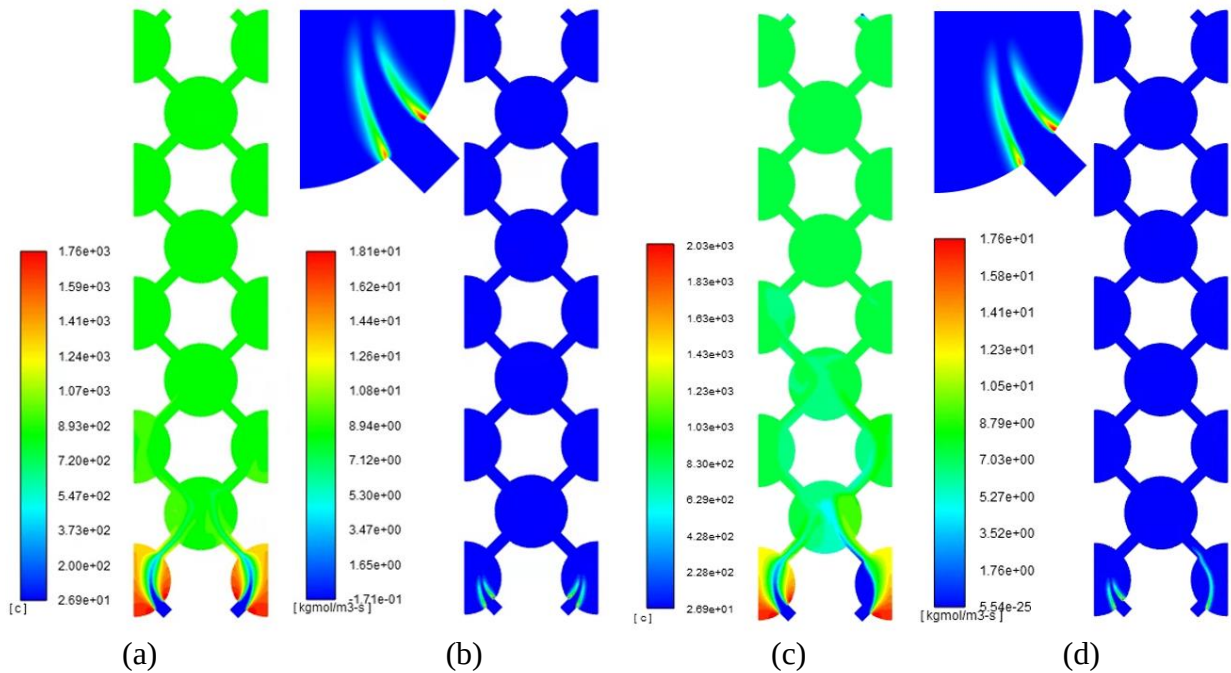


Figure V.39 *B7* maps of: (a) temperature and (b) reaction rate. *M2* maps of: (c) temperature and (d) reaction rate.

With a low amount of fuel in the reactive mixture, there is a large similarity between the maps of the two approaches, as shown in Figure V.40. The hotspots have nearly the same size and the

major difference between *B9* and *M3* is the decrease of temperature towards the outlet, which is lower for *B9*. The maximum reaction rate is the same for both approaches.

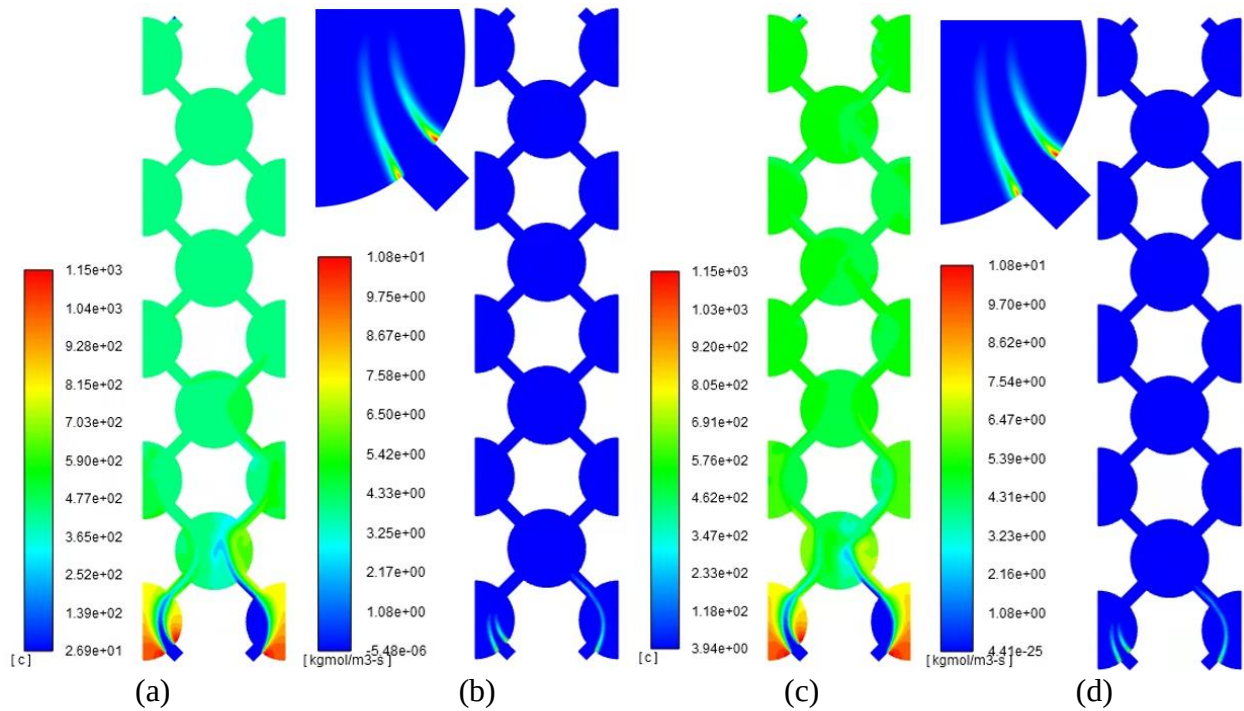


Figure V.40 *B9* maps of: (a) temperature and (b) reaction rate. *M3* maps of: (c) temperature and (d) reaction rate.

For non-premixed combustion, the difference in the size of the hotspots is noticeable in Figure V.41. As previously said, the hotspot occupies a larger space if the reverse rate is used in *B10*. Moreover, the decrease of temperature towards the outlet is lower. The maximum reaction rate of *B10* is ca. 5% lower than *M4*.

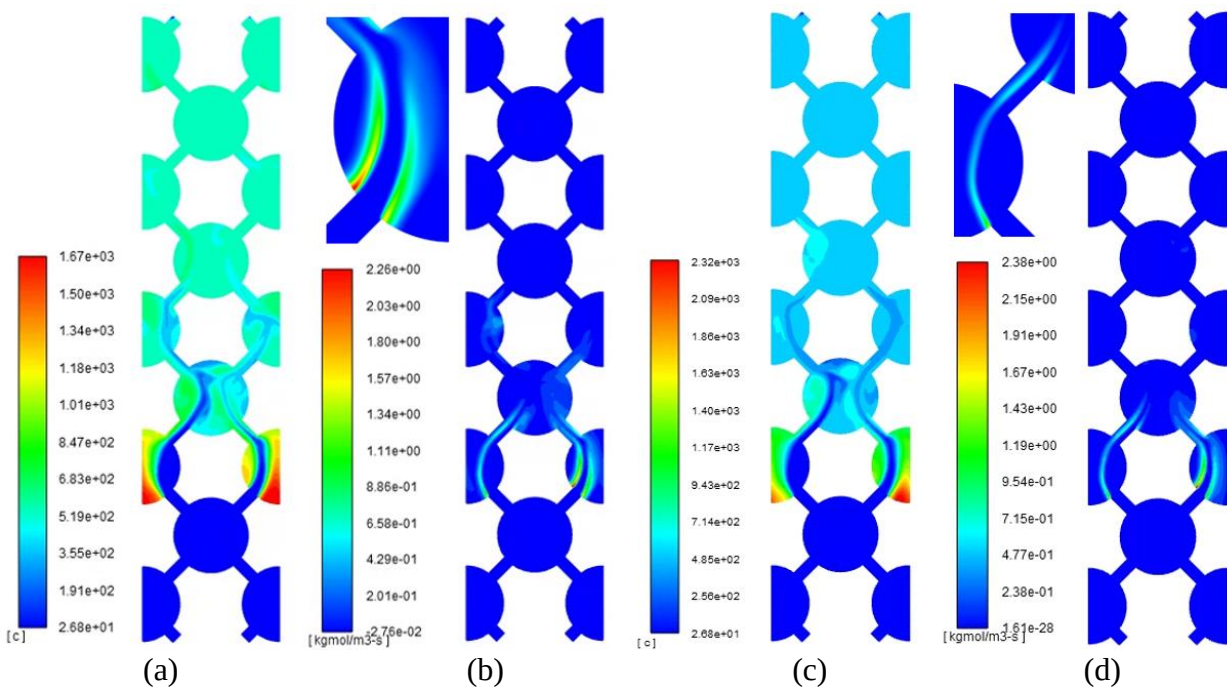


Figure V.41 *B10* maps of: (a) temperature and (b) reaction rate. *M4* maps of: (c) temperature and (d) reaction rate.

For a larger amount of fuel in the reactive mixture, the difference in the maps is more visible. As shown in Figure V.42a, with the reverse reaction the maximum temperature is attained in a larger portion of the reactor, and not only in the hotspots as in Figure V.42c. In *B11*, the maximum reaction rate is ca. 32% higher than *M5*. As visible in Figure V.42b and in Figure V.42d, with the reverse rate, the reaction front occurs in a similar zone of the reactor.

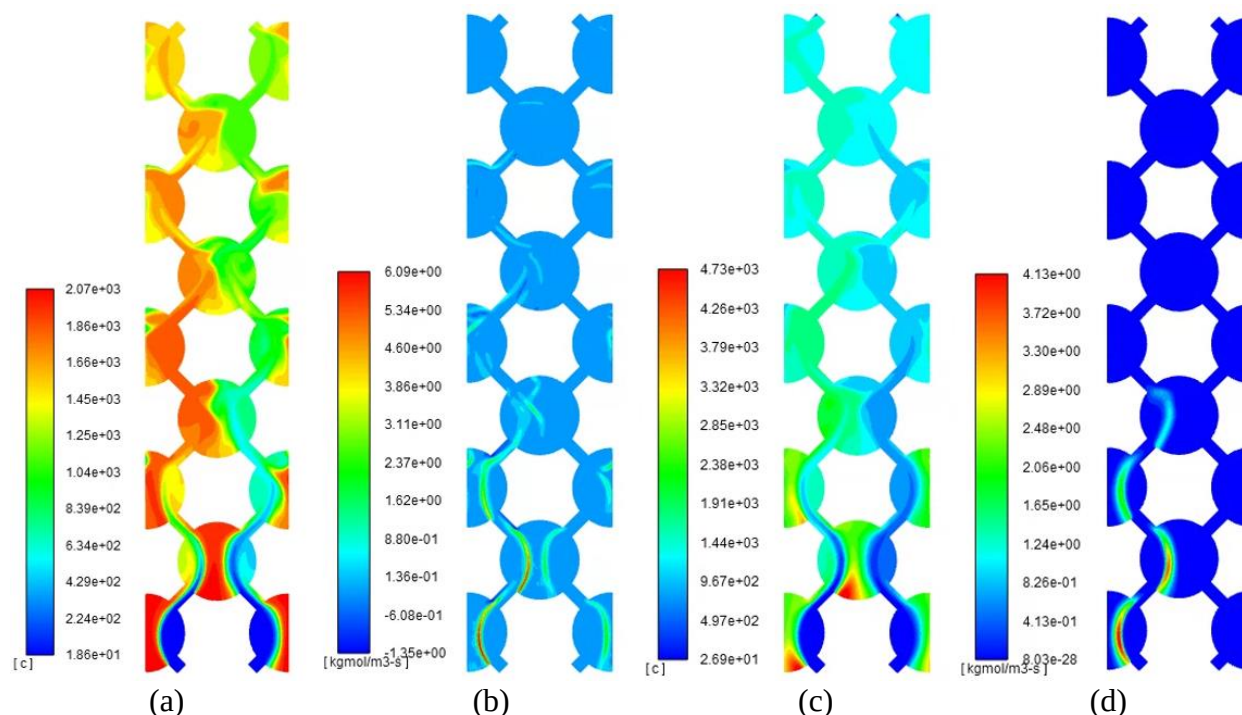


Figure V.42 *B11* maps of: (a) temperature and (b) reaction rate. *M5* maps of: (c) temperature and (d) reaction rate.

In similarity to the previous case, in *B12*, the highest temperature occupies a larger portion of the reactor and is not restricted to the hotspot, as visible in Figure V.43a. The extension of the reaction is similar to the case without reverse rate, *M6*, as shown in Figure V.43b and in Figure V.43d. The maximum reaction rate is 23% higher in *B12*.

The maps in Appendix C show that one of the reactants of *B1* to *B12* is completely consumed in the same zone of the reactor as the correspondent cases *M1* to *M6* without the reverse rate. Thus, although negative rates are present, the extension of the reaction is similar with and without the reverse rate.

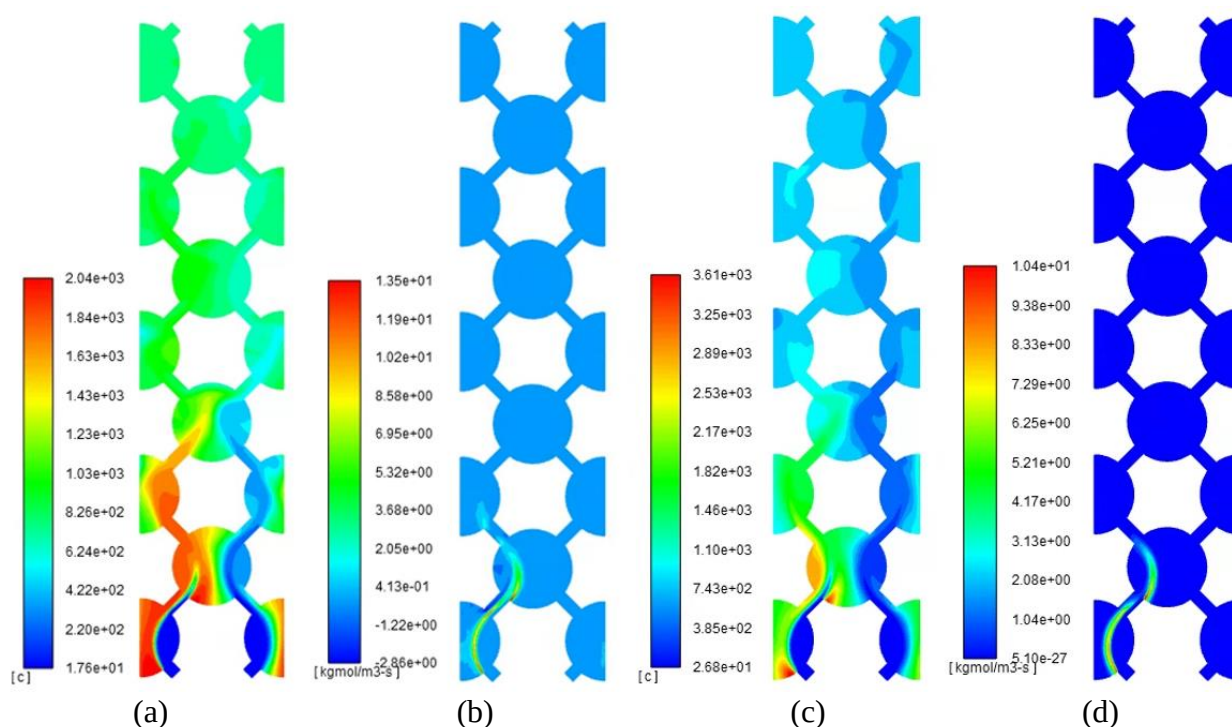


Figure V.43 *B12* maps of: (a) temperature and (b) reaction rate. *M6* maps of: (c) temperature and (d) reaction rate.

Premixed Combustion

All premixed cases considering the backward rate, *B1* to *B9*, will be presented next.

The cases without N_2 are shown in Table V.15. For a large amount of fuel, in *B1* and *B2*, it is not possible to reach complete conversion of the reactants. In *B2*, the conversion of fuel is higher and the maximum temperature increases. In *B3*, for a lower amount of fuel, hydrogen is completely consumed and the oxygen is in excess. Since lean combustion occurs, the maximum temperature is the lowest between the cases, *B1* to *B3*.

In similarity to section V.3.2.2, it is not possible to have temperatures below 1500 °C without N_2 .

Table V.15 Premixed cases without N_2 , including the backward reaction.

Premixed Combustion without N_2								
	Species	$y_{in,left}$	$y_{in,right}$	$\bar{y}_{out}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{C8}(^{\circ}C)$
B1 $\theta = 2.00$ $Da = 0.51$ $Ka = 1.97$	H_2	0.8	0.8	0.59	0.37	0.75	2300	2277
	O_2	0.2	0.2	0.059				
	N_2	0	0	0				
	H_2O	0	0	0.35				
B2 $\theta = 0.50$ $Da = 3.75$ $Ka = 0.27$	H_2	0.5	0.5	0.19	0.68	0.34	2410	2388
	O_2	0.5	0.5	0.40				
	N_2	0	0	0				
	H_2O	0	0	0.41				

B3 $\theta = 0.13$ $Da = 3.78$ $Ka = 0.26$	H ₂	0.2	0.2	0	1	0.13	2050	1517
	O ₂	0.8	0.8	0.78				
	N ₂	0	0	0				
	H ₂ O	0	0	0.22				

B1 to B3 – Premixed mixtures without N₂, simulated with Maxwell, including the reverse rate

Cases B4 to B9, which have N₂, are presented in Table V.16.

Although the temperatures are lower if the reverse reaction is considered, as stated in the beginning of this section, in similarity to Section V.3.2.2., it is only possible to have a maximum temperature below 1500 °C with low $\theta = 0.071$. The temperatures at C8 are below 1000 °C from B6 to B9. As the amount of N₂ doubles, from B4 to B5, the maximum temperature decreases ca. 4%. If the amount of hydrogen is reduced, in B6, the maximum temperature decreases approximately 9%. The maximum temperature between B6 and B8 is similar, as the amount of oxygen in the reactive mixture is either reduced or increased, respectively.

The largest decrease in the maximum temperature occurs in B9 where a small θ is used with a lower amount of fuel. In all cases, the conversion of fuel is total.

Table V.16 Premixed cases with N₂, including the backward reaction.

Premixed Combustion with N ₂								
	Species	$y_{in,left}$	$y_{in,right}$	$\bar{y}_{out}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{C8}(^{\circ}C)$
B4 $\theta = 0.20$ $Da = 3$ $Ka = 0.33$	H ₂	0.2	0.2	0	1	0.20	2080	1557
	O ₂	0.5	0.5	0.44				
	N ₂	0.3	0.3	0.33				
	H ₂ O	0	0	0.22				
B5 $\theta = 0.50$ $Da = 3.77$ $Ka = 0.27$	H ₂	0.2	0.2	0	1	0.50	1990	1557
	O ₂	0.2	0.2	0.11				
	N ₂	0.6	0.6	0.67				
	H ₂ O	0	0	0.22				
B6 $\theta = 0.17$ $Da = 1.74$ $Ka = 0.58$	H ₂	0.1	0.1	0	1	0.17	1780	843
	O ₂	0.3	0.3	0.26				
	N ₂	0.6	0.6	0.63				
	H ₂ O	0	0	0.11				
B7 $\theta = 0.25$ $Da = 1.42$ $Ka = 0.70$	H ₂	0.1	0.1	0	1	0.25	1760	851
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
B8 $\theta = 0.13$ $Da = 2$ $Ka = 0.50$	H ₂	0.1	0.1	0	1	0.13	1750	842
	O ₂	0.4	0.4	0.37				
	N ₂	0.5	0.5	0.53				
	H ₂ O	0	0	0.11				

B9	H ₂	0.05	0.05	0	1	0.07	1150	473
$\theta = 0.071$	O ₂	0.35	0.35	0.33				
Da = 1.36	N ₂	0.6	0.6	0.62				
Ka = 0.74	H ₂ O	0	0	0.051				

B4 to B9 – Premixed mixtures with N₂, simulated with Maxwell, including the reverse rate

In similarity to what was shown previously for the hydrogen combustion with the forward rate, if the reverse reaction is considered, as the amount of fuel in the reactive mixture decreases, from B1 to B7, the reaction front occurs further in the reactor, as shown in Figure V.44. Moreover, the maximum reaction rate decreases. In B1, the reaction front is in the inlet channel. As the amount of fuel is reduced, in B3, the reaction front moves to the end of the inlet channel. In B4, although N₂ is used, θ is larger than in B3, and the reaction front occurs nearly in the same place. In B7, the reaction front is extended to half of the chamber. The maximum reaction rate of B7 is one order of magnitude lower than B1.

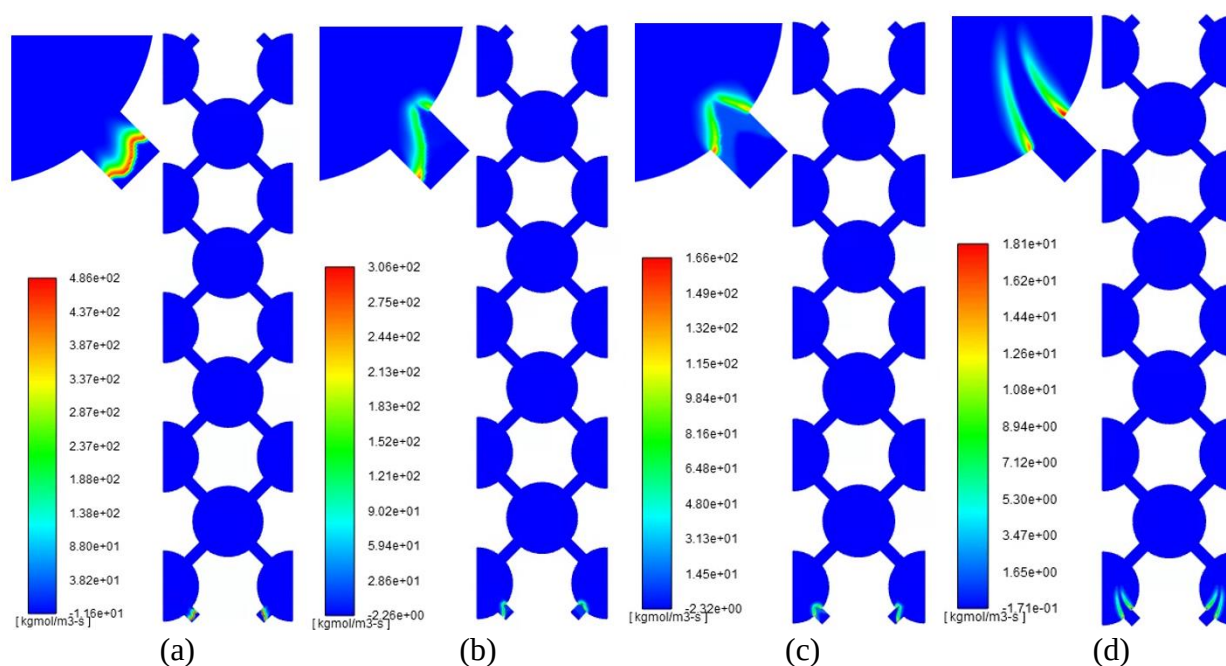


Figure V.44 Reaction rate maps of: (a) B1, (b) B3, (c) B4 and (d) B7.

In B1, the maximum temperature is attained immediately after the reaction front and is maintained nearly constant in the entire reactor. From B3 to B7, the temperature rises on the sides of the reaction front and then decreases towards the outlet, as visible in Figure V.45.

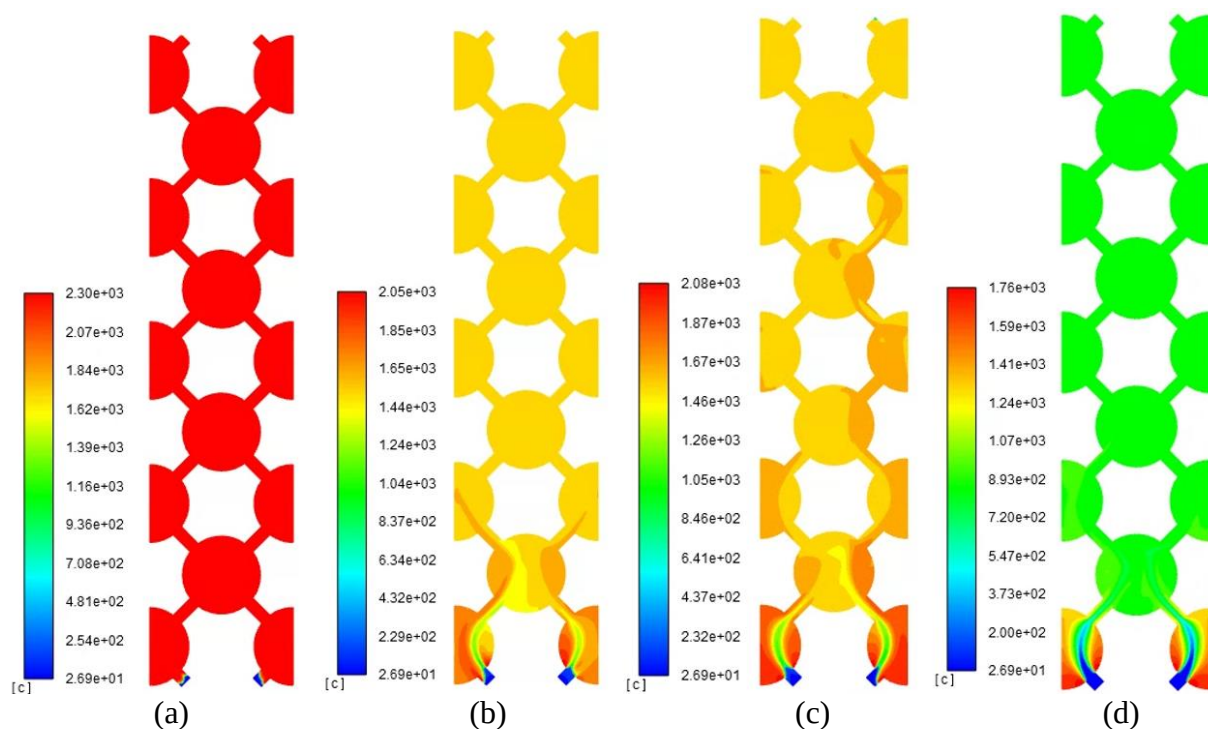


Figure V.45 Temperature maps of: (a) B1, (b) B3, (c) B4 and (d) B7.

Non-premixed Combustion

Non-premixed cases considering the backward rate, *B10* to *B12*, are presented in Table V.17. It is visible that the difference in the maximum temperature between the three cases is ca. 17%, while without the reverse reaction the difference was higher than 53%. In this way, the inclusion of the reverse rate enables to decrease the concentration of heat in the reactor as the fuel and air streams are mixed. In fact, the reverse reaction is endothermic, decreasing locally the temperature as the reactants are formed, which enables to extend the reactive zone.

In similarity to Section V.3.2.3, the maximum temperature increases as the amount of fuel is increased in the reactive mixture, in *B11* and *B12*. In fact, all the oxygen is consumed, in contrast to *B10* where lean combustion (complete conversion of oxygen) occurs.

Table V.17 Non-premixed cases, including the backward reaction.

Non-premixed Combustion								
	Species	$y_{in,left}$	$y_{in,right}$	$\bar{y}_{out}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{c8}(^{\circ}C)$
B10 $\theta = 0.27$ $Da = 0.73$ $Ka = 1.38$	H ₂	0.1	0	0	1	0.26	1670	560
	O ₂	0	0.2	0.071				
	N ₂	0.9	0.8	0.86				
	H ₂ O	0	0	0.066				
B11 $\theta = 2.14$ $Da = 1.38$ $Ka = 0.73$	H ₂	0.5	0	0.13	0.57	1	2070	1536
	O ₂	0	0.2	0				
	N ₂	0.5	0.8	0.68				
	H ₂ O	0	0	0.19				

B12	H ₂	0.9	0.	0.63	0.13	1	2040	805
$\theta = 8.99$	O ₂	0	0.2	0				
Da = 1.02	N ₂	0.1	0.8	0.27				
Ka = 0.98	H ₂ O	0	0	0.095				

B10 to B12 – Non-premixed mixtures, simulated with Maxwell, including the reverse rate

With a low amount of fuel in the reactive mixture, *B10*, the reaction front occurs in the 3rd row of chambers, where the maximum temperature is attained. For a larger amount of fuel, in *B12*, the reaction front is extended to the first two rows of chambers, as shown in Figure V.46. The maximum reaction rate is 17% higher in *B12*.

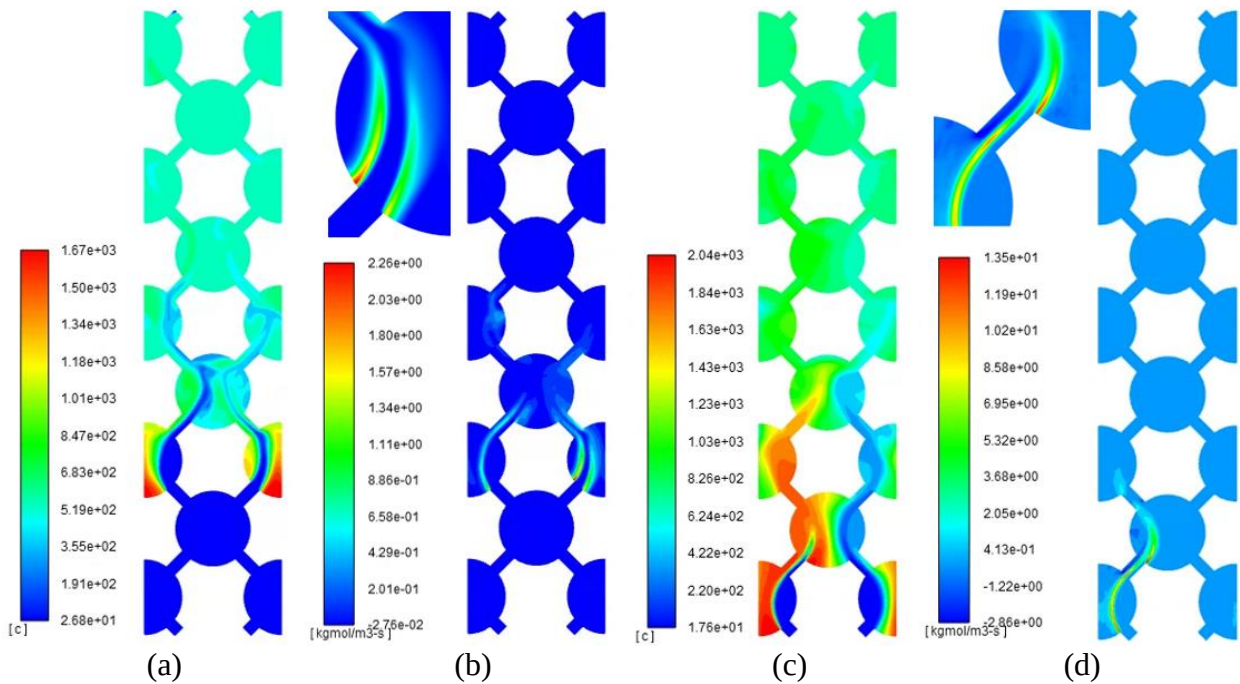


Figure V.46 *B10* maps of: (a) temperature and (b) reaction rate. *B12* maps of: (c) temperature and (d) reaction rate.

Effect of kb

In the previous sections, kb was calculated in function of kf , according to $kf =$

$kb \left(\frac{p}{RT} \right)^d e^{\frac{-\Delta H_f^\circ + T \Delta S_f^\circ}{RT}}$ (Equation V.4b). In this section, kb will be calculated using the Arrhenius

reaction rate expression, $kb' = \mathcal{A}' T^{\delta'} e^{\frac{-E_{a'}}{RT}}$ (Equation V.4a) with larger parameters, $\mathcal{A}' = 1 \times 10^{15}$ m³/(kmols), $\delta' = 0$ and $E_{a'} = 1 \times 10^8$ J/kmol, provided by default in ANSYS® FLUENT™.

If kb is calculated with the Arrhenius reaction rate expression with larger parameters, at 1000 °C $kb' = 8.19 \times 10^{10}$ m³/(kmols), as shown in Figure V.47. In this case, the order of magnitude of kb' is higher than kf and the reverse rate will have a major impact in combustion. In fact, the use of kb' will result in an unrealistic decrease of the temperature of combustion since the values of

kb' are larger than the values of kb of validated mechanisms for the hydrogen combustion (see Section V.1.2.1).

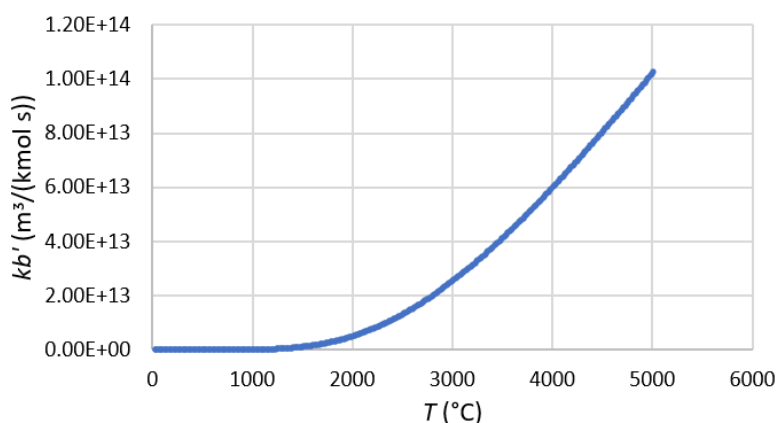


Figure V.47 kb' evolution from 25 °C to 5000 °C.

To understand the effect of kb' , premixed cases were repeated: *B1* without N_2 ; *B4* and *B5* with N_2 and temperature at C8 higher than 1000 °C (initial molar fraction of fuel 0.2); *B7* and *B9* with N_2 and temperature at C8 lower than 1000 °C (initial molar fraction of fuel ≤ 0.1); and three non-premixed cases, *B10*, *B11* and *B12*.

The results are shown in Table V.18, in which is visible that cold combustion occurs in all cases, i.e., the temperature is below 585 °C.

The conversions of fuel and oxygen are less than 0.5 for all cases and total conversion is never attained.

Table V.18 Combustion with large kb .

Premixed Combustion with Large kb								
	Species	$y_{in,left}$	$y_{in,right}$	$\bar{y}_{out}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{C8}(^{\circ}C)$
<i>B1'</i> $\theta = 2$	H ₂	0.8	0.8	0.79	0.020	0.040	250	249
	O ₂	0.2	0.2	0.19				
	N ₂	0	0	0				
	H ₂ O	0	0	0.018				
<i>B4'</i> $\theta = 0.2$	H ₂	0.2	0.2	0.18	0.13	0.024	236	234
	O ₂	0.5	0.5	0.49				
	N ₂	0.3	0.3	0.30				
	H ₂ O	0	0	0.026				
<i>B5'</i> $\theta = 0.5$	H ₂	0.2	0.2	0.18	0.11	0.059	213	212
	O ₂	0.2	0.2	0.19				
	N ₂	0.6	0.6	0.61				
	H ₂ O	0	0	0.023				
<i>B7'</i> $\theta = 0.5$	H ₂	0.1	0.1	0.081	0.17	0.022	214	194
	O ₂	0.2	0.2	0.19				
	N ₂	0.7	0.7	0.71				
	H ₂ O	0	0	0.020				

<i>B9'</i> <i>θ</i> = 0.071	H ₂	0.05	0.05	0.031	0.32	0.070	198	186
	O ₂	0.35	0.35	0.34				
	N ₂	0.6	0.6	0.61				
	H ₂ O	0	0	0.019				
Non-premixed Combustion with Large <i>kb</i>								
<i>B10'</i> <i>θ</i> = 0.27	H ₂	0.1	0	0.034	0.42	0.17	210	163
	O ₂	0	0.2	0.094				
	N ₂	0.9	0.8	0.86				
	H ₂ O	0	0	0.016				
<i>B11'</i> <i>θ</i> = 2.14	H ₂	0.5	0	0.27	0.097	0.13	210	201
	O ₂	0	0.2	0.075				
	N ₂	0.5	0.8	0.63				
	H ₂ O	0	0	0.021				
<i>B12'</i> <i>θ</i> = 8.99	H ₂	0.9	0	0.71	0.056	0.25	218	207
	O ₂	0	0.2	0.030				
	N ₂	0.1	0.8	0.24				
	H ₂ O	0	0	0.021				

B1' to B9' – Premixed mixtures, simulated with Maxwell, including the reverse rate with larger kb'

B10' to B12' – Non-premixed mixtures, simulated with Maxwell, including the reverse rate with larger kb'

For the premixed cases, $B1'$ to $B7'$, as the initial amount of fuel decreases and the amount of inert/oxygen increases, the reaction front moves away from the inlet. In $B1'$ and $B4'$, the reaction front is in the end of the inlet channel, as shown in Figure V.48a and in Figure V.48b. The maximum reaction rate is one order of magnitude higher than $B5'$ and $B7'$. Note that, the maximum reaction rate is approximately the triple if no inert is used, as shown previously. As visible in Figure V.48b and in Figure V.48c, the maximum reaction rate for $B5'$ is slightly higher than $B7'$ and the reaction front is extended to less than $D/2$. In $B7'$, which has a lower amount of fuel in the reactive mixture, the reaction front is prolonged to the first half, $\cong D/2$, of the chamber.

It is possible to conclude that with kb' the maximum reaction rate is two orders of magnitude lower when compared to the previous cases with kb (see Figure V.44). Moreover, with kb , the difference between the maximum and the minimum reaction rate differs two orders of magnitude, while with kb' the values are apart one order of magnitude.

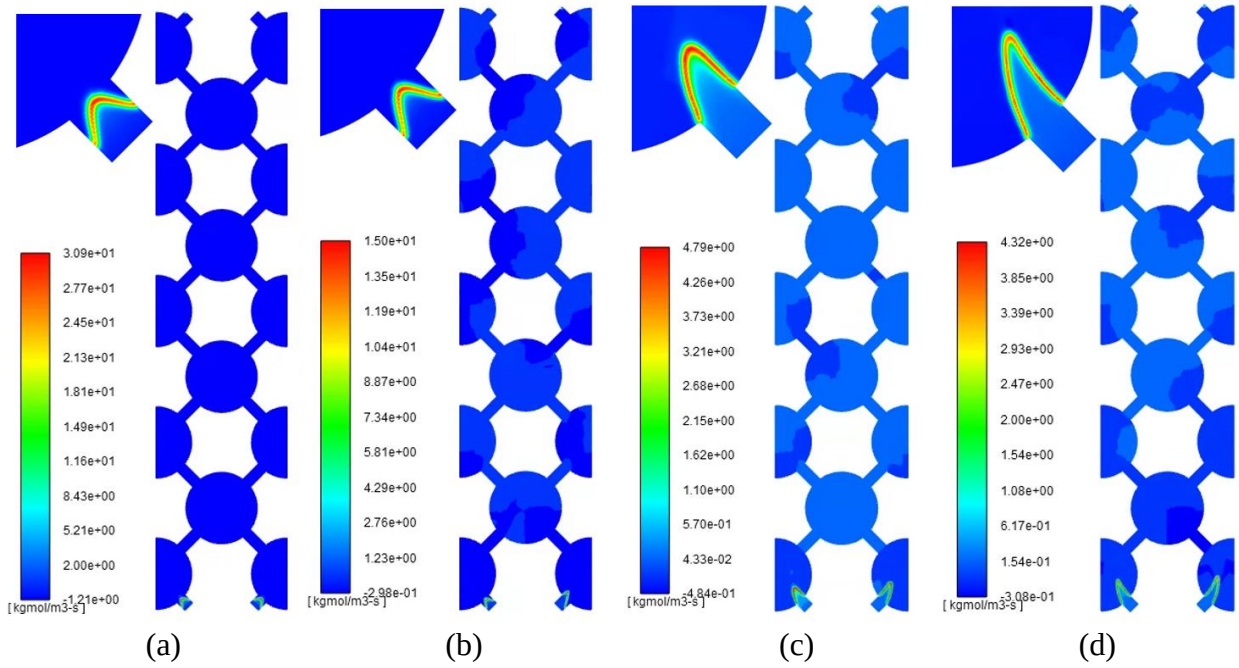


Figure V.48 Reaction rate maps of: (a) $B1'$, (b) $B4'$, (c) $B5'$ and (d) $B7'$.

In similarity to Section V.3.2.3., where several physical properties were constant, if the backward rate with large kb' is included with variable properties, the temperature increases after the reaction front and stays nearly constant in the entire reactor, as shown in Figure V.49. The highest temperature is attained in $B1'$ which has the largest amount of fuel in the initial mixture and does not have nitrogen. $B5'$ and $B7'$ have close temperatures. While with kb the temperature decreases towards the outlet (see Figure V.45), with kb' the temperature at the outlet is close to the maximum temperature, since no hotspots are formed.

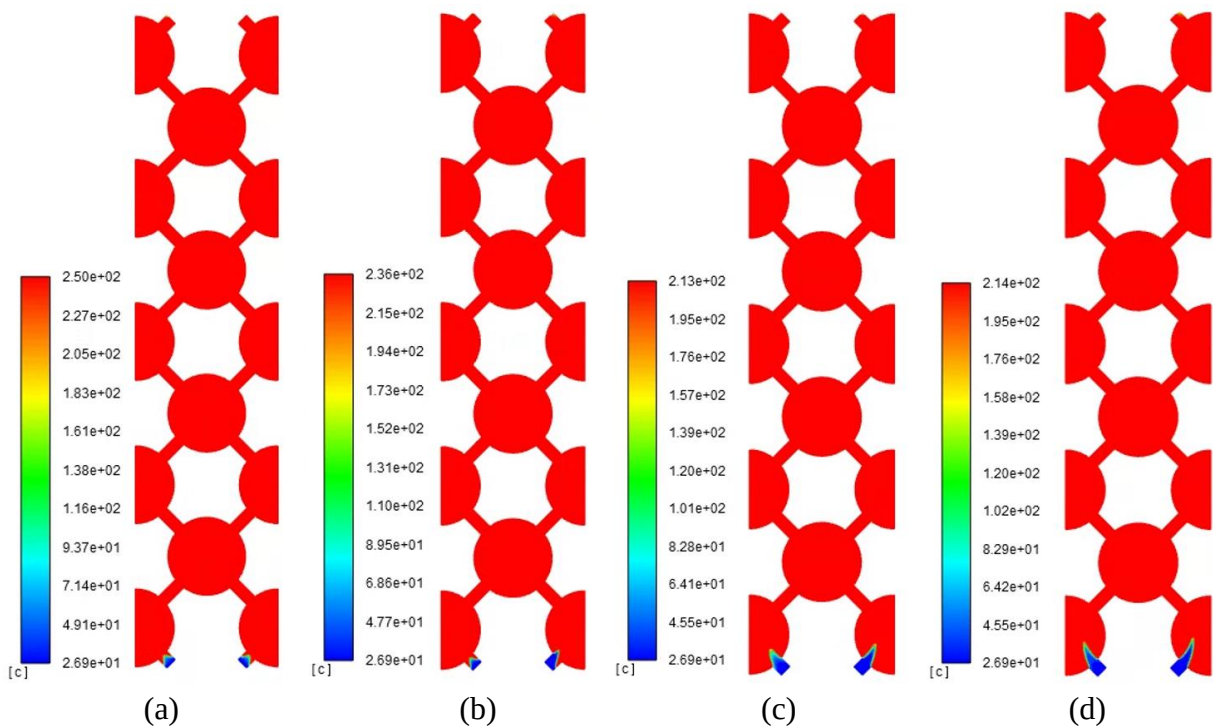


Figure V.49 Temperature maps of: (a) $B1'$, (b) $B4'$, (c) $B5'$ and (d) $B7'$.

In the previous cases, the reaction rate maps have shown that in most of the reactor, the reaction rate has a small negative value. If a low amount of fuel in the initial mixture is used, in $B9'$, a defined reaction front occurs in the interior of the chambers of the first row and the reaction rate is positive in most of the reactor, as shown in Figure V.50a. In fact, the reverse reaction is endothermic, decreasing locally the temperature as the reactants are formed, which enables to extend the reactive zone. As expected, the maximum reaction rate of $B9'$ is ca. one order of magnitude smaller when compared to the cases, $B1'$ to $B7'$.

As shown in Figure V.46, if non-premixed combustion with kb , $B10$, is simulated with a low amount of fuel in the initial mixture, the reaction front occurs in the third row of chambers and the maximum rate is low in most of the reactor. Using kb' , in $B10'$, a reaction front can be distinguished in the third row of chambers, but the maximum value is present in a large portion of the reactor, as shown in Figure V.50b. The maximum reaction rate is one order of magnitude lower when compared to $B10$. The maximum reaction rate of $B10'$ is one order of magnitude lower than $B9'$. For a larger amount of fuel, in $B11'$ and $B12'$, the maximum reaction rate occurs in the first chamber and has a higher value when compared to $B10'$, as shown in Figure V.50c and in Figure V.50d. The reaction rate is positive in most of the reactor, in similarity to $B10'$. In non-premixed combustion with kb' , $B10'$ to $B12'$, the reaction rate is one to two orders of magnitude lower, in comparison to the cases with kb , $B10$ to $B12$.

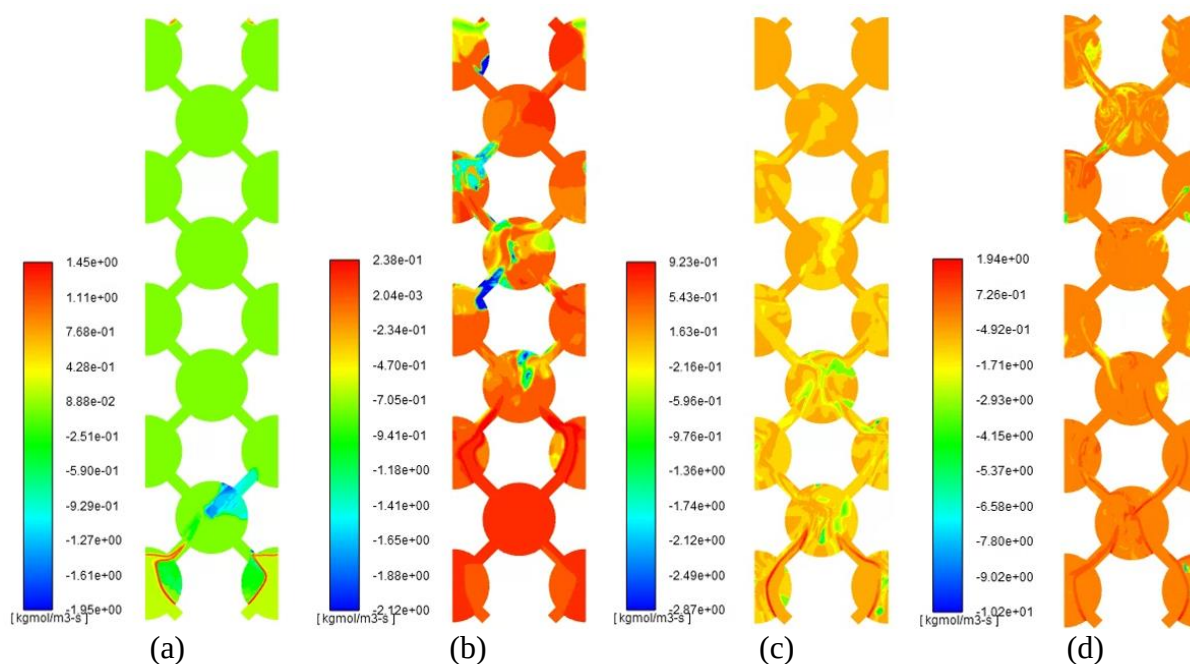


Figure V.50 Reaction rate maps of: (a) $B9'$, (b) $B10'$, (c) $B11'$ and (d) $B12'$.

As expected, the temperature increases after the reaction front. $B9'$ has the lowest maximum temperature when compared to the premixed cases, $B4'$ to $B7'$, since the initial amount of fuel is

lower. Non-premixed cases, $B10'$ and $B11'$, have the same maximum temperature which is lower than the maximum temperature of $B12'$, since the amount of fuel in the reactive mixture is larger.

As previously said, while with kb the temperature decreases towards the outlet (see Figure V.46), if kb' is used, the temperature at the outlet is close to the maximum temperature, since hotspots are not formed.

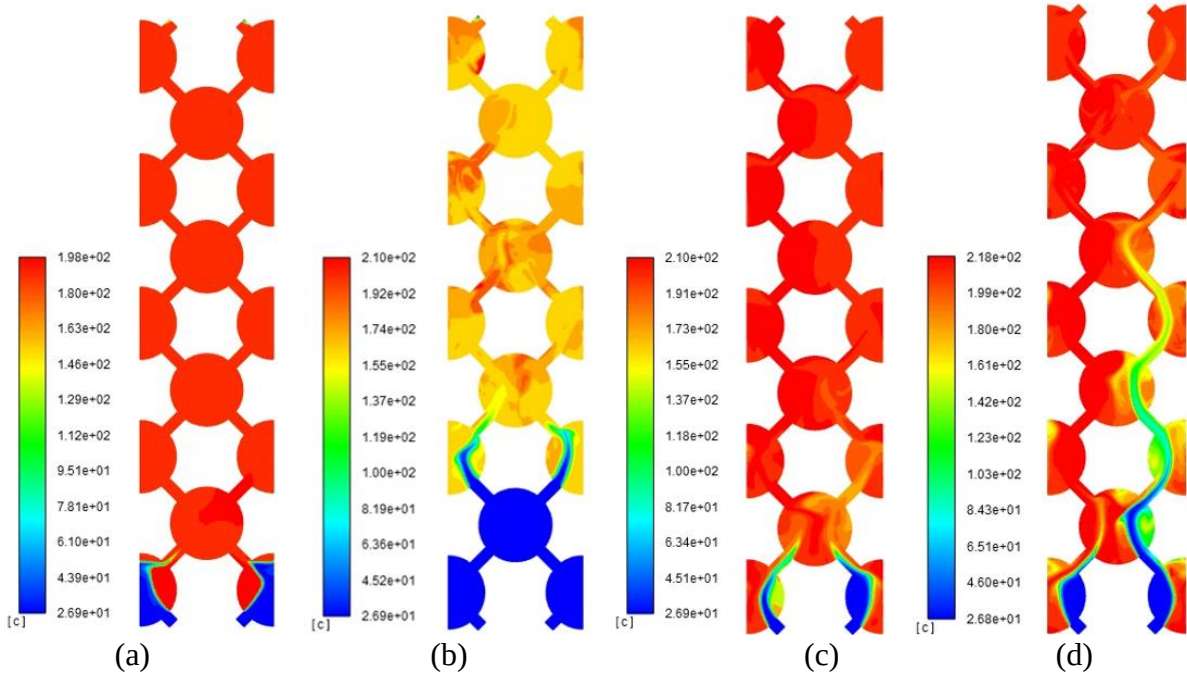


Figure V.51 Temperature maps of: (a) $B9'$, (b) $B10'$, (c) $B11'$ and (d) $B12'$.

V.3.2.7 Transient vs Steady

In the previous sections, the simulations were solved with transient-state equations, as shown in V.3.1. In this section, it is assumed that a steady-state solution is reached after a certain number of iterations. For that, the temporal discretization uses an implicit or explicit time-marching algorithm. In the case of this work, an implicit algorithm was used, the Pseudo-transient under relaxation method, which assumes a pseudo time step, Δt . For the pressure-velocity coupling, the Coupled method was used. The spatial discretization was performed with the Least Squares Cell Based algorithm for the gradient, the Second Order for the pressure and the Second Order Upwind for the momentum, energy and species. The convergence criterion for the maximum residuals of continuity and momentum is 10^{-5} , for the energy is 10^{-6} and for the species is 10^{-3} .

In similarity with the previous section, the reactants enter at 25 °C and 1 bar (constant) at both inlets. For the steady simulation, a Re number below the critical value was chosen, $Re = 100$, and the velocity at each inlet was calculated from Equation V.51.

Premixed Combustion

For premixed combustion, the influence of using a steady-state approach at $Re = 100$ will be compared with the transient-state approach for the three models, Fick (*S7*), Maxwell (*M2*) and Thickened Flame with and without UDF (*F2* and *F2u*).

The results are shown in Table V.19. It is visible that if the steady-state is used, the maximum temperatures have a maximum difference of 3% between the four models. This result is similar to the prediction of the transient simulations which differ ca. 2% (for most cases) between the four models.

The prediction of the temperature at C8 differs less than 1% with steady-state, while with the transient approach the difference is ca. 2% (for most cases).

The maximum temperature prediction with steady-state is approximately 25% lower than the prediction with the transient-state. In contrast, the temperature at C8 is ca. 18% higher than the prediction with the transient approach.

Table V.19 Transient vs steady-state.

Transient vs Steady Model								
	Species	$y_{in,left}$	$y_{in,right}$	$\overline{y_{out}}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{C8}(^{\circ}C)$
M2s Steady $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	1460	1101
	O ₂	0.2	0.2	0.13				
	N ₂	0.7	0.7	0.71				
	H ₂ O	0	0	0.15				
M2 Transient $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	2030	851
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
F2s Steady $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	1450	1009
	O ₂	0.2	0.2	0.14				
	N ₂	0.7	0.7	0.73				
	H ₂ O	0	0	0.13				
F2 Transient $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	2020	867
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
F2us Steady $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	1450	1004
	O ₂	0.2	0.2	0.14				
	N ₂	0.7	0.7	0.73				
	H ₂ O	0	0	0.13				

<i>F2u UDF</i> <i>Transient</i> $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	2000	826
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
<i>S7ps</i> <i>Steady</i> $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	1500	1034
	O ₂	0.2	0.2	0.14				
	N ₂	0.7	0.7	0.72				
	H ₂ O	0	0	0.14				
<i>S7p</i> <i>Transient</i> $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	2060	843
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				

M2s, F2s, F2us, S7ps – Cases with Maxwell, Flame, Flame with UDF and Fick, simulated in steady-state
M2, F2, F2u, S7p – Cases with Maxwell, Flame, Flame with UDF and Fick, simulated in transient-state

As previously shown, the temperature maps are similar for the three models, Fick, Maxwell and Thickened Flame. As an example, Figure V.52 shows the maps for the steady-state approach and Figure V.53 for the transient-state of case *M2* (see Appendix C).

As expected, if the steady-state is used, the flow is nearly symmetrical and no vortices are formed, as shown in Figure V.52a. If the transient-state is used, the oscillating behaviour inside the chambers is promoted and vortices are formed especially at the top of the mixing chambers, as shown in Figure V.53a. The *y*-velocity history of *M2s* in the centre of C2, C4, C6 and C8 is shown in Figure V.54 where is visible that after the initial stabilization (ca. 15000 iterations), the velocity remains nearly constant. From C2 to C8, the average of v_y decreases from -0.35 m/s to -0.45 m/s.

If the steady approach is used, the reaction occurs in the inlet channel and presents two fronts which are nearly symmetrical, as visible in Figure V.52b. In contrast, if the transient-state is used, the reaction front is extended from the end of the inlet channels to the first half of the chambers, as shown in Figure V.53b. The maximum reaction rate is ca. 5% lower for the steady approach.

As expected, for both approaches, the temperature rises after the reaction front and a hotspot is formed at the bottom of the first chamber. In the steady approach, the temperature decreases after the hotspot, and increases in the three upper rows of chambers of the reactor. In contrast, if the transient-state is used, the temperature decreases and remains nearly constant towards the outlet. The temperature history of *M2s* in the centre of C2, C4, C6 and C8 is shown in Figure V.55 where is visible that after ca. 15000 iterations, the temperature rises and stays nearly constant. From C2 to C6, the temperature is close to 1000 °C and increases to approximately 1100 °C at C8, as previously said when the temperature map of Figure V.52c was analysed.

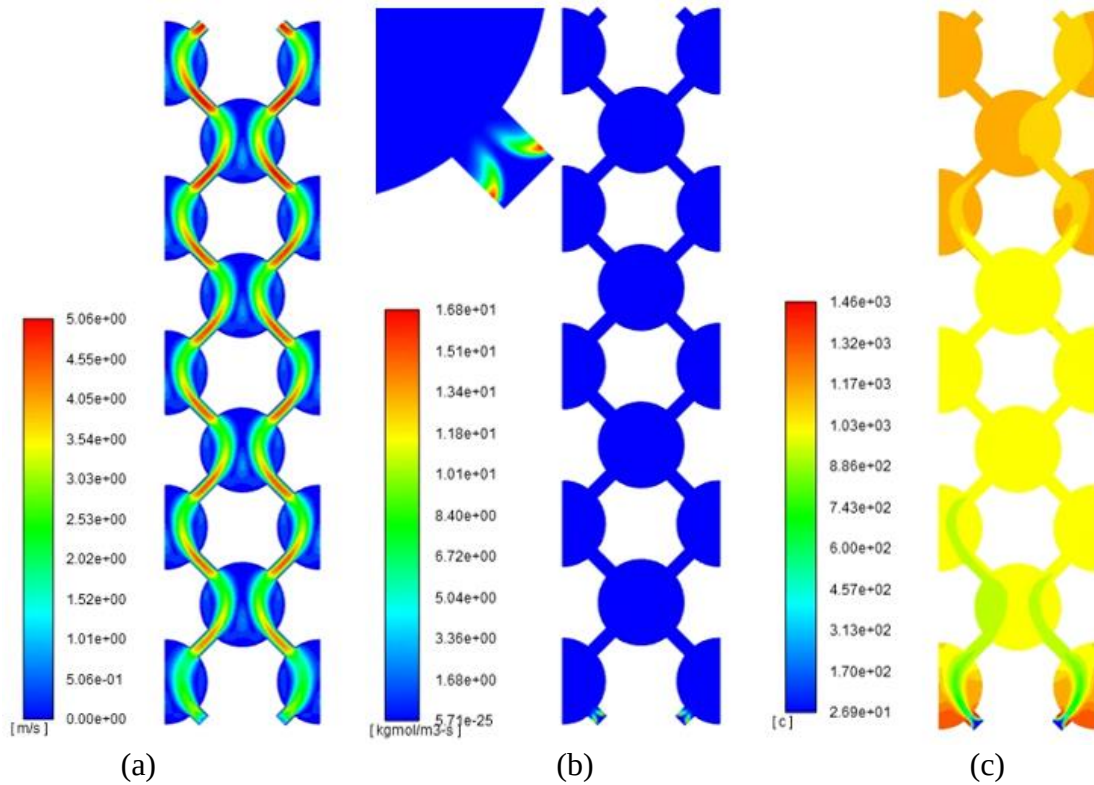


Figure V.52 *M2s* (steady-state) maps of (a) velocity magnitude, (b) reaction rate and (c) temperature.

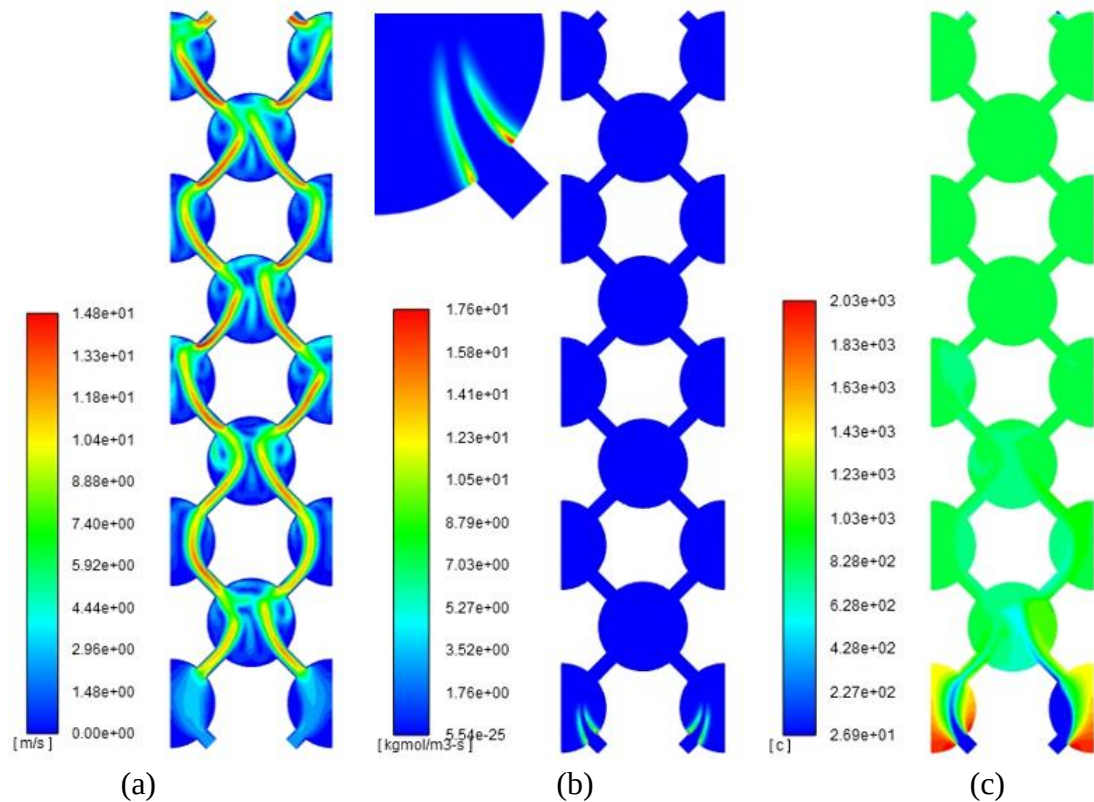


Figure V.53 *M2* (transient-state) maps of (a) velocity magnitude, (b) reaction rate and (c) temperature.

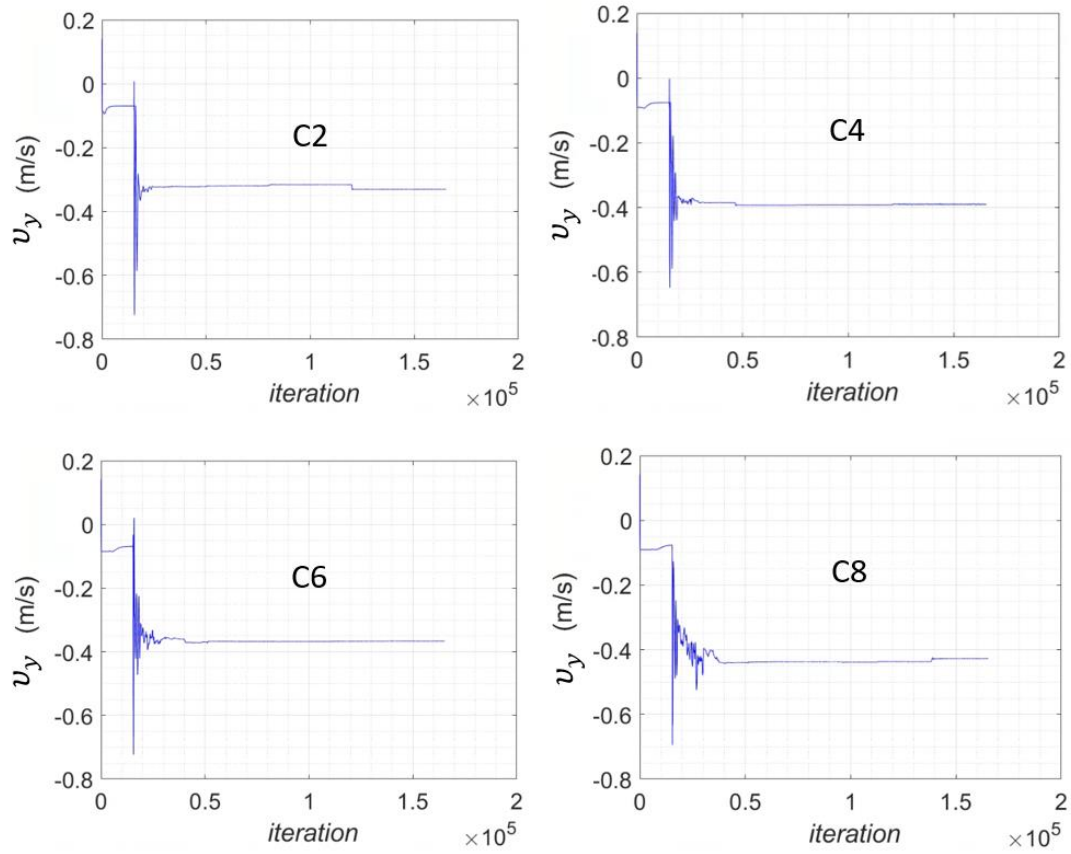
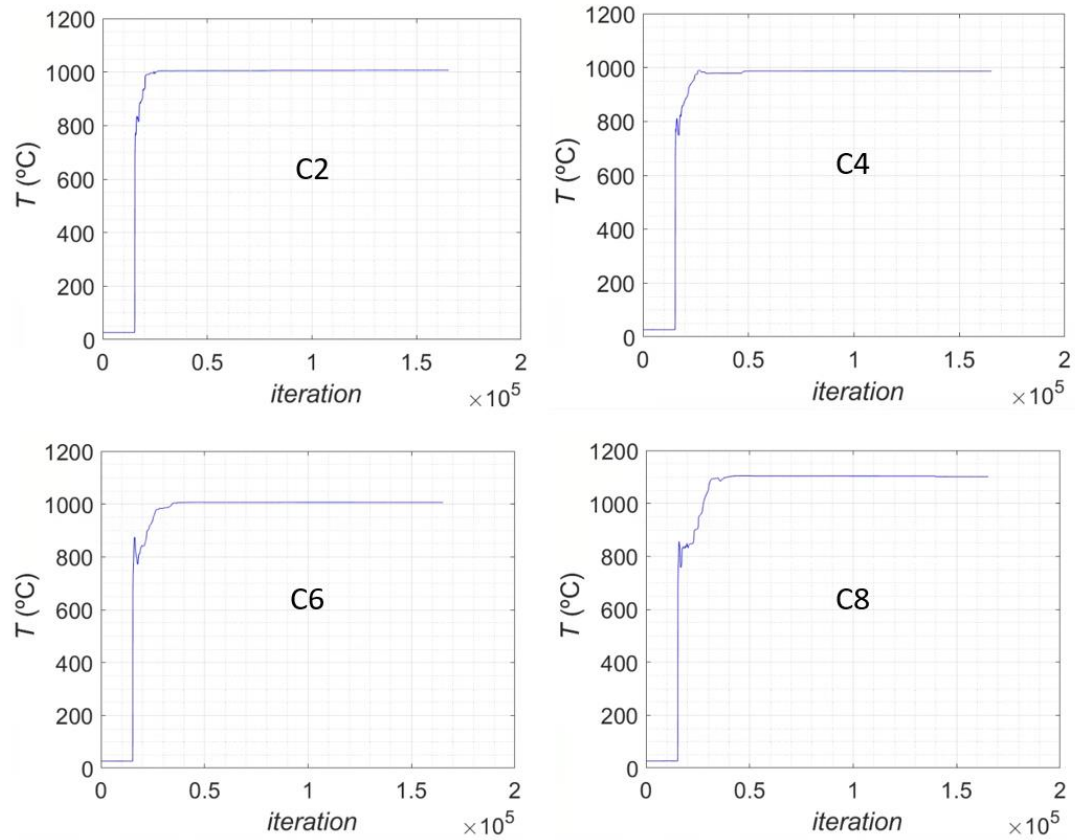
Figure V.54 y -velocity history of M2s in the centre of C2, C4, C6 and C8.

Figure V.55 Temperature history of M2s in the centre of C2, C4, C6 and C8.

Non-premixed Combustion

To study the steady-state approach in non-premixed combustion, case *M4* was used. In Table V.20 is shown the comparison between *M4s* and *M4*. In non-premixed combustion, if the steady approach is used, the maximum temperature is ca. 14% higher. The temperature at C8 of *M4s* is approximately 6% higher than *M4*.

Table V.20 Comparison between steady and transient simulations of *M4*.

Transient vs Steady Model								
	Species	$y_{in,left}$	$y_{in,right}$	$\overline{y_{out}}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{C8}(^{\circ}C)$
<i>M4s (Re = 100)</i> <i>Steady</i> $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	2730	605
	O ₂	0	0.2	0.066				
	N ₂	0.9	0.8	0.86				
	H ₂ O	0	0	0.072				
<i>M4 (Re = 300)</i> <i>Transient</i> $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	2320	550
	O ₂	0	0.2	0.066				
	N ₂	0.9	0.8	0.87				
	H ₂ O	0	0	0.064				

M4s – Non-premixed case with Maxwell, simulated in steady-state

M4 – Non-premixed case with Maxwell, simulated in transient-state

Figure V.56 shows the maps for the steady-state approach, and Figure V.57 for the transient-state.

As expected, if the steady-state is used, the flow is nearly symmetrical and no vortices are formed, as shown in Figure V.56a. If the transient-state is used, the oscillating behaviour inside the chambers is promoted and vortices are formed especially at the top of the mixing chambers, as shown in Figure V.57a. This behaviour is similar to the results reported for premixed combustion.

If the steady approach is used, the reaction front is in the first row of chambers, while with the transient-state the reaction front was in the 3rd row of chambers, as visible in Figure V.56b and in Figure V.57b. The maximum reaction rate is one order of magnitude lower for the steady approach.

As expected, for both approaches, the temperature rises after the reaction front. Although the temperature raise occurs in different chambers, the hotspot has the same shape and is formed at the bottom of the reaction chamber. The temperature decreases then towards the outlet, as shown in Figure V.56c and in Figure V.57c.

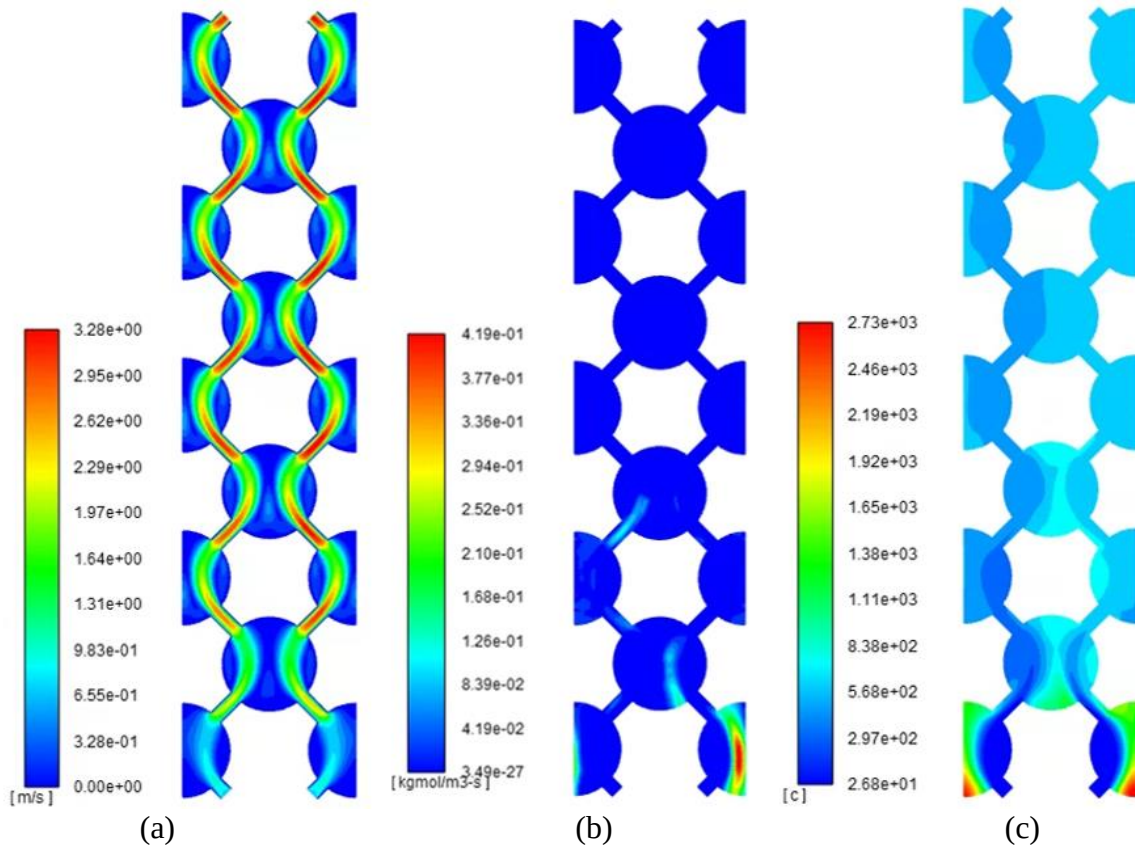


Figure V.56 *M4s* (steady-state) maps of: (a) velocity magnitude, (b) reaction rate and (c) temperature.

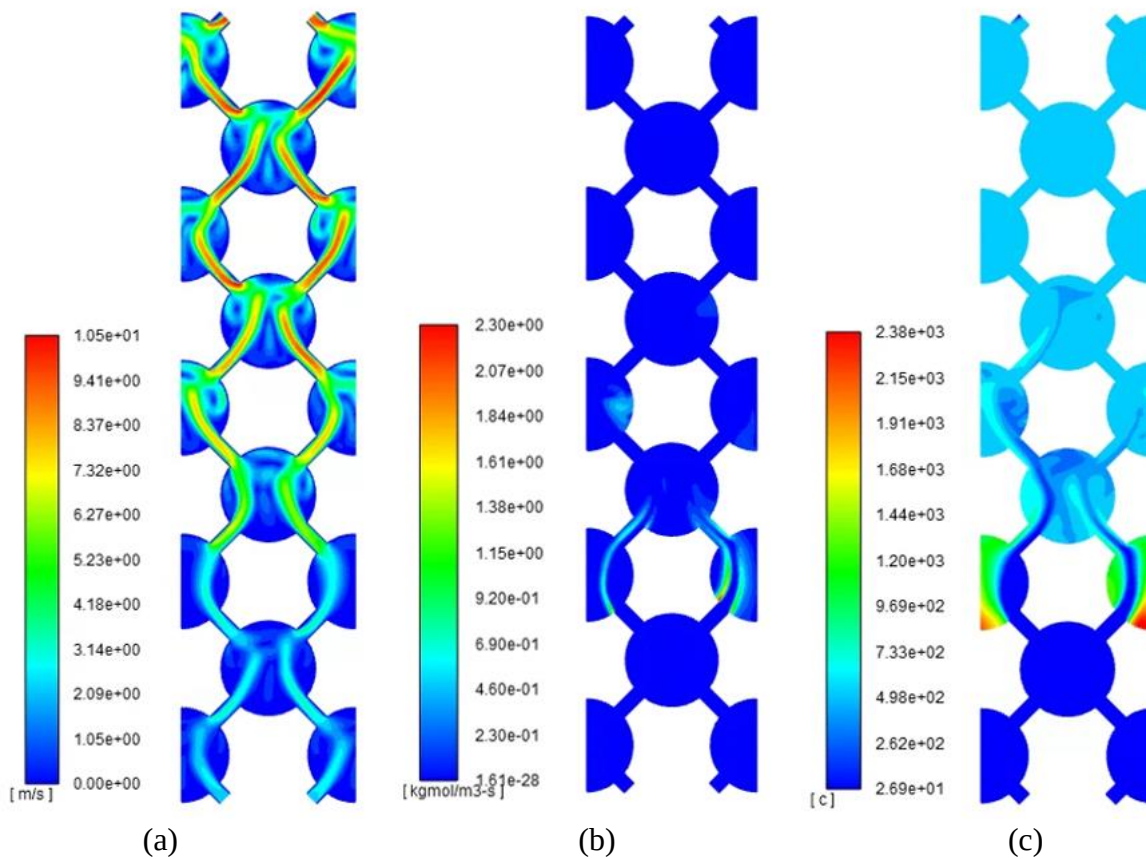


Figure V.57 *M4* (transient-state) maps of: (a) velocity magnitude, (b) reaction rate and (c) temperature.

V.3.3 19-Reactions Scheme Simulation

In the previous sections, the global scheme of hydrogen combustion with one reaction was used. In this section, a reduced mechanism with 19 reactions will be used. The mechanism was previously shown in Section V.1.2.1.

To compare the 19-reactions scheme approach with the global scheme, the initial reactive mixtures that were previously presented will be simulated. A premixed case, *C1*, which will be compared with *B7* (including the backward reaction) and with *M2* (excluding the backward reaction); and a non-premixed case, *C2*, which will be compared with *B10* (including the backward reaction) and with *M4* (excluding the backward reaction).

As shown in Section V.1.2.1, the first reaction of the 19-reactions scheme has H instead of H₂. The initial molar fraction of H will, then, be provided to the software for numerical reasons. The results will still be analysed in terms of the fuel, H₂, considering the equilibrium $\text{H}_2 \leftrightarrow 2\text{H}$.

Table V.21 shows that in premixed combustion, *C1*, the maximum temperature for the 19-reactions scheme is lower when compared to the global scheme, ca. 34% in comparison to *B7* and ca. 42% in comparison to *M2*. For non-premixed combustion, *C2*, the maximum temperature is higher if the 19-reactions scheme is used (30% higher than *B10* and 7% higher than *M4*).

For premixed combustion with the 19-reactions scheme, *C1*, the temperature at C8 is closer to the prediction of *B7* which considers the backward reaction. In contrast, for non-premixed combustion, the result of *C2* is closer to *M4*, which uses only the forward rate.

For premixed combustion, if the 19-reactions scheme is used the difference between the maximum temperature and the temperature at C8 is ca. 3%, while with the global scheme the difference is higher than 50%. For non-premixed combustion, the difference between T_{max} and T_{C8} is higher than 70% for both approaches.

Table V.21 Premixed and non-premixed combustion with the 19-reactions scheme.

H₂ Combustion with the 19-reactions Scheme								
	Species	$y_{in,left}$	$y_{in,right}$	$\bar{y}_{out}$	X_{H_2}	X_{O_2}	$T_{max}(\text{°C})$	$T_{C8}(\text{°C})$
<i>C1</i> $\theta = 0.25$	H	0.1	0.1	0	1	0.07	1070	1025
	O ₂	0.2	0.2	0.19				
	N ₂	0.7	0.7	0.76				
	H ₂ O	0	0	0.054				
	H ₂	0	0	0				
	O	0	0	0				
	OH	0	0	0				
	HO ₂	0	0	0				
	H ₂ O ₂	0	0	0				

B7 $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	1760	851
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
M2 $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	2030	851
	O ₂	0.2	0.2	0.16				
	N ₂	0.7	0.7	0.74				
	H ₂ O	0	0	0.11				
C2 $\theta = 0.27$	H	0.1	0	0	1	0.15	2520	663
	O ₂	0	0.2	0.086				
	N ₂	0.9	0.8	0.89				
	H ₂ O	0	0	0.029				
	H ₂	0	0	0				
	O	0	0	0				
	OH	0	0	0				
	HO ₂	0	0	0				
	H ₂ O ₂	0	0	0				
B10 $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	1670	560
	O ₂	0	0.2	0.071				
	N ₂	0.9	0.8	0.86				
	H ₂ O	0	0	0.066				
M4 $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	2320	550
	O ₂	0	0.2	0.066				
	N ₂	0.9	0.8	0.87				
	H ₂ O	0	0	0.064				

C1, C2 – Case with Maxwell, simulated with the 19-reactions scheme

B7, B10 – Cases with Maxwell, simulated with the global scheme, including the reverse rate

M2, M4 – Cases with Maxwell, simulated with the global scheme

The 19-reactions scheme is composed of 21 reactions (19 plus two double reactions, as shown in Section V.1.2.1). Table V.22 shows the maximum and minimum reaction rate for each reaction.

Table V.22 Maximum and minimum rate of each reaction.

Rate Amplitude				
	<i>C1</i>		<i>C2</i>	
<i>Reaction</i>	r_{min} (kmol/(m ³ s))	r_{max} (kmol/(m ³ s))	r_{min} (kmol/(m ³ s))	r_{max} (kmol/(m ³ s))
1	-4.67×10^0	1.56×10^{-1}	-1.11×10^0	2.38×10^0
2	-1.33×10^0	5.23×10^{-2}	-4.00×10^0	2.55×10^{-1}
3	-3.41×10^{-7}	9.82×10^{-1}	-2.51×10^0	1.32×10^0
4	-1.81×10^0	3.81×10^{-3}	-6.04×10^{-1}	1.09×10^{-1}
5	-1.89×10^0	6.37×10^{-14}	-5.68×10^0	2.11×10^{-15}
6	1.83×10^{-10}	4.06×10^{-3}	-2.53×10^{-20}	3.8×10^2
7	1.83×10^{-11}	1.60×10^0	-1.16×10^{-21}	1.45×10^{-3}
8	2.49×10^{-9}	4.58×10^1	-3.18×10^{-19}	4.69×10^{-1}
9	-8.70×10^{-6}	3.66×10^2	-1.22×10^{-6}	3.27×10^0
10	-1.01×10^{-8}	6.66×10^0	-6.94×10^{-10}	6.92×10^{-1}
11	-1.65×10^{-8}	4.32×10^1	-3.81×10^{-9}	3.50×10^{-2}
12	8.14×10^{-8}	7.58×10^{-1}	-6.10×10^{-15}	2.12×10^{-1}
13	2.62×10^{-6}	1.43×10^0	0	1.23×10^{-1}
14	-8.59×10^{-9}	8.98×10^{-4}	-2.47×10^{-5}	1.12×10^{-1}
15	-5.25×10^{-10}	6.04×10^{-4}	-1.55×10^{-7}	5.53×10^{-4}
16	-5.14×10^{-1}	6.02×10^{-6}	-1.20×10^{-2}	3.56×10^{-3}
17	-2.34×10^{-11}	4.31×10^{-1}	-3.88×10^{-21}	7.18×10^{-3}
18	-3.64×10^{-8}	5.67×10^{-2}	-5.57×10^{-8}	1.35×10^{-3}
19	1.19×10^{-10}	1.13×10^{-2}	-2.63×10^{-10}	2.30×10^{-3}
20	3.11×10^{-8}	1.81×10^{-2}	-3.31×10^{-9}	5.30×10^{-4}
21	7.75×10^{-11}	3.85×10^{-2}	-1.23×10^{-8}	8.15×10^{-3}

Figure V.58 shows the reaction rate map for the first reaction of *C1*, which is representative of all reactions since the aspect of the maps is similar.

Comparing *C1* with *B7* and *M2*, it is visible that the reaction front is in the beginning of the inlet channel, while in the global scheme the reaction front is in the first row of chambers. If the 19-reactions scheme is used, the maximum rate is lower and the reaction rate is close to zero inside most of the reactor, as shown in Figure V.58a. Differently, in the global scheme with the backward reaction, the reaction rate is negative inside most of the reactor; without the backward reaction, the reaction rate is close to zero, as shown in Figure V.58b and in Figure V.58c. In this way, the forward reaction is promoted if the 19-reactions scheme is used.

Table V.22 shows that in the first two reactions of *C1*, both the forward and backward reactions are promoted since the maximum and minimum rates differ one or two orders of magnitude, respectively. In the third reaction, only the forward reaction is promoted, since the maximum reaction rate differs six orders of magnitude in relation to the minimum rate, which is close to

zero; thus, the reaction is more "positive" than "negative". In contrast, in the fifth reaction, $\text{H}_2 + \text{M} = \text{H} + \text{H} + \text{M}$, the backward reaction is promoted, favouring the formation of H_2 . From the sixth to the thirteenth reactions, the forward reaction is promoted. The highest reaction rate is obtained in the ninth reaction, $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$. The fourteenth and fifteenth reactions, $\text{H} + \text{HO}_2 = \text{OH} + \text{OH}$, have a low reaction rate; thus, the production of OH is low. The formation of H_2O_2 occurs in the sixteenth reaction, $\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$, where the backward reaction is promoted. From the seventeenth to the last reactions, the forward reactions are promoted.

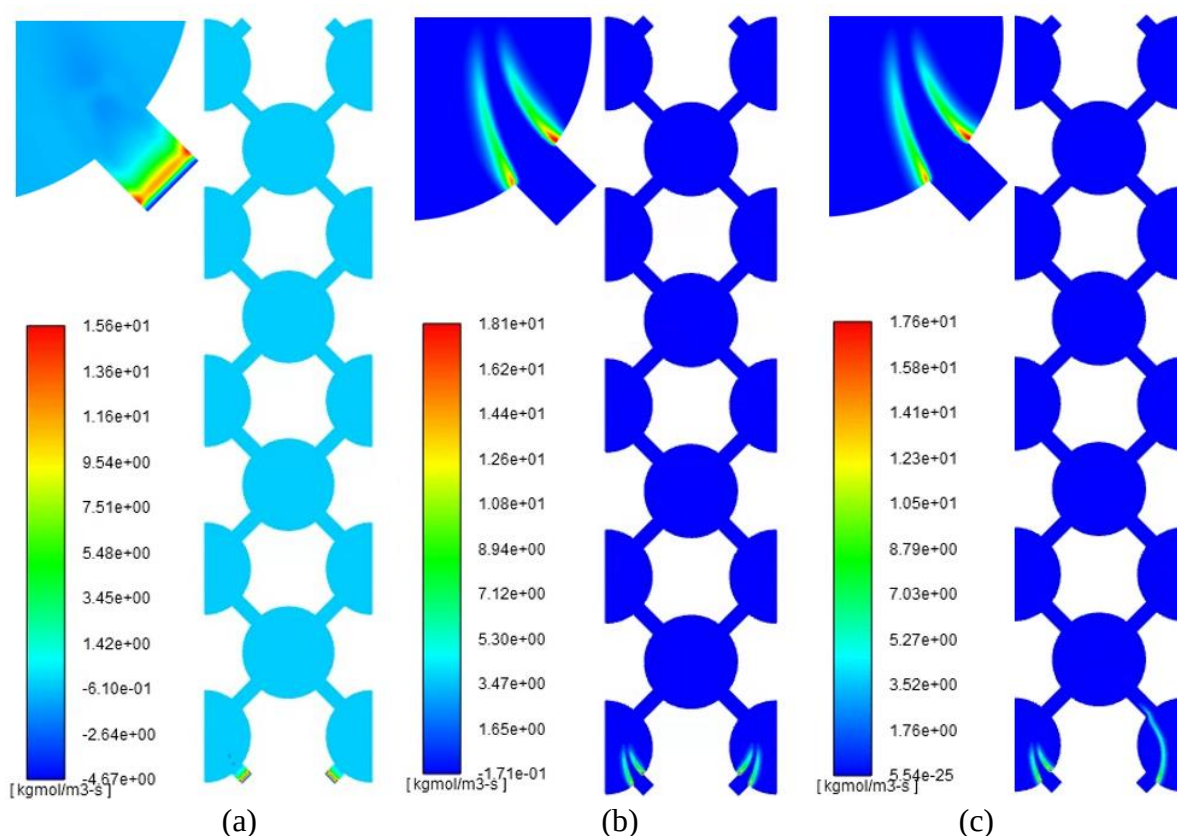


Figure V.58 Reaction rate maps of: (a) C1, (b) B7 and (c) M2.

In Figure V.59 are shown the temperature maps. It is visible that, as expected, the temperature rises after the reaction front. Differently from the global reaction scheme, if the 19-reactions scheme is used, there are no hotspots, and it is possible to maintain the temperature in most of the reactor.

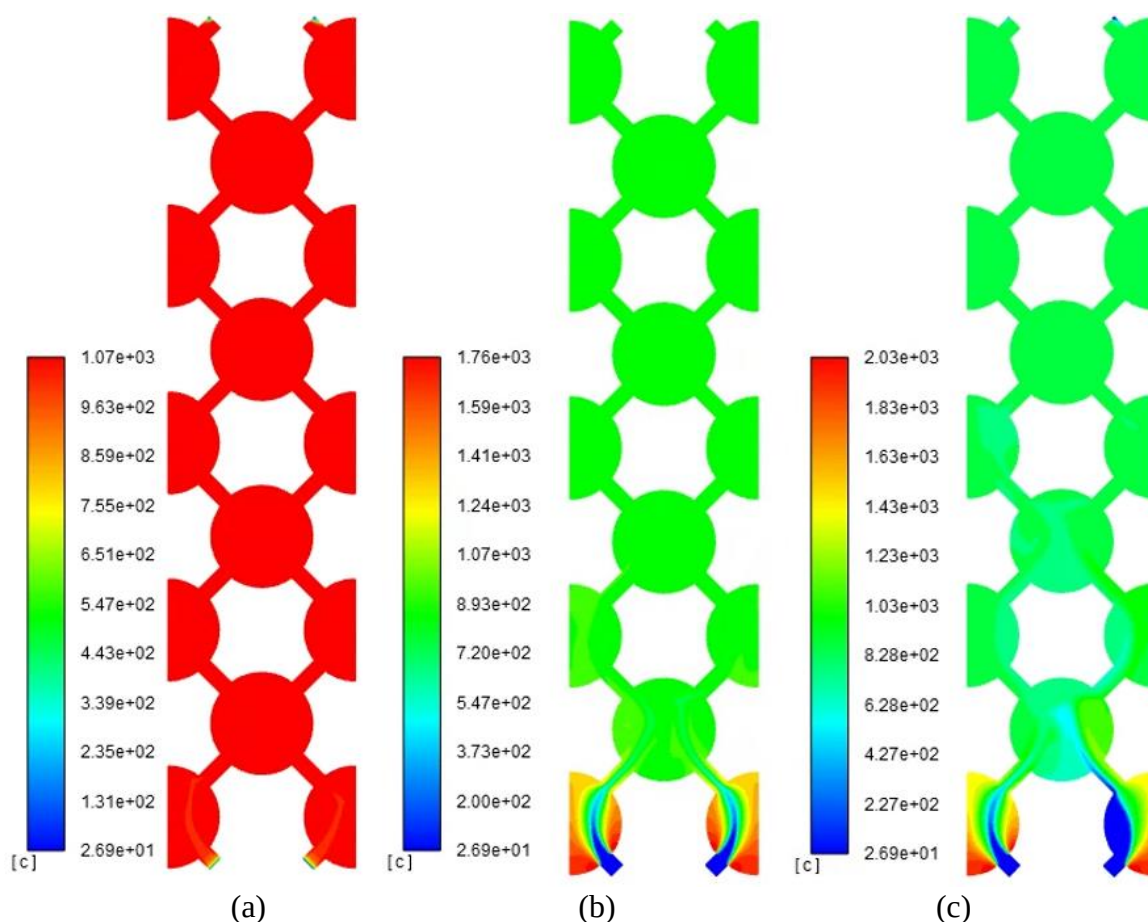


Figure V.59 Temperature maps of: (a) C2, (b) B7 and (c) M2.

In Figure V.60 are shown the reaction rate maps for non-premixed combustion. While for the global reaction scheme the reaction front is in the third row of chambers, for the 19-reactions scheme, C2, the maximum reaction front is in the first row of chambers. As visible, the maximum reaction rate is close for the three cases. In C2 and M4, the reaction rate is close to zero in most of the reactor; in B10 it is negative.

Table V.22 shows that in the first four reactions both the forward and backward reactions are promoted since they are of the same order of magnitude. In contrast, in the fifth reaction, $\text{H}_2 + \text{M} = \text{H} + \text{H} + \text{M}$, the backward reaction is promoted, favouring the formation of H_2 . From the sixth to the fourteenth reactions, the forward reaction is promoted. The highest reaction rate is obtained in the sixth reaction, $\text{O} + \text{O} + \text{M} = \text{O}_2 + \text{M}$. The fifteenth reaction, $\text{H} + \text{HO}_2 = \text{OH} + \text{OH}$, has a low reaction rate; thus, the production of OH is low. The formation of H_2O_2 occurs in the sixteenth reaction, $\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$, where the backward reaction is promoted. From the seventeenth to the last reactions, the forward reaction is promoted; however, they have a low rate in the order of $10^{-3} \text{ kmol}/(\text{m}^3 \text{ s})$ or $10^{-4} \text{ kmol}/(\text{m}^3 \text{ s})$.

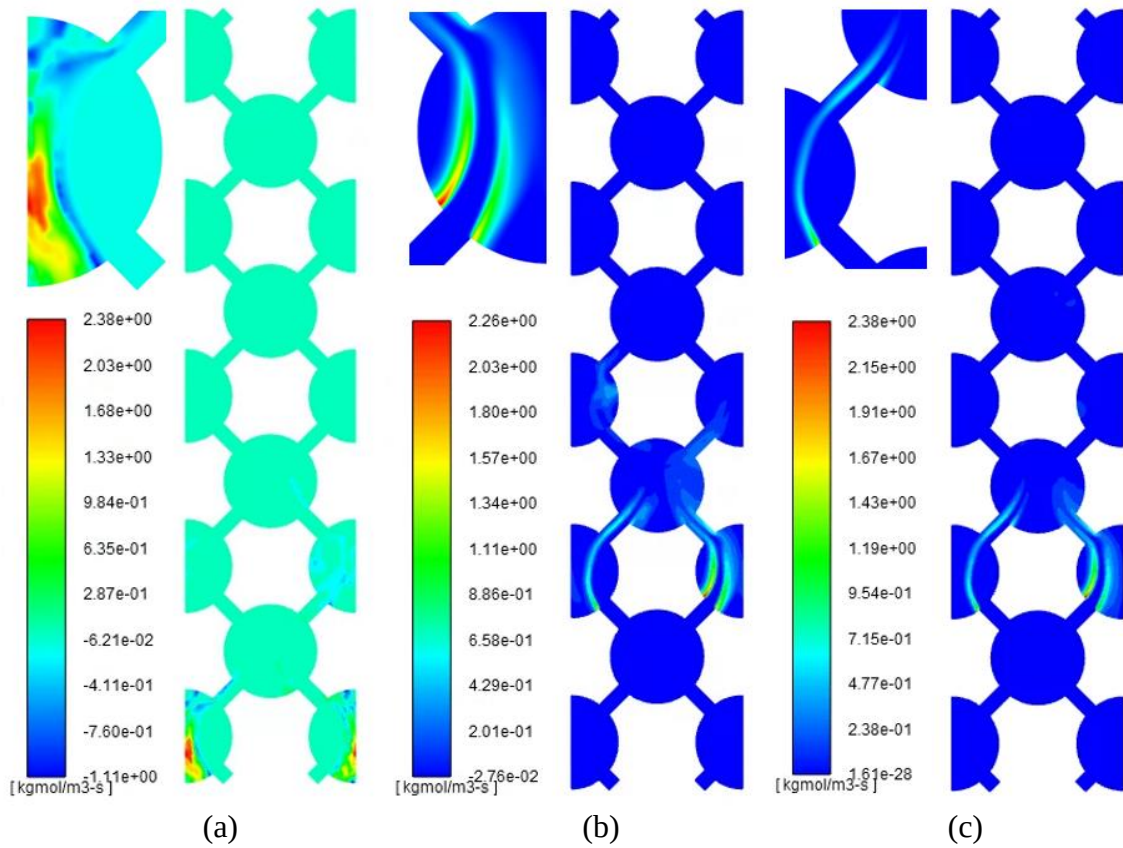


Figure V.60 Reaction rate maps of: (a) C_2 , (b) B_{10} and (c) M_4 .

In Figure V.61 are represented the temperature maps. It is visible that the maximum temperature is attained in the region of the maximum reaction rate. Differently from premixed combustion, in non-premixed, hotspots are present if the 19-reactions scheme is used. In non-premixed combustion the temperature is similar in the entire reactor, except in the hotspot.

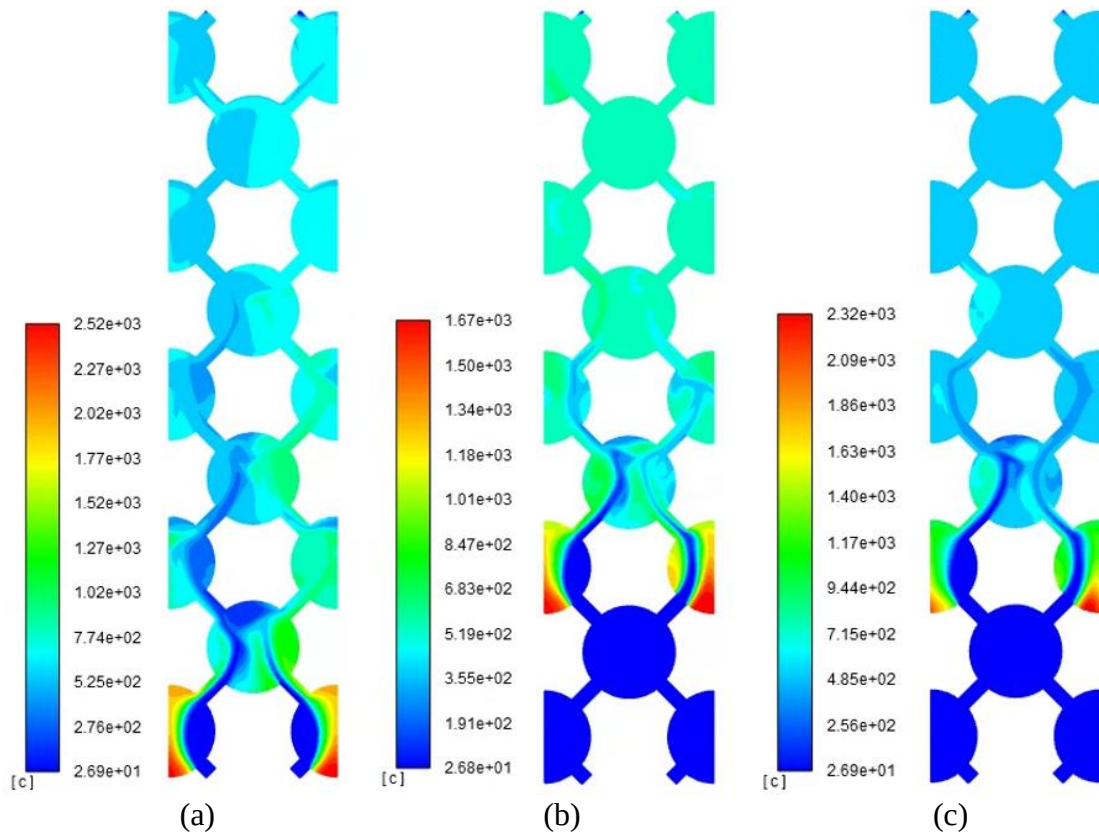


Figure V.61 Temperature maps of: (a) C3, (b) B10 and (c) M4.

V.3.3.1 Effect of Pressure-Dependent Reactions

In Section V.3.3, the complete 19-reactions scheme was used, including pressure-dependent reactions, as shown in Section V.1.2.1. To analyse the effect of these reactions, the Troe fall-off was not considered in *C1* and *C2*. The results, *C1p* and *C2p*, are compared with the original case.

The results are shown in Table V.23 where is visible that the prediction of the maximum temperature without the fall-of kinetics is less than 1% higher. The prediction of the temperature at C8 has ca. 1% difference to the original scheme in *C1p* and approximately 8% in *C2p*.

Table V.23 Combustion without fall-off.

Combustion without Fall-off								
	Species	$y_{in,left}$	$y_{in,right}$	$\bar{y}_{out}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$T_{C8}(^{\circ}C)$
<i>C1p</i> (no fall-off) $\theta = 0.25$	H	0.1	0.1	0	1	0.11	1090	1039
	O ₂	0.2	0.2	0.19				
	N ₂	0.7	0.7	0.75				
	H ₂ O	0	0	0.057				
	H ₂	0	0	0				
	O	0	0	0				
	OH	0	0	0				
	HO ₂	0	0	0				
	H ₂ O ₂	0	0	0				

C1 $\theta = 0.25$	H	0.1	0.1	0	1	0.07	1070	1025
	O ₂	0.2	0.2	0.19				
	N ₂	0.7	0.7	0.76				
	H ₂ O	0	0	0.054				
	H ₂	0	0	0				
	O	0	0	0				
	OH	0	0	0				
	HO ₂	0	0	0				
	H ₂ O ₂	0	0	0				
C2p (no fall-off) $\theta = 0.27$	H	0.1	0	0	1	0.11	2540	590
	O ₂	0	0.2	0.090				
	N ₂	0.9	0.8	0.88				
	H ₂ O	0	0	0.023				
	H ₂	0	0	0				
	O	0	0	0				
	OH	0	0	0				
	HO ₂	0	0	0				
	H ₂ O ₂	0	0	0				
C2 $\theta = 0.27$	H	0.1	0	0	1	0.15	2520	663
	O ₂	0	0.2	0.086				
	N ₂	0.9	0.8	0.89				
	H ₂ O	0	0	0.029				
	H ₂	0	0	0				
	O	0	0	0				
	OH	0	0	0				
	HO ₂	0	0	0				
	H ₂ O ₂	0	0	0				

C1p, C2p – Cases with Maxwell, simulated with the 19-reactions scheme without fall-off

C1, C2 – Cases with Maxwell, simulated with the 19-reactions scheme

In Figure V.62 and in Figure V.63 are shown the maps for premixed and non-premixed combustion with and without fall-off. In similarity to the original case, *C1*, if the fall-off is not considered, *C1p*, the reaction front occurs in the first row of chambers. The reaction rate of the first reaction is ca. 40% higher in *C1p*, as shown in Figure V.62c and in Figure V.62d. For both cases, the temperature rises after the reaction front and is maintained nearly constant in the rest of the reactor, as visible in Figure V.62a and in Figure V.62b.

In similarity to *C2*, in *C2p*, the reaction front is in the first chamber. The maximum reaction rate is ca. 35% lower if the fall-off is not considered, as shown in Figure V.63c and in Figure V.63d. For both approaches, a hotspot is present at the left (oxygen) side of the half chambers of the first row where the maximum temperature is attained. The temperature inside reactor decreases then towards the outlet, as shown in Figure V.63a and in Figure V.63b.

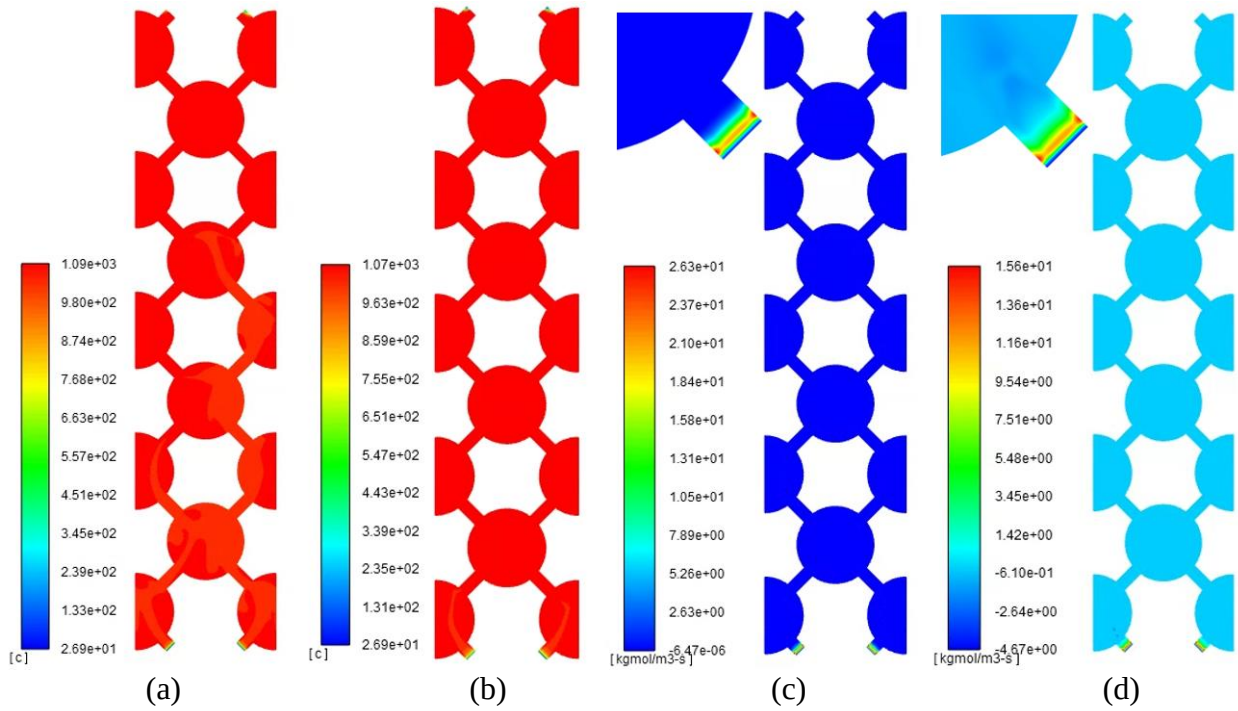


Figure V.62 Temperature maps of: (a) $C1p$ and (b) $C1$. Reaction rate maps of reaction 1 of: (c) $C2p$ and (d) $C2$.

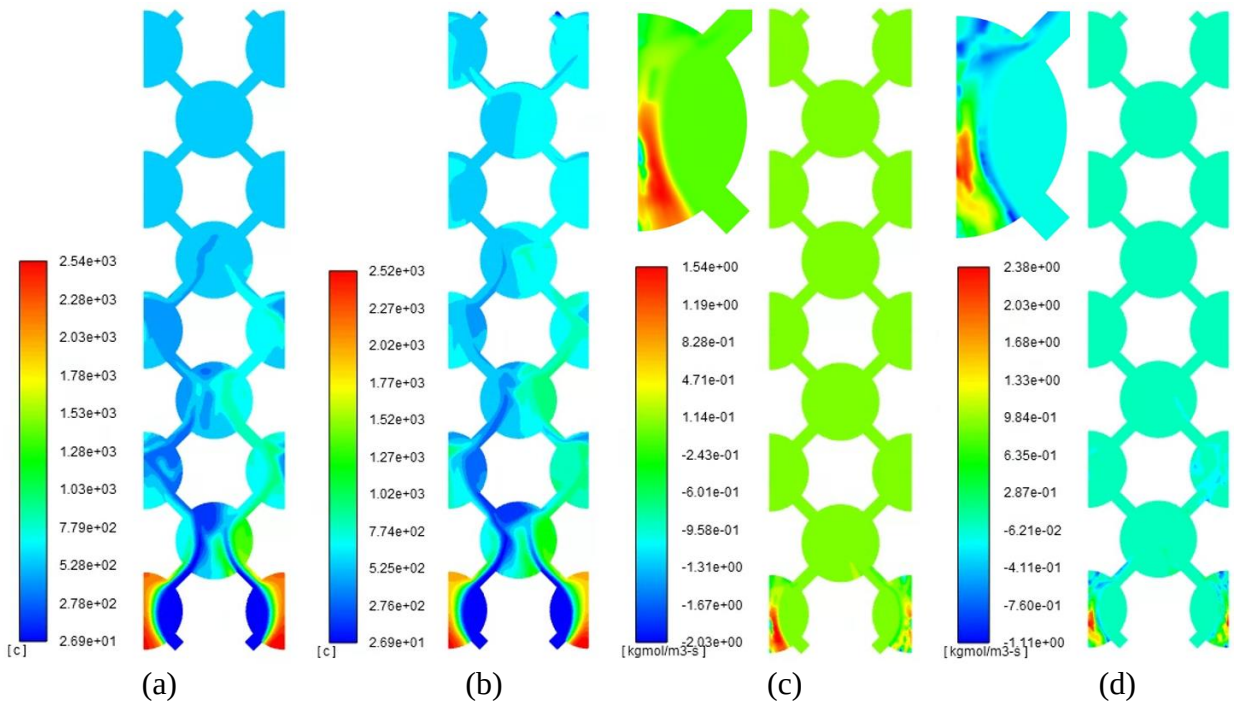


Figure V.63 Temperature maps of: (a) $C2p$ and (b) $C2$. Reaction rate maps of reaction 1 of: (c) $C2p$ and (d) $C2$.

V.4 Lamellar Micromixing Model for Combustion

In this section, the Lamellar Micromixing Model (see section V.1.3.3) will be adapted for combustion reactions and applied to the NETmix chambers.

As shown in Section V.1.3.3, the Lamellar Micromixing Model can be expressed through

$$\frac{\partial C_i}{\partial t} + \psi x \frac{\partial C_i}{\partial x} = \mathcal{D}_i \frac{\partial^2 C_i}{\partial x^2} + r c_i \quad (\text{V.64})$$

in which C_i is the concentration, $\mathcal{D}_i$ is the diffusion coefficient and $r c_i$ is the rate of production of species. $\psi(\mathbf{X}, t) = -(\mathbf{D} : \mathbf{nn})$ is the stretching function, where $\mathbf{D}$ is the stretching tensor and $\mathbf{n}$ is the direction of the mass transfer which is normal to the surface (Ranz 1979, Ottino 1979, Ottino 1980, Chella and Ottino 1984).

Considering a change of variable, $Z = x/S(t)$, in which $S(t)$ is the striation thickness, the Lamellar Micromixing Model equation assumes the form

$$\frac{\partial C_i}{\partial t} = \mathcal{A}(t)Z \frac{\partial C_i}{\partial Z} + \frac{\mathcal{D}_i}{S(t)^2} \frac{\partial^2 C_i}{\partial Z^2} + r c_i \quad (\text{V.65})$$

in which $\mathcal{A}(t) = -\frac{\partial \ln(S(t))}{\partial t}$ is a stretching function (Ottino 1980, Ottino 1982).

The Lamellar Micromixing Model for Combustion was based on the Flamelet models. The composition of the mixture and temperature equations are given by

$$\frac{\partial C_i}{\partial t} = \mathcal{A}(t)Z \frac{\partial C_i}{\partial Z} + \frac{\mathcal{D}_i}{S(t)^2} \frac{\partial^2 C_i}{\partial Z^2} + r c_i \quad (\text{V.66a})$$

$$\frac{\partial T}{\partial t} = \mathcal{A}(t)Z \frac{\partial T}{\partial Z} + \frac{\mathcal{D}_i \text{Le}_i}{S(t)^2} \frac{\partial^2 T}{\partial Z^2} - \frac{1}{c_{p_M}} \sum_{i=1}^n h_i r c_i \quad (\text{V.66b})$$

where Le_i is the Lewis number, which relates the thermal diffusivity with the mass diffusivity. In fully turbulent or flamelet regimes, the diffusivities are considered equal for all the species, and $\text{Le} = \frac{\lambda}{\rho \mathcal{D} c_p} = 1$ (see Section V.1.3). c_{p_M} is the specific heat capacity of the mixture, h_i and $r c_i$ are the specific enthalpy and production rate of each element i of the mixture, respectively.

V.4.1 Application to the NETmix Chambers

V.4.1.1 Model Implementation

The Lamellar Micromixing Model for Combustion was applied to the global reaction of hydrogen combustion, $\text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O}$. The system of equations is given by,

$$\frac{\partial C_{\text{H}_2}}{\partial t} = \mathcal{A}(t)Z \frac{\partial C_{\text{H}_2}}{\partial Z} + \frac{\mathcal{D}_{\text{H}_2-\text{Air}}}{S(t)^2} \frac{\partial^2 C_{\text{H}_2}}{\partial Z^2} + r c_{\text{H}_2} \quad (\text{V.67a})$$

$$\frac{\partial C_{O_2}}{\partial t} = \alpha(t)Z \frac{\partial C_{O_2}}{\partial Z} + \frac{\mathcal{D}_{H_2-Air}}{S(t)^2} \frac{\partial^2 C_{O_2}}{\partial Z^2} + r_{C_{O_2}} \quad (V.67b)$$

$$\frac{\partial C_{H_2O}}{\partial t} = \alpha(t)Z \frac{\partial C_{H_2O}}{\partial Z} + \frac{\mathcal{D}_{H_2-Air}}{S(t)^2} \frac{\partial^2 C_{H_2O}}{\partial Z^2} + r_{C_{H_2O}} \quad (V.67c)$$

$$\frac{\partial C_{N_2}}{\partial t} = \alpha(t)Z \frac{\partial C_{N_2}}{\partial Z} + \frac{\mathcal{D}_{H_2-Air}}{S(t)^2} \frac{\partial^2 C_{N_2}}{\partial Z^2} \quad (V.67d)$$

$$\frac{\partial T}{\partial t} = \alpha(t)Z \frac{\partial T}{\partial Z} + \frac{\mathcal{D}_{H_2-Air}}{S(t)^2} \frac{\partial^2 T}{\partial Z^2} - \frac{1}{\rho_M c_{p_M}} (h_{H_2} r_{C_{H_2}} + h_{O_2} r_{C_{O_2}} + h_{H_2O} r_{C_{H_2O}}) \quad (V.67e)$$

in which $\mathcal{D}_{H_2-Air} = 2.88 \times 10^{-5} \text{ m}^2/\text{s}$ (Ansys 2021), and ρ_M is the molar density of the mixture.

In similarity to Section V.3.2, the global scheme of the hydrogen combustion was used, with $r = kfC_{H_2}C_{O_2}$. The Arrhenius parameters for the calculation of kf (Equation V.4a) are $A = 9.87 \times 10^8 \text{ m}^3/(\text{kmols})$, $b = 0$ and $E_a = 3.10 \times 10^7 \text{ J/kmol}$ (Ansys 2021). The reaction rate of each species is $r_{C_{H_2}} = -r$, $r_{C_{O_2}} = -0.5r$ and $r_{C_{H_2O}} = r$, respectively.

In the previous equations, $S(t)$ is obtained from LMS, through the relation proposed by Ranz (1979), $\ln(\alpha) = \ln\left(\frac{S}{S_0}\right)$ (Equation III.21). In section V.2.1, it was shown that the interfacial area generation, α , in chamber C6 of NETmix (considering gaseous mixtures) is given by $\alpha = 66e^{295t}$ ($R^2 = 0.99$). In this way, the striation thickness is expressed by $S = S_0 e^{-\ln(66e^{295t})}$, and the stretching function is $\alpha(t) = -\frac{\partial \ln(S_0 e^{-\ln(66e^{295t})})}{\partial t} = -295 \text{ s}^{-1}$.

The Lamellar Micromixing Model for Combustion was used to predict the temperature in premixed and non-premixed hydrogen combustion inside NETmix. For that, a normalized 1D domain (0 to 1) was considered to represent the flow in one NETmix chamber.

To solve the system of Partial Differential Equations, PDE, (Equation V.61), the MATLAB[®] function *pdepe* was used. For that, the 1D domain was discretized considering $\Delta x = 10^{-3}$. The time step, $\Delta t = 7.8 \times 10^{-6} \text{ s}$, was the same as Section V.2 (ExtendedNUB simulation for gases at $Re = 300$).

As shown in section V.2.1, the interfacial area generation was calculated during 3τ , corresponding to 0.224 s flow time, which was used as the final time of the simulation with the Lamellar Micromixing Model for Combustion.

The 1D domain was initialized uniformly, according to

$$\begin{aligned}
C_{\text{H}_2}(Z, 0) &= C_{\text{H}_2}^i \\
C_{\text{O}_2}(Z, 0) &= C_{\text{O}_2}^i \\
C_{\text{N}_2}(Z, 0) &= C_{\text{N}_2}^i \\
C_{\text{H}_2\text{O}}(Z, 0) &= 0 \\
T(Z, 0) &= T^i
\end{aligned} \tag{V.68}$$

in which $C_{\text{H}_2}^i$, $C_{\text{O}_2}^i$ and $C_{\text{N}_2}^i$ are the initial concentrations of the reactants. T^i is the initial temperature, which is set to the hydrogen ignition temperature, 585 °C, since the Lamellar Micromixing Model for Combustion can only be applied to combustion in flame mode.

The boundary conditions consider the gradient of concentrations at the edge of a single stria zero,

$$\begin{aligned}
\left. \frac{\partial C_{\text{H}_2}}{\partial Z} \right|_{Z=0; 1} &= 0 \\
\left. \frac{\partial C_{\text{O}_2}}{\partial Z} \right|_{Z=0; 1} &= 0 \\
\left. \frac{\partial C_{\text{H}_2\text{O}}}{\partial Z} \right|_{Z=0; 1} &= 0 \\
\left. \frac{\partial C_{\text{N}_2}}{\partial Z} \right|_{Z=0; 1} &= 0 \\
\left. \frac{\partial T}{\partial Z} \right|_{Z=0; 1} &= 0
\end{aligned} \tag{V.69}$$

Thermodynamic Properties

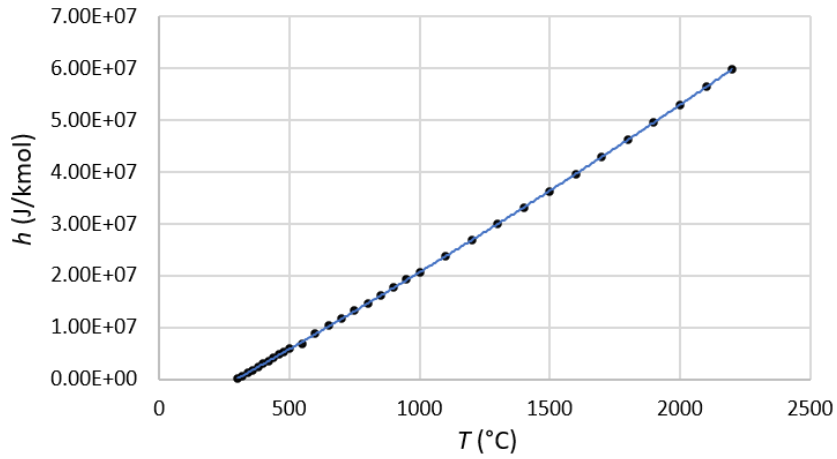
The enthalpy of each species is obtained from data points (Perry and Green 1997) to which a polynomial fitting was made ($R^2 = 0.999$). The variation of h with T is given by

$$h_{\text{H}_2} = 1.73T^2 + 2.71 \times 10^4 T - 8.16 \times 10^6 \tag{V.70a}$$

$$h_{\text{O}_2} = 2.19T^2 + 2.99 \times 10^4 T - 9.32 \times 10^6 \tag{V.70b}$$

$$h_{\text{H}_2\text{O}} = 5.54T^2 + 3.00 \times 10^4 T - 9.49 \times 10^6 \tag{V.70c}$$

As an example, the plot of h is shown in Figure V.64 for H_2 .

Figure V.64 Evolution of the H₂ Enthalpy with the temperature.

The specific heat of each compound was calculated according to

$$c_p = C1 + c2 \left(\frac{c3}{T} / \sinh\left(\frac{c3}{T}\right) \right)^2 + c4 \left(\frac{c5}{T} / \cosh\left(\frac{c5}{T}\right) \right)^2 \quad (\text{V.71})$$

in which $C1$, $C2$, $C3$ and $C4$ are parameters (Perry and Green 1997), listed in Table V.24.

Table V.24 Specific heat parameters.

Specific Heat				
	H ₂	O ₂	H ₂ O	N ₂
$C1$	27620	29100	33360	29110
$C2$	9560	10040	26790	8610
$C3$	2466	2526.5	2610.5	1701.6
$C4$	3760	9360	8900	100
$C5$	567.6	1153.8	1169	909.79

A polynomial fitting ($R^2 = 0.999$) was made and the expressions of the variation of c_p with T are given by

$$c_{p_{H_2}} = 2.16 \times 10^{-12}T^5 - 1.40 \times 10^{-8}T^4 + 3.10 \times 10^{-5}T^3 - 2.96 \times 10^{-2}T^2 + 1.35 \times 10^1T + 2.68 \times 10^4 \quad (\text{V.72a})$$

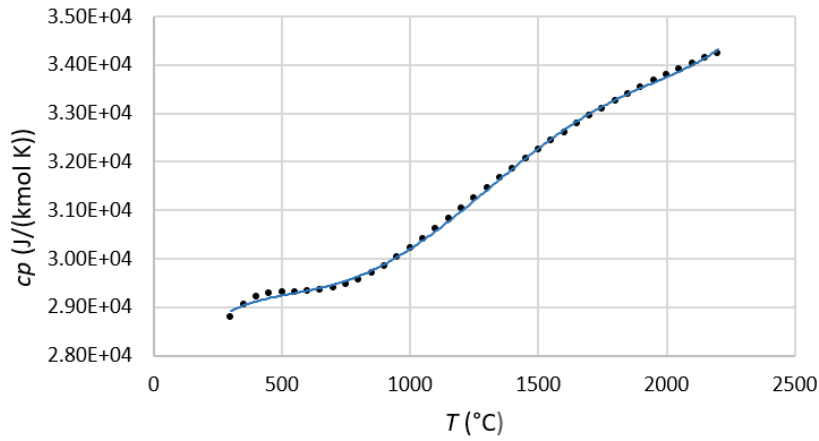
$$c_{p_{O_2}} = 1.25 \times 10^{-6}T^3 - 7.44 \times 10^{-3}T^2 + 1.62 \times 10^1T - 2.49 \times 10^4 \quad (\text{V.72b})$$

$$c_{p_{H_2O}} = -2.08 \times 10^{-6}T^3 + 6.11 \times 10^{-3}T^2 + 6.26T + 3.09 \times 10^4 \quad (\text{V.72c})$$

$$c_{p_{N_2}} = 2.01 \times 10^{-9}T^4 - 1.09 \times 10^{-5}T^3 + 1.88 \times 10^{-2}T^2 - 7.01T + 2.97 \times 10^4 \quad (\text{V.72d})$$

$$c_{p_M} = y_{H_2}c_{p_{H_2}} + y_{O_2}c_{p_{O_2}} + y_{H_2O}c_{p_{H_2O}} + y_{N_2}c_{p_{N_2}} \quad (\text{V.72e})$$

As an example, the plot of c_p is shown in Figure V.65 for H₂.

Figure V.65 Evolution of the H₂ specific heat with the temperature.

The density of the mixture was obtained from the incompressible ideal gas law (Ansys 2021),

$$\rho_M = \frac{p}{RT} \quad (\text{V.73})$$

in which the operating pressure is $p = 10^5$ Pa and the ideal gas constant is $R = 8314$ J/(kmol K). A polynomial fitting was made ($R^2 = 0.999$) and the expression of the variation of ρ_M with T is given by

$$\rho_M = -1.47 \times 10^{-17}T^5 + 1.03 \times 10^{-13}T^4 - 2.82 \times 10^{-10}T^3 + 3.84 \times 10^{-7}T^2 - 2.72 \times 10^{-4}T + 9.32 \times 10^{-2} \quad (\text{V.74})$$

The plot of ρ_M is shown in Figure V.66.

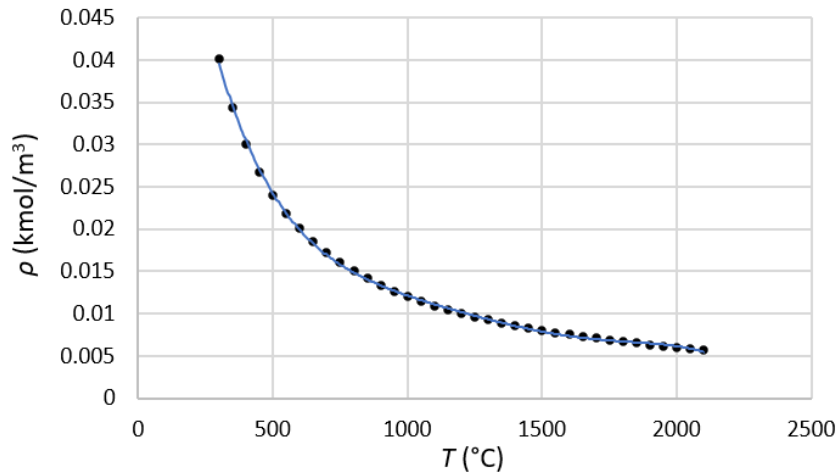


Figure V.66 Evolution of the mixture density with the temperature.

V.4.1.2 Premixed Combustion

To apply the Lamellar Micromixing Model for Combustion in the NETmix chambers, premixed cases, $L1$ to $L5$, were simulated. As visible in Table V.25, the reactive mixtures have $Ka < 1$; thus, the flamelet regime assumptions can be applied (see Section V.1.3).

The results were compared with the CFD simulations presented in Section V.3.2.2, which considered a mass diffusivity, $\mathcal{D} = 2.88 \times 10^{-5} \text{ m}^2/\text{s}$, and used the incompressible-ideal-gas law for the prediction of the mixture density in similarity to the Lamellar Micromixing Model for Combustion. The results are presented in Table V.25 which shows that the outlet molar fractions are similar for both models. The prediction of the temperature at C8, which has a dynamic behaviour close to C6 in which LMS was applied to obtain $\alpha(t)$ and $S(t)$, has a maximum 12% difference between the two models (ca. 3%, 1%, 11%, 5%, 12%, for each case, respectively). The case with the largest difference is *L5* and the closest result is *L1*.

In general, it is possible to conclude that the Lamellar Micromixing Model for Combustion provides a good prediction of combustion in NETmix. In fact, the difference to the CFD results is small, considering the large differences between the two models, as well as the simplifications that were made to the original Lamellar Micromixing Model and the thermodynamic assumptions.

Table V.25 Simulation of premixed combustion with the Lamellar Micromixing Model for Combustion.

Premixed Combustion					
	Species	$y_{in,left}$	$y_{in,right}$	$\bar{t}_{out}$	$T_{C8}(^{\circ}\text{C})$
L1 Ka = 0.33 $\theta = 0.2$	H ₂	0.2	0.2	0	1600
	O ₂	0.5	0.5	0.44	
	N ₂	0.3	0.3	0.33	
	H ₂ O	0	0	0.22	
S4 (ExtendedNUB) Ka = 0.33 $\theta = 0.2$	H ₂	0.2	0.2	0	1549
	O ₂	0.5	0.5	0.44	
	N ₂	0.3	0.3	0.33	
	H ₂ O	0	0	0.22	
L2 Ka = 0.27 $\theta = 0.5$	H ₂	0.2	0.2	0	1535
	O ₂	0.2	0.2	0.11	
	N ₂	0.6	0.6	0.67	
	H ₂ O	0	0	0.22	
S5 (ExtendedNUB) Ka = 0.27 $\theta = 0.5$	H ₂	0.2	0.2	0	1545
	O ₂	0.2	0.2	0.11	
	N ₂	0.6	0.6	0.67	
	H ₂ O	0	0	0.22	
L3 Ka = 0.58 $\theta = 0.167$	H ₂	0.1	0.1	0	725
	O ₂	0.3	0.3	0.26	
	N ₂	0.6	0.6	0.63	
	H ₂ O	0	0	0.11	
S6 (ExtendedNUB) Ka = 0.58 $\theta = 0.167$	H ₂	0.1	0.1	0	832
	O ₂	0.3	0.3	0.26	
	N ₂	0.6	0.6	0.63	
	H ₂ O	0	0	0.11	

L4 Ka = 0.70 $\theta = 0.25$	H ₂	0.1	0.1	0	805
	O ₂	0.2	0.2	0.16	
	N ₂	0.7	0.7	0.74	
	H ₂ O	0	0	0.11	
S7 (ExtendedNUB) Ka = 0.70 $\theta = 0.25$	H ₂	0.1	0.1	0	864
	O ₂	0.2	0.2	0.16	
	N ₂	0.7	0.7	0.74	
	H ₂ O	0	0	0.11	
L5 Ka = 0.50 $\theta = 0.125$	H ₂	0.1	0.1	0	702
	O ₂	0.4	0.4	0.37	
	N ₂	0.5	0.5	0.53	
	H ₂ O	0	0	0.11	
S8 (ExtendedNUB) Ka = 0.250 $\theta = 0.125$	H ₂	0.1	0.1	0	823
	O ₂	0.4	0.4	0.37	
	N ₂	0.5	0.5	0.53	
	H ₂ O	0	0	0.11	

L1 to L5 – Premixed cases, simulated with the Lamellar Micromixing Model for Combustion

S4 to S8 – Premixed cases, simulated with CFD, using Fick and constant properties

As an example, the histories of temperature and average molar fractions of *L1* are presented in Figure V.67. It is visible that the temperature rises and attains a first value, ca. 1060 °C, as shown in Figure V.67b, which coincides with the consumption of the reactants and the water formation (see Figure V.67a). The temperature continues then to increase reaching 1600 °C, as visible in Figure V.67c and in Figure V.67d.

Case *L1* was used for illustration purposes. The map of the temperature is shown in Figure V.68 and the maps of the molar fractions are shown in Figure V.69. It is visible that the initial molar fractions are uniform in the entire domain as well as the initial temperature, which was set at the hydrogen ignition temperature, 585 °C. As the reaction occurs, the temperature increases as shown in Figure V.68. The molar fraction of the reactants decreases, and the molar fraction of water increases. The molar fraction of N₂ is nearly constant, as shown in Figure V.69.

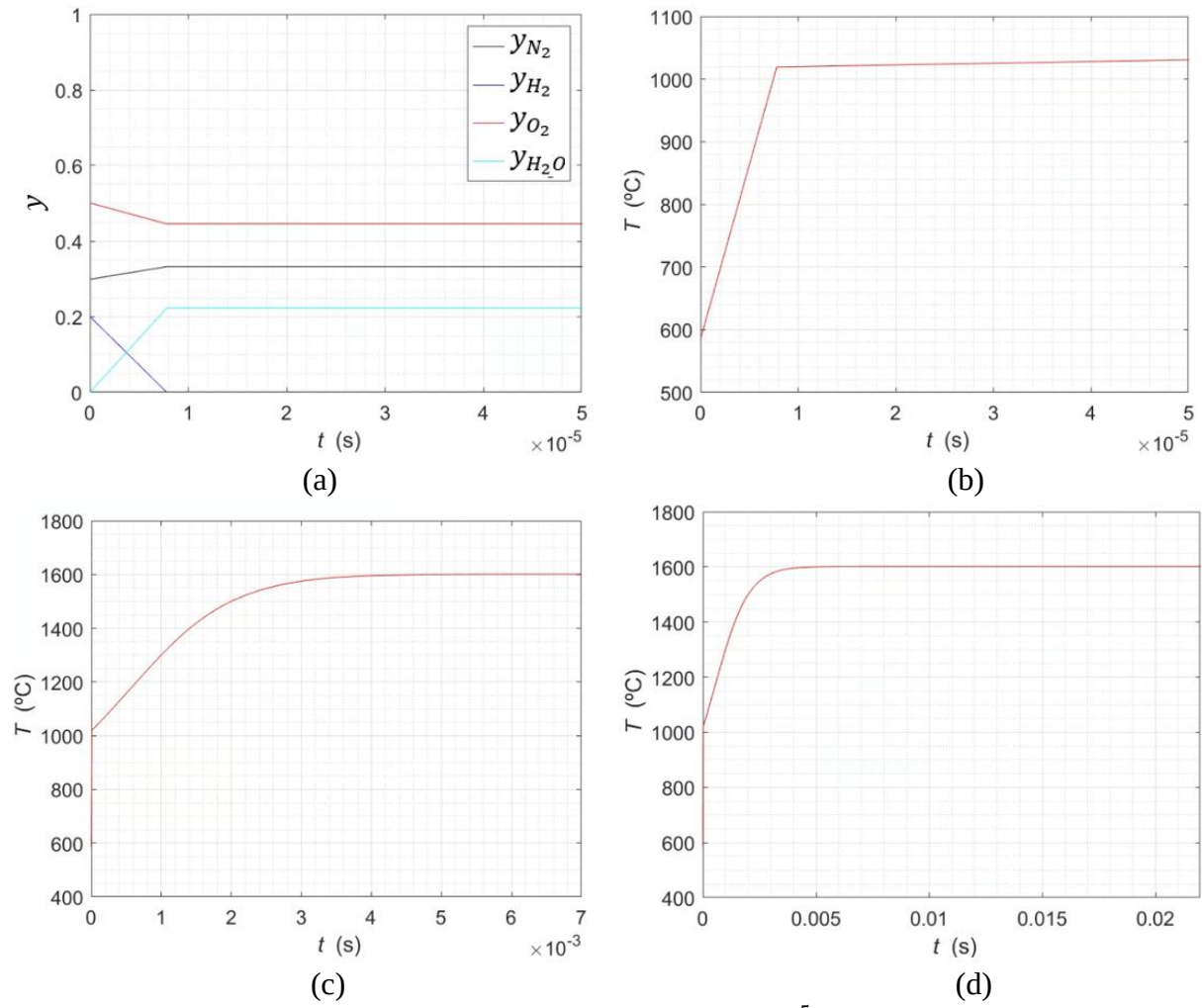


Figure V.67 (a) History of the average molar fractions of $L1$ during 5×10^{-5} s. Histories of temperature during: (b) 5×10^{-5} s, (c) 7×10^{-5} s, and (d) 0.022 s.

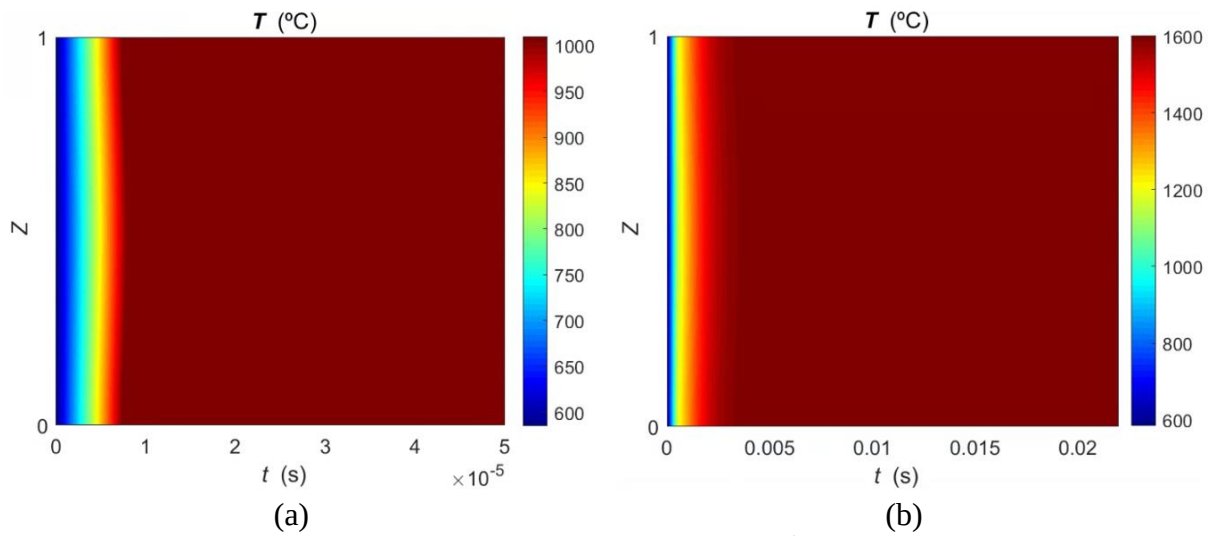
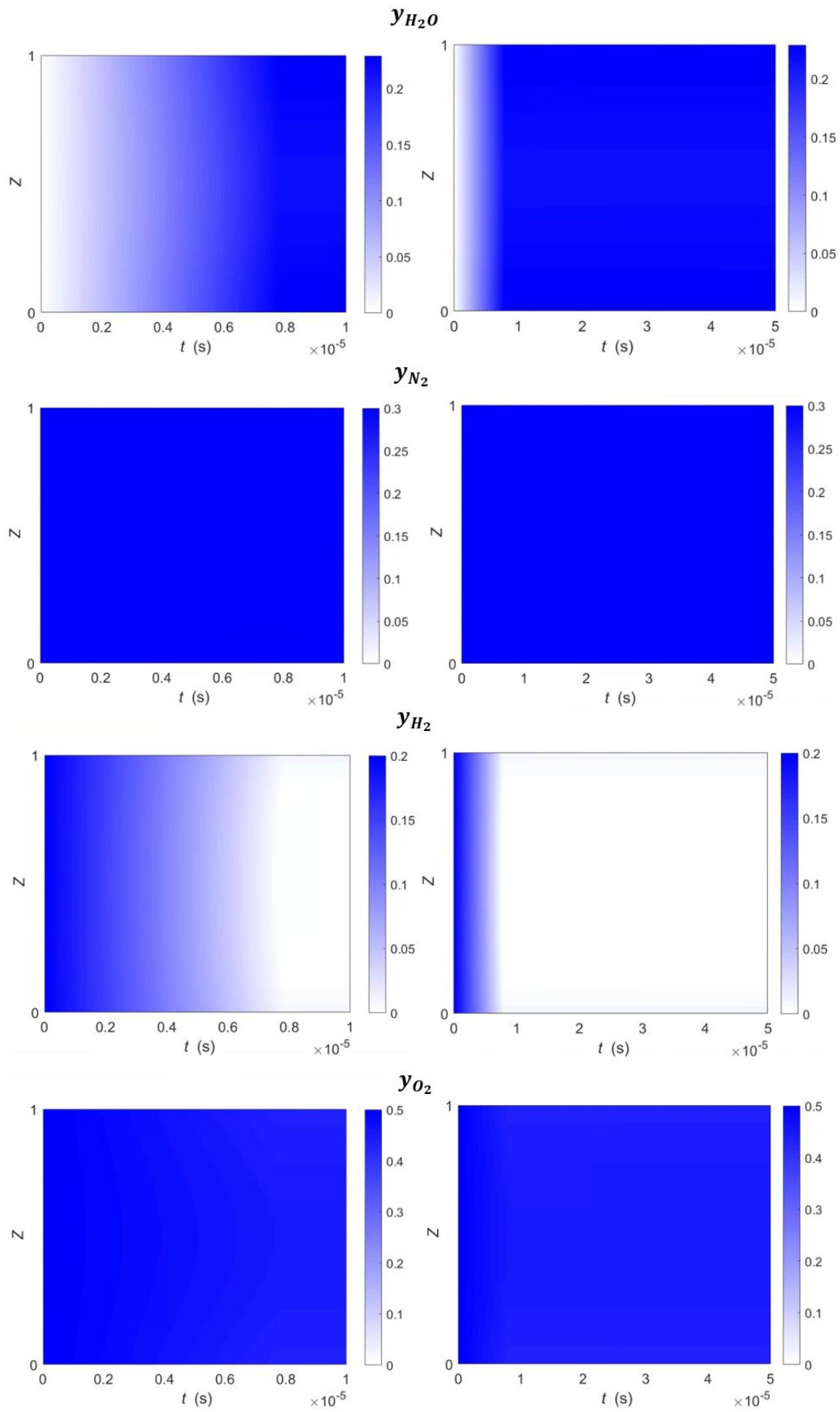


Figure V.68 Temperature maps of $L1$ at: (a) 5×10^{-5} s and (b) 0.022 s.

Figure V.69 Molar fraction maps of $L1$.

The evolution of the striation thickness with the flow time was analysed. The history of S is shown in Figure V.70, in which is visible that, as expected, S decreases as the interfacial area generation increases (see Section V.2.1).

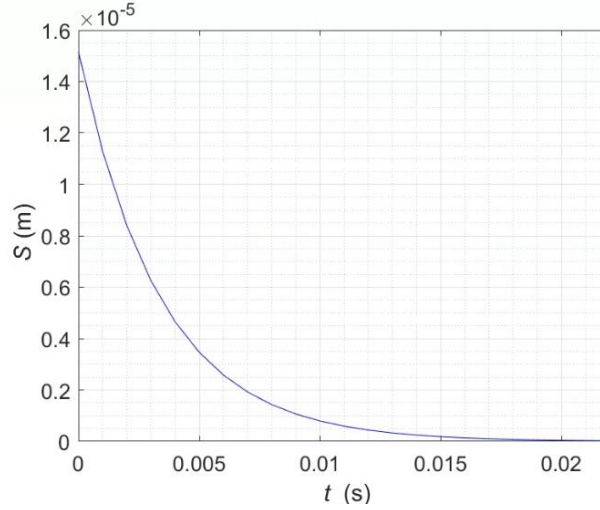


Figure V.70 History of the striation thickness.

V.4.1.3 Non-premixed Combustion

Three non-premixed cases, $L6$ to $L8$, were simulated as shown in Table V.26. The non-premixed reactive mixtures that were analysed in previous chapters of this work were used: a fuel stream at the left of the domain and an air stream at the right of the domain. The fuel stream was enriched in fuel from 0.1 to 0.9 (molar fraction) in $L6$ to $L8$, respectively. In order to set the initial concentration of the reactive mixture, a Heaviside function, *heaviside*, was used in the initial condition:

$$\begin{aligned}
 C_{H_2}(Z, 0) &= C_{H_2}^l \text{heaviside}(Z) + C_{H_2}^r \text{heaviside}(-Z) \\
 C_{O_2}(Z, 0) &= C_{O_2}^l \text{heaviside}(Z) + C_{O_2}^r \text{heaviside}(-Z) \\
 C_{N_2}(Z, 0) &= C_{N_2}^l \text{heaviside}(Z) + C_{N_2}^r \text{heaviside}(-Z) \\
 C_{H_2O}(Z, 0) &= 0 \\
 T(Z, 0) &= T^i(\text{heaviside}(Z) + \text{heaviside}(-Z))
 \end{aligned} \tag{V.75}$$

in which $C_{H_2}^l$, $C_{H_2}^r$, $C_{O_2}^l$, $C_{O_2}^r$, $C_{N_2}^l$ and $C_{N_2}^r$ are the initial concentrations of the reactants at the left, l , and right, r , sides of the domain. T^i is the initial temperature, which is uniform in the entire domain. To apply the *heaviside* function, Z varied between -0.5 and 0.5 (the domain was then normalized between 0 and 1 to represent the results).

As shown in Table V.26, it is visible that $L6$ has the lowest temperature at C8 since the oxygen is in excess. In contrast, $L7$ and $L8$ have higher temperatures since the fuel is in excess.

The difference to the CFD results is similar to the premixed cases, 12% between *L6* and *S10p*, and 4% between *L8* and *S12p*. The difference between *L7* and *S11p* is expectable since the Lamellar Micromixing Model for Combustion does not predict hotspots. Moreover, the comparison was performed with a CFD case with variable mass diffusivity.

Table V.26 Simulation of non-premixed combustion with the Lamellar Micromixing Model for Combustion.

Non-premixed Combustion					
	Species	$y_{in,left}$	$y_{in,right}$	$\overline{y_{out}}$	$T_{c8}(^{\circ}\text{C})$
<i>L6</i> $Ka = 1.38$ $\theta = 0.27$	H ₂	0.1	0	0	633
	O ₂	0	0.2	0.075	
	N ₂	0.9	0.8	0.87	
	H ₂ O	0	0	0.053	
<i>S10p</i> (ExtendedNUB) $Ka = 1.38$ $\theta = 0.27$	H ₂	0.1	0	0	525
	O ₂	0	0.2	0.075	
	N ₂	0.9	0.8	0.87	
	H ₂ O	0	0	0.053	
<i>L7</i> $Ka = 0.72$ $\theta = 2.14$	H ₂	0.5	0	0.14	836
	O ₂	0	0.2	0	
	N ₂	0.5	0.8	0.68	
	H ₂ O	0	0	0.18	
<i>S11p</i> (ExtendedNUB) $Ka = 0.72$ $\theta = 2.14$	H ₂	0.5	0	0.14	1349
	O ₂	0	0.2	0	
	N ₂	0.5	0.8	0.68	
	H ₂ O	0	0	0.18	
<i>L8</i> $Ka = 0.98$ $\theta = 8.99$	H ₂	0.9	0	0.63	814
	O ₂	0	0.2	0	
	N ₂	0.1	0.8	0.27	
	H ₂ O	0	0	0.095	
<i>S12p</i> (ExtendedNUB) $Ka = 0.98$ $\theta = 8.99$	H ₂	0.9	0	0.63	775
	O ₂	0	0.2	0	
	N ₂	0.1	0.8	0.27	
	H ₂ O	0	0	0.095	

L6 to *L8* – Non-premixed cases, simulated with the Lamellar Micromixing Model for Combustion
S10p to *S12p* – Non-premixed cases, simulated with CFD, using Fick and variable properties

For illustration purposes, in Figure V.71 are shown the histories of temperature and molar fractions of *L6*. In Figure V.71a is visible that the hydrogen is consumed in the first 8×10^{-5} s, which coincides with the raise of temperature, as shown in Figure V.71b. If a larger simulation time is plotted, 0.022 s, it is visible that the temperature has a slight decrease, as represented in Figure V.71d.

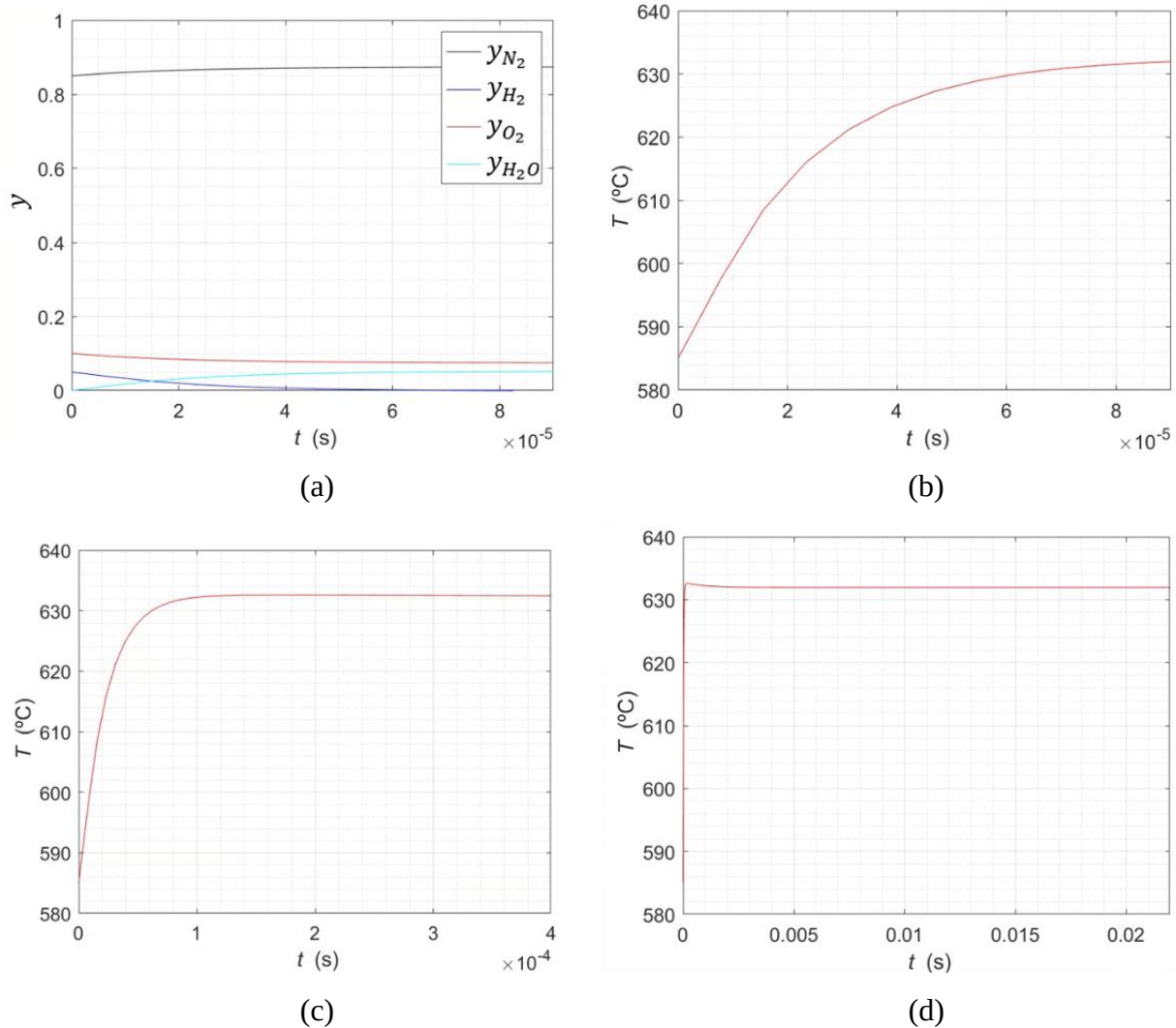
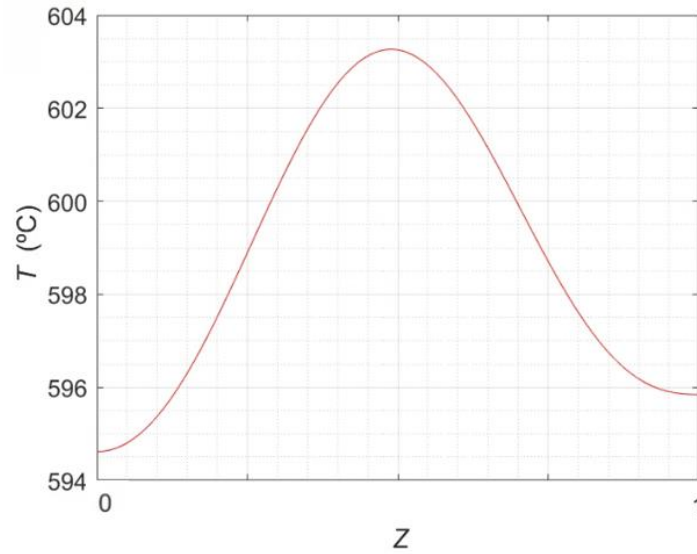


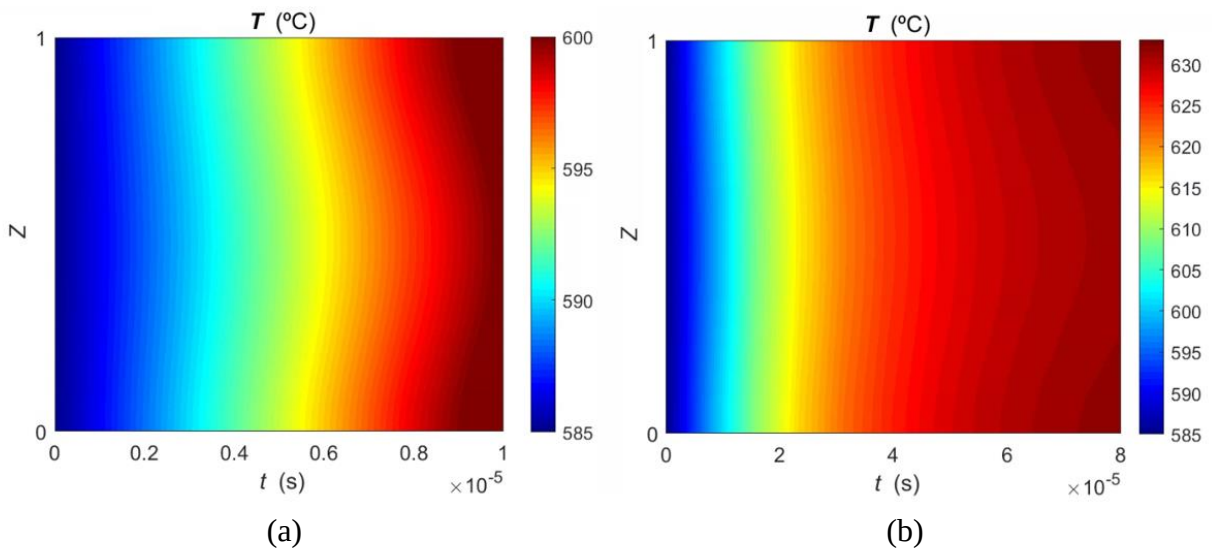
Figure V.71 (a) History of the average molar fractions of $L6$ during 8×10^{-5} s. Histories of temperature during: (b) 8×10^{-5} s, (c) 4×10^{-5} s, and (d) 0.022 s.

Comparing with premixed combustion, it is possible to conclude that for non-premixed cases, the consumption of the reactants is less abrupt as well as the raise of temperature. In fact, the reactants are being mixed which slows the reaction. In this way, for non-premixed combustion, the graphics are not characterized by the presence of peaks.

The temperature profile at 1×10^{-5} s is shown in Figure V.72 where is visible that the temperature raise occurs in the middle of the domain, Z , in the interface between the fuel and oxygen.

Figure V.72 Temperature profile of *L6* at 1×10^{-5} s.

The maps of the evolution of the temperature are shown in Figure V.73. As previously shown, the raise of temperature starts in the middle of *Z* and then becomes uniform, as visible in Figure V.73.

Figure V.73 Temperature maps of *L6* at: (a) 1×10^{-5} s and (b) 8×10^{-5} s.

The maps of the evolution of the molar fractions are shown in Figure V.74. The different initial concentrations are visible in *Z*: half of the domain with fuel and the other half with air. As the reactants are mixed, the fractions of the species become uniform, and water is produced.

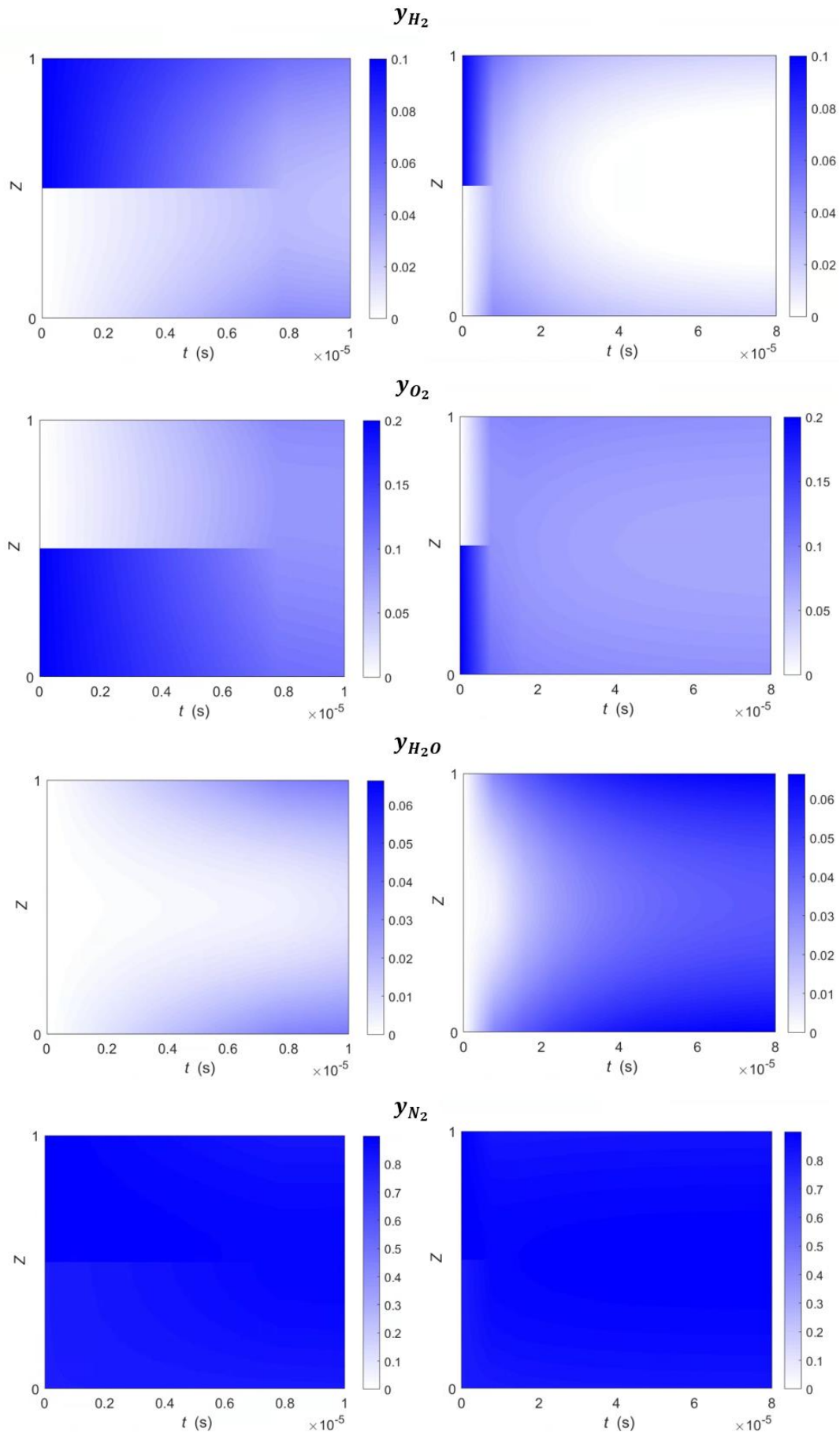


Figure V.74 Molar fraction maps of L6.

The evolution of the striation thickness, S , is the same as previously shown for premixed combustion, as represented in Figure V.75.

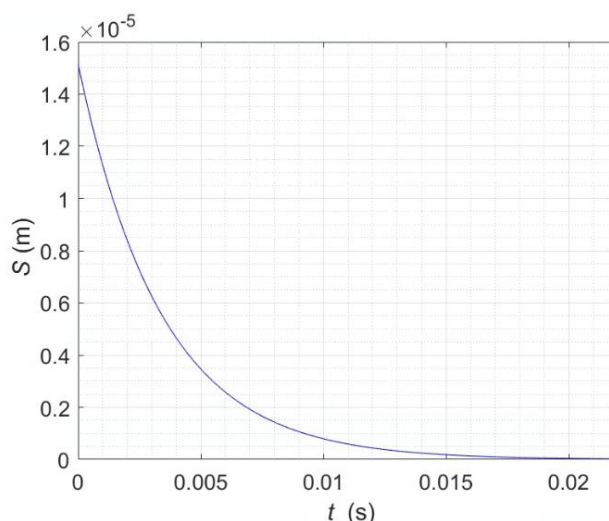


Figure V.75 Striation thickness evolution.

V.5 Computational Aspects

For the numerical validation of the ExtendedNUB for gases, the CFD simulation was run in 2 nodes of a computational cluster (FEUP) Intel® Xeon® with 16 cores at 2.1 GHz and 64 GB of RAM, and took ca. 3 days to perform 1.5×10^5 time steps.

For LMS, the data was saved from ANSYS® FLUENT™ in files with ASCII format. The data processing was made in MATLAB® R2018a. The conversion of the data to files .mat and their processing are shown in Appendix D.2. The run time of LMS for gases is similar to the time for liquids (see Section IV.4.2).

V.5.1 Combustion in ExtendedNUB Analysis

The CFD transient-state simulations of combustion in ExtendedNUB were run in two different machines: in 2 nodes of a computational cluster (FEUP) Intel® Xeon® with 16 cores at 2.1 GHz and 64 GB of RAM; and in 8 nodes of the supercomputer BOB (MACC) with an Intel 8-cores "Sandy Bridge" Xeon (2 processors) at 2.7 GHz and 32 GB of RAM.

For the global scheme of hydrogen, if the computational cluster (FEUP) is used, the simulation takes approximately 15 days to perform 1.5×10^5 time steps. If the supercomputer BOB is used, the simulation takes ca. 3 days perform 1.5×10^5 time steps. For the 19-reactions scheme of hydrogen, if the computational cluster (FEUP) is used, the simulation takes approximately 3

weeks to perform 1.5×10^5 time steps. If the supercomputer BOB is used, the simulation takes ca. 6 days to perform 1.5×10^5 time steps.

The steady-state simulations were run in a x64-based processor Intel® Xeon® X5687 with 8 cores at 3.60 GHz and 24 GB of RAM, and took ca. 2 days to perform 1.5×10^5 iterations.

For the hydrodynamics analysis, the data was saved from ANSYS® FLUENT™ in text files .out. The conversion of the data to files .xlsx was made in Visual Basic for Applications (VBA). The processing was made in MATLAB® R2018a. The data conversion and processing are shown in Appendix D.3.

For the Thickened Flame Model, a UDF to predict the flame speed was developed. The code is shown in Appendix D.10.

V.5.2 Lamellar Micromixing Model for Combustion Analysis

The CFD simulation with gases without combustion was used to implement LMS and obtain the interfacial area generation (see the beginning of this chapter).

The Lamellar Micromixing Model for Combustion was developed and run in MATLAB® R2018a, using a x64-based processor Intel® Core™ i7-9700 with 8 cores at 3.00 GHz and 32 GB of RAM. The codes of the Lamellar Micromixing Model for Combustion are in Appendix D.11.

V.6 Conclusions

The ExtendedNUB model was numerically validated for gases. The CFD maps have shown a similar pattern for liquids and gases, characterized by the presence of vortices inside the mixing chambers. From velocity histories and spectral analysis, it was shown that the chaotic behaviour of NETmix is maintained. Moreover, the interfacial area generation is exponential, characteristic of this type of flow. The strange attractors have a similar shape for liquids and gases.

The ExtendedNUB model with gases was used to study combustion in NETmix for the first time. If combustion occurs in NETmix, the flow remains chaotic with a larger interfacial area generation when compared to the flow without reaction, as shown from the application of DLMS.

CFD simulations of the hydrogen combustion were performed with three schemes: the global reaction scheme, with and without the reverse rate, and the 19-reactions scheme. Two different types of combustion were applied, premixed and non-premixed.

For premixed and non-premixed combustion, as the reactive mixture is diluted in fuel, i.e., more nitrogen is added or more oxygen is added, the maximum temperature decreases. Moreover, the reaction front occurs further in the reactor and the maximum reaction rate decreases. In general, the maximum temperature for non-premixed combustion is higher when compared to the maximum temperature of premixed cases. In most cases, hotspots were formed in a zone of the reactor. Cases with lean combustion, i.e., oxygen in excess, have a lower temperature of combustion, as well as reactive mixtures with a low equivalence ratio, θ .

If the reverse reaction is included in the reactive scheme, the maximum temperature is lower for premixed and non-premixed combustion.

The influence of the mixture properties as well as the diffusion model were studied. It was shown that the physical properties exert a major influence and should be predicted by models, enabling their variation with the temperature. The best diffusion model is the Maxwell diffusion which has closer values to at least one of the other two models (Fick and Flame).

The Lamellar Micromixing Model was adapted for combustion by adding a temperature equation in the PDE system. Moreover, the LMS results were included in the model to represent the flow dynamics of the NETmix system. The difference in the prediction of the temperature between the Lamellar Micromixing Model for Combustion and the CFD simulations is less than 12%.

Chapter VI – NETcombustor

This chapter is dedicated to a technological approach to simulate combustion in NETmix. In the previous chapter, a reduced model, ExtendedNUB, of the NETmix reactor was used to perform the hydrogen combustion at a micro-scale level. Here, a whole network similar to a device that could be used for industrial applications will be developed, the NETcombustor model.

The State of the Art of this chapter starts by approaching the NETmix reactors that were previously developed and their applications. A review on combustion devices, from industrial equipment to micro and meso reactors, will then be made.

In this chapter, NETcombustor will be presented and numerically validated. The combustion of hydrogen in NETmix will be simulated through NETcombustor, using the global reaction scheme with and without the reverse rate. The difference between premixed and non-premixed reactive mixtures will be assessed. Moreover, the influence of the injection scheme in the combustion temperature and products will be evaluated. The results of NETcombustor will be compared with the CFD simulations. To conclude the NETcombustor studies, a combustion curve for the system H₂-Air in NETmix will be designed.

VI.1 State of the Art

VI.1.1 NETmix Technology

Over the years, the NETmix technology was kept according to the original patent (Lopes et al. 2005) which covers two alternatives, *NETmix 3D* and *NETmix 2D*. Historically, the configuration and layout of the reactor have been improved. In this section, the evolution of the NETmix technology will be assessed.

NETmix 3D

The first NETmix reactor, *NETmix 3D* (Figure VI.1b), was constituted by spherical chambers connected by cylindrical channels at an angle of $\phi = 45^\circ$ (Figure VI.1a). The rows of the device alternate between 15 and 16 chambers (in each row), starting with 15 chambers in the first row. The total number of rows is $n_x = 49$. The number of columns, n_y , is equal to the maximum number

of chambers in a row, in this case $n_y = 16$. Since each chamber has two inlets, this unit has a total of 30 inlet and 30 outlet channels.

This device was used for academic studies such as tracer experiments, shown in Figure VI.1c (Laranjeira 2005, Laranjeira et al. 2011), as well as for the industrial production of nanocrystalline hydroxyapatite (Silva et al. 2008, Gomes 2011), illustrated in Figure VI.1d.

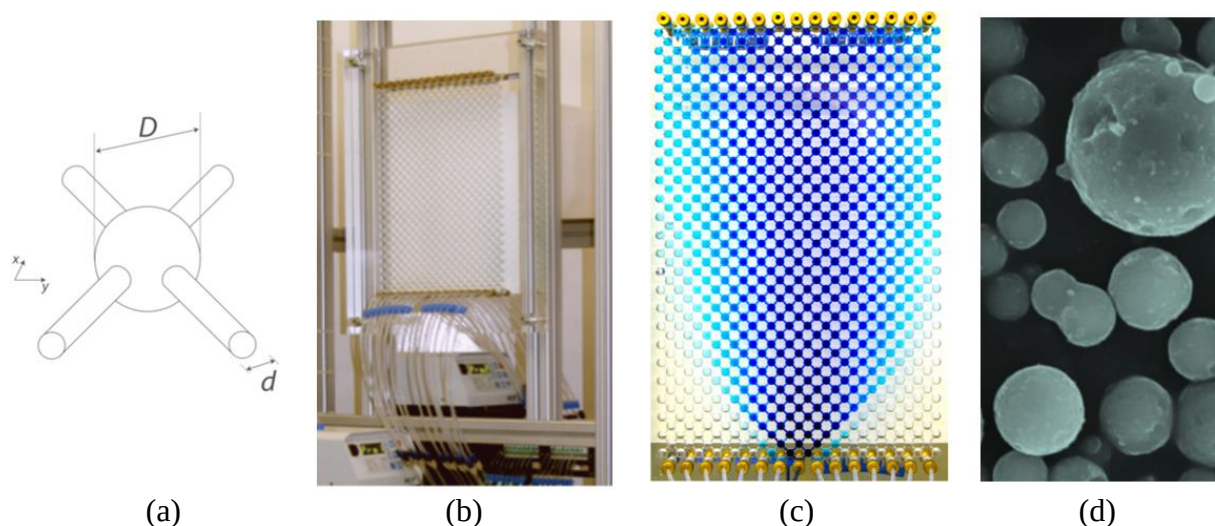


Figure VI.1 (a) NETmix 3D unit cell, (b) NETmix 3D device (Gomes 2011), (c) NETmix 3D flow, (d) Nanocrystalline hydroxyapatite (<https://www.fluidinova.com/hydroxyapatite-properties-uses-and-applications>).

Multi-inlet NETmix 2D

As the mixing mechanisms are mainly 2D in the xy plane, a 2D NETmix *Multi-inlet NETmix 2D* (Figure VI.2b), was developed. The chambers are cylindrical, and the channels are prismatic with depth, w , perpendicular to the xy plane (Figure VI.2a). In this reactor, additional injection ports to feed reactants or collect products were added in three equally spaced rows, forming a multi-inlet injection system, as shown in Figure VI.2c.

The Multi-inlet NETmix 2D reactor was used to perform tracer studies (Figure VI.2b) and for industrial applications (Gomes 2011).

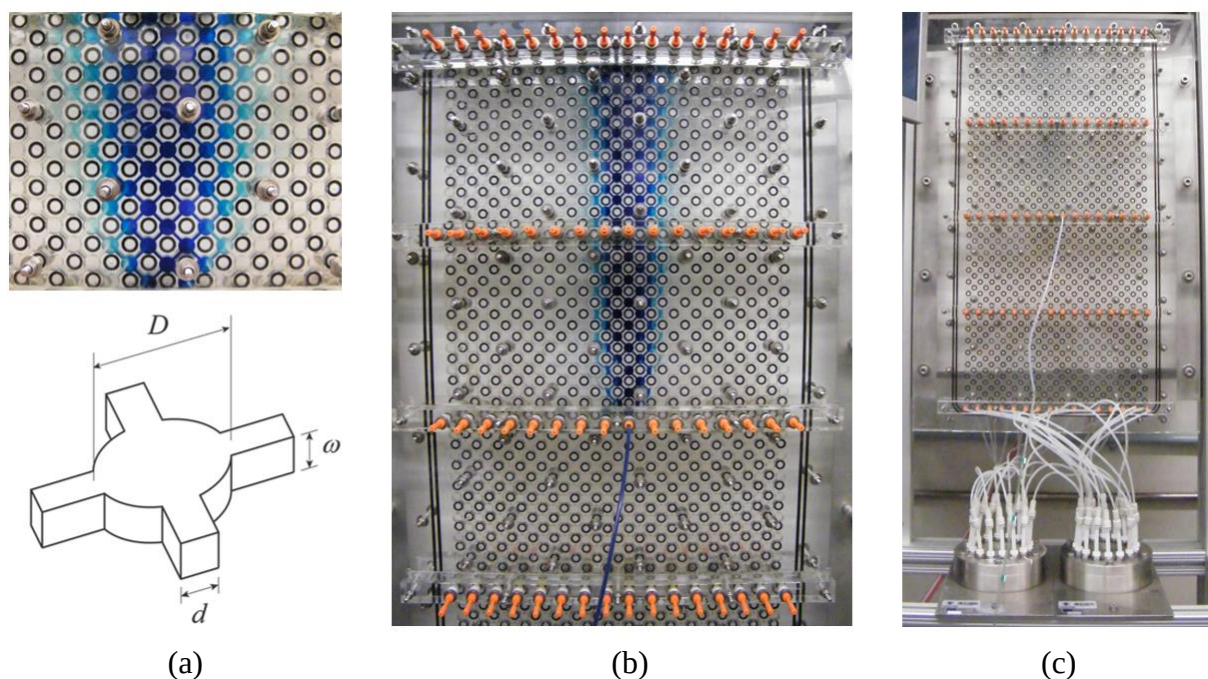


Figure VI.2 (a) NETmix 2D unit cell, (b) NETmix Multi-inlet tracer, (c) NETmix Multi-inlet device (adapted from Gomes 2011).

Lab-scale NETmix

Smaller 2D devices were built for laboratorial testing, the *lab-scale NETmix 2D* reactors. In the Lab-scale NETmix, the network is formed by cylindrical chambers and prismatic channels, which are etched in plates. The closest chambers to the right and left side edges (except the chambers of the first and last rows) have a diameter, $D/\sqrt{2}$, to avoid uneven distribution of flow and residence times along the network. The unit has 8 inlet chambers (4 in the front and 4 at the back) and 8 outlet chambers which are joined by a collector in only 1 outlet stream (Figure VI.3a and Figure VI.3b).

In 2013, the lab-scale NETmix was used to perform pressure drop measurements (Fonte 2013, Fonte et al. 2013). Since 2017, the Lab NETmix has been used for laboratory flow studies, such as hydrodynamics and multiphase analysis (Figure VI.3c), for the production of micro-capsules for textile applications (Moreira et al. 2020) and for Pickering emulsions (Ribeiro et al. 2021), shown in Figure VI.3d.

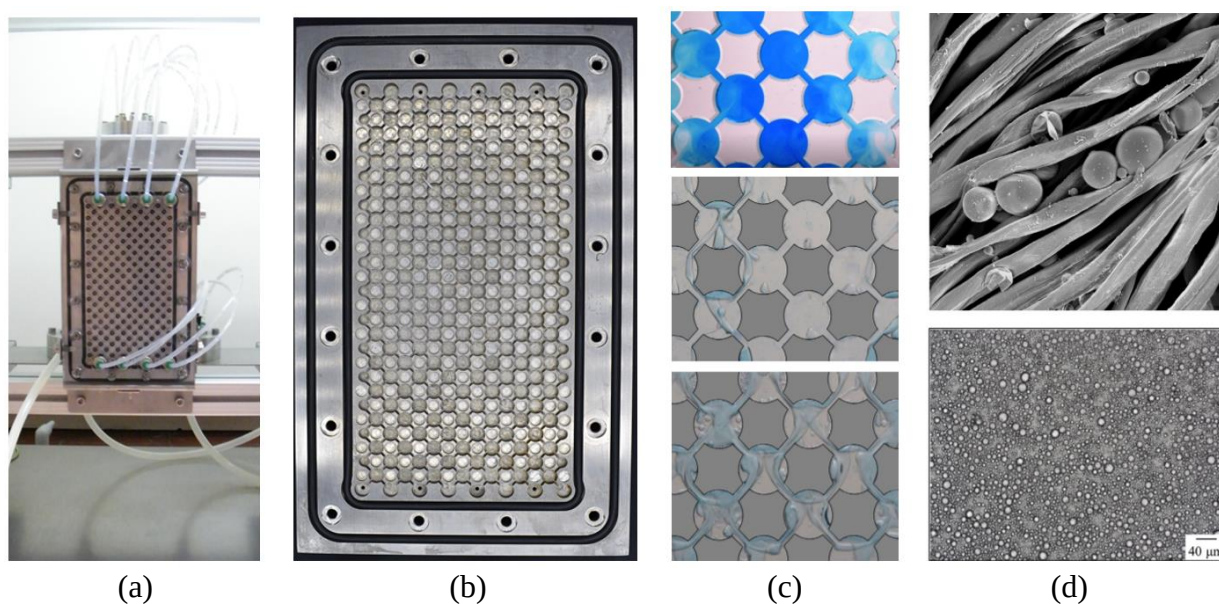


Figure VI.3 (a) Lab-scale NETmix device, (b) 2D NETmix plate, (c) NETmix flow and multiphasic flow (Fernandes et al. 2021), (d) impregnated microcapsules in cotton (Moreira et al. 2020) and Pickering emulsions (Ribeiro et al. 2021).

NETmix Photoreactor

Since 2016, the Lab-Scale NETmix reactor was adapted to perform photocatalysis, *NETmix Photoreactor*. The reactor has 8 inlets and 8 outlets, in similarity with the lab-scale NETmix device (Figure VI.4a). To perform photocatalysis, NETmix Photoreactor includes photocatalyst plates (Lima et al. 2016). The photocatalyst sheets are inserted upon the NETmix plate and the device is then placed in a solar radiation simulator (Figure VI.4b) or in contact with UV-LEDs (Figure VI.4c).

This device has been used to perform photocatalysis studies such as the homogeneous and heterogeneous photo-Fenton (Lima et al. 2017) and the intensification of the heterogeneous TiO₂ photocatalysis (Filho et al. 2017, Marinho et al. 2017, Santos et al. 2019). Recently, the reactor has been used for ozonation studies for water treatment (Filho et al. 2019) and kinetic modelling (Santos et al. 2021).

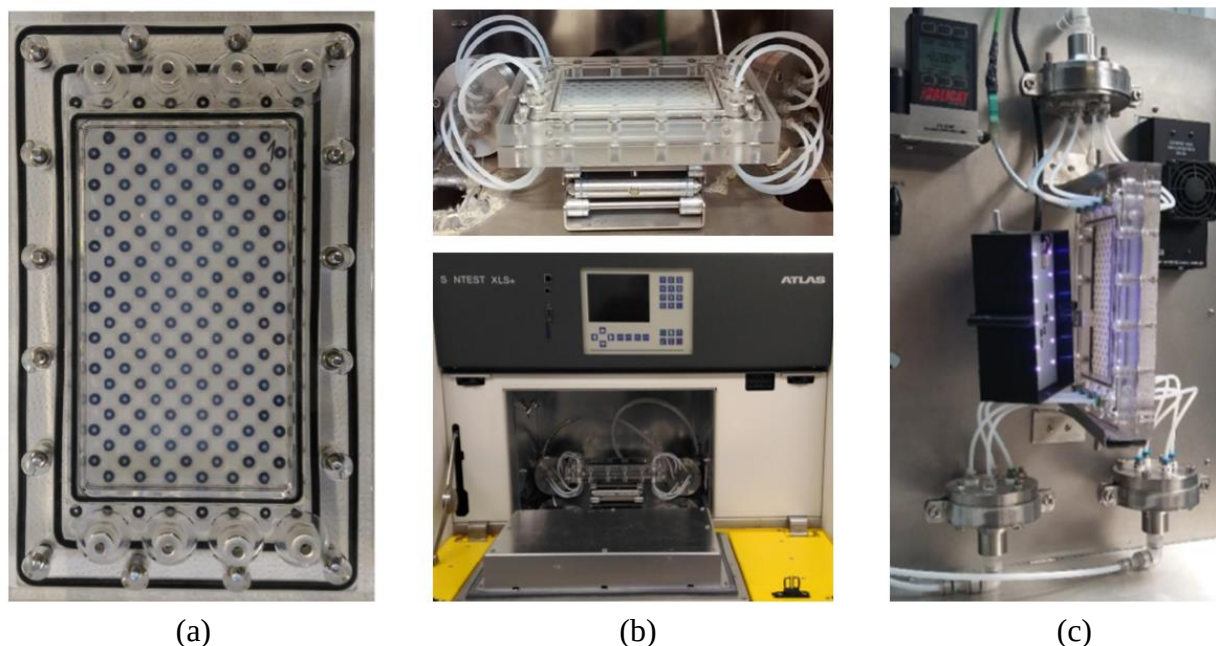
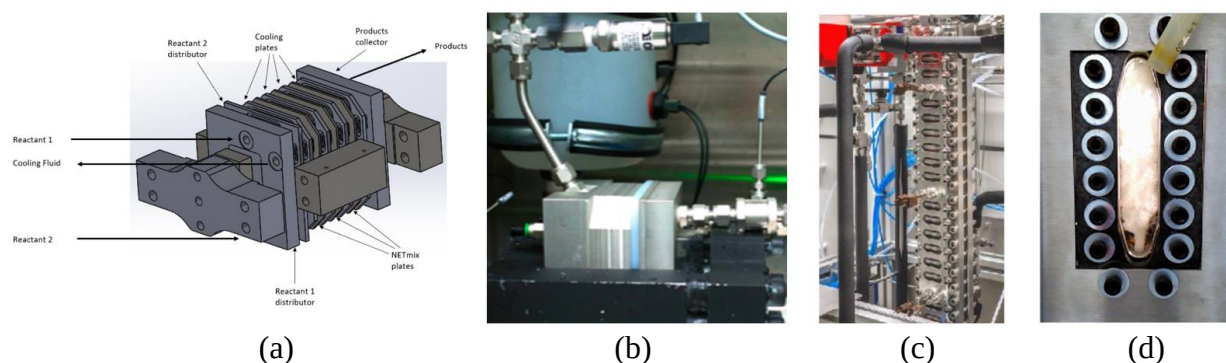


Figure VI.4 (a) NETmix Photoreactor device (Marinho et al. 2017), (b) NETmix Photoreactor inside a solar radiation simulator (Marinho et al. 2017, Filho et al. 2017), (c) NETmix Photoreactor in contact with UV-LEDs (Filho et al. 2019).

MicroNETmix

A device with smaller chambers, *MicroNETmix*, was developed in 2017. The structure of the MicroNETmix network is similar to the Lab-scale NETmix reactor (Table VI.1). The device has a total of 4 inlets (which are distributed along the eight chambers of the first row) and one outlet. MicroNETmix has been used for microencapsulation (Moreira et al. 2020), Pickering emulsions (Ribeiro et al. 2021) and MOF production (see Figure VI.3).

Studies have shown that in MicroNETmix it is possible to control the temperature if a heat exchanger is coupled to the device (Costa 2017). In this way, two variants of MicroNETmix were designed to perform processes that include heat exchange, *MicroNETmix UG* and *MicroNETmix U12*, which were developed for the continuous production of gas hydrates at the CoLAB NET4CO₂, shown in Figure VI.5d (<https://www.net4co2.pt/p138-co2-capture-en>). Differently from the NETmix devices that were previously described which were constituted by one network plate, the MicroNETmix UG unit (Figure VI.5c) is constituted by three plates assembled in a block to enable high-pressure operations. In order to remove the heat from NETmix, the network plates are alternated with cooling plates (Costa 2017, Lopes et al. 2018, Lopes et al. 2019), a scheme is shown in Figure VI.5a. The MicroNETmix U12 unit is similar to the MicroNETmix UG unit, but with five NETmix plates and 8 inlets (Figure VI.5b).



Micro2D-REACTmix

Since 2020, a new device, *Micro2D-REACTmix* shown in Figure VI.6, is being developed for Fischer-Tropsch processes to produce synthetic fuels, at the CoLAB NET4CO₂. In this device, the network plates include a catalytic plate in which the catalyst is immobilized as a 2D film. The reactor is built with a material compatible with the operating conditions of the Fischer-Tropsch process, which tolerates pressures up to 30 bar and temperatures up to 400 °C. Heat exchange plates are also incorporated to maintain the feed gas between 180 °C and 250 °C, and to remove the heat of the reaction.



Figure VI.6 Micro2D-REACTmix device.

MesoHGtS U3

In 2019, at the CoLAB NET4CO₂, the MicroNETmix UG unit was adapted to a mesoreactor format (D in the order of 10 mm), *MesoHGtS U3*, to produce hydrates in a pilot (Figure VI.7a). In similarity with the MicroNETmix UG unit, two NETmix plates are installed in parallel and each plate is assembled with two cooling plates (Figure VI.7b), using the Armadillo® technology shown in Figure VI.7c (Costa 2017, Lopes et al. 2018, Lopes et al. 2019).

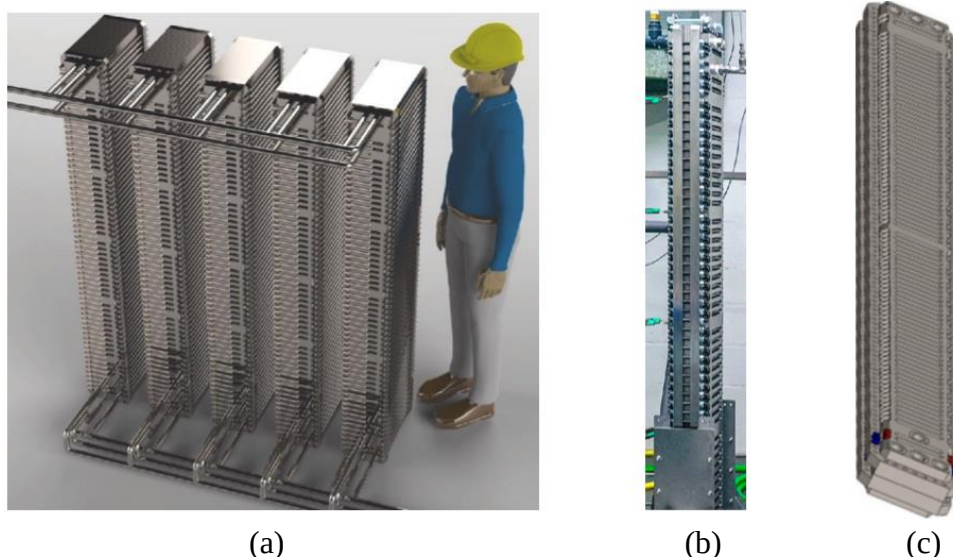


Figure VI.7 (a) MesoHGtS U3 unit, (b) MesoHGtS U3 device, (c) Exterior Armadillo® tech.

NETmix Devices Topology

The topology and characteristics of the NETmix devices that were previously described are listed in Table VI.1 and in Table VI.2.

Table VI.1 NETmix network characteristics.

NETmix Network				
	Type of network	Number of plates	Number of inlets	Number of outlets
NETmix 3D	3D	1	16	16
Multi-inlet NETmix 2D	2D	1	16	16
Lab-scale NETmix 2D	2D	1	8	8
NETmix Photoreactor	2D	1	8	8
MicroNETmix	2D	1	8	8
MicroNETmix UG	2D	3	8	8
MicroNETmix U12	2D	5	8	8

Table VI.2 NETmix network topology.

NETmix Network Topology							
	n_x	n_y	D (mm)	d (mm)	D/d	l (mm)	ω (mm)
NETmix 3D	49	16	7.0	1.5	4.66	3	-
Multi-inlet NETmix 2D	49	16	8.5	1.5	5.66	5.5	5.9
Lab-scale NETmix 2D	29	8	6.5	1.0	6.50	2.0	3.0
NETmix Photoreactor	29	8	6.5	1.0	6.50	2.0	3.0
MicroNETmix	25	8	3.3	0.5	6.6	1.8	0.5
MicroNETmix UG	25	8	3.3	0.5	6.6	1.8	0.5
MicroNETmix U12	25	8	3.3	0.5	6.6	1.8	0.5

VI.1.2 Combustion Technology

In this section, different combustion devices will be presented. The review starts with combustion equipment that is mainly used in industrial plants and ends with more recent technologies to perform combustion at meso and micro-scales.

In industry, such as petrochemical and refineries, combustion is mostly used for heating and to produce steam. For that purpose, furnaces and boilers are the most common devices.

Furnaces

A furnace, or direct-fired heater, represented in Figure VI.8, is a type of enclosed chamber where heat is generated by the combustion of fuel. A blower introduces air into the heating chamber, where the oxygen is combined with the fuel. In the radiant section, the heat from the burning fuel heats the Heat Transfer Fluid (HTF) in the tubes of the chamber. An additional recover of heat occurs in the convection section, where thinner tubes are used to maximize the heat transfer (Jenkins and Mullinger 2011).

A furnace can be used to produce heat energy which can be used for heating purposes or converted into mechanical energy to drive a process, or into electrical energy, as in a power plant. The generated heat can be transferred from the furnace through tubes filled with water, air, or heat-transfer oil. All types of fuel can be used.

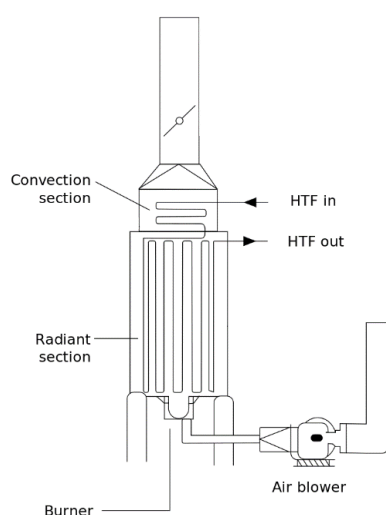


Figure VI.8 Furnace scheme (adapted from Jenkins and Mullinger 2011).

Boilers

Boilers can be used to produce steam or heated water to run industrial processes or to provide heat for buildings. The major types of industrial boilers are water-tube and fire-tube.

In water-tube boilers, represented in Figure VI.9a, the water is inside the tubes and the fuel is burned in a furnace chamber. The heat of combustion is transferred through the walls of the tubes and heats the water, producing steam.

In fire-tube boilers, represented in Figure VI.9b, heated gases from combustion pass through the tubes which are in contact with a water chamber. The water is heated and vaporizes into steam (Snow 2002).

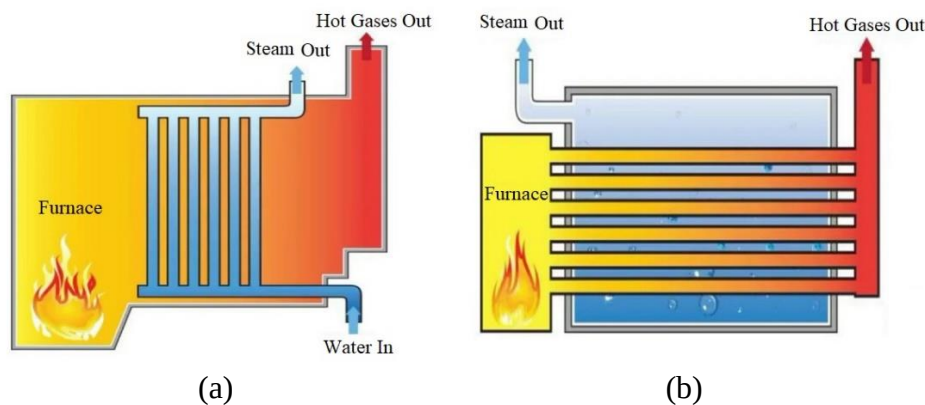


Figure VI.9 Water and fire-tube boilers (adapted from Industrial Boiler Mechanical 2019).

Another field that depends mostly on combustion is the power generation. For that, gas turbines and internal combustion engines are the most used devices.

Gas Turbines

In turbines, power is generated by the rotation of blades or vanes through the movement of gas or liquid. For gases, as shown in Figure VI.10, a compressor is used to pressurize the air which is then mixed with the fuel in the combustion chamber, generating high-pressure gas that moves the rotor of the turbine (Schobeiri 2018).

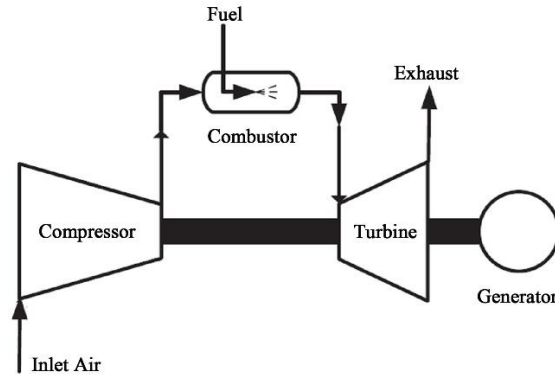


Figure VI.10 Turbine scheme (adapted from Darwish 2013).

Internal Combustion Engines

In Internal Combustion (IC) engines, energy is produced by the ignition of fuel under high pressure in an enclosed space. The gas expansion created by the burning fuel is turned into mechanical energy to move a crankshaft or rotor. Other than power generation, IC engines are also used in automobiles, pumps and in industrial machinery.

There are two types of combustion in IC engines: Spark-ignition (SI) and Compression Ignition (CI), also known as diesel.

In SI engines, represented in Figure VI.11a, the mixture Air-Fuel is introduced into the cylinder of the engine and compressed, inducing ignition by a spark. The pistons are then pushed by the gases that are released from the combustion reaction.

CI engines, shown in Figure VI.11b, do not need an ignition system. The air is compressed and as the fuel is sprayed into the compressed air, the temperature increases and ignition occurs (Kenneth 1935).

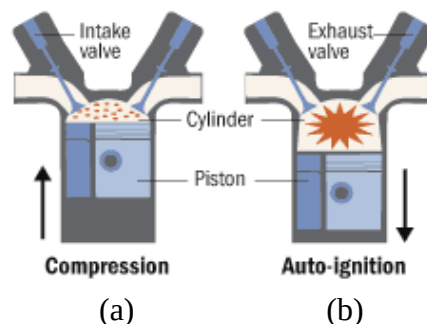


Figure VI.11 CI and SI engines (adapted from Encyclopædia Britannica 2019).

Combustion is easier to control if gaseous fuels are used. Specifically for gases, there are three principal types of gas burners: Premix, Radiant and Nozzle Mix.

Premix Burners

Also called Aerated or Atmospheric burners, in Premix burners, the gas is ejected from nozzles to the air inside a close space. After, the mixture Air-Fuel reacts and flows through slots, holes or grilles. The shape and size of the chamber can be varied, depending on the application. An example of a typical burner is shown in Figure VI.12. An even output distribution of heat is desired in order to avoid hotspots which would promote the NO_x formation (Snow 2002).

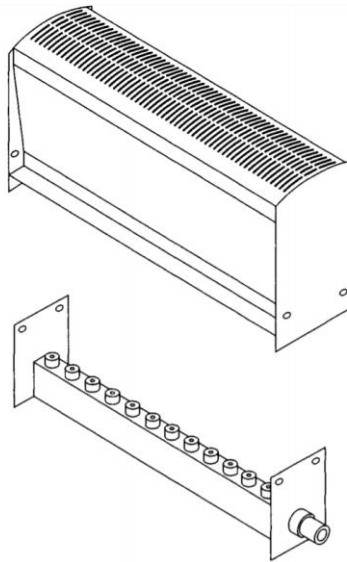


Figure VI.12 Gas burner scheme (from Snow 2002).

Radiant Burners

In radiant burners, in order to increase the heat released by radiation, a ceramic matrix is added at the top of the nozzles surface. Combustion at the surface of the ceramic matrix raises the temperature, increasing the energy release from gases in the radiant form. A scheme of this type of nozzles is shown in Figure VI.13 (Snow 2002).

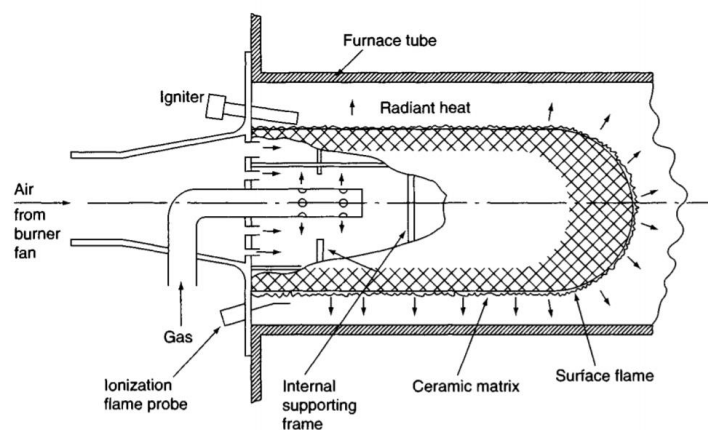


Figure VI.13 Radiant burner scheme (from Snow 2002).

Nozzle Mix Burners

In Nozzle Mix burners, the stability and shape of the flames are controlled by the use of a forced fan. The gas exits the nozzles or holes on the head of the burner. The gas is then mixed with a high velocity air stream in a blast tube (Snow 2002). A schematic representation is given in Figure VI.14.

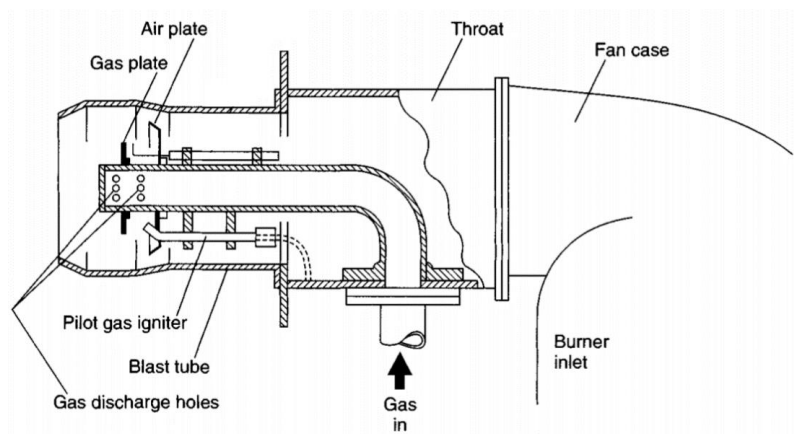


Figure VI.14 Nozzle mix burner scheme (adapted from Snow 2002).

VI.1.2.1 Meso and Micro-Scale Combustion Devices

Meso and micro-scale combustion devices have been gaining attention in the last years. In fact, for chemical systems that can function in a small scale, micro and meso combustors have a reduced cost, less pollutant emissions and are easier to transport (Avci et al. 2010). Moreover, in micro and meso reactors, the combustion reaction is easier to control. Combustion-driven micro devices using hydrocarbons have a growing importance due to the specific energy of hydrocarbons (55.5 MJ/kg for methane), which is higher than, for example, the commonly used lithium batteries, 1.2 MJ/kg (Fernandez-Pello 2002, Wu et al. 2007). Micro-combustion has four main areas of applications: *chemical propulsion* which includes micro air vehicles and microthrusters, *chemical process industry* such as gas reforming, *laboratory analytics*, for example, PCR reactions, and *communication devices*, comprising sensors, computers and mobile phones (Jejurkar and Mishra 2009). Reviews on meso and micro-combustors can be found in the works of Hessel et al. (2008) and Jejurkar and Mishra (2009). Several micro and meso-combustor devices will be presented next.

Vortex Chambers

In vortex chambers, vortex flows are used to stabilize the combustion flames. The fuel is injected perpendicularly to the oxidizer. The direct impinging of the fuel and oxidizer enhances mixing at the inlets. The exhaust of the combustion products is done perpendicularly to the fuel inlet (Figure VI.15). A vortex chamber with 10.6 mm^3 , shown in Figure VI.15, has been used to study the combustion of hydrogen, methane and propane (Wu et al. 2007).

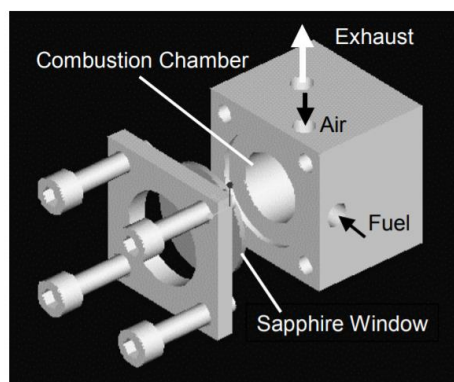


Figure VI.15 3D Vortex chamber scheme (from Wu et al. 2007).

Micro-tube Combustor

Micro-tube combustors have a Tee shape, with the inlet of fuel and oxidizer at opposite sides. The reactants are mixed at the Tee node and then flow into the micro-tube. An ignition source is connected to the micro-tube where combustion occurs, and the flame stabilizes (Figure VI.16a). Micro-tubes can have several topologies, such as the configuration of Figure VI.16b, which is used to study heat loss in CH_4 combustion (Junwei and Beijing 2008).

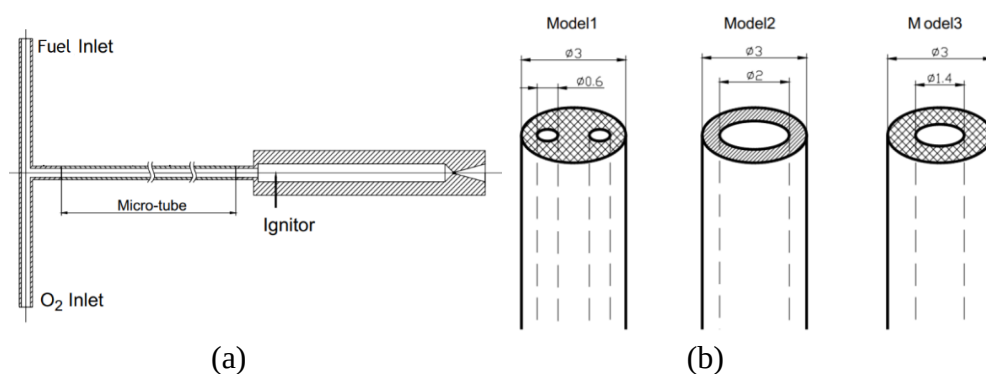


Figure VI.16 (a) Micro-tube combustor scheme and (b) micro-tube configurations with diameter, ϕ (adapted from Junwei and Beijing 2008).

Catalytic Micro-reactor

Micro reactors have been used for process intensification due to the temperature control and improved mass transfer that can be achieved. The catalytic micro-reactor was developed for the integration of two processes, combustion and steam reforming. The use of catalytic combustion has several advantages, such as the reduction of NO_x emissions. The reactor, shown in Figure VI.17, is composed of several parts. The reforming gases pass through the interior channel and the combustion gases through the exterior channels. The catalytic layers are located in the middle of the two channels (Vaccaro et al. 2010).

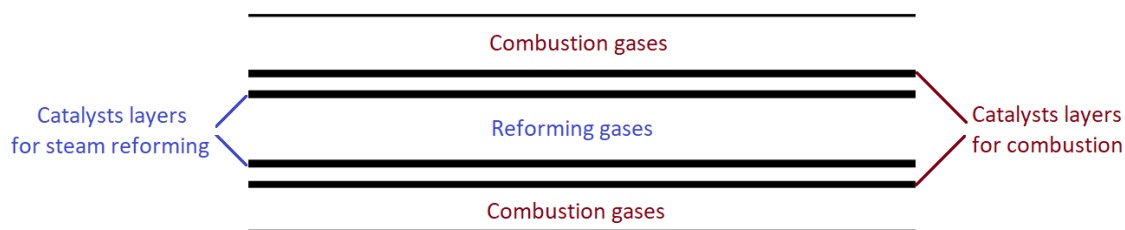


Figure VI.17 Catalytic micro-reactor (adapted from Vaccaro et al. 2010).

Other versions of catalytic micro-reactors for combustion and steam reforming have already been developed, as shown in the work of Moon et al. (2016).

Different designs for catalyst support, such as pellets and honeycomb (Figure VI.18) substrates, can be found in Cybulski and Moulijn's book (2006).

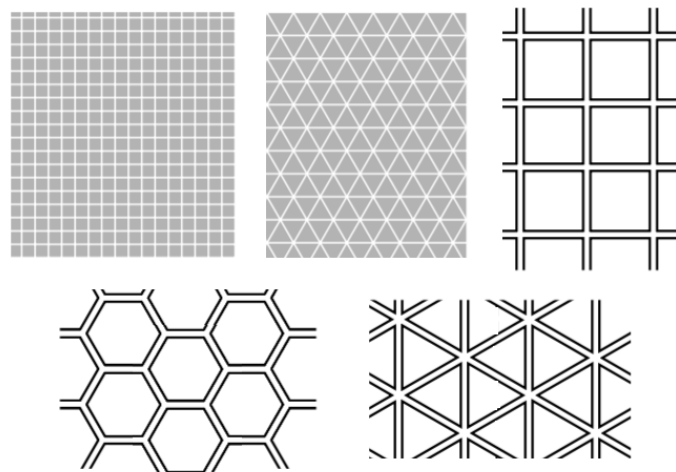


Figure VI.18 Catalyst substrates (adapted from Cybulski and Moulijn 2006).

VI.2 NETcombustor Model

A first network model to represent NETmix was proposed by Laranjeira (2005) to perform Residence Time Distribution (RTD) studies, tracer and reaction simulations (Laranjeira et al. 2009). In that approach, the NETmix chambers were modelled as perfectly mixed Continuous Stirred Tank Reactors (CSTR), zones of complete micromixing, and the channels as Plug-Flow Reactors (PFR), zones of segregation (Laranjeira 2005). From the comparison with experiments, it was shown that the network model represents perfectly the mixing features of NETmix, as visible in Figure VI.19.

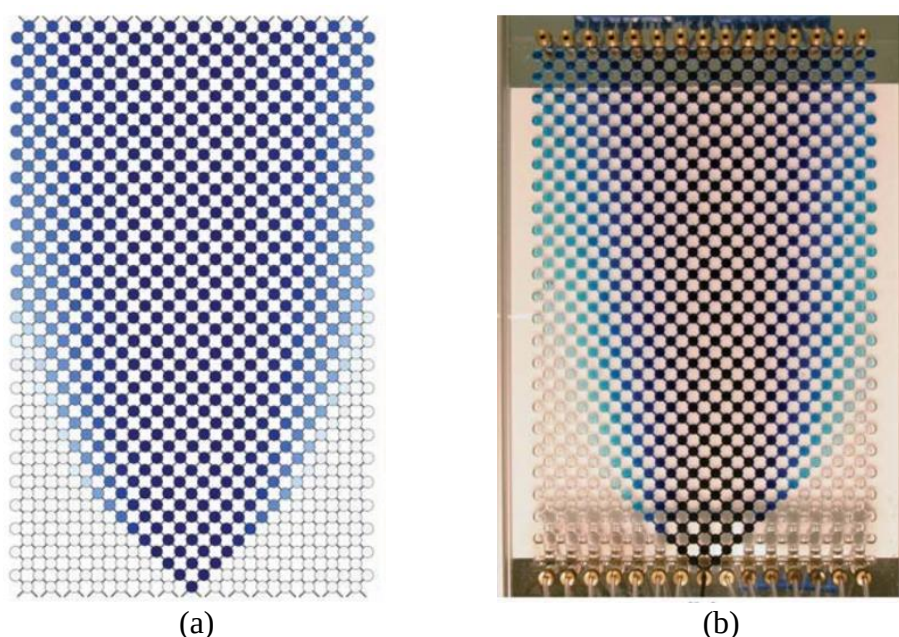


Figure VI.19 Tracer in: (a) NETmix network model, (b) NETmix device (adapted from Laranjeira et al. 2011).

In this work, a network model to perform combustion was developed, NETcombustor. The NETmix chambers were modelled as perfectly mixed Continuous Stirred Tank Reactors (CSTR) and the channels as Plug-Flow Reactors (PFR). To study the combustion of H_2 in NETmix, the energy balances were included in the model.

The schematic NETmix network is represented in Figure VI.20a. As visible, the inlet channels are in the bottom row and the outlet channels are in the top row. The network was developed using the Aspen Custom Modeler[®] V10 software and is shown in Figure VI.20b. The network is composed of 17 rows and 8 columns, with 14 inlet channels (I1 to I14) and 14 outlet channels (O1 to O14). The first block, (B1), is used to give the inlet conditions to the inlet row of the network. In this model, the chambers are considered as perfectly mixing zones. Thus, the balance equations for the Continuous Stirred-Tank Reactor (CSTR) are applied. The channels are used to connect the chambers and no reaction occurs in them.

The 3D network is represented by a 2D model, in which the chambers have a diameter, D , and the channels have a width, d . The volume of the chambers that will be further used in this work is given by $\frac{\pi D^2}{4} \omega$, in which ω is the depth of the 3D network.

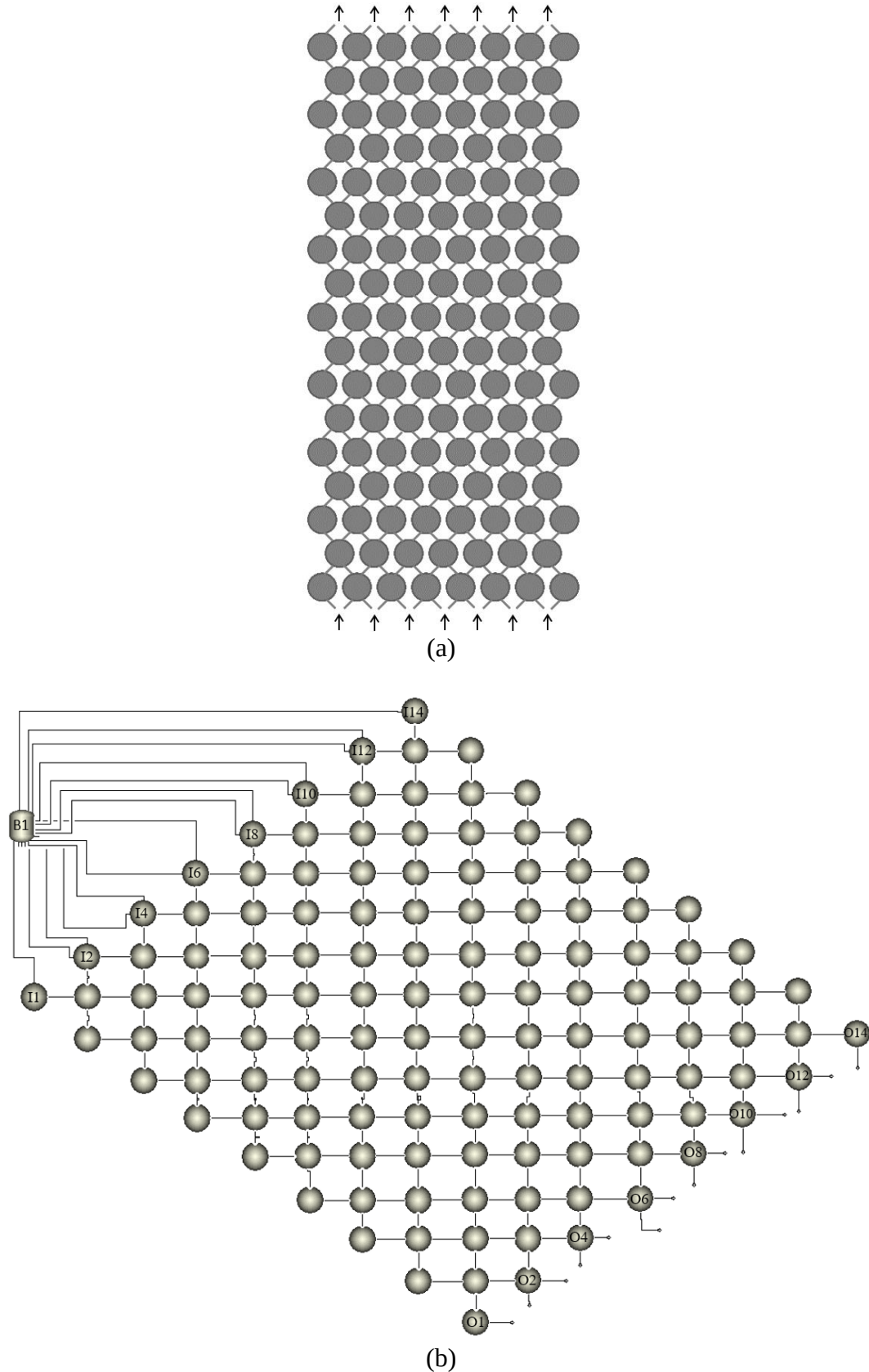


Figure VI.20 (a) NETmix network scheme. (b) NETcombustor network.

Network Topology

The study was performed considering the diameter of the NETmix chambers in the meso scale, in the order of 10 mm. The width of the channels was calculated in order to have a ratio $D/d = 6.65$, at which the best mixing is obtained (see Section IV.2.3.2). In this way, the dimensions of the network (Figure VI.20) are $D = 10.0$ mm, $d = 1.50$ mm and $\omega = 1$ mm.

Mass and Energy Balances

Since the chambers where combustion will take place are perfect mixing zones, the CSTR model equations for the mass balance are used. The mass balance for each component in each chamber is given by

$$V \frac{dC_i}{dt} = \sum_{j=1}^{nj} F_j y_{i,j} - \sum_{k=1}^{nk} F_k y_{i,k} + V r c_i \quad (\text{VI.1})$$

in which t is the time, V is the volume of the network chamber, C is the molar concentration of component i , y is the molar fraction of component i in stream j or k , and F is the molar flow rate that goes through inlet, j , or outlet, k . The total number of inlets and outlets in which component i is present is given by n_j and n_k , respectively, which can be 1 or 2. rc is the rate of production/consumption of component i .

The molar concentration, C_i , is given by $y_i \rho_{out}$ in which ρ_{out} is calculated with the Aspen Custom Modeler® V10 function, pDens_Mol_Vap. The value of the molar flow rate, F , is directly obtained from Aspen Custom Modeler® V10.

The energy balance for adiabatic chambers is given by

$$V \frac{d(\rho_{out} h_{out})}{dt} - V \frac{dp}{dt} = \sum_{j=1}^{nj} F_j h_j - h_{out} \sum_{k=1}^{nk} F_k \quad (\text{VI.2})$$

in which ρ_{out} is the molar density inside the chamber, p is the pressure and h is the specific enthalpy of the inlet j , or outlet, k . As the streams of each chamber are in equilibrium at the outlet, the properties of the mixture are the same for both outlets. In this way, there is no need to consider $\sum_{j=1}^{nk} F_k h_k$, and one value is used for the enthalpy of the outlets, h_{out} .

The enthalpy, h , and the molar density, ρ , were calculated with the Aspen Custom Modeler® V10 functions, pEnth_Mol and pDens_Mol_Vap, respectively.

The Aspen Custom Modeler® V10 functions consider the ideal gas equation, $pV = nRT$, in which $p = 10^5$ Pa is the pressure, V is the volume of each NETmix chamber, n is the number of moles, $R = 8314$ J/(kmol K) is the ideal gas constant and T is the temperature.

The physical properties of the components were calculated with the *ideal* model available in Aspen Custom Modeler® V10.

Boundary Conditions

The inlet row is composed of 14 inlet streams. The Reynolds number was set to $Re = 300$ at the inlet row. The inlet velocity for each inlet, j , is given by

$$v_j^{in} = Re\mu_j^{in}/(\rho_j^{in}D_h) \quad (VI.3)$$

in which μ and ρ are the viscosity and density of the mixture that goes through inlet j , respectively. μ^{in} and ρ^{in} are obtained from Aspen Custom Modeler® V10 functions, pDens_Mass_Vap and pVisc_Vap, respectively. The hydraulic diameter is $D_h = 2\omega d/(\omega + d)$.

The volumetric flow rate, F , of each inlet is given by

$$F = v_j^{in}A_c \quad (VI.4)$$

in which $A_c = \omega d$ is the inlet channel area.

The equivalence ratio is given by

$$\theta = \sum_{j=1}^{nj} \frac{F_j y_{H_2,j}}{2F_j y_{O_2,j}} \quad (VI.5)$$

in which F is the molar flow rate of inlet j , and y is the molar fraction of H_2 or O_2 .

For the hydrogen combustion (with the global scheme), the Damköhler number, which relates the reaction rate with the mass transfer, is written as $Da = \overline{C}_{H_2}^{in0.5} \overline{C}_{O_2}^{in0.5} \tau K$, in which the passage time is $\tau = \frac{\pi D^2}{8d\overline{v}^{in}}$, and $\overline{v}^{in}$ is the average of the velocity at the inlet row.

Each chamber of the first row of NETcombustor has two inlets (see Figure VI.19 and Figure VI.20) where the reactive mixture is injected. In premixed combustion, all the inlet streams include the oxygen, fuel and inert compound. Thus, the injection scheme is AAAAAAAAAAAAAA. In non-premixed combustion, the fuel and oxygen are injected in different streams. The injection scheme is then variable. In the cases that will be presented further in this work, A represents the fuel, B the oxygen and C the inert.

VI.2.1 NETcombustor Numerical Validation - Instantaneous H₂ Combustion

For the numerical validation of the network model, H₂ combustion was simulated with the global reaction scheme, $\text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O}$. The combustion was considered instantaneous, i.e., a large rate coefficient is used, $k = 1 \times 10^7 \text{ s}^{-1}$. The rate of the reaction, r_{in} , is given by $r_{in} = kC_{\text{H}_2}C_{\text{O}_2}$. The inert nitrogen, N₂, was added to the mixture in order to dilute the reactants.

For this case, the mass balances are as follows:

$$V \frac{dC_{\text{H}_2}}{dt} = \sum_{j=1}^{nj} F_j y_{\text{H}_2,j} - \sum_{k=1}^{nk} F_k y_{\text{H}_2,k} + 2Vr_{in} \quad (\text{VI.6a})$$

$$V \frac{dC_{\text{O}_2}}{dt} = \sum_{j=1}^{nj} F_j y_{\text{O}_2,j} - \sum_{k=1}^{nk} F_k y_{\text{O}_2,k} + Vr_{in} \quad (\text{VI.6b})$$

$$V \frac{dC_{\text{H}_2\text{O}}}{dt} = \sum_{j=1}^{nj} F_j y_{\text{H}_2\text{O},j} - \sum_{k=1}^{nk} F_k y_{\text{H}_2\text{O},k} - 2Vr_{in} \quad (\text{VI.6c})$$

$$V \frac{dC_{\text{N}_2}}{dt} = \sum_{j=1}^{nj} F_j y_{\text{N}_2,j} - \sum_{k=1}^{nk} F_k y_{\text{N}_2,k} \quad (\text{VI.6d})$$

The heat of combustion, Q , is calculated for each chamber as

$$Q = 2h_v M_{\text{H}_2} \left(\sum_{j=1}^{nj} F_j y_{\text{H}_2,j} - \sum_{k=1}^{nk} F_k y_{\text{H}_2,k} \right) \quad (\text{VI.7})$$

in which $h_v = 141.65 \text{ MJ/kg}$ is the heating value of hydrogen.

The velocity, v , and Reynolds number, Re , of each outlet stream, k , are calculated as follows:

$$v_k = \frac{1}{A_c} F_k \frac{\mathcal{M}_k}{\rho_k} \quad (\text{VI.8})$$

$$\text{Re}_k = D_h \frac{\rho_k v_k}{\mu_k} \quad (\text{VI.9})$$

in which $\mathcal{M}_k$ is the molecular mass of stream k .

The conversion of H₂ or O₂ is given by

$$X_i = \frac{\sum_{j=1}^{nj} F_j y_{i,j} - \sum_{k=1}^{nk} F_k y_{i,k}}{\sum_{j=1}^{nj} F_j y_{i,j}} \quad (\text{VI.10})$$

in which i represents the compound, j represents the inlets and k represents the outlets.

For the numerical validation of NETcombustor, at the middle inlets, I7 and I8 (see Figure VI.20), a pure compound will be injected, either pure H₂ or pure O₂. At the rest of the inlets, a mixture of O₂ or H₂ (depending on which is the pure compound injected at the middle inlets) with N₂ is injected. In the *First Set*, the pure compound is H₂ (A), and the injection scheme is given by BBBBBAABBBBBB. In the *Second Set*, the pure compound is O₂ (B), and the injection scheme is given by AAAAAABBAAAAAA.

VI.2.1.1 First Set

For the previously mentioned injection scheme, BBBBBAABBBBBB, in the *First Set*, pure H₂ is injected at the middle inlets, A, and a mixture of O₂ with N₂ is injected at the other inlets, B. The molar fraction of O₂ was varied from 0.1 to 0.4, and the molar fraction of N₂ was varied from 0.9 to 0.6. The injection was made at 25°C and 1 bar. The *First Set* is composed of four different cases. The specifications of *Case1* to *Case4* are presented in Table VI.3.

Table VI.3 NETcombustor *First Set* simulations.

First Set											
	Species	$y_{in} (A)$	$y_{in} (B)$	$\overline{y_{out}}$	X_{H_2}	X_{O_2}	r_{max} ($\frac{kmol}{m^3s}$)	Q_{max} (kJ/h)	T_{max} (°C)	$\overline{T_{out}}$ (°C)	$\overline{Re_{out}}$
Case1 Da = 266 $\theta = 5.81$	H ₂	0	1	0.44	0.17	1	0.53	28.2	1268	817	120
	O ₂	0.1	0	0							
	N ₂	0.9	0	0.46							
	H ₂ O	0	0	0.10							
Case2 Da = 234 $\theta = 2.90$	H ₂	0	1	0.35	0.34	1	1.05	56.0	2057	1550	81
	O ₂	0.2	0	0							
	N ₂	0.8	0	0.43							
	H ₂ O	0	0	0.22							
Case3 Da = 264 $\theta = 1.93$	H ₂	0	1	0.26	0.52	1	1.56	83.3	2683	2238	61
	O ₂	0.3	0	0							
	N ₂	0.7	0	0.65							
	H ₂ O	0	0	0.086							
Case4 Da = 329 $\theta = 1.44$	H ₂	0	1	0.17	0.67	0.97	2.06	109.8	3062	2788	50
	O ₂	0.4	0	0.011							
	N ₂	0.6	0	0.72							
	H ₂ O	0	0	0.11							

The results of Table VI.3 show that as the mole fraction of oxygen increases (smaller θ), the conversion of fuel, H₂, increases. In fact, for lower molar fractions of oxygen, there is not enough

oxidizer to burn all the fuel, *Case4* is the only simulation in which oxygen is not in excess, i.e., $X_{O_2} < 1$.

As the conversion of H_2 increases, the maximum heat of combustion and temperature increase, as well as the outlet temperature.

As shown in Figure VI.21d, for a larger initial fraction of oxygen (higher conversion of fuel), the reaction is extended to every row of NETmix. In contrast, for the lower fraction of oxygen, *Case1*, the reaction occurs just in the first half of the network, as shown in Figure VI.21a. Moreover, Figure VI.21 shows that the reaction rate increases as the initial fraction of oxygen increases, attaining a maximum of $2.06 \text{ kmol}/(\text{m}^3\text{s})$ in *Case4*. However, for lower initial fractions of oxygen, the number of rows with the maximum reaction rate is larger. It is also visible that the reaction starts to occur in the chambers of the first row, which have a fuel and an oxygen inlet stream (middle chambers), and then continues in the adjacent chambers of the next rows, forming a V shaped map.

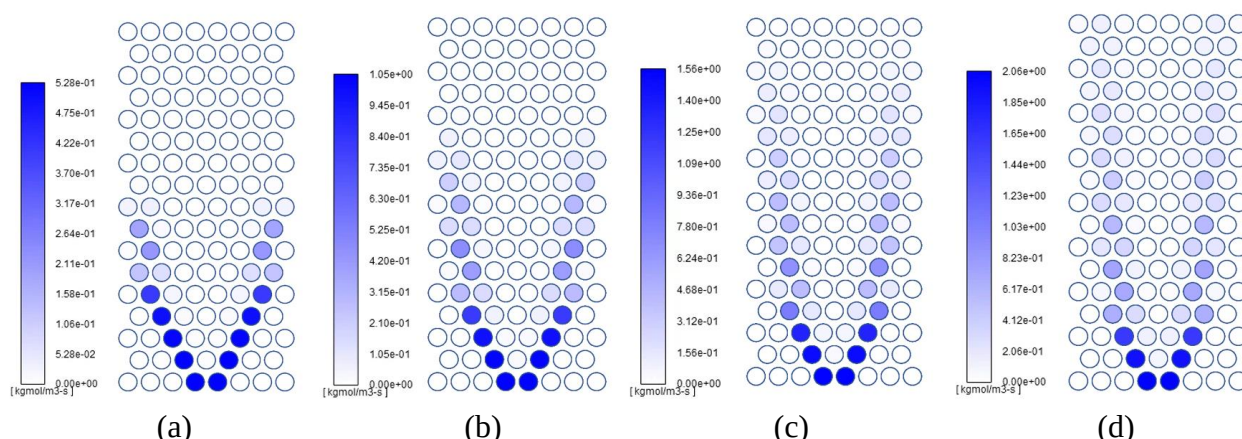


Figure VI.21 First set reaction rate, r , map of: (a) *Case1*, (b) *Case2*, (c) *Case3* and (d) *Case4*

The maximum heat of combustion is larger in *Case4* where the conversion of fuel is higher, as shown in Figure VI.22d. In similarity to the reaction rate, the heat of combustion maps are V shaped and the number of rows with the maximum value is higher for lower conversions of fuel, as visible in Figure VI.22.

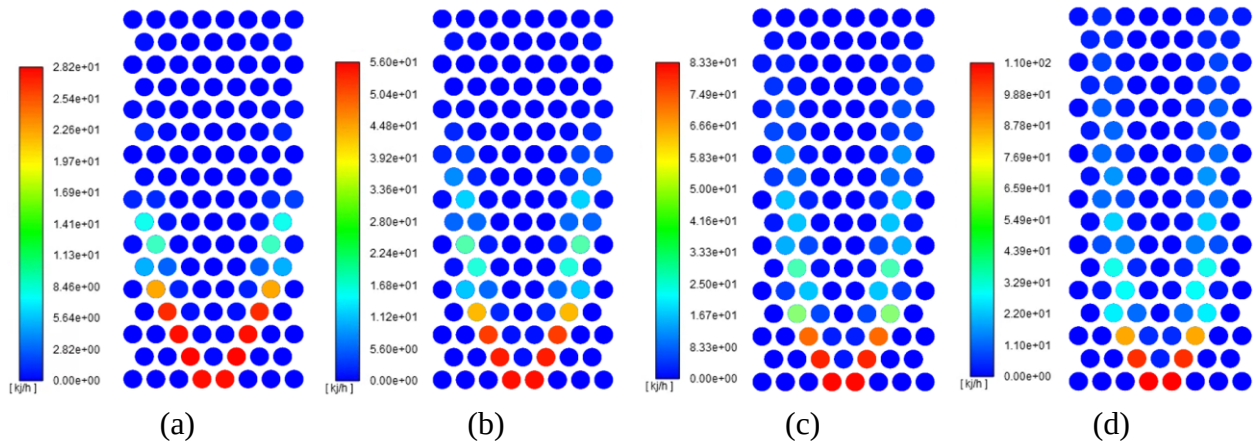


Figure VI.22 First set combustion heat, Q , map of: (a) Case1, (b) Case2, (c) Case3 and (d) Case4.

The temperature maps of Figure VI.23 show that for a larger initial fraction of oxygen the highest temperatures are attained from a lower row and a larger number of chambers have the maximum temperature. The temperature starts to increase in the middle chambers of the first row, where the reaction starts. The maps have an *arrow* shape with gets thinner as the initial fraction of oxygen increases. Figure VI.23 also shows that the temperature attains higher values in the edge columns than in the middle columns.

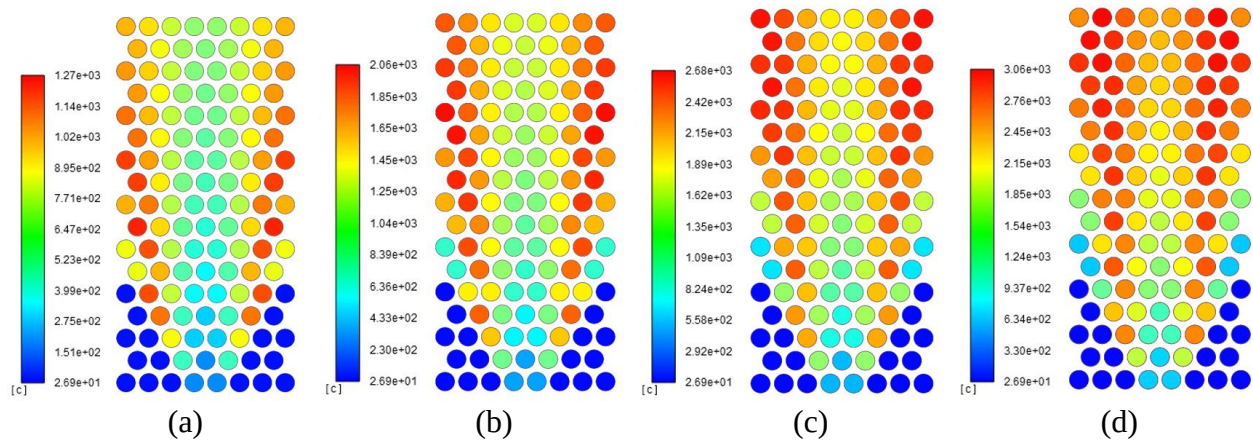


Figure VI.23 First set temperature, T , map of: (a) Case1, (b) Case2, (c) Case3 and (d) Case4.

As expected, as the initial fraction of oxygen increases from Case1 to Case4, the consumption of fuel increases, as shown in Figure VI.24. In fact, the number of chambers without fuel is higher in Case4, which is the only case without fuel in the last row. For all the cases, the molar fraction of H_2 is smaller in the chambers with higher temperature, as shown in Figure VI.24.

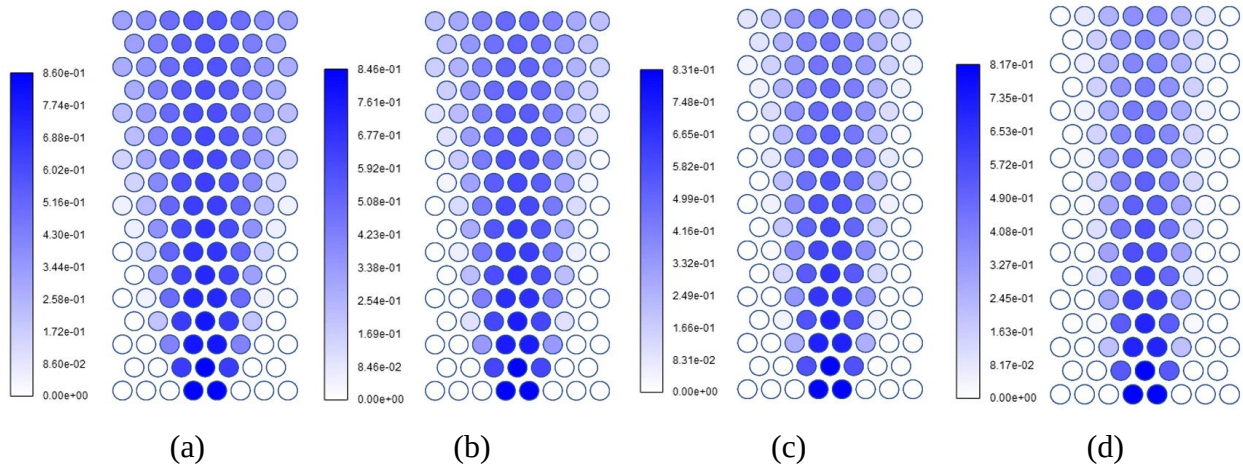


Figure VI.24 First set molar fraction of H_2 , y_{H_2} , map of: (a) Case1, (b) Case2, (c) Case3 and (d) Case4.

In Case1, where the initial oxygen fraction is lower, all the oxygen is consumed until the 8th row of chambers. As the initial fraction of oxygen increases, its consumption is slower and for the largest initial fraction of oxygen, Case4, oxygen is present in the last row of chambers, as shown in Figure VI.25.

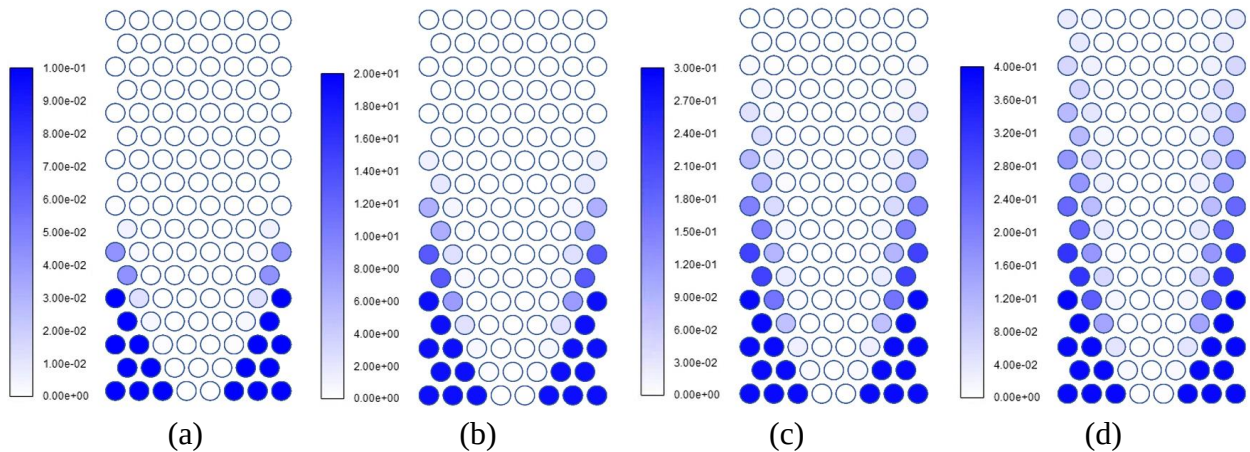


Figure VI.25 First set molar fraction of O_2 , y_{O_2} , map of: (a) Case1, (b) Case2, (c) Case3 and (d) Case4.

As the conversion of fuel increases from Case1 to Case4, a larger amount of water is produced, as shown in Figure VI.26. The maps of the molar fraction of the reactants are V shaped, in similarity to the heat of combustion map. Differently, in the water production map it is possible to distinguish an *arrow* shape, in similarity with the temperature maps.

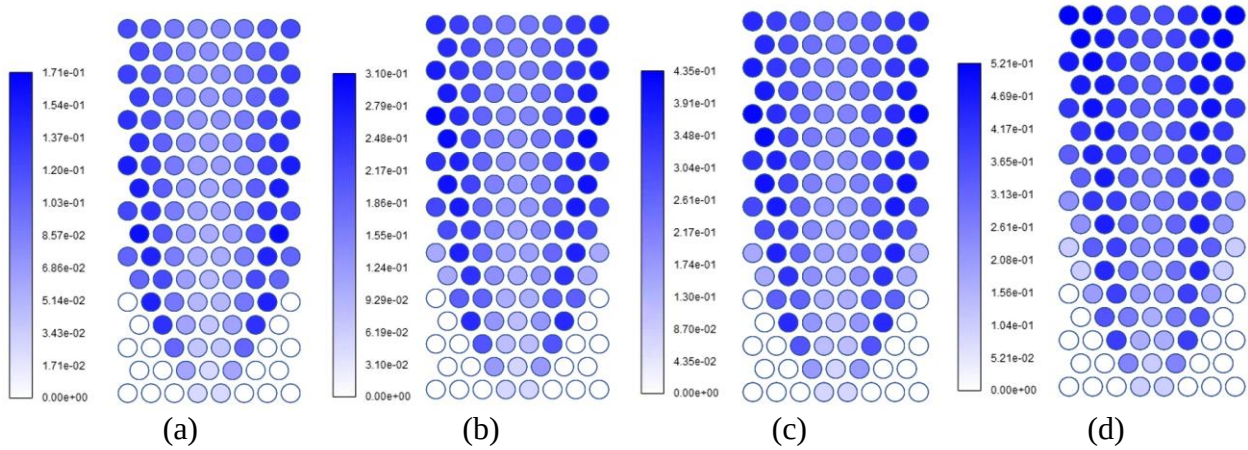


Figure VI.26 First set molar fraction of H_2O , y_{H_2O} , map of: (a) *Case1*, (b) *Case2*, (c) *Case3* and (d) *Case4*.

As the reaction occurs, the physical properties of the mixture change, especially due to the formation of water and temperature raise. In Figure VI.27 are shown the maps of the viscosity where is visible that as the temperature increases and water is produced, the viscosity increases. Between *Case1* and *Case4* the increase in the maximum temperature is more than $1500\text{ }^{\circ}\text{C}$, and the viscosity increases one order of magnitude.

The density decreases for higher temperatures, as water is formed, as visible in Figure VI.28. From *Case1* to *Case4*, the density increases ca. 0.05 kg/m^3 .

As a result of the temperature raise and changes in the mixture properties, the velocity increases, as shown in Figure VI.29. From *Case1* to *Case4* the velocity doubles, approximately.

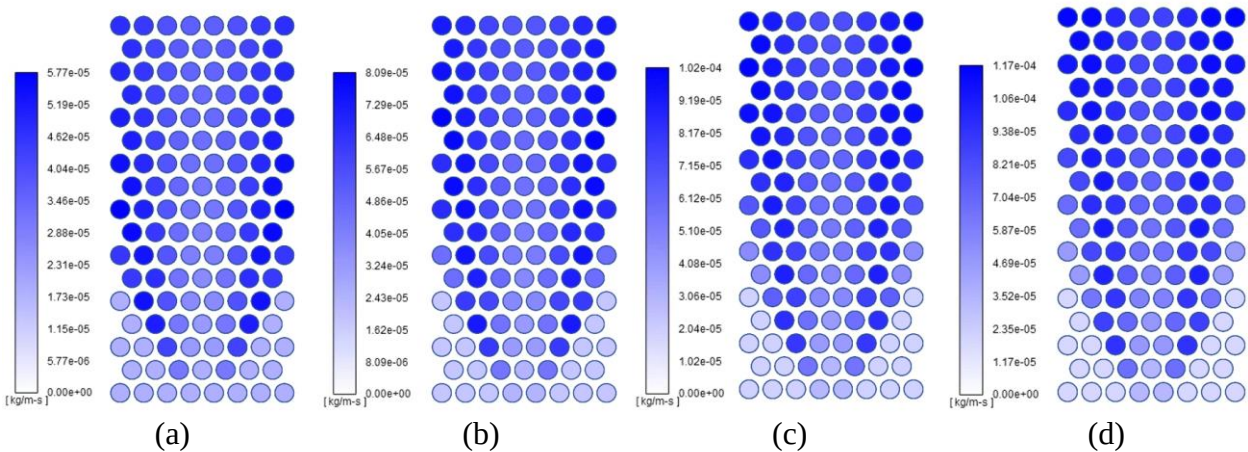
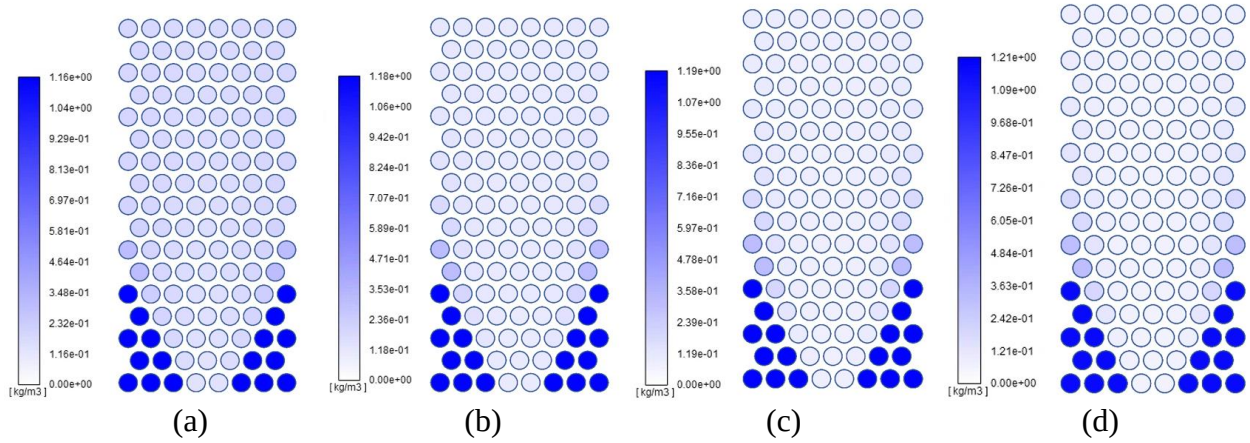
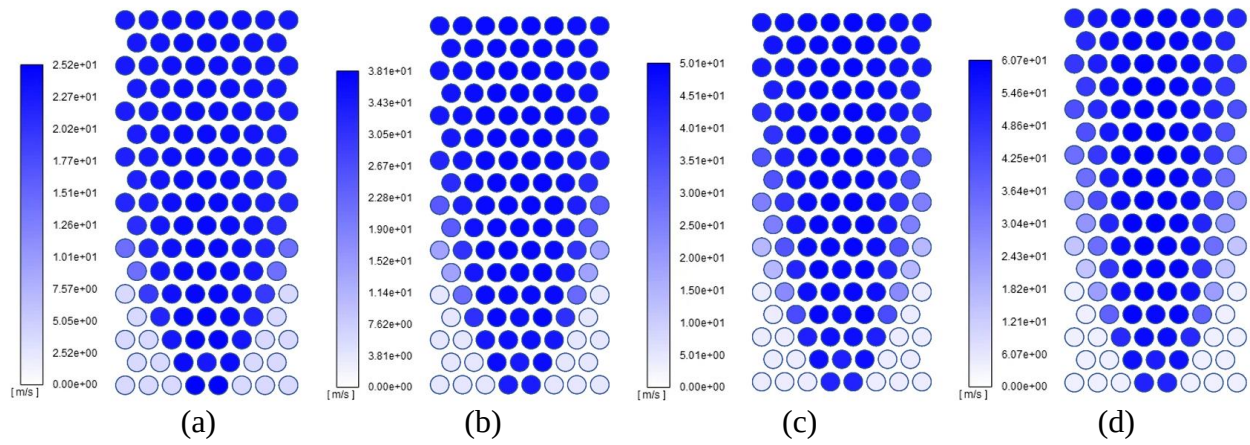


Figure VI.27 First set viscosity, μ , map of: (a) *Case1*, (b) *Case2*, (c) *Case3* and (d) *Case4*.


 Figure VI.28 First set density, ρ , map of: (a) Case1, (b) Case2, (c) Case3 and (d) Case4.

 Figure VI.29 First set velocity, v , map of: (a) Case1, (b) Case2, (c) Case3 and (d) Case4.

As shown in Table VI.3, for higher temperatures the Re number decreases. For an outlet temperature of 817 °C, in Case1, the Reynolds in the last row is 120, more than a half lower, in relation to the initial Re. In Case4, with an outlet temperature of 2788 °C, the Re in the last row of chambers is 50. In Figure VI.30 is also visible that the Re number is lower in the chambers with the maximum temperature.

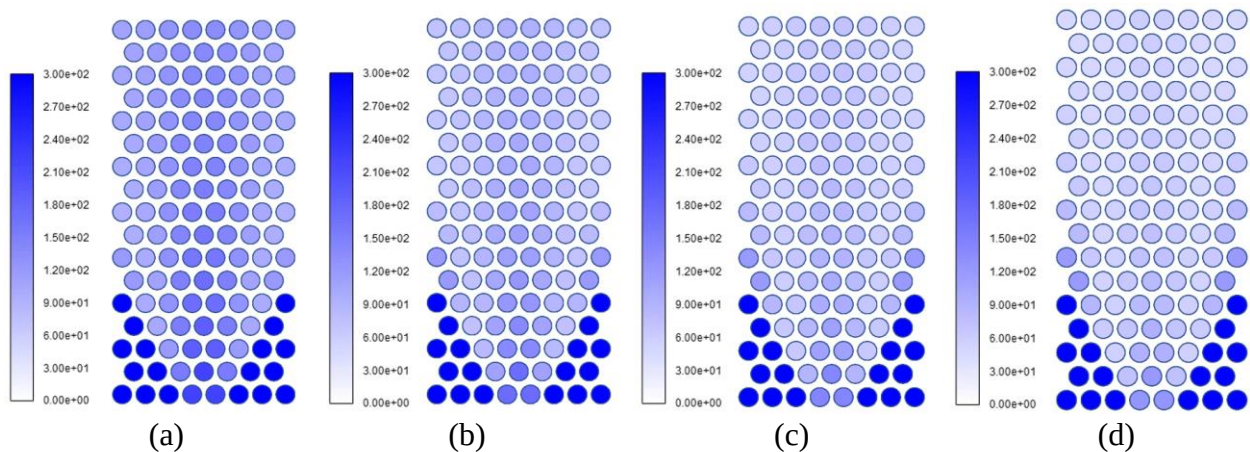


Figure VI.30 First set Reynolds number, Re, map of: (a) Case1, (b) Case2, (c) Case3 and (d) Case4.

VI.2.1.2 Second Set

With the injection scheme, AAAAAABBBAAAAA, in the *Second Set*, pure O₂ is injected at the middle inlets, B, and a mixture of H₂ with N₂ is injected at the other inlets, A. The molar fraction of H₂ was varied from 0.1 to 0.4 and the molar fraction of N₂ was varied from 0.9 to 0.6. The injection was made at 25°C and 1 bar. The *Second Set* is composed of four different cases. The specifications of *Case1* to *Case4* are presented in Table VI.4.

Table VI.4 NETcombustor *Second Set* simulations.

Second Set											
	Species	$y_{in} (A)$	$y_{in} (B)$	$\overline{y}_{out}$	X_{H_2}	X_{O_2}	r_{max} $\left(\frac{kmol}{m^3s}\right)$	Q_{max} (kJ/h)	T_{max} (°C)	$\overline{T}_{out}$ (°C)	$\overline{Re}_{out}$
Case1 Da = 283 $\theta = 0.32$	H ₂	0.1	0	0	1	0.32	0.29	15.5	779	728	126
	O ₂	0	1	0.089							
	N ₂	0.9	0	0.82							
	H ₂ O	0	0	0.091							
Case2 Da = 368 $\theta = 0.97$	H ₂	0.2	0	0.008	0.97	0.69	0.63	33.8	1391	1344	89
	O ₂	0	1	0.037							
	N ₂	0.8	0	0.77							
	H ₂ O	0	0	0.18							
Case3 Da = 410 $\theta = 1.18$	H ₂	0.3	0	0.071	0.79	0.94	1.04	55.7	1953	1591	80
	O ₂	0	1	0.007							
	N ₂	0.7	0	0.69							
	H ₂ O	0	0	0.23							
Case4 Da = 427 $\theta = 1.78$	H ₂	0.4	0	0.18	0.56	1	1.53	81.6	2427	1535	83
	O ₂	0	1	0							
	N ₂	0.6	0	0.60							
	H ₂ O	0	0	0.22							

Table VI.4 shows that as the initial molar fraction of hydrogen increases (larger θ), the conversion O₂, increases and the conversion of H₂ decreases. For the lowest fraction of fuel, *Case1*, the conversion of H₂ is complete since the oxygen is in excess. For the largest initial fraction of fuel, *Case4*, the fuel is in excess, and all the oxygen is consumed.

As the conversion of H₂ increases, the maximum heat of combustion and temperature increase, as well as the outlet temperature. Comparing with the *First Set* (see Table VI.3), the heat of combustion is ca. 20 kJ/h lower. The temperature is more than 500 °C higher in the first two cases and more than 1000 °C higher in the last two cases, since a larger amount of fuel was injected.

As shown in Figure VI.31, the maximum reaction rate increases as the initial fraction of hydrogen increases. In all cases, the maximum reaction rate is smaller when compared to the *First Set*. It is also visible that in *Case2* and *Case3*, the reaction is extended to every row of NETmix. Differently, in *Case1* and *Case4*, which have the lowest and highest initial fractions of hydrogen, respectively, the reaction does not occur in every row. In similarity to the *First Set*, the number of chambers with the maximum reaction rate is higher for lower initial fractions of fuel, and the maps are V shaped.

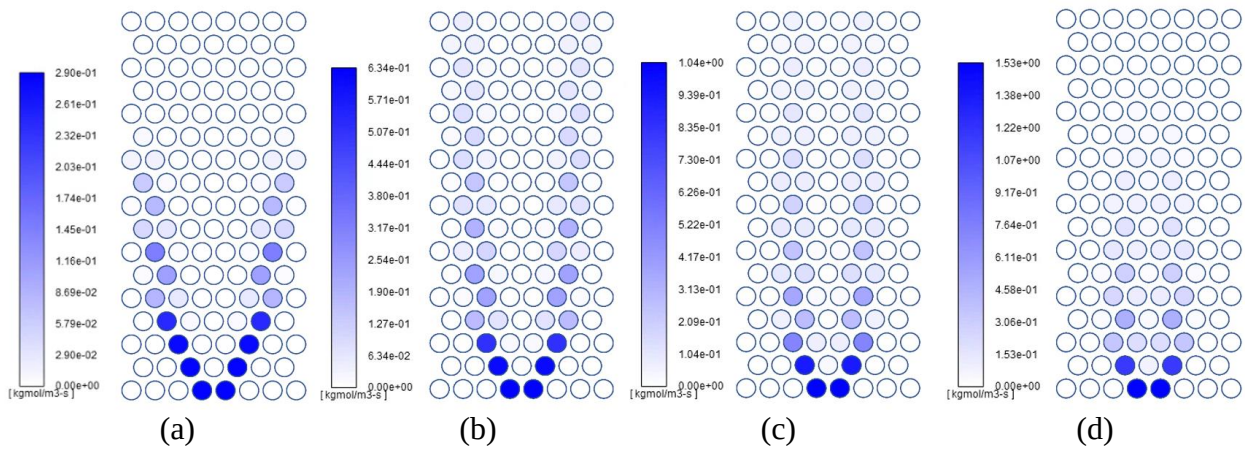


Figure VI.31 Second set reaction rate, r , map of: (a) *Case1*, (b) *Case2*, (c) *Case3* and (d) *Case4*.

In similarity with the *First Set*, the maximum heat of combustion is larger in *Case4*, where the initial fraction of hydrogen is higher, as shown in Figure VI.32d. However, for all the cases, the maximum heat of combustion is ca. 30 kJ/h smaller in comparison to the *First Set*. In similarity with the reaction rate, the heat of combustion maps are V shaped and the number of rows with the maximum value is higher for lower initial fractions of fuel, as visible in Figure VI.32.

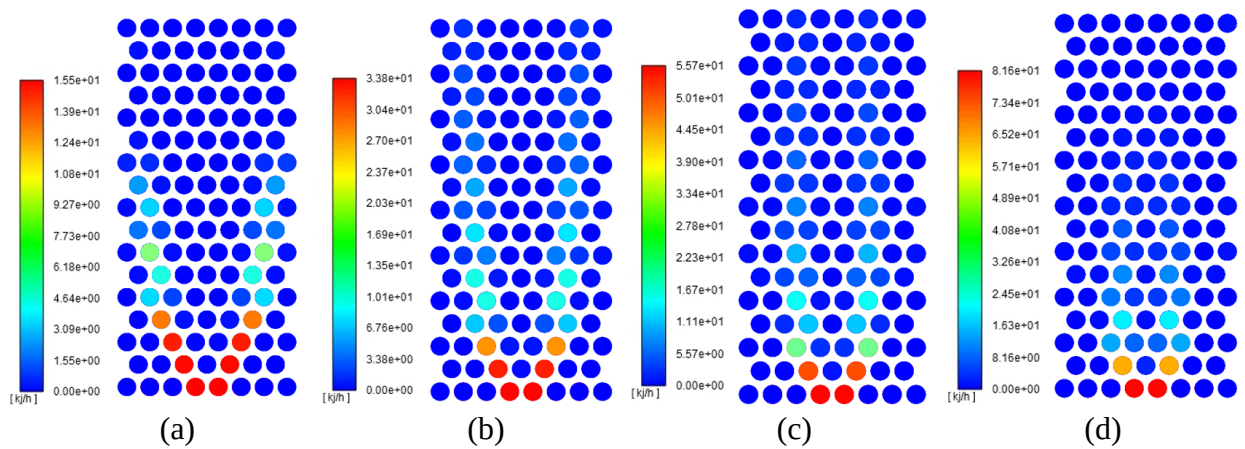


Figure VI.32 Second set heat of combustion, Q , map of: (a) *Case1*, (b) *Case2*, (c) *Case3* and (d) *Case4*.

In the temperature maps of Figure VI.33, it is visible that for a larger initial fraction of hydrogen the maximum temperature is higher. However, in contrast to the *First Set*, from *Case1* to *Case4*,

the number of chambers with the maximum temperature is smaller. Moreover, in the *First Set*, the temperatures were higher at the edges of NETmix and in the *Second Set* the temperatures are higher in the middle chambers. The temperature starts to increase in the middle chambers of the first row, where the reaction starts, assuming an arrow shape which gets thinner as the initial fraction of oxygen increases, as shown in Figure VI.33.

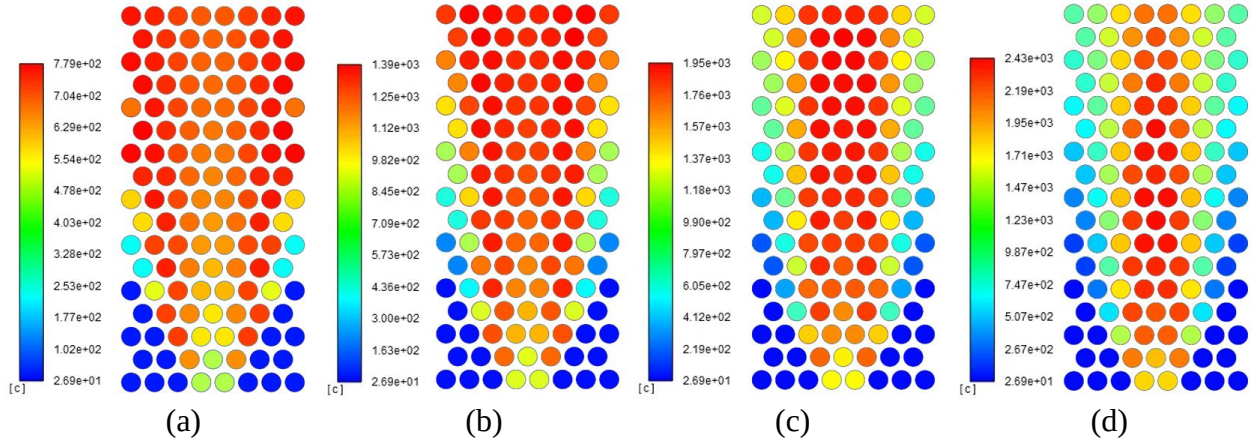


Figure VI.33 *Second set* temperature, T , map of: (a) *Case1*, (b) *Case2*, (c) *Case3* and (d) *Case4*.

As expected, as the initial fraction of hydrogen increases from *Case1* to *Case4*, the consumption of fuel decreases, as shown in Figure VI.34. In fact, the number of chambers without fuel is higher in *Case1* which is the only case without fuel in the chambers of the last row. For all cases, the molar fraction of H_2 is smaller in the rows where the temperature is higher, as shown in Figure VI.34.

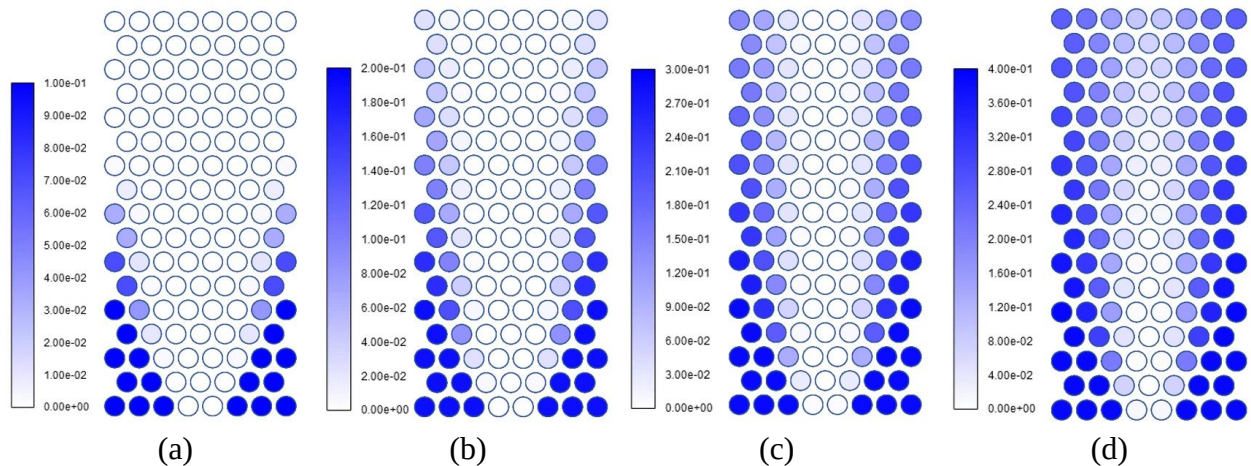


Figure VI.34 *Second set* molar fraction of H_2 , y_{H_2} , map of: (a) *Case1*, (b) *Case2*, (c) *Case3* and (d) *Case4*.

In *Case4*, where the initial hydrogen fraction is higher, all the oxygen is consumed until the 10th row of chambers. As the initial fraction of hydrogen decreases, the consumption of oxygen is slower. In fact, from *Case1* to *Case3*, there is oxygen in NETmix until the last row of chambers, as visible in Figure VI.35.

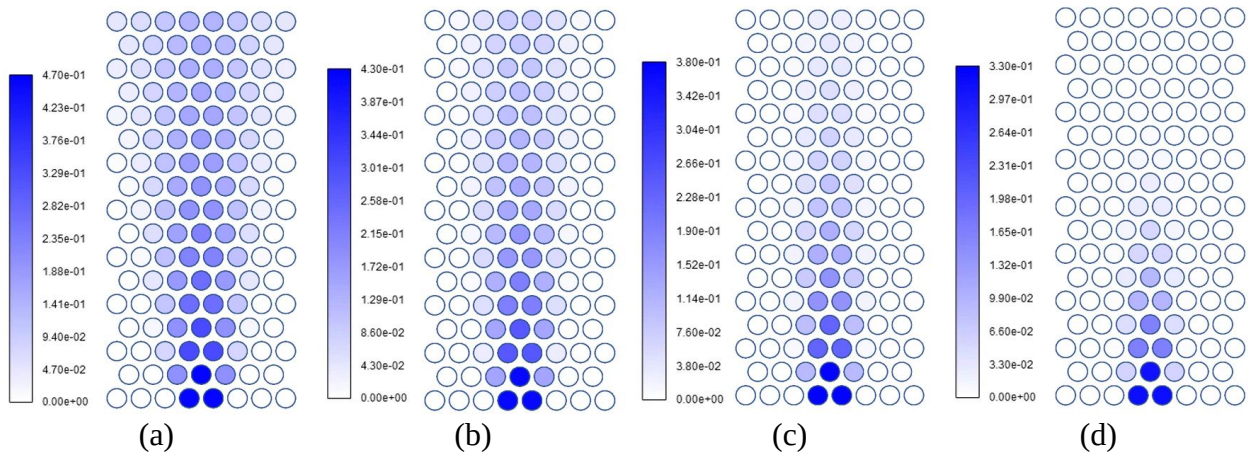


Figure VI.35 Second set molar fraction of O_2 , y_{O_2} , map of: (a) *Case1*, (b) *Case2*, (c) *Case3* and (d) *Case4*.

As the initial fraction of fuel decreases, from *Case1* to *Case4*, the maximum fraction of produced water increases. However, the number of chambers with the maximum fraction of water is smaller, as visible in Figure VI.36. It is possible to distinguish an *arrow* in the maps of Figure VI.36, in similarity to temperature maps.

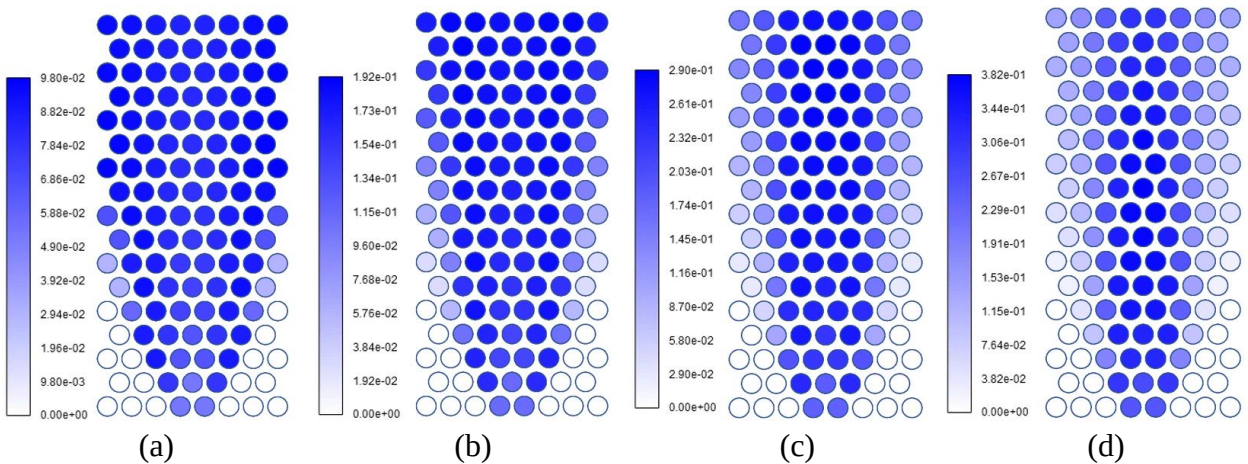
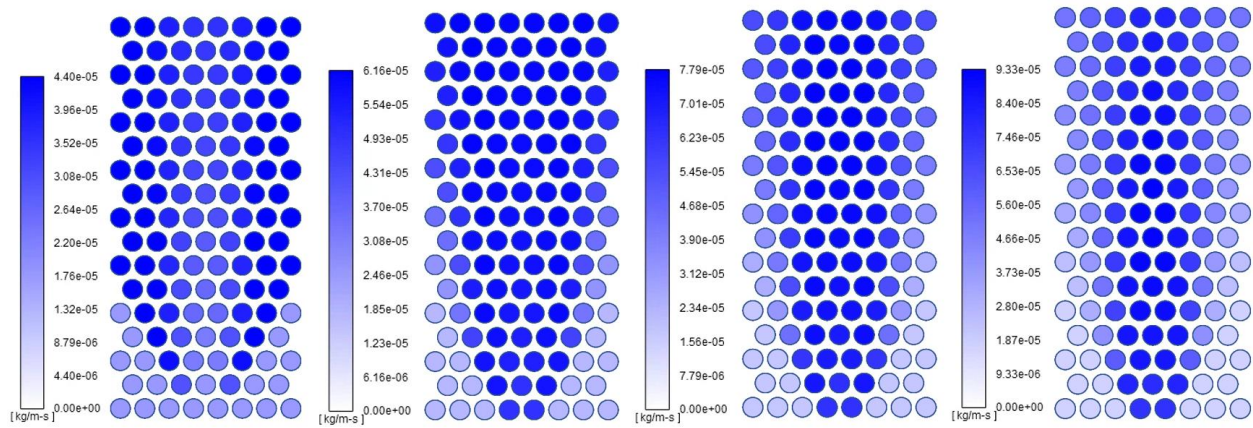


Figure VI.36 Second set molar fraction of H_2O , y_{H_2O} , map of: (a) *Case1*, (b) *Case2*, (c) *Case3* and (d) *Case4*.

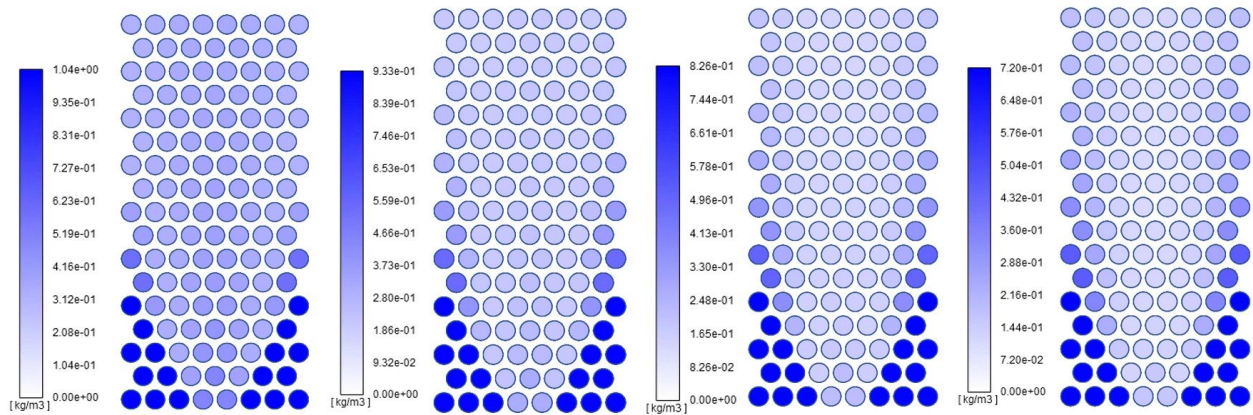
As the reaction occurs, the physical properties of the mixture change, especially due to the water formation and temperature raise. In Figure VI.37 are shown the maps of the viscosity which show that as the temperature increases and water is produced, the viscosity increases. From *Case1* to *Case4* the viscosity doubles, approximately.

In contrast, the density decreases for higher temperatures and in the presence of water, as shown in Figure VI.38, from *Case1* to *Case4*.

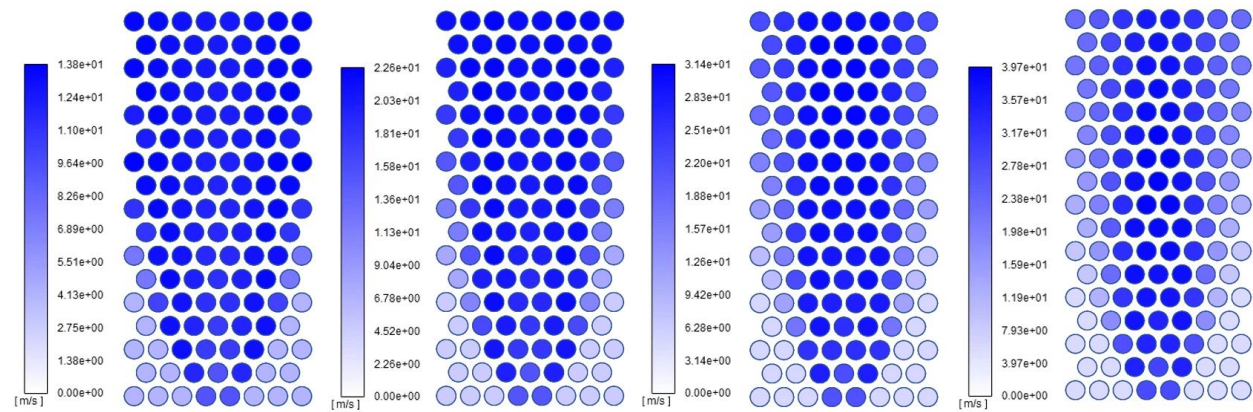
As a result of the temperature raise and changes in the mixture properties, the velocity increases, as shown in Figure VI.39. From *Case1* to *Case4* the velocity triples, approximately.



(a) (b) (c) (d)
Figure VI.37 Second set viscosity, μ , map of: (a) Case1, (b) Case2, (c) Case3 and (d) Case4.



(a) (b) (c) (d)
Figure VI.38 Second set density, ρ , map of: (a) Case1, (b) Case2, (c) Case3 and (d) Case4.



(a) (b) (c) (d)
Figure VI.39 Second set velocity, v , map of: (a) Case1, (b) Case2, (c) Case3 and (d) Case4.

As shown in Table VI.4, for higher temperatures the Re number decreases, for an outlet temperature of 728 °C, in Case1, the Reynolds in the last row is 126, nearly a half of the initial Re. In Case4, with an outlet temperature of 1535 °C, the Re in the last row of chambers is 83. In Figure VI.40 is also visible that the Re number is lower in the chambers where the temperature is higher.

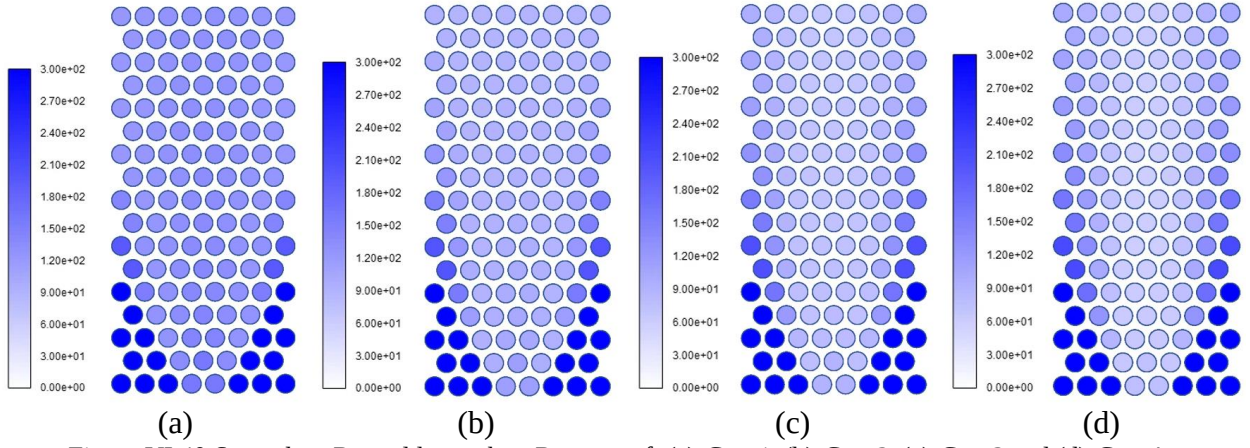


Figure VI.40 Second set Reynolds number, Re , map of: (a) Case1, (b) Case2, (c) Case3 and (d) Case4.

VI.2.2 Global H_2 Combustion in NETcombustor

In this section, NETcombustor will be used to study the hydrogen combustion in the NETmix reactor. Different reactive mixtures will be used, including premixed and non-premixed cases, in similarity to the analysis of section V.3.2. The reactive mixtures have $Da < 1$; thus, the reaction is not limited by diffusion.

The results of NETcombustor will be compared with the CFD simulations that were performed in the previous chapters with ExtendedNUB, the reduced geometric model of the NETmix reactor.

Reaction Kinetics

The global scheme for the hydrogen combustion with one reaction will be used, $H_2 + 0.5O_2 \rightarrow H_2O$, (see Section V.1.2.1). The reaction rate is given by

$$r = kfC_{H_2}C_{O_2} \quad (VI.11)$$

in which C is the molar concentration of the reactants. The Arrhenius parameters for the calculation of kf (Equation V.4a) are $A = 9.87 \times 10^8 \text{ m}^3/(\text{kmol s})$, $b = 0$ and $E_a = 3.10 \times 10^7 \text{ J/kmol}$.

If the backward reaction is included, $H_2 + 0.5O_2 \leftrightarrow H_2O$, the reaction rate is given by

$$r = kfC_{H_2}C_{O_2} - kbC_{H_2O} \quad (VI.12)$$

in which the backward rate coefficient, kb , is calculated with Equation V.4b.

VI.2.2.1 Premixed Combustion

The global scheme was used to simulate the hydrogen combustion in NETcombustor. For premixed combustion, a mixture of $\text{H}_2\text{-O}_2\text{-N}_2$ was injected at each inlet stream, at 25°C and 1 bar, with the injection scheme AAAAAAAAAAAAAA. Since NETcombustor is based on the CSTR equations to represent the NETmix chambers, the model is not as sensitive as the CFD equations to predict the formation of hotspots inside the chambers. The outlet temperature of NETcombustor will then be compared with the temperature in the centre of chamber C8 of the CFD simulations where the temperature is homogeneous in most cases. Note that, the comparison is not performed with the outlet of ExtendedNUB due to the presence of backflow, as shown in the maps of Chapter V (see Appendix C).

Table VI.5 shows the reactive systems that were simulated: *R1* and *R2* without the reverse reaction, *R1b* and *R2b* with the reverse reaction, and the respective comparison with the CFD simulations. In *R1b*, the value of kb , in the order of $10^6 \text{ kmol}/(\text{m}^3 \text{ s})$, is two orders of magnitude lower when compared to kf , in the order of $10^8 \text{ kmol}/(\text{m}^3 \text{ s})$. The difference of the outlet temperature between *R1* and *R1b* is then ca. 39%. In fact, for a large amount of fuel in the reactive mixture, $\theta = 2$, which is not diluted by N_2 , the temperature of combustion is higher, and the effect of kb is more pronounced, as shown in Section V.3.2.6 (see Figure V.36). It is visible that if the reverse reaction is considered it is not possible to attain complete conversion of oxygen. Thus, the temperature is lower. In *R2b*, the reactive mixture is diluted by N_2 and has a lower amount of fuel, $\theta = 0.25$. The value of kb , in the order of $10^{-3} \text{ kmol}/(\text{m}^3 \text{ s})$, is largely lower when compared to kf , in the order of $10^7 \text{ kmol}/(\text{m}^3 \text{ s})$. In this way, the influence of the reverse reaction is not visible and the outlet temperature of *R2b* is the same as *R2*. In fact, for $T < 2500^\circ\text{C}$, the effect of kb is not significant (see Figure V.36).

Comparing with the CFD simulations, the outlet temperature between *R1* and *M1* (without backward reaction) differs less than 1%. With the reverse rate, the difference between the two models, *R1b* and *R1*, is ca. 20%. With N_2 , *R2* and *M2* differ ca. 3%. Including the reverse rate, the two models, *R2b* and *B7* differ approximately 5%.

NETcombustor and ExtendedNUB use distinct models for the energy and mass equations, as shown in the previous sections. Moreover, NETcombustor represents a network where only macromixing studies in steady state are simulated, while ExtendedNUB is a reduced model of the reactor where micromixing is analysed in each chamber, using CFD. The outlet temperature of NETcombustor was compared with the temperature at chamber C8 which is not uniform for several CFD cases due to the changes in the mixing features after the hotspot at the reaction front.

In this way, the differences between the two models are expectable and NETcombustor is numerically validated. In fact, the results are similar considering that the two reactor models present large differences.

Table VI.5 Premixed combustion in NETcombustor, at $Re = 300$.

Premixed Combustion							
	Species	$y_{in,left} (A)$	$y_{in,right} (A)$	$\overline{y}_{out}$	X_{H_2}	X_{O_2}	$\overline{T}_{out} (^{\circ}C) / T_{C8} (^{\circ}C)$
R1 Da = 0.14 $\theta = 2$	H ₂	0.8	0.8	0.50	0.50	1	3031
	O ₂	0.2	0.2	0			
	N ₂	0	0	0			
	H ₂ O	0	0	0.50			
ExtendedNUB M1 $\theta = 2$	H ₂	0.8	0.8	0.50	0.50	1	3016
	O ₂	0.2	0.2	0			
	N ₂	0	0	0			
	H ₂ O	0	0	0.50			
R1b Da = 0.14 $\theta = 2$	H ₂	0.8	0.8	0.65	0.27	0.55	1758
	O ₂	0.2	0.2	0.10			
	N ₂	0	0	0			
	H ₂ O	0	0	0.25			
ExtendedNUB B1 $\theta = 2$	H ₂	0.8	0.8	0.59	0.37	0.75	2277
	O ₂	0.2	0.2	0.059			
	N ₂	0	0	0			
	H ₂ O	0	0	0.35			
R2 Da = 0.13 $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	824
	O ₂	0.2	0.2	0.16			
	N ₂	0.7	0.7	0.74			
	H ₂ O	0	0	0.11			
ExtendedNUB M2 $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	851
	O ₂	0.2	0.2	0.16			
	N ₂	0.7	0.7	0.74			
	H ₂ O	0	0	0.11			
R2b Da = 0.13 $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	824
	O ₂	0.2	0.2	0.16			
	N ₂	0.7	0.7	0.74			
	H ₂ O	0	0	0.11			
ExtendedNUB B7 $\theta = 0.25$	H ₂	0.1	0.1	0	1	0.25	871
	O ₂	0.2	0.2	0.16			
	N ₂	0.7	0.7	0.74			
	H ₂ O	0	0	0.11			

R1, R2 – Premixed cases simulated in NETcombustor

R1b, R2b – Premixed cases simulated in NETcombustor, including the reverse rate

M1, M2 – Premixed cases simulated in CFD with Maxwell

B1, B7 – Premixed cases simulated in CFD with Maxwell, including the reverse rate

In similarity to the CFD simulations of the previous chapters, if nitrogen is not used to dilute the initial reactive mixture, higher temperatures are attained.

As an example, in Figure VI.41 and in Figure VI.42 are shown the NETcombustor maps of *R1* (both cases have a similar pattern).

If a premixed mixture is used, all the fuel or oxygen is consumed in the first row of chambers, as shown in Figure VI.41a, where it is visible that the reaction rate is different from zero. Moreover, Figure VI.42a shows that the molar fraction of oxygen is zero from the 2nd to the last row of chambers.

In the chambers that have the maximum reaction rate, the heat of combustion is maximum, as shown in Figure VI.41b. The maximum temperature is attained in the first row, where the reaction occurs, as visible in Figure VI.41c, and its value is maintained towards the outlet of the reactor. As the reaction occurs, water is produced, as shown in Figure VI.42b.

In Figure VI.42c it is shown that the Re number decreases in the first row, where the maximum temperature is attained, and is then maintained in the rest of the reactor.

For *R1*, which does not have N_2 in the reactive mixture, a high temperature of 3031 °C is attained. The maximum reaction rate is 6.17 kmol/(m³ s), and the heat of combustion reaches 1184 kJ/h. If N_2 is used in the reactive mixture, *R2*, a lower temperature is attained, 824 °C. The maximum reaction rate is lower, 0.58 kmol/(m³ s), as well as the maximum heat of combustion, 111 kJ/h. The Re number is nearly the triple ($Re = 40$ in *R1* and $Re = 118$ in *R2*) since the temperature is lower.

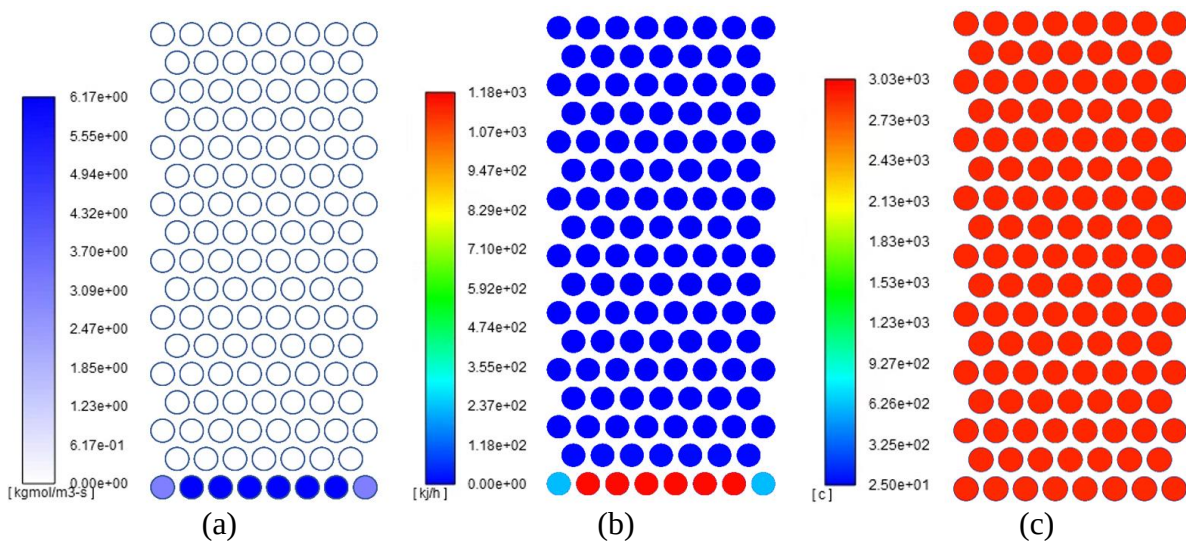


Figure VI.41 *R1* NETcombustor map of: (a) reaction rate, (b) heat of combustion and (c) temperature.

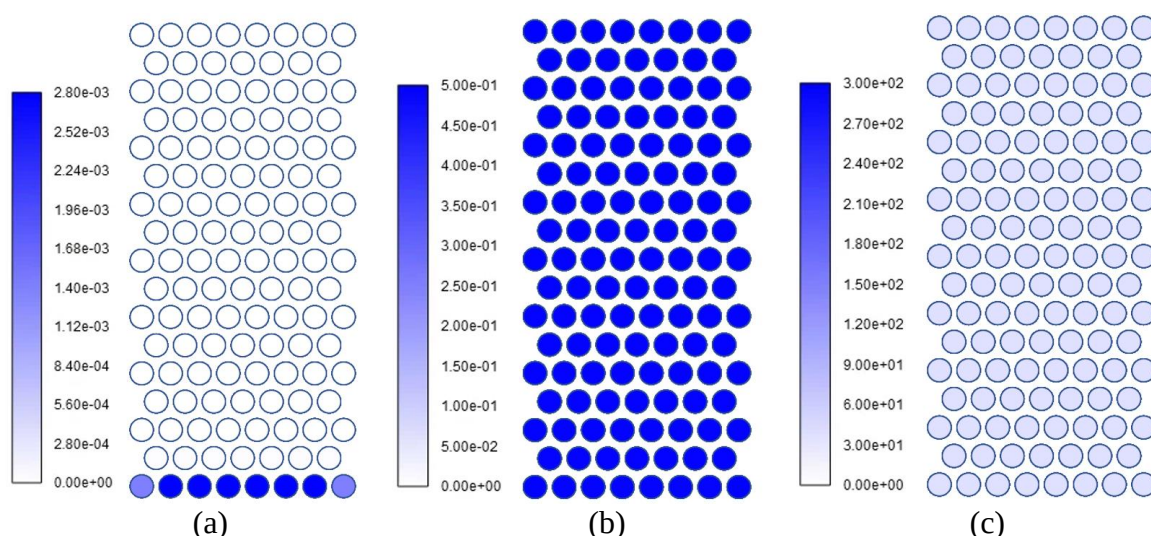


Figure VI.42 *R1* NETcombustor map of: (a) y_{O_2} , (b) y_{H_2O} and (c) Re number.

The maps of *R1b* and *R2b* are similar to the maps of *R1* and *R2*. If the backward reaction is considered, *R1b*, the maximum reaction rate, $3.42 \text{ kmol}/(\text{m}^3 \text{ s})$, is nearly a half of the reaction rate of *R1*. The heat of combustion of *R1b*, 656 kJ/hr , is also approximately a half of the heat of combustion of *R1*. As previously said, the temperature inside the reactor is lower if the reverse reaction is considered, having a maximum of 1758°C . As visible in Table VI.5, the result of *R2b* is the same as *R2* since k_b is considerably smaller than k_f . In this way, the reaction rate as well as the heat of combustion of *R2b* are similar to *R2*.

Effect of k_b

To analyse the effect of k_b in NETcombustor, in similarity to Section V.3.2.5, k_b' will be calculated using the Arrhenius reaction rate expression (Equation V.4a) with large parameters, $A = 1 \times 10^{15} \text{ m}^3/(\text{kmol s})$, $b = 0$ and $E_a = 1 \times 10^8 \text{ J/kmol}$.

In Table VI.6 are shown the results of this approach for the cases that were previously presented, *R1* and *R2*, as well as the comparison with the CFD simulations. In similarity to the CFD simulations of Section V.3.2.5, if k_b' is used, the temperatures are significantly lower as well as the conversions. As expected for a large k_b , in Table VI.6 is shown that cold combustion occurs, i.e., the temperatures are below 585°C , and the conversions are not total. The difference in the outlet temperature between the CFD simulations and NETcombustor is ca. 14% and 7% for *R1'* and *R2'*, respectively.

Table VI.6 Non-premixed combustion with large kb in NETcombustor, at $Re = 300$.

Premixed Combustion with large kb							
	Species	$y_{in,right}(A)$	$y_{in,left}(A)$	$\overline{y}_{out}$	X_{H_2}	X_{O_2}	$\overline{T}_{out}(^{\circ}C)/T_{C8}(^{\circ}C)$
<i>R1' (with backward)</i> $\theta = 2$	H ₂	0.8	0.8	0.79	0.020	0.040	176
	O ₂	0.2	0.2	0.19			
	N ₂	0	0	0			
	H ₂ O	0	0	0.018			
<i>B1' (ExtendedNUB)</i> $\theta = 2$	H ₂	0.8	0.8	0.78	0.027	0.060	249
	O ₂	0.2	0.2	0.19			
	N ₂	0	0	0			
	H ₂ O	0	0	0.027			
<i>R2' (with backward)</i> $\theta = 0.25$	H ₂	0.1	0.1	0.077	0.24	0.060	226
	O ₂	0.2	0.2	0.19			
	N ₂	0.7	0.7	0.71			
	H ₂ O	0	0	0.025			
<i>B7' (ExtendedNUB)</i> $\theta = 0.25$	H ₂	0.1	0.1	0.081	0.17	0.022	194
	O ₂	0.2	0.2	0.19			
	N ₂	0.7	0.7	0.71			
	H ₂ O	0	0	0.020			

R1', R2' – Premixed cases simulated in NETcombustor, including the reverse rate with large kb'

B1', B7' – Premixed cases simulated in CFD with Maxwell, including the reverse rate with large kb'

As an example, in Figure VI.43 and in Figure VI.44 are shown the NETcombustor maps of *R1'* (both cases have a similar pattern). Differently from *R1* and *R2*, if kb' is used, the reaction occurs mainly in the first two rows, as shown in Figure VI.43a. The reaction rate is maximum in the first row, and minimum in the second row. In most of the reactor, the reaction rate is close to zero. The maximum reaction rate is larger in *R1'*, 3.10×10^{-1} kmol/(m³ s), than in *R2'*, 1.49×10^{-1} kmol/(m³ s), since the amount of fuel in the reactive mixture is larger. The heat of combustion is also higher, 59 kJ/h in *R1'* and approximately a half in *R2'*, 29 kJ/h. Note that, as expected, the heat of combustion is higher in the chambers with a higher reaction rate, as shown in Figure VI.43b.

While in *R1* and *R2* the outlet temperature was similar to the maximum temperature, with kb' the decrease of temperature is more pronounced, as shown in Figure VI.43c. Moreover, the temperature at the side chambers of the reactor is higher. If a large kb is used, the maximum temperature is lower in *R1'*, 190 °C, than in *R2'*, 249 °C.

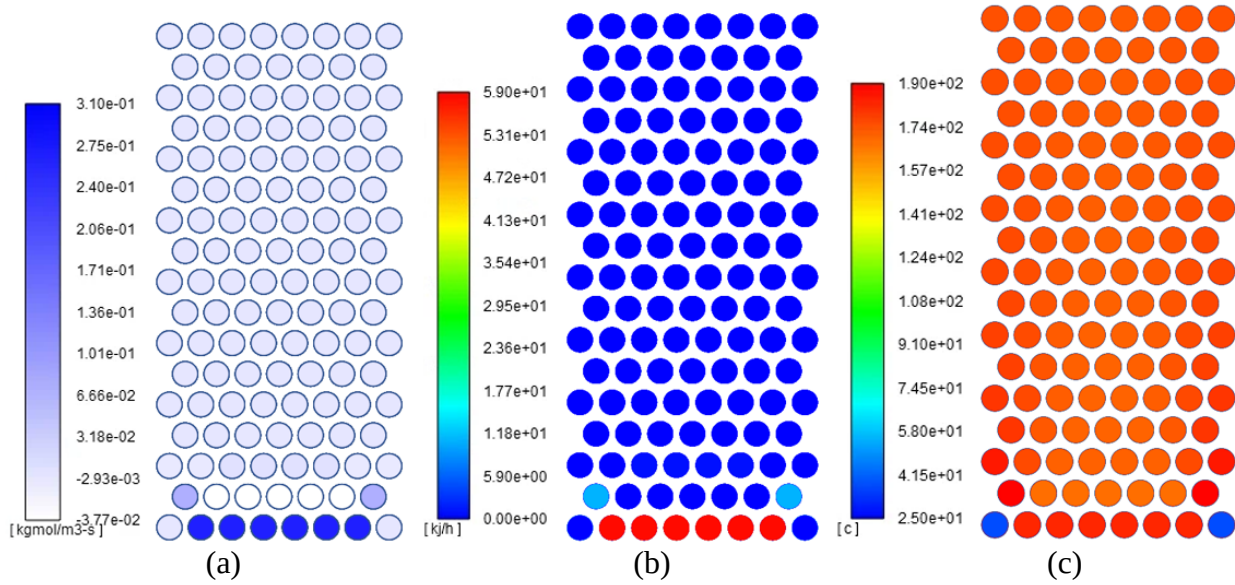


Figure VI.43 *R1* ' NETcombustor map of: (a) reaction rate, (b) heat of combustion and (c) temperature.

Figure VI.44a shows that oxygen is consumed in nearly all the rows of the reactor and attains lower values at the side chambers. The production of water is uniform, as visible in Figure VI.44b.

The Re number is higher when compared with *R1* and *R2* since the temperature inside the reactor is lower, as shown in Figure VI.44c. The lowest Re is 202 in *R1* and 217 in *R2*.

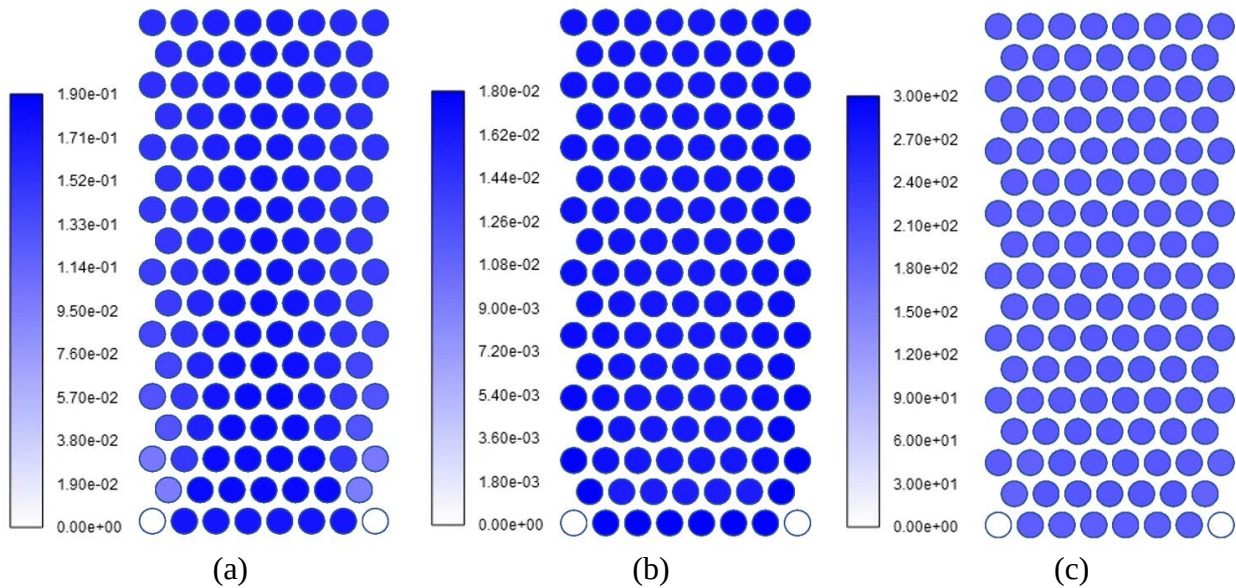


Figure VI.44 *R1* ' NETcombustor map of: (a) y_{O_2} , (b) y_{H_2O} and (c) Re number.

VI.2.2.2 Non-premixed Combustion

In non-premixed combustion, the fuel and oxygen enter the reactor from different streams. In order to compare the results with the CFD simulations of Section V.3.2.3, an alternated injection scheme was used in order to represent six ExtendedNUBs in parallel, CABABABABABABC. At the side chambers, the injector, C, only has the inert compound, N_2 ; in the other chambers, the injector is alternated between the fuel stream, A, and the oxygen stream, B. The injection is made at 25 °C and 1 bar.

In Table VI.7 are presented the cases that were simulated, *R3* to *R5* and *R3b* to *R5b*, as well as the comparison with the ExtendedNUB simulations. In similarity to the previous section, in non-premixed combustion, the influence of the reverse reaction is only noticed for high temperatures. In this way, between the three cases that were simulated *R3* to *R5*, *R4* is the only case in which a small difference of ca. 1% is visible in the outlet temperature when compared to *R4b*.

Table VI.7 shows that the prediction of the outlet temperature by NETcombustor is lower than the CFD result. From *R3* to *R5*, the outlet temperature of NETcombustor differs ca. 12%, 9% and 10%, respectively, of the temperature at C8 of the CFD simulation. With the reverse reaction, the difference to the CFD result is ca. 13%, 19% and 11% for *R3b* to *R5b*, respectively.

In similarity with the previous section, the deviation between NETcombustor and the CFD simulations is acceptable, given the differences between the two models.

Table VI.7 Non-premixed combustion in NETcombustor, at $Re = 300$.

Non-premixed Combustion							
	Species	$y_{in,left}(A)$	$y_{in,right}(B)$	$\overline{y_{out}}$	X_{H_2}	X_{O_2}	$\overline{T_{out}}(^{\circ}C)/T_{C8}(^{\circ}C)$
<i>R3</i> Da = 0.14 $\theta = 0.27$	H ₂	0.1	0	0	1	0.27	454
	O ₂	0	0.2	0.061			
	N ₂	0.9	0.8	0.89			
	H ₂ O	0	0	0.046			
ExtendedNUB <i>M4</i> $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	550
	O ₂	0	0.2	0.066			
	N ₂	0.9	0.8	0.87			
	H ₂ O	0	0	0.064			
<i>R3b</i> Da = 0.14 $\theta = 0.27$	H ₂	0.1	0	0	1	0.27	454
	O ₂	0	0.2	0.061			
	N ₂	0.9	0.8	0.89			
	H ₂ O	0	0	0.046			

ExtendedNUB B10 $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	560
	O ₂	0	0.2	0.071			
	N ₂	0.9	0.8	0.86			
	H ₂ O	0	0	0.066			
R4 Da = 0.23 $\theta = 2.14$	H ₂	0.5	0	0.16	0.47	1	1200
	O ₂	0	0.2	0			
	N ₂	0.5	0.8	0.70			
	H ₂ O	0	0	0.14			
ExtendedNUB M5 $\theta = 2.14$	H ₂	0.5	0	0.14	0.57	1	1341
	O ₂	0	0.2	0			
	N ₂	0.5	0.8	0.68			
	H ₂ O	0	0	0.18			
R4b Da = 0.23 $\theta = 2.14$	H ₂	0.5	0	0.16	0.47	1	1189
	O ₂	0	0.2	0			
	N ₂	0.5	0.8	0.70			
	H ₂ O	0	0	0.14			
ExtendedNUB B11 $\theta = 2.14$	H ₂	0.5	0	0.13	0.57	1	1536
	O ₂	0	0.2	0			
	N ₂	0.5	0.8	0.68			
	H ₂ O	0	0	0.19			
R5 Da = 0.17 $\theta = 8.99$	H ₂	0.9	0	0.62	0.11	1	691
	O ₂	0	0.2	0			
	N ₂	0.1	0.8	0.30			
	H ₂ O	0	0	0.078			
ExtendedNUB M6 $\theta = 8.99$	H ₂	0.9	0	0.63	0.13	1	802
	O ₂	0	0.2	0			
	N ₂	0.1	0.8	0.27			
	H ₂ O	0	0	0.095			
R5b Da = 0.17 $\theta = 8.99$	H ₂	0.9	0	0.62	0.11	1	691
	O ₂	0	0.2	0			
	N ₂	0.1	0.8	0.30			
	H ₂ O	0	0	0.078			
ExtendedNUB B12 $\theta = 8.99$	H ₂	0.9	0	0.63	0.13	1	805
	O ₂	0	0.2	0			
	N ₂	0.1	0.8	0.27			
	H ₂ O	0	0	0.095			

R3 to R5 – Non-premixed cases simulated in NETcombustor

R3b to R5b – Non-premixed cases simulated in NETcombustor, including the reverse rate

M3 to M5 – Non-premixed cases simulated in CFD with Maxwell

B10 to B12 – Non-premixed cases simulated in CFD with Maxwell, including the reverse rate

In non-premixed combustion one of the reactants is nearly completely consumed in the first row of chambers, as visible in Figure VI.45a for *R3*. The maximum reaction rate occurs then in the first row. In the second and third rows the reaction rate is lower than 10^{-2} kmol/(m³ s), as visible in Figure VI.45b. As expected, the maximum heat of combustion is released in the first row, as shown in Figure VI.45c for *R3*.

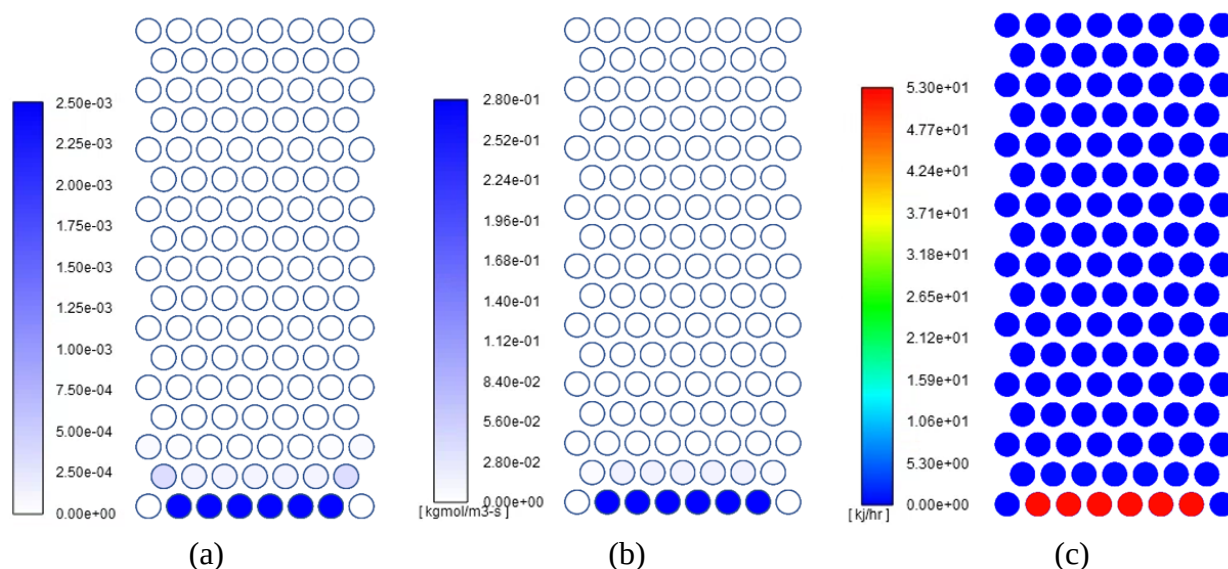


Figure VI.45 *R3* map of: (a) hydrogen mass fraction, (b) reaction rate and (c) heat of combustion.

If a smaller amount of fuel is used in the initial mixture, *R3*, all the fuel is consumed ($X_{H_2} = 1$) and the maximum reaction rate attains 0.28 kmol/(m³ s). In *R4* and *R5*, where a larger amount of fuel is present in the reactive mixture, all the oxygen is consumed and the maximum reaction rate is higher, 1.05 kmol/(m³ s).

The heat of combustion is mainly released in the first row, as previously said. As expected, in *R3*, the total heat of combustion, 335 kJ/h, is lower than in *R4* and *R5*, 1223 kJ/h and 1228 kJ/h, respectively. The maximum heat of combustion is also lower for *R3*, 53 kJ/h, in comparison to *R4* and *R5*, 202 kJ/h.

In *R3*, the amount of fuel in the reactive mixture is low and the oxygen is in excess ($X_{H_2} = 1$). Thus, the maximum temperature, 454 °C, is lower when compared to *R4* and *R5*, as visible in Figure VI.46. *R5* has the highest initial the amount of fuel; however, the oxygen is only enough to burn a small amount of fuel ($X_{H_2} = 0.11$). In this way, the maximum temperature of *R5*, 691 °C, is lower than *R4*, which is the case with the highest temperature, 1200 °C, since the conversion of fuel is higher ($X_{H_2} = 0.47$). Figure VI.46 shows that the highest temperatures are attained in the middle of the reactor.

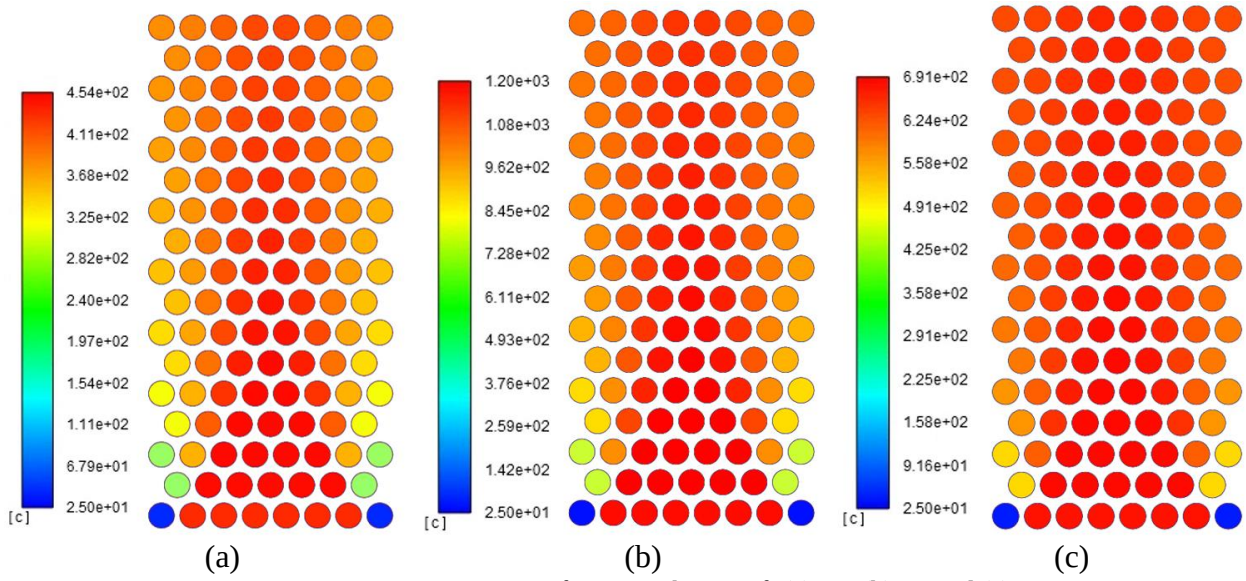


Figure VI.46 Temperature maps of NETcombustor of: (a) *R3*, (b) *R4* and (c) *R5*.

In similarity with the temperature maps, the largest amount of water is produced mainly in the first row where the maximum reaction rate occurs, as shown in Figure VI.47b.

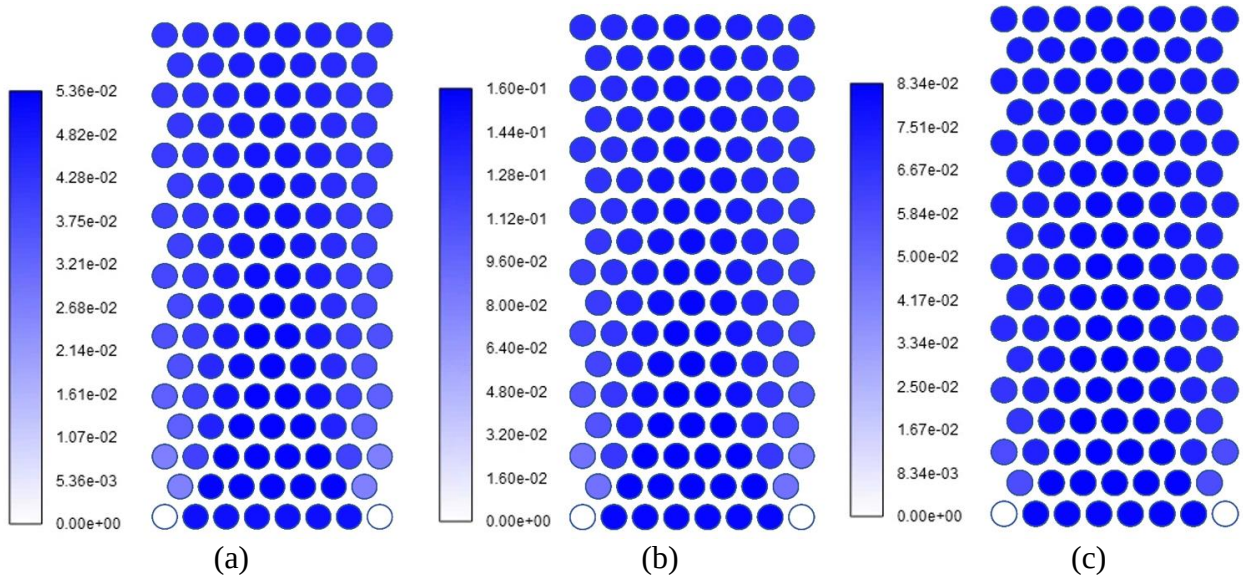


Figure VI.47 y_{H_2O} maps of NETcombustor of: (a) *R3*, (b) *R4* and (c) *R5*.

The outlet Re number is lower for higher temperatures. In this way, as visible in Figure VI.48, *R4* is the case with the smallest Reynolds. For all cases, it is visible that the lowest Re is attained in the middle of the reactor, where the temperature is higher. The lowest Re are 157, 95 and 129 for *R3*, *R4* and *R5*, respectively.

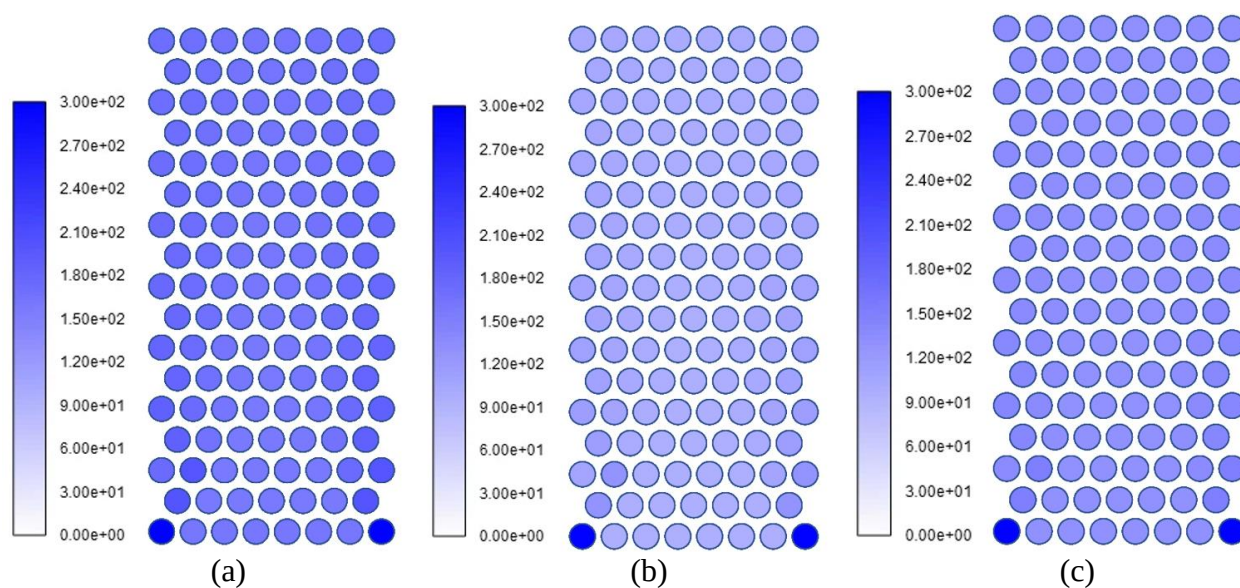


Figure VI.48 Re maps of NETcombustor of: (a) R3, (b) R4 and (c) R5.

The maps of the cases with the reverse reaction are similar to the maps that were shown for the cases without the backward rate. Moreover, since the influence of kb is small, as previously stated in the analysis of Table VI.7, the maximum reaction rate and heat of combustion are similar for both approaches, with and without the reverse reaction. The mole fraction of the reactants and products of R3b to R5b are also the same as R3 to R5.

Effect of kb

In similarity to Section VI.2.2.1 for premixed cases, the effect of using a large kb' will be assessed for non-premixed combustion. In Table VI.8 are shown the previous initial mixtures, R3' to R5', which were simulated with a different reaction rate, and the comparison with the CFD results for the same mixtures.

As expected, the maximum temperatures are lower than 585 °C for all cases and cold combustion occurs. Moreover, the conversion of fuel and oxygen is never total.

The difference of the outlet temperatures between NETcombustor and the CFD simulations is less than 2% for the three cases.

Table VI.8 Non-premixed combustion with large kb in NETcombustor at $Re = 300$.

Non-premixed Combustion with Large kb							
	Species	$y_{in,left}(A)$	$y_{in,right}(B)$	$\overline{y_{out}}$	X_{H_2}	X_{O_2}	$\overline{T_{out}}(^{\circ}C)/T_{C8}(^{\circ}C)$
<i>R3' (with backward)</i> Da = 0.14 $\theta = 0.27$	H ₂	0.1	0	0.024	0.46	0.13	167
	O ₂	0	0.2	0.073			
	N ₂	0.9	0.8	0.88			
	H ₂ O	0	0	0.021			
<i>ExtendedNUB B10'</i> $\theta = 0.27$	H ₂	0.1	0	0.034	0.42	0.17	163
	O ₂	0	0.2	0.094			
	N ₂	0.9	0.8	0.86			
	H ₂ O	0	0	0.016			
<i>R4' (with backward)</i> Da = 0.23 $\theta = 2.14$	H ₂	0.5	0	0.26	0.070	0.17	204
	O ₂	0	0.2	0.054			
	N ₂	0.5	0.8	0.69			
	H ₂ O	0	0	0.025			
<i>ExtendedNUB B11'</i> $\theta = 2.14$	H ₂	0.5	0	0.27	0.097	0.13	201
	O ₂	0	0.2	0.075			
	N ₂	0.5	0.8	0.63			
	H ₂ O	0	0	0.021			
<i>R5' (with backward)</i> Da = 0.17 $\theta = 8.99$	H ₂	0.9	0	0.66	0.070	0.29	209
	O ₂	0	0.2	0.026			
	N ₂	0.1	0.8	0.29			
	H ₂ O	0	0	0.024			
<i>ExtendedNUB B12'</i> $\theta = 8.99$	H ₂	0.9	0	0.71	0.056	0.25	207
	O ₂	0	0.2	0.030			
	N ₂	0.1	0.8	0.24			
	H ₂ O	0	0	0.021			

R3' to R5' – Non-premixed cases simulated in NETcombustor, including the reverse rate with large kb'

B10' to B12' – Non-premixed cases simulated in CFD with Maxwell, including the reverse rate with large kb'

In similarity to the result of *R3*, if the backward reaction is included with kb' , the maximum reaction rate is attained in the first row of chambers, as shown in Figure VI.49. However, with kb' , the reaction occurs nearly in all the chambers of the network and not only in the first row. Figure VI.49a shows that *R3'* has the largest number of rows with a high rate of reaction. In fact, *R3'* is the case with the largest $kb' = 9.07 \times 10^5 \text{ m}^3/(\text{kmol s})$ and $kf = 5.78 \times 10^2 \text{ m}^3/(\text{kmol s})$, while *R4'* has $kb' = 4.59 \times 10^4 \text{ m}^3/(\text{kmol s})$ and $kf = 5.05 \times 10^2 \text{ m}^3/(\text{kmol s})$, and *R5'* has $kb' = 5.90 \times 10^4 \text{ m}^3/(\text{kmol s})$ and $kf = 5.11 \times 10^2 \text{ m}^3/(\text{kmol s})$. Although *R3'* has a larger number of rows with a higher reaction rate, in relation to the maximum reaction rate for that case,

$1.88 \times 10^{-1} \text{ kmol}/(\text{m}^3 \text{ s})$, $R5'$ has the highest reaction rate, $3.39 \times 10^{-1} \text{ kmol}/(\text{m}^3 \text{ s})$, since the amount of fuel in the initial mixture is higher.

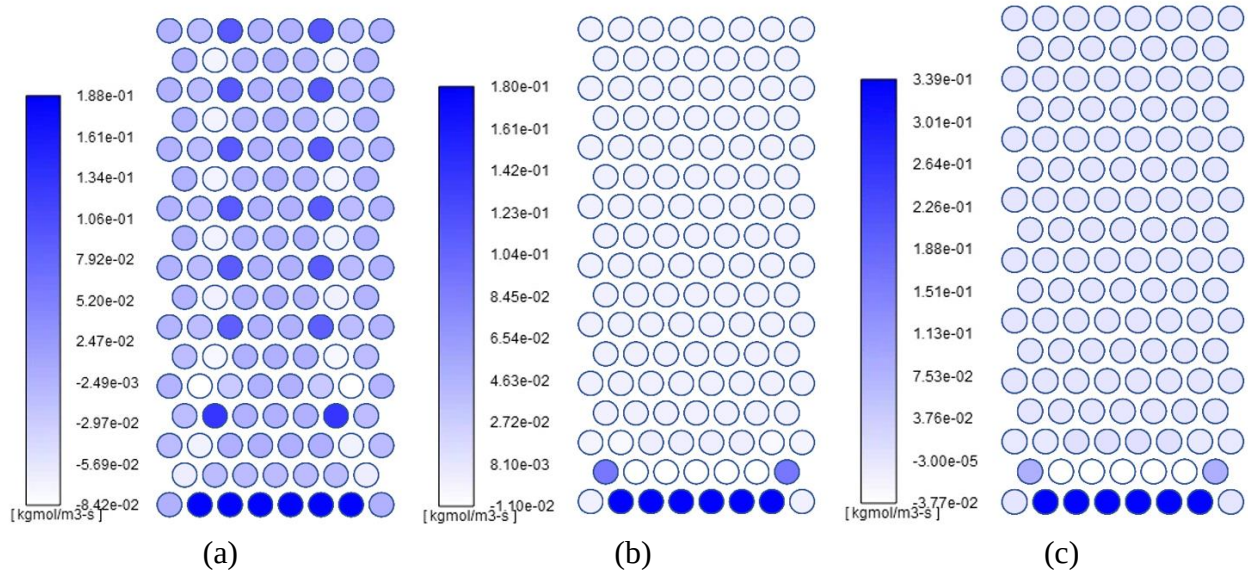


Figure VI.49 Reaction rate maps of NETcombustor of: (a) $R3'$, (b) $R4'$ and (c) $R5'$.

The heat of combustion is higher in the rows with the maximum reaction rate, as shown in Figure VI.50. As expected, if the backward reaction is promoted, the heat of combustion is lower, 32% between $R3$ and $R3'$, and more than 50% lower for $R4'$ and $R5'$.

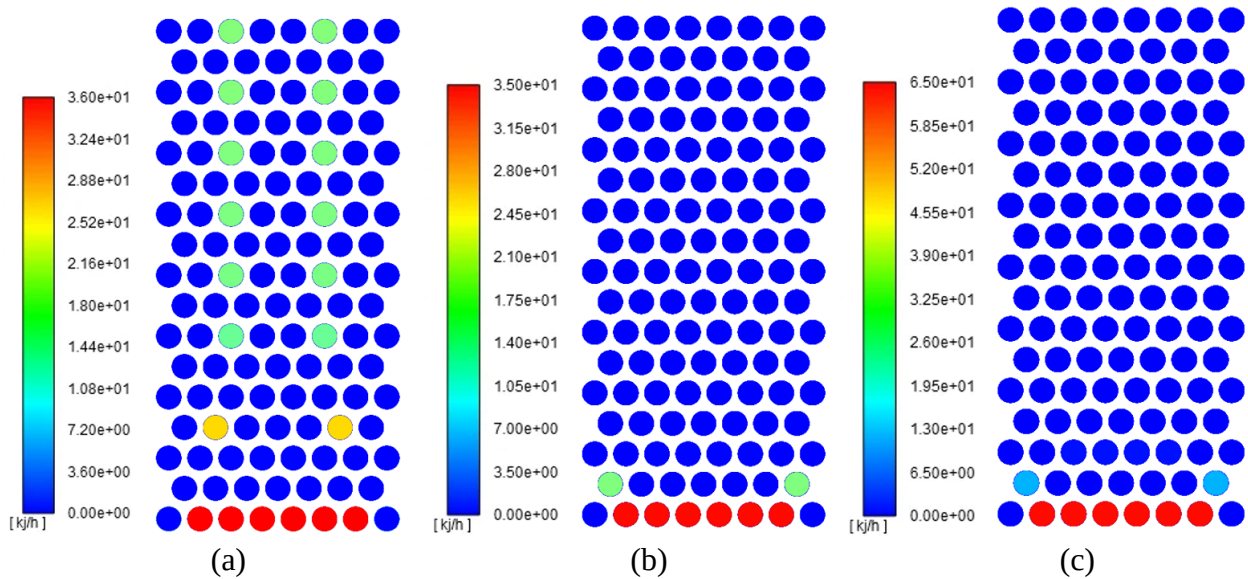


Figure VI.50 Heat of combustion maps of NETcombustor of: (a) $R3'$, (b) $R4'$ and (c) $R5'$.

As shown in Figure VI.51, as the initial amount of fuel increases, the number of chambers with the maximum temperature is larger. However, the highest temperature is attained for $R3'$ which has the largest value of kb' and a higher conversion of fuel. While in $R3'$ the highest temperature is reached in the middle of the reactor, as the initial amount of fuel increases, in $R4'$ and $R5'$, the highest temperature is attained at the edge columns.

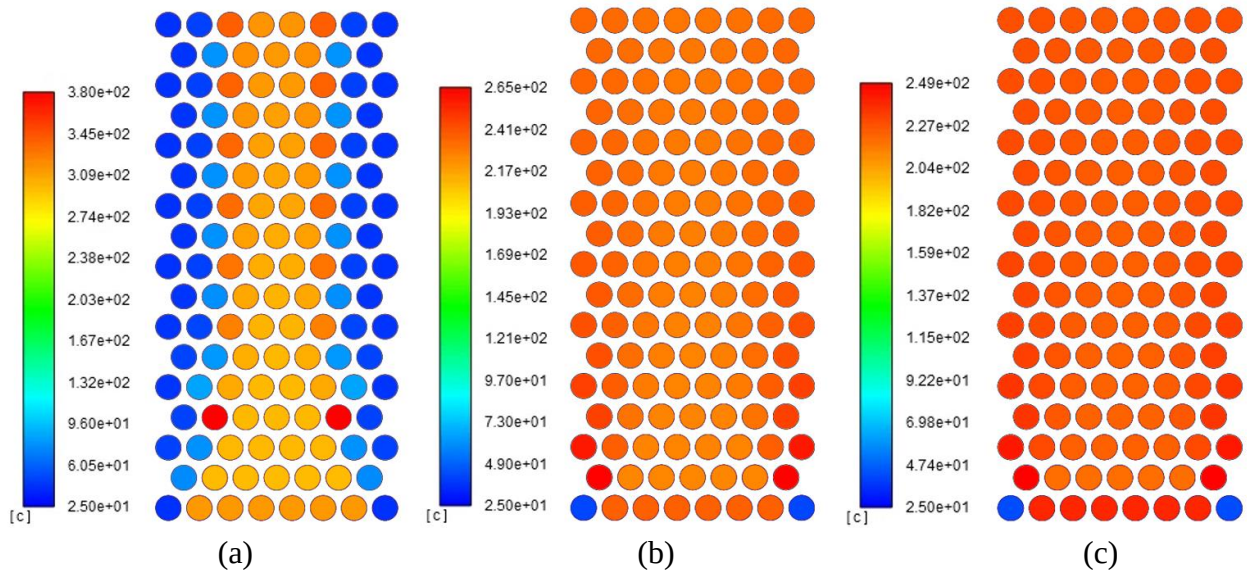


Figure VI.51 Temperature maps of NETcombustor of: (a) $R3'$, (b) $R4'$ and (c) $R5'$.

Figure VI.52 shows that the amount of produced water is larger in the chambers with higher temperature. In this way, in $R3'$ water is mainly produced in the middle columns of chambers. Moreover, the water molar fraction is higher, since the conversion of H_2 , 0.46, is larger when compared to $R4'$ and $R5'$, 0.07.

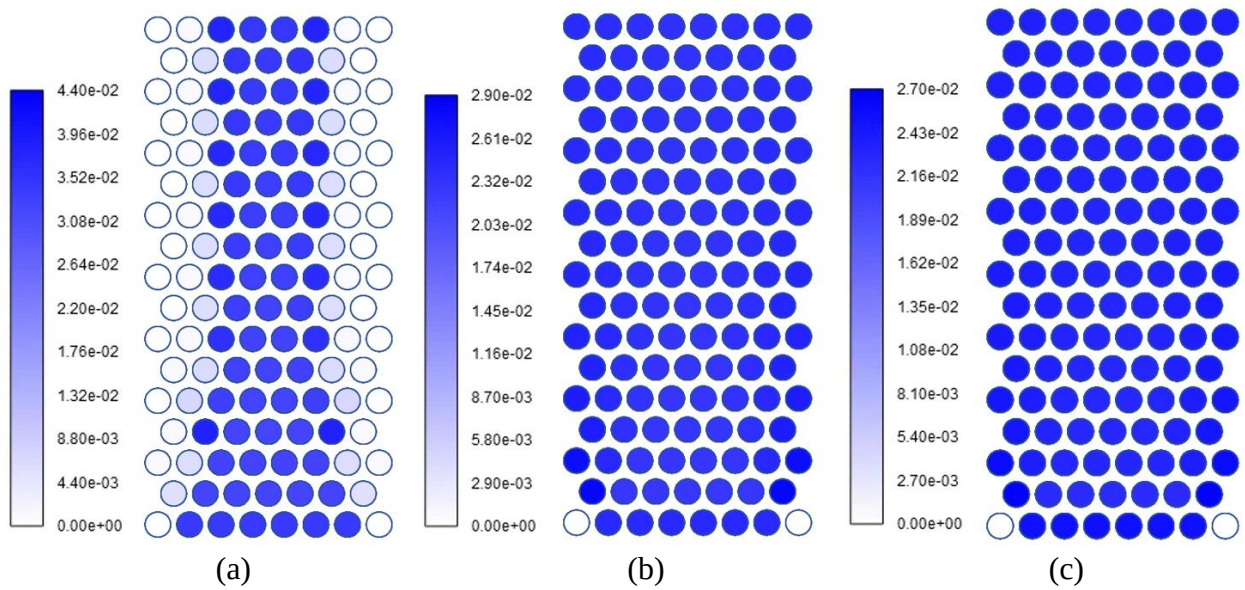
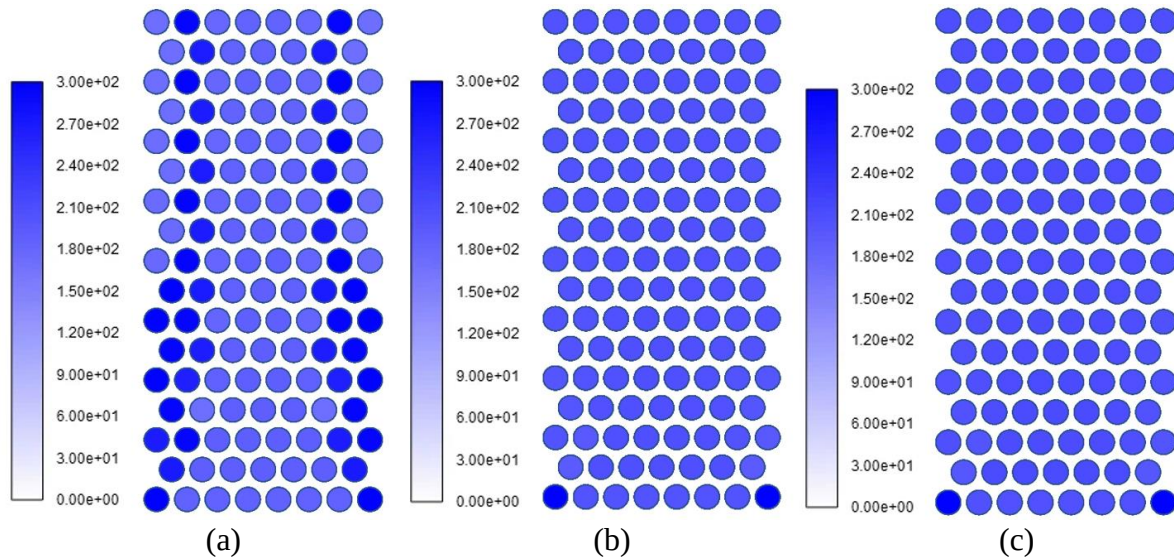


Figure VI.52 y_{H_2O} maps of NETcombustor of: (a) $R3'$, (b) $R4'$ and (c) $R5'$.

As previously said, if the backward reaction is promoted with a large kb , the temperature that is attained in the reaction is lower. Thus, the Re number is higher and there is a smaller difference between the initial value and the Reynolds inside the reactor after combustion, as shown in Figure VI.53. The lowest values of Re are 185, 194 and 199 for $R3'$, $R4'$ and $R5'$, respectively.

Figure VI.53 Re maps of NETcombustor of: (a) $R3'$, (b) $R4'$ and (c) $R5'$.

Injection Scheme Influence

In order to evaluate the influence of the injection scheme, combustion will be simulated with four inlet configurations: the *alternated* scheme, CABABABABABABC, which was previously used; the *right-left* scheme, AAAAAAABBBBBBBB, with the fuel injections at the left side of the reactor and the oxygen injections at the right; the *middle* scheme, BBBBBAABBBBBB, where the fuel injections are in the middle inlets; and the *edge* scheme, AAAAAABBAAAAAA, which has the fuel injections in all inlets except in the middle.

Table VI.9 shows the several injection schemes for the cases $R3$, $R4$ and $R5$.

Table VI.9 Injection scheme influence in NETcombustor, at $Re = 300$.

Non-premixed Combustion									
	Species	$y_{in} (A)$	$y_{in} (B)$	$\overline{y_{out}}$	X_{H_2}	X_{O_2}	$T_{max} (^\circ C)$	$\overline{T_{out}} (^\circ C)$	$\overline{Re_{out}}$
$R3$ <i>alternated</i> $\theta = 0.27$	H ₂	0.1	0	0	1	0.27	454	394	167
	O ₂	0	0.2	0.061					
	N ₂	0.9	0.8	0.89					
	H ₂ O	0	0	0.046					
$R3$ <i>right-left</i> $\theta = 0.27$	H ₂	0.1	0	0.015	0.77	0.21	636	329	190
	O ₂	0	0.2	0.080					
	N ₂	0.9	0.8	0.88					
	H ₂ O	0	0	0.030					
$R3$ <i>middle</i> $\theta = 0.050$	H ₂	0.1	0	0	1	0.050	453	147	233
	O ₂	0	0.2	0.16					
	N ₂	0.9	0.8	0.81					
	H ₂ O	0	0	0.023					

R3 edge $\theta = 1.64$	H ₂	0.1	0	0.037	0.61	1	664	444	161
	O ₂	0	0.2	0					
	N ₂	0.9	0.8	0.93					
	H ₂ O	0	0	0.033					
R4 alternated $\theta = 2.14$	H ₂	0.5	0	0.16	0.47	1	1196	1068	101
	O ₂	0	0.2	0					
	N ₂	0.5	0.8	0.70					
	H ₂ O	0	0	0.14					
R4 right-left $\theta = 2.14$	H ₂	0.5	0	0.20	0.29	0.63	1647	750	139
	O ₂	0	0.2	0.041					
	N ₂	0.5	0.8	0.71					
	H ₂ O	0	0	0.042					
R4 middle $\theta = 0.36$	H ₂	0.5	0	0	1	0.36	1701	872	116
	O ₂	0	0.2	0.11					
	N ₂	0.5	0.8	0.84					
	H ₂ O	0	0	0.047					
R4 edge $\theta = 12.87$	H ₂	0.5	0	0.43	0.080	1	1196	308	186
	O ₂	0	0.2	0					
	N ₂	0.5	0.8	0.54					
	H ₂ O	0	0	0.027					
R5 alternated $\theta = 8.99$	H ₂	0.9	0	0.62	0.11	1	691	647	133
	O ₂	0	0.2	0					
	N ₂	0.1	0.8	0.30					
	H ₂ O	0	0	0.078					
R5 right-left $\theta = 8.99$	H ₂	0.9	0	0.53	0.11	0.96	2023	892	148
	O ₂	0	0.2	0.0054					
	N ₂	0.1	0.8	0.42					
	H ₂ O	0	0	0.042					
R5 middle $\theta = 1.50$	H ₂	0.9	0	0.11	0.66	0.99	2069	1885	70
	O ₂	0	0.2	0.0026					
	N ₂	0.1	0.8	0.81					
	H ₂ O	0	0	0.075					
R5 edge $\theta = 53.9$	H ₂	0.9	0	0.86	0.02	1	691	154	234
	O ₂	0	0.2	0					
	N ₂	0.1	0.8	0.13					
	H ₂ O	0	0	0.016					

In R3, where the fuel stream has a small amount of H₂ (molar fraction of 0.1), the *alternated* scheme is the only case in which combustion occurs in every chamber of the first row (except the edge chambers which only have the inert N₂), as shown in Figure VI.54a. The maximum reaction

rate is the same for all the schemes, $0.28 \text{ kmol}/(\text{m}^3 \text{ s})$. For the *alternated* scheme, the reaction rate is maximum in the first row and zero in the rest of the reactor since nearly all the fuel is consumed in the inlet chambers, $X_{\text{H}_2} = 1$, as shown in Figure VI.57a. In these chambers, the heat of combustion is 53 kJ/h , as shown in Figure VI.55a. Note that, the maximum heat of combustion is the same for the other configurations since for all schemes there are chambers with complete conversion of hydrogen. In the *alternated* scheme, the maximum temperature is attained in a larger number of chambers, as shown in Figure VI.56. However, the maximum temperature is higher for the *right-left* and *edge* schemes. The production of water occurs in the first row as shown in Figure VI.59. In this case, the oxygen is in excess, $X_{\text{O}_2} = 0.26$, as visible in Figure VI.58a.

If the *right-left* scheme is used, the reaction starts in the second row in the interface between the fuel side (right) and the oxygen side (left). The maximum reaction rate is attained in the first two rows and. Differently from the *alternated* scheme, the reaction occurs in all the rows towards the outlet, as shown in Figure VI.54b. Note that the reaction starts in the middle chamber of the second row and is displaced to the fuel side. The maximum heat of combustion is obtained in the chambers with the maximum reaction rate (second and third rows), as shown in Figure VI.55a. In these chambers, the maximum temperature is attained, $636 \text{ }^\circ\text{C}$, as shown in Figure VI.56b. With this scheme the reactants are not completely consumed, $X_{\text{H}_2} = 0.77$ and $X_{\text{O}_2} = 0.21$ (see Figure VI.57b and Figure VI.58b), thus it is possible to extend the reaction to all the rows.

When the *middle* scheme is used, since the fuel is injected at the middle chambers, the reaction rate attains $0.28 \text{ kmol}/(\text{m}^3 \text{ s})$ in those chambers, as shown in Figure VI.54c. In these chambers, the heat of combustion attains 53 kJ/h (which is the same in all schemes, as previously stated) and the temperature rises to $453 \text{ }^\circ\text{C}$. Note that this scheme has the lowest maximum temperature, as visible in Figure VI.56. In similarity to the *alternated* scheme, all the fuel is consumed in the first row (see Figure VI.57c), $X_{\text{H}_2} = 1$, and the oxygen is in excess (see Figure VI.58c). Thus, it is not possible to extend the reaction to the rest of the reactor. As expected, the production of water occurs in the first row, as shown in Figure VI.59c,

If the *edge* scheme is used, the reaction starts to occur in the middle chambers of the first row, in similarity to the *middle* scheme, since these are the chambers where the fuel contacts with the oxygen. The reaction rate attains its maximum, $0.28 \text{ kmol}/(\text{m}^3 \text{ s})$, in the first and second rows. Differently from the *middle* scheme, the oxygen is not fully consumed in the first row and it is possible to extend the reaction until the 13th row, as shown in Figure VI.54d, which is the row where the oxygen is completely consumed (see Figure VI.58d). The maximum heat of combustion is released in the first two rows where the reaction rate is maximum, and then decreases until the 13th row of chambers, as visible in Figure VI.55d. In R3, the highest temperature, $664 \text{ }^\circ\text{C}$, is

reached with the *edge* scheme. However, differently from the previous schemes, the chambers with the highest temperature do not coincide with the higher reaction rate values, as shown in Figure VI.56d.

Concerning the Reynolds, for all schemes the Re number is smaller in the chambers with a higher temperature, as shown in Figure VI.60.

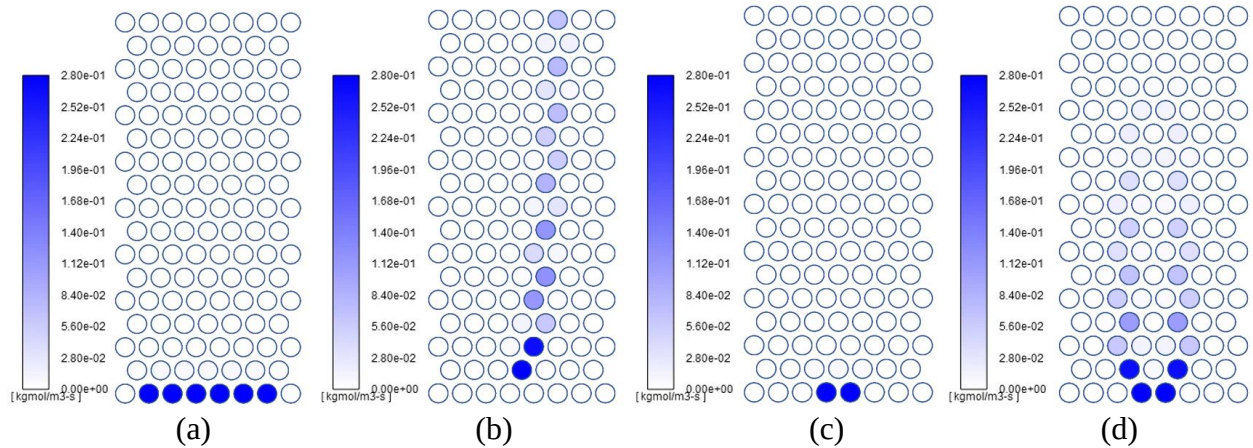


Figure VI.54 Reaction rate maps in NETcombustor of R3 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

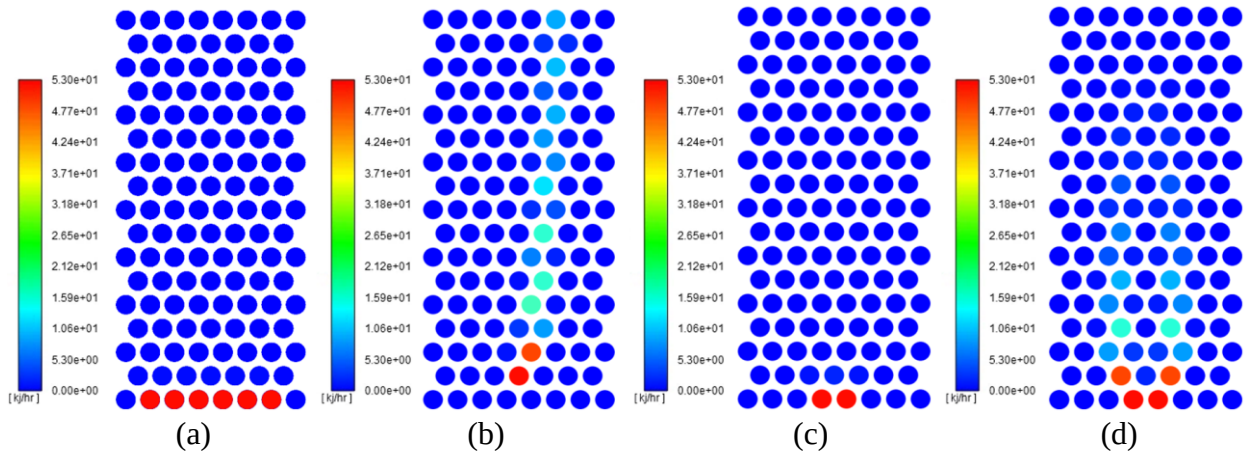


Figure VI.55 Heat of combustion maps in NETcombustor of R3 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

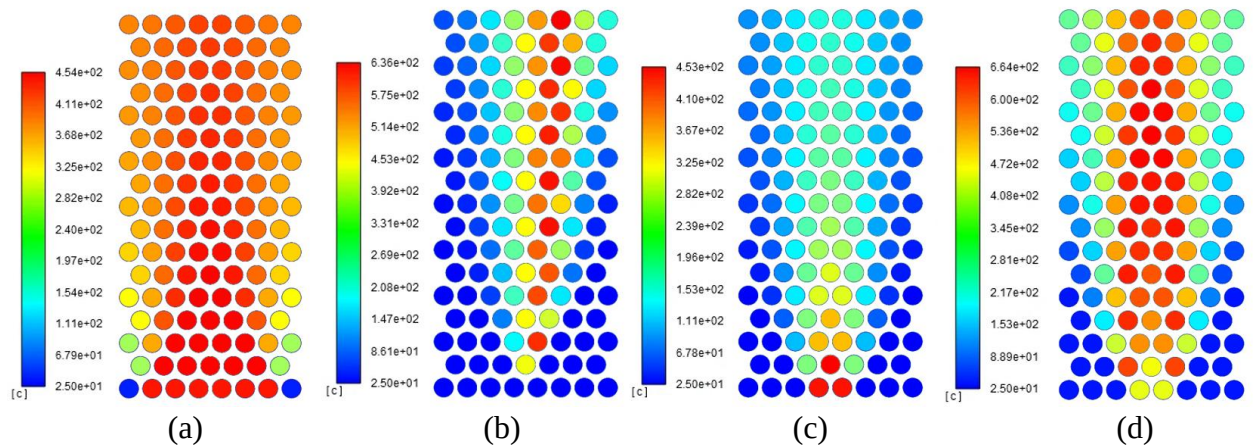


Figure VI.56 Temperature maps in NETcombustor of R3 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

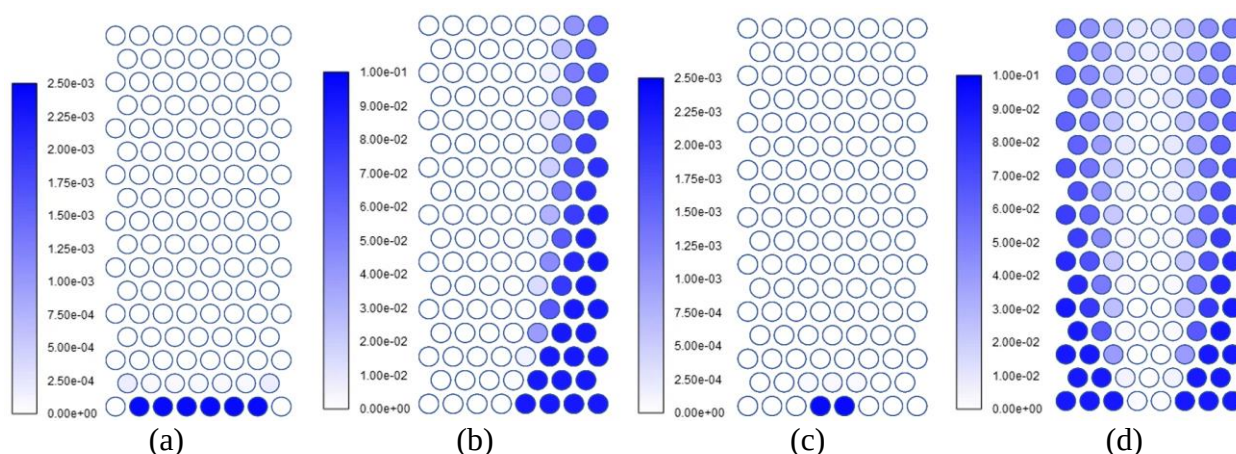


Figure VI.57 H₂ molar fraction maps in NETcombustor of R3 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

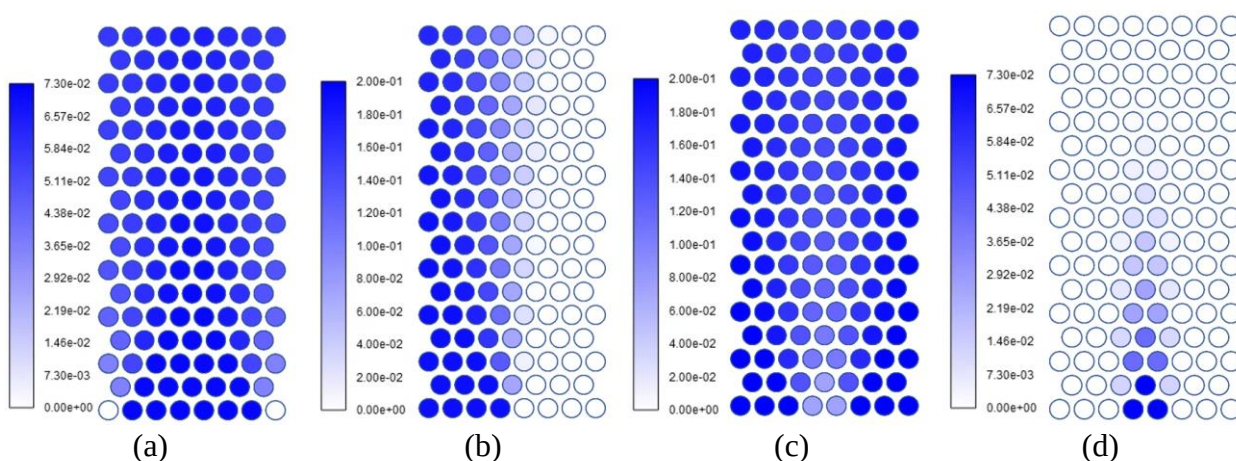


Figure VI.58 O₂ molar fraction maps in NETcombustor of R3 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

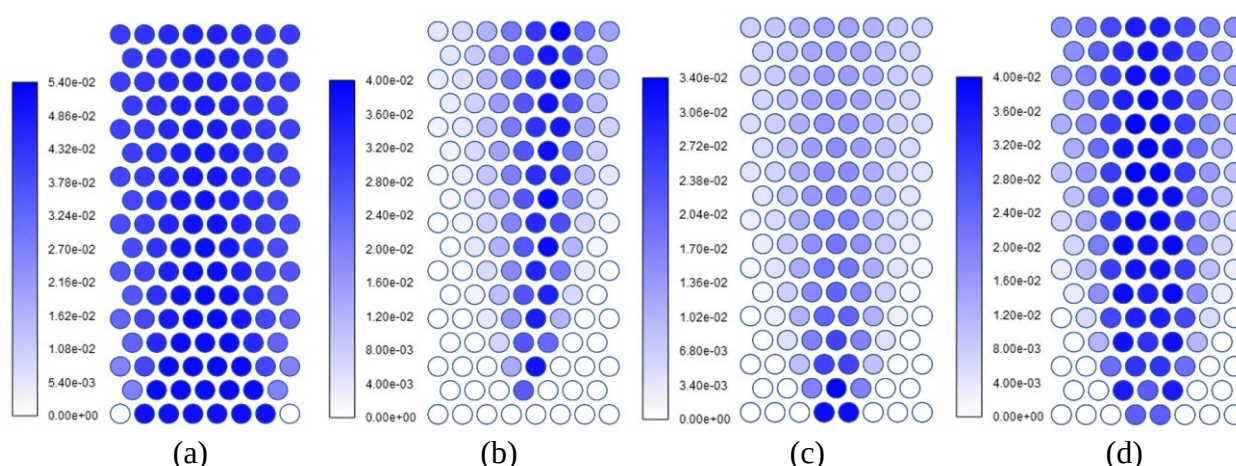


Figure VI.59 H₂O molar fraction maps in NETcombustor of R3 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

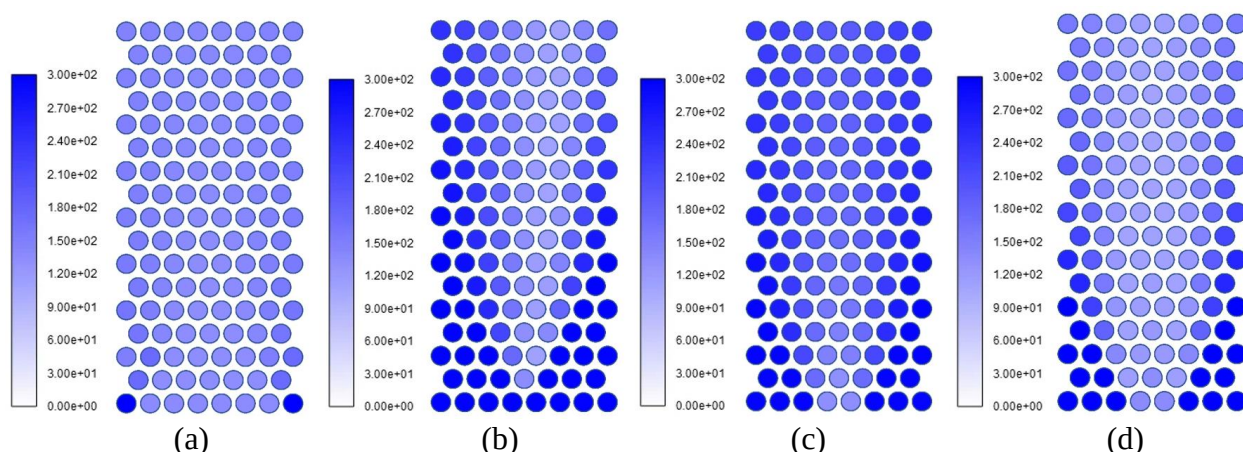


Figure VI.60 Re number maps in NETcombustor of $R3$ with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

In $R4$, the fuel stream is richer in H_2 (molar fraction 0.5) than $R3$ (molar fraction 0.1). In similarity with $R3$, the *alternated* scheme is the only configuration in which the reaction occurs in every chamber of the first row (see Figure VI.61a). The reaction rate reaches a maximum of $1.05 \text{ kmol}/(\text{m}^3 \text{ s})$, which is higher than in $R3$, $0.28 \text{ kmol}/(\text{m}^3 \text{ s})$. The maximum heat of combustion is produced in the first row, 202 kJ/h , which is higher than in $R3$. Note that, the maximum heat of combustion is the same for all schemes, since there are chambers with complete conversion of oxygen in all cases, as shown in Figure VI.62. The maximum temperature, 1196°C , which is higher than in $R3$ (454°C), is attained in the first row, as shown in Figure VI.63a. In similarity to $R3$, with the *alternated* scheme a larger number of rows have the maximum temperature, as visible in Figure VI.63. Since all the oxygen is consumed in the first row ($X_{O_2} = 1$ and $X_{H_2} = 0.46$), as shown in Figure VI.65a and Figure VI.64a, it is not possible to extend the reaction to the other rows, and water is produced only in the first row (see Figure VI.66a).

If the *right-left* scheme is used, in similarity with $R3$, the reaction starts to occur in the middle chambers of the second row, where the fuel contacts with the oxygen. Differently from $R3$, in the chambers above the second row, the reaction is displaced to the oxygen side, as shown in Figure VI.61b. With this scheme, as in $R3$, neither the fuel or oxygen are completely consumed ($X_{H_2} = 0.29$ and $X_{O_2} = 0.63$), as shown in Figure VI.64b and in Figure VI.65b. In this way, the reaction is extended to the outlet (see Figure VI.61b). In similarity to $R3$, the maximum heat of combustion is produced in the middle chambers which have the highest reaction rate, as shown in Figure VI.62b. The temperature rises from the first chamber of reaction. However, the maximum temperature is not attained in the chambers with the highest reaction rate, as visible in Figure VI.63b. The maximum temperature, 1647°C , is higher than in $R3$ since the fuel stream is richer in H_2 .

When the *middle* scheme is used, the reaction starts in the middle chambers of the first row, in similarity with *R3*. However, since the fuel stream is richer in H_2 , the reaction is only extended until the fifth row, as shown in Figure VI.61c. In this case, the oxygen is in excess and all the fuel is consumed in the first five rows ($X_{O_2} = 0.36$ and $X_{H_2} = 1$), as shown in Figure VI.64c and in Figure VI.65c. The maximum heat of combustion is produced in the middle chambers of the first row where the reaction rate is maximum, as visible in Figure VI.62c. For *R4*, this scheme has the highest temperature, 1701 °C. Differently from *R3*, the highest temperature is not reached in the first row where the reaction rate is the maximum. As shown in Figure VI.63c, the highest temperature is in the fifth row.

In the *edge* scheme, the reaction occurs in the middle chambers of the first row, as shown in Figure VI.61d. In contrast with *R3*, the reaction is not extended to the upper rows. In fact, in *R4*, since the fuel is richer in H_2 , all the oxygen is consumed in the first row ($X_{O_2} = 1$ and $X_{H_2} = 0.080$), as shown in Figure VI.65d. As expected, water is produced in the middle chambers of the first row, as shown in Figure VI.66d. In the same chambers, the heat of combustion is released, as visible in Figure VI.62d. The temperature attains the maximum value of 1196 °C, decreasing then towards the outlet, as shown in Figure VI.63d.

Concerning the Reynolds, for all schemes the Re number is smaller in the chambers that have a higher temperature, as shown in Figure VI.67.

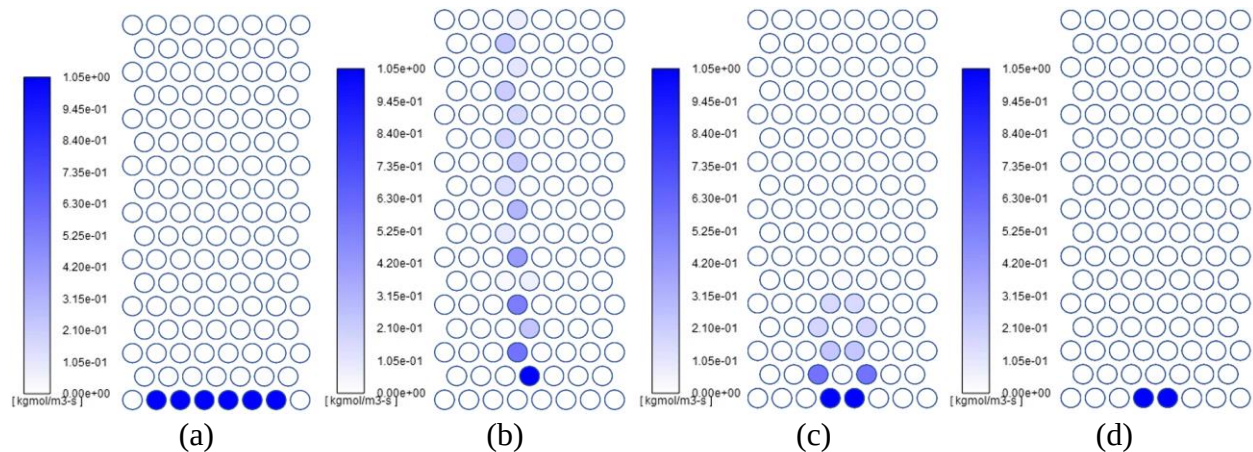


Figure VI.61 Reaction rate maps in NETcombustor of *R4* with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

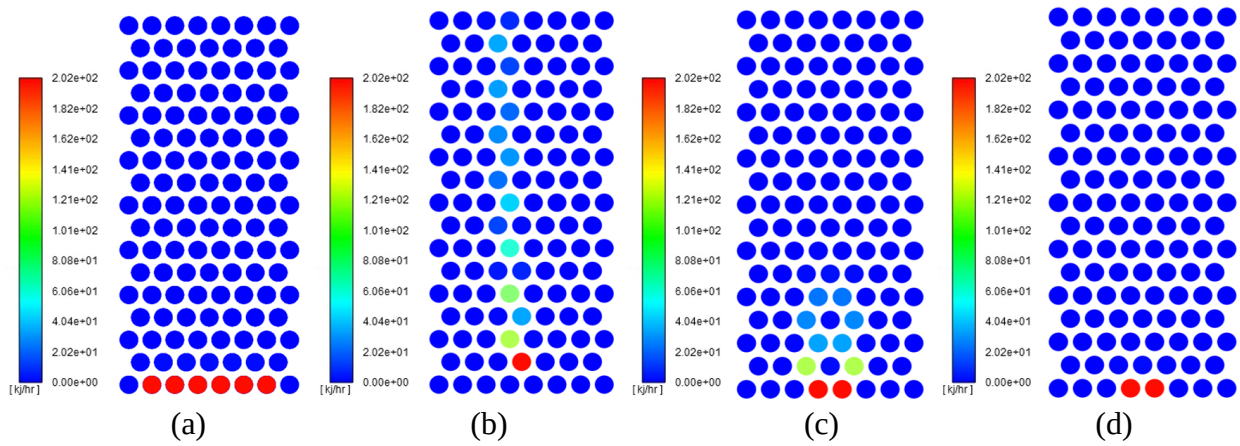


Figure VI.62 Heat of combustion maps in NETcombustor of R4 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

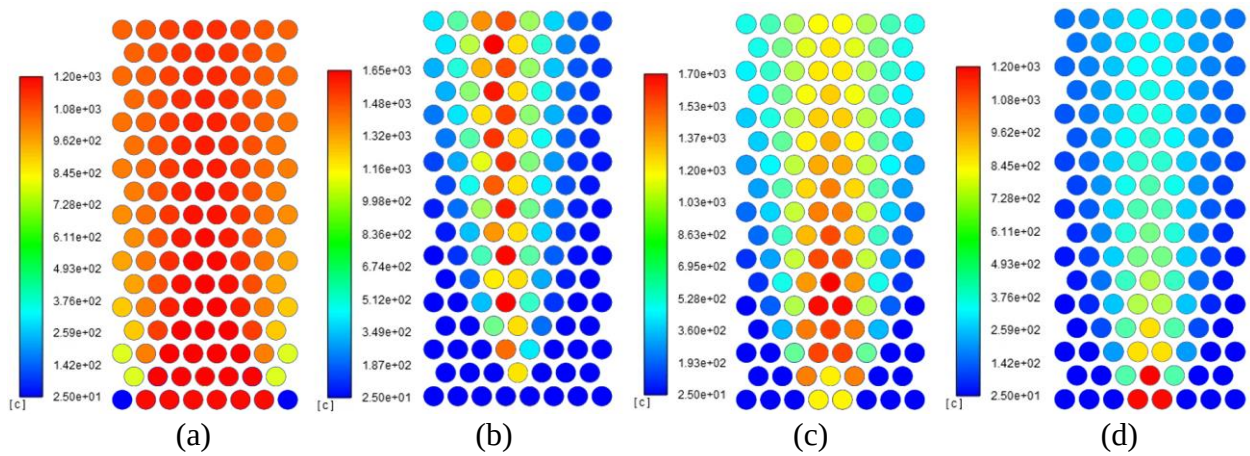


Figure VI.63 Temperature maps in NETcombustor of R4 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

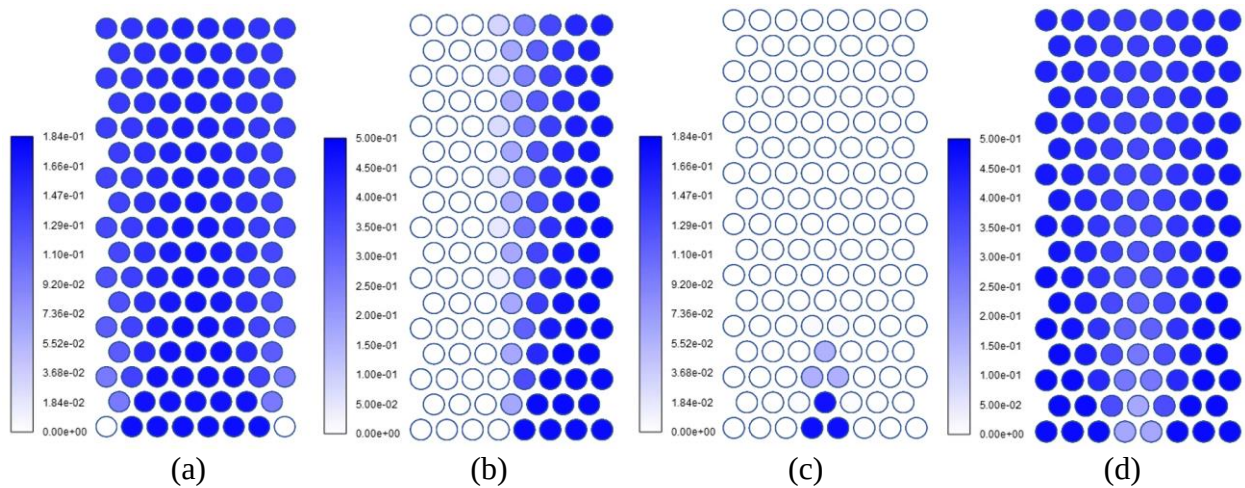


Figure VI.64 H₂ molar fraction maps in NETcombustor of R4 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

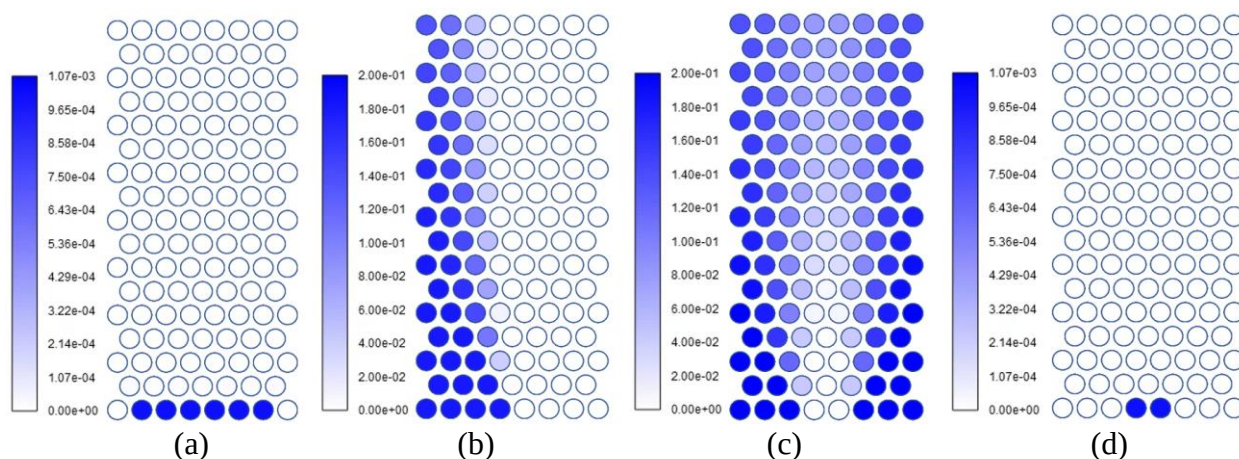


Figure VI.65 O_2 molar fraction maps in NETcombustor of *R4* with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

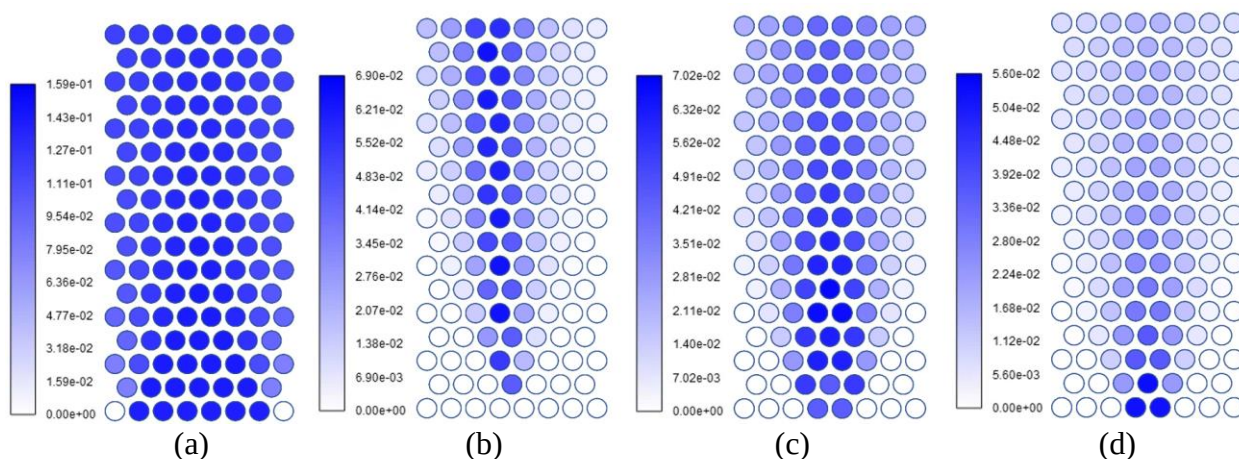


Figure VI.66 H_2O molar fraction maps in NETcombustor of *R4* with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

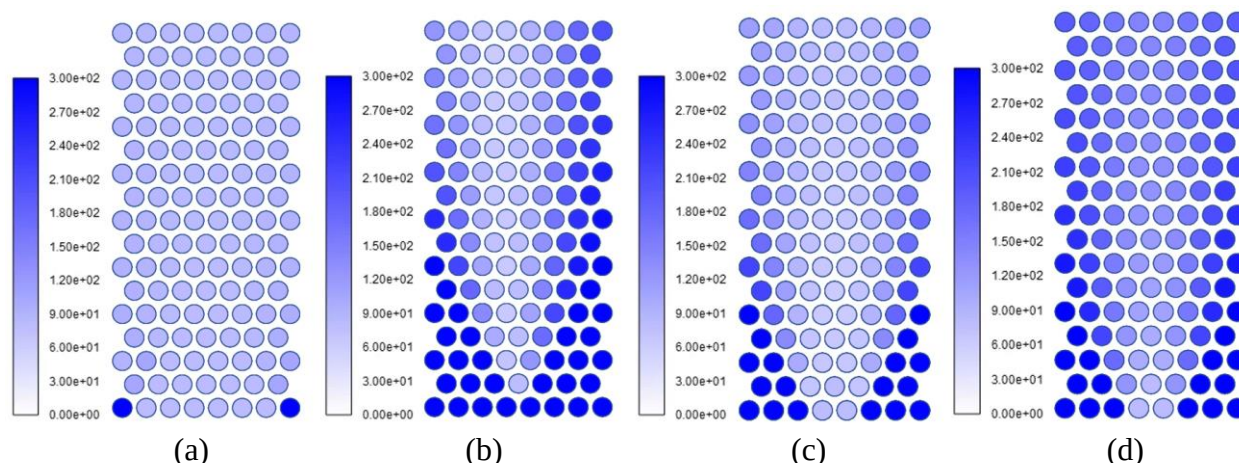


Figure VI.67 Re number maps in NETcombustor of *R4* with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

In *R5*, the molar fraction of H_2 in the fuel stream is increased to 0.9. In the *alternated* scheme, in similarity with *R3* and *R4*, the reaction occurs in all the chambers of the first row, as shown in Figure VI.68a. Note that the maximum reaction rate is the same as *R4*. In similarity to *R4*, all the

oxygen is consumed in the first row, $X_{O_2} = 1$ and $X_{H_2} = 0.11$ (see Figure VI.71a and Figure VI.72a), where water is produced (see Figure VI.73a). The heat of combustion is also released in the first row, attaining the same value as $R4$, as shown in Figure VI.69a. In the first row, the temperature reaches 691 °C which is maintained in most of the chambers, as represented in Figure VI.70a.

In the *right-left* scheme, the reaction starts to occur in the middle chambers of the second row in similarity with $R3$ and $R4$. The maximum reaction rate, $1.05 \text{ kmol}/(\text{m}^3 \text{ s})$, occurs in the first three rows, and from the first row the reaction is displaced towards the oxygen side, as in $R4$ (see Figure VI.68b). The fuel and oxygen are not consumed completely, $X_{H_2} = 0.11$ and $X_{O_2} = 0.96$, as shown in Figure VI.71b and in Figure VI.72b. Thus, the reaction is extended to the last row. The maximum heat of combustion, 202 kJ/h, is attained in the three chambers with the maximum reaction rate, as shown in Figure VI.69b. In $R3$ and $R4$, the highest temperature of the *right-left* scheme was attained in the chambers with the highest reaction rate. In $R5$, the highest temperature, 2023 °C, occurs in a larger portion of the left side of the reactor, as shown in Figure VI.70b.

When the *middle* scheme is used, the reaction starts in the middle chambers of the first row where the highest reaction rate is attained, $1.05 \text{ kmol}/(\text{m}^3 \text{ s})$. Differently from the *middle* scheme results of $R3$ and $R4$, the reactants are not consumed in the first row and the reaction is extended until the outlet row, as shown in Figure VI.68c. Figure VI.71c and Figure VI.72c show the molar fraction of the reactants, where is visible that the oxygen is nearly completely consumed, $X_{O_2} = 0.99$ and $X_{H_2} = 0.66$. For $R5$, the *middle* scheme has the highest maximum temperature, 2069 °C. Differently from $R3$ and $R4$, the maximum temperature is attained in the side chambers of the upper rows, as shown in Figure VI.70c.

If the *edge* scheme is used, the amount of oxygen is very small in relation to the fuel, $\theta = 53.9$. In this way, the reaction occurs only in the middle chambers of the first row, as shown in Figure VI.68d. The maximum heat of combustion and temperature are reached in these chambers, as shown in Figure VI.69d and in Figure VI.70d, respectively. The oxygen is exhausted in the first row, $X_{O_2} = 1$, and a small amount of fuel is consumed, $X_{H_2} = 0.02$, as visible in Figure VI.71 and in Figure VI.72. Water is produced in the middle chambers of the first row where the reaction occurs, as shown in Figure VI.73d.

Concerning the Reynolds, for all schemes the Re number is smaller in the chambers that have a higher temperature, as visible in Figure VI.74.

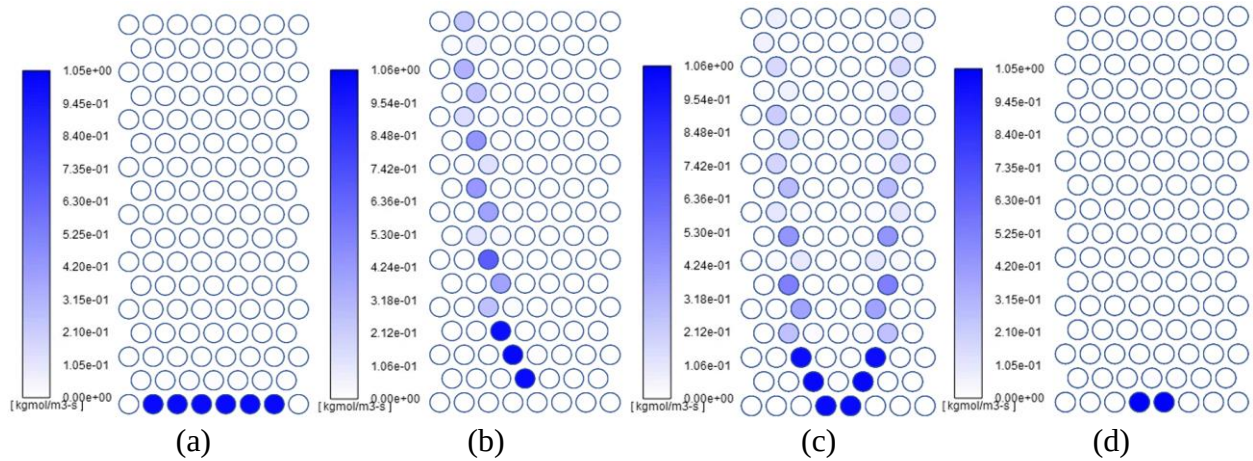


Figure VI.68 Reaction rate maps in NETcombustor of R5 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

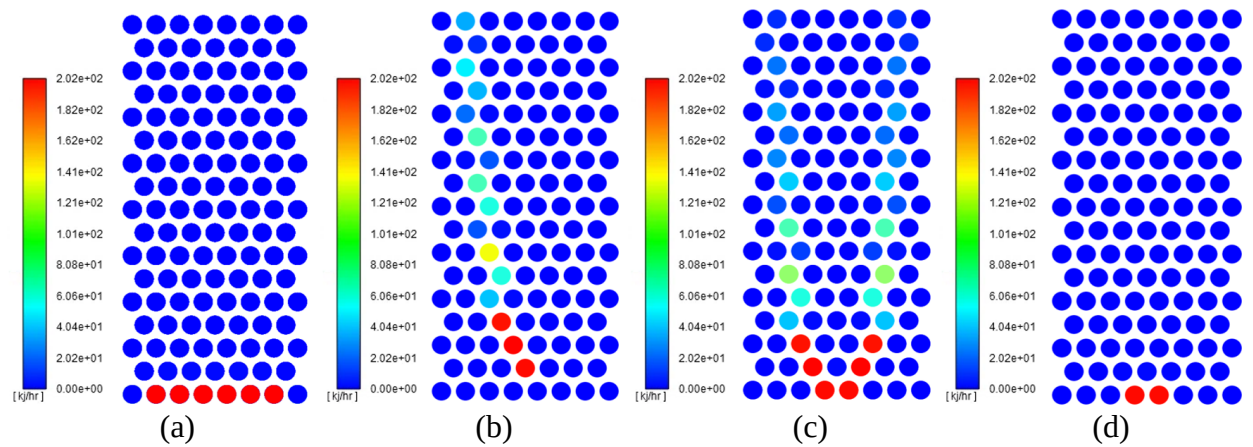


Figure VI.69 Heat of combustion maps in NETcombustor of R5 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

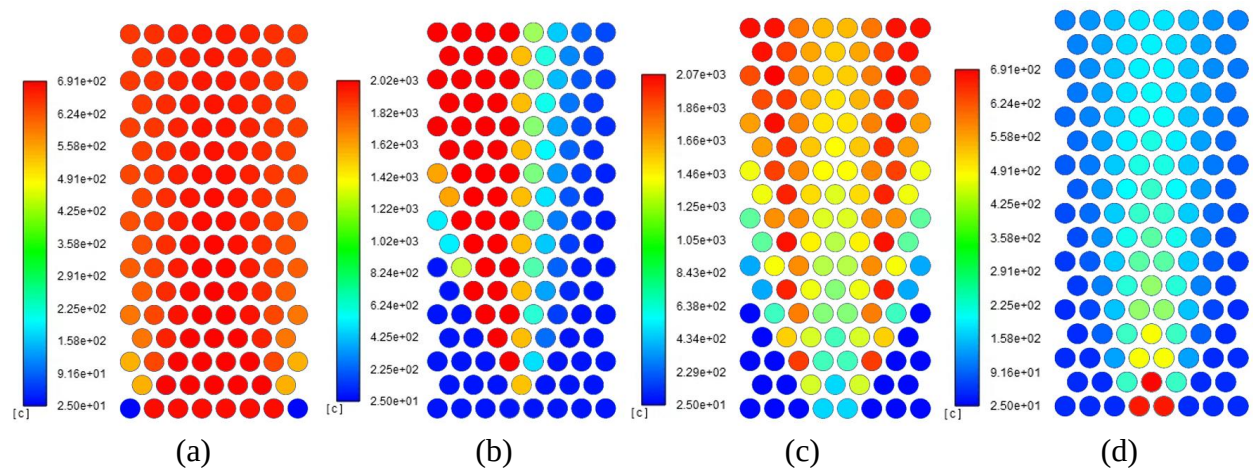


Figure VI.70 Temperature maps in NETcombustor of R5 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

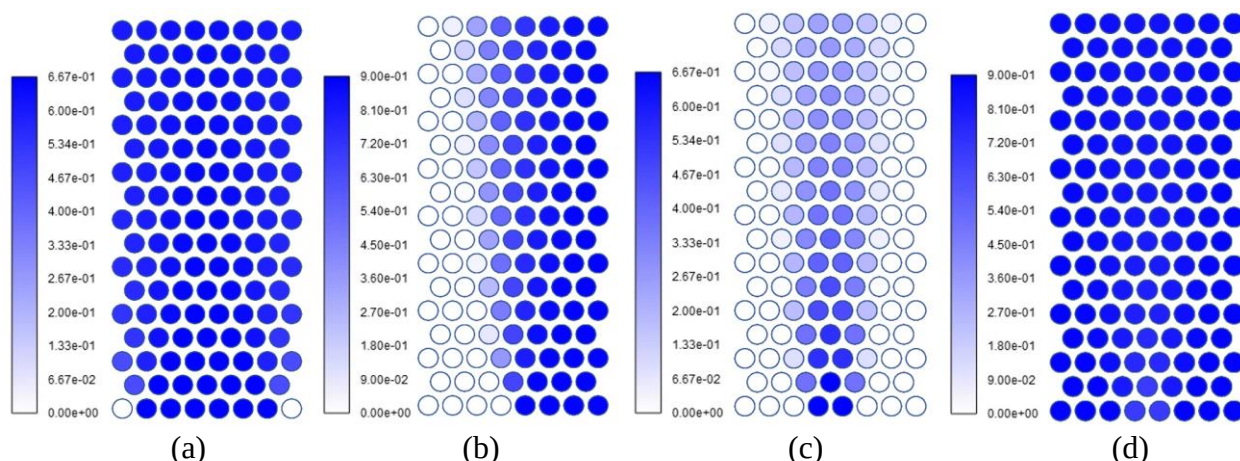


Figure VI.71 H_2 molar fraction maps in NETcombustor of $R5$ with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

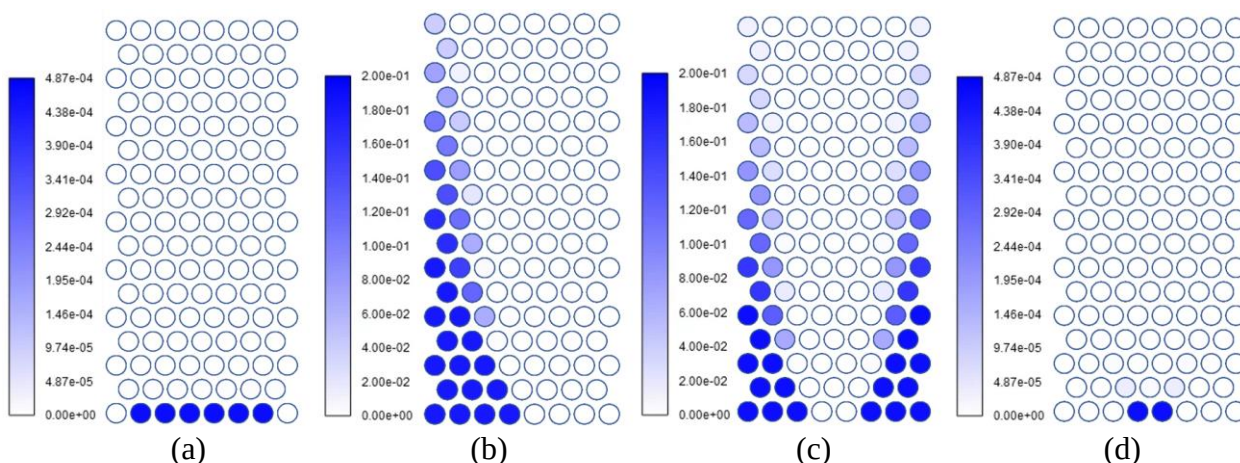


Figure VI.72 O_2 molar fraction maps in NETcombustor of $R5$ with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

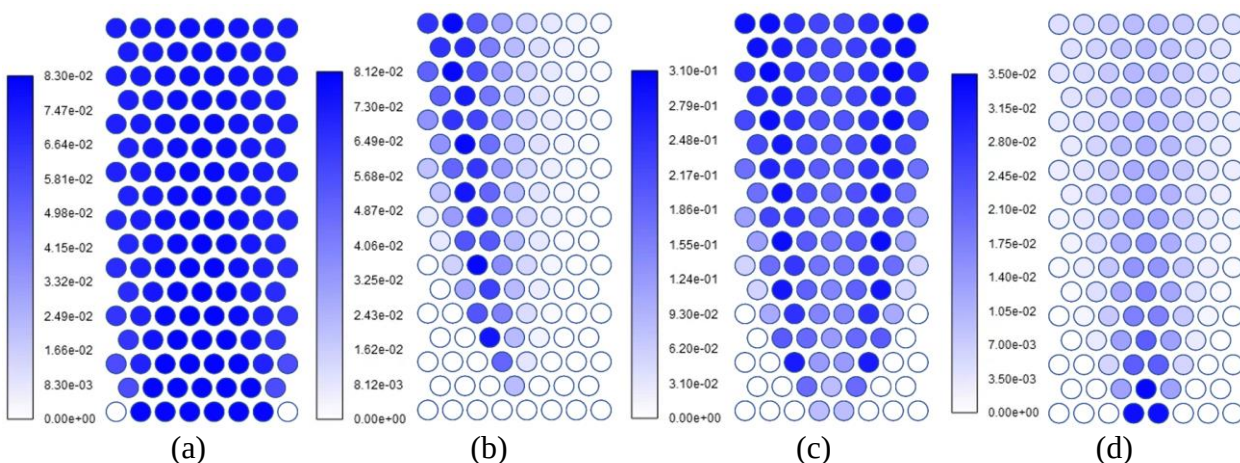


Figure VI.73 H_2O molar fraction maps in NETcombustor of $R5$ with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

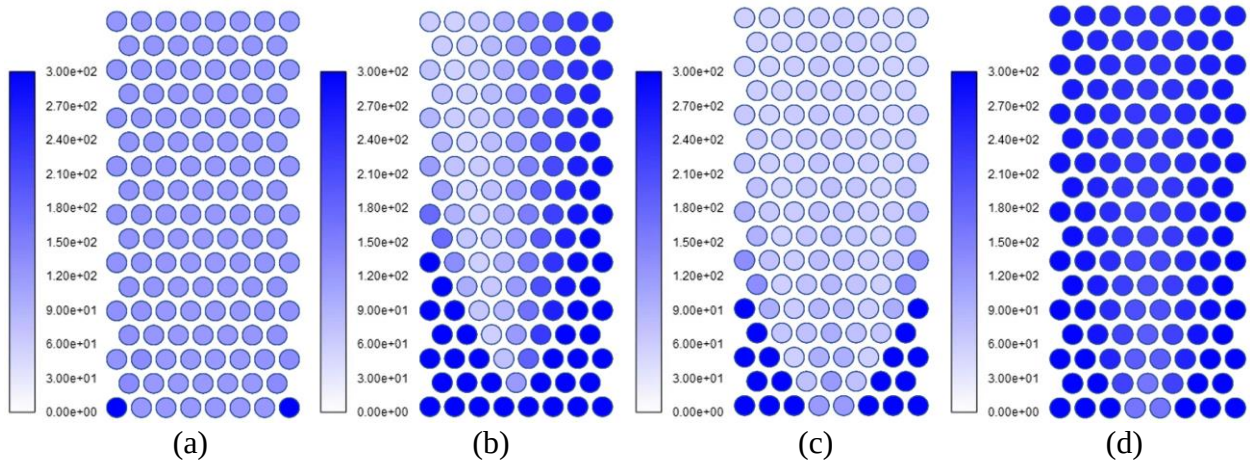


Figure VI.74 Re number maps in NETcombustor of R5 with: (a) *alternated*, (b) *right-left*, (c) *middle* and (d) *edge* schemes.

In general, highest temperatures are attained in the injection schemes where the reaction is extended to the interface between the fuel and the oxygen. In the cases where one of the reactants is fully consumed in the first rows, the maximum temperatures are lower.

NETmix Combustion Curve for H_2 -Air

Non-premixed combustion was used to obtain the combustion curve for the system H_2 -Air. For that, the scheme CABABABABABABC was used in which A is the fuel stream, B is the air stream and C is pure nitrogen. The composition of the fuel stream was varied in order to obtain mixtures with a different θ . The maximum temperature of combustion with these mixtures in NETcombustor is shown in Table VI.10.

Table VI.10 Fuel mixtures with $0.27 < \theta < 9$.

θ vs T			
θ	$y_{H_2}(A)$	$y_{N_2}(A)$	$T(^{\circ}C)$
0.27	0.1	0.9	454
0.63	0.2	0.8	784
1.07	0.3	0.7	1200
1.64	0.4	0.6	1136
2.14	0.5	0.5	1068
3.5	0.6	0.4	990
5	0.7	0.3	898
7.5	0.8	0.2	770
9	0.9	0.1	691

The plot of the temperature inside the NETmix chambers for $0.27 < \theta < 9$ is shown in Figure VI.75, where is visible that the shape of the curve is similar to the adiabatic flame temperature graphic, presented in the State of the Art of Section V.1.2 (Figure V.2). For both curves, the maximum temperature is obtained at $\theta = 1.07$. In NETmix, using the NETcombustor approach,

the maximum temperature of the chambers is approximately 1000 °C lower than the adiabatic flame temperature measured in a Smithells burner. Moreover, the decrease of temperature after the maximum value is slower, i.e., the lower temperatures are attained for a higher θ . As expected, a mesoreactor as NETmix with large heat transfer capacity is a potential via to perform complete combustion with lower temperatures, when compared with common experimental tubes in which the control of the reactive mixture is harder.

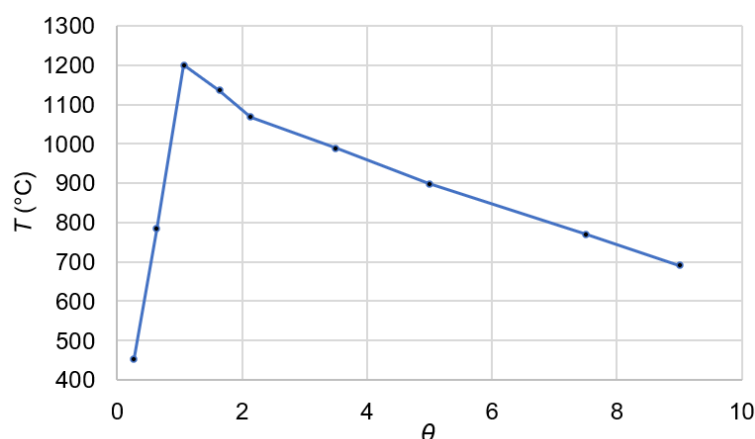


Figure VI.75 Adiabatic flame temperature of NETmix for the system H₂-Air.

VI.3 Computational Aspects

NETcombustor was developed in Aspen Custom Modeler® V10 and run in a x64-based processor Intel® Core™ i7-2600 with 4 cores at 3.40 GHz and 8 GB of RAM. The model codes are shown in Appendix D.12.

The simulation was run with the Steady approach. The non-linear solver was set in the Standard mode with the Newton method, considering a residual convergence. The linear solver was MA48. The integration method Implicit Euler was chosen, and the tolerances were set to 10^{-5} . The Least Squares estimator was used with NL2SOL, and the optimiser was FEASOPT.

The maps of NETcombustor were programmed in Visual Basic for Applications (VBA) and run in a x64-based processor Intel® Core™ i7-7500U with 2 cores at 2.70 GHz and 8 GB of RAM. The codes are listed in Appendix D.13.

VI.4 Conclusions

A network of reactors to model macromixing was developed to study combustion in NETmix, the NETcombustor model. In this approach, CSTR equations are used to represent the NETmix chambers.

NETcombustor was used to study the hydrogen combustion in NETmix with the global scheme for *premixed* and *non-premixed* reactive mixtures.

In general, the temperature that is predicted by NETcombustor is lower than the temperature obtained with the CFD simulations. For most cases, the difference between the two models is less than 10%. The maximum difference is 20%.

In similarity with the CFD results, in NETcombustor, as the amount of fuel of the reactive mixture decreases, the temperature inside the chambers decreases, as well as the maximum reaction rate and the heat of combustion. If the backward reaction is considered, lower temperatures are obtained.

For non-premixed combustion, the injection scheme was studied. It was shown that the distribution of the fuel and oxygen exerts a major influence in the temperature of combustion. In fact, if the injection scheme enables the extension of the reaction to the interface between the fuel and the oxygen, higher temperatures are attained. In contrast, if one of the reactants is fully consumed in the first reaction chambers, the maximum temperatures are lower.

The maximum temperature in function of θ (ratio between the fuel and oxygen of the initial mixture) was studied and a H₂-Air combustion curve was built for NETmix. The shape of the NETmix combustion curve is similar to a typical H₂-Air adiabatic flame temperature curve, measured with conventional experimental tubes. Moreover, the temperature of combustion in NETmix is ca. 1000 °C lower, showing that this reactor is a potential via to perform combustion with low temperatures, reducing the emissions of pollutants as NO_x.

Chapter VII – Applied Combustion in NETmix

In Chapters V and VI, combustion was studied in the NETmix reactor, using a reduced geometric model, ExtendedNUB, which enabled to analyse the reactions at a micro-scale level; and using a complete network, NETcombustor, which enabled to have a macro-scale and global approach of combustion.

The energy that is released from combustion can be used as heat supply in lab-scale or industrial processes, reducing the energy consumption and pollutant emissions. Due to the large heat transfer capacity of the NETmix reactor, the heat of combustion is expected to have an efficient transfer.

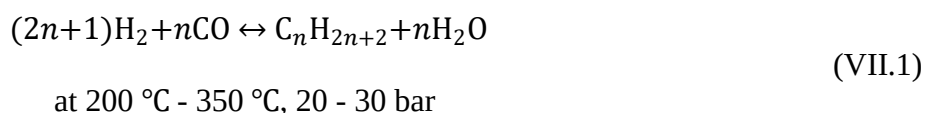
Here, combustion with heat removal will be assessed in NETmix. In the beginning of the chapter, a process context in which NETmix with combustion could be integrated will be suggested. After that, CFD and NETcombustor will be used to simulate combustion in NETmix, including heat transfer. From that, it will be possible to study the temperature of the reactor, considering heat release to the exterior. The studies will be performed for premixed and non-premixed combustion, using the reaction schemes of hydrogen of the previous chapters: the global scheme and the 19-reactions scheme.

VII.1 Process Context

Combustion reactions in NETmix could be incorporated in a process unit to obtain synthetic fuels integrated in the NET4CO₂ strategy (see Figure VII.1, <https://www.net4co2.pt/p134-co2-economy-en>), which aims the development of NETmix units to produce synthetic fuels with a sustainable technology.

As stated in the Introduction chapter of this work, the main purpose of performing controlled combustion is to reduce the emissions of NO_x and SO_x. The production of synthetic fuels from syngas enables to reduce the pollutant emissions, since the combustion of synthetic fuels is cleaner when compared to the combustion of conventional fossil fuels, such as coal, oil and gas (Longwell 1977, Sullivan 2012, Josephine et al. 2012, Bosch 2017, Evo 2021).

Syngas such as CO, CO₂ and H₂ are by-products of combustion which can be reused in Fischer-Tropsch (FT) reactions to obtain synthetic fuels (Klerk 2011):



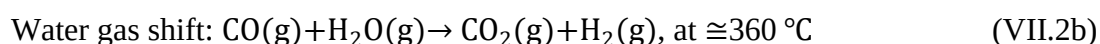
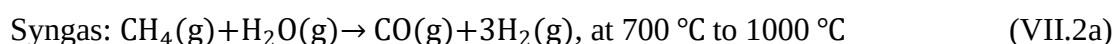
Moreover, the heat of combustion from NETmix could be used to maintain the temperature of the feed gas between 180 °C and 250 °C. A NETmix reactor, Micro2D-REACTmix (see Section VI.1.1) is already being developed to perform FT processes, which includes heat transfer plates.

Another objective of the NET4CO₂ strategy is the development of NETmix units for the production of syngas from the reforming of methane.

As stated in Section V.1.2., hydrogen is mainly obtained from reforming processes. In fact, nearly 50% of the global hydrogen is produced via steam reforming (Dincer et al. 2015). Lately, new technologies are being developed to reduce the pollutant emissions associated to the production of syngas, namely, carbon capture and storage (CCS) methods (Abad et al. 2017, Abdulla et al. 2020).

In the NET4CO₂ strategy, CCS methods are included in a circular economy for the production of syngas in a sustainable route (see Figure VII.1).

The reforming of methane is performed at high temperatures, through the following reactions (Press et al., 2008):



Industrially, the reforming of methane is mainly performed in large fixed or fluidized bed reactors, using two ways: the Autothermal reforming and the Steam reforming, with efficiencies between 60% and 70% (Reimert et al. 2012, Speight 2020).

Since NETmix has a higher heat transfer capacity when compared to large tanks (see the Chapter I), improved efficiencies of the process are expected, using a smaller unit. In this way, combustion can be performed with $T < 1300 \text{ }^\circ\text{C}$, preventing the formation of pollutants as NO_x (See Section V.1.1). One of the challenges of the methane reforming is related to the high temperatures that are required. To this end, NETmix plates with combustion could be directly coupled to the methane reforming plates to supply heat to the reactive mixture. The heat released from combustion could also be used through heat exchange plates. Moreover, the water produced in combustion could be reused as reactant in the reforming reactions.

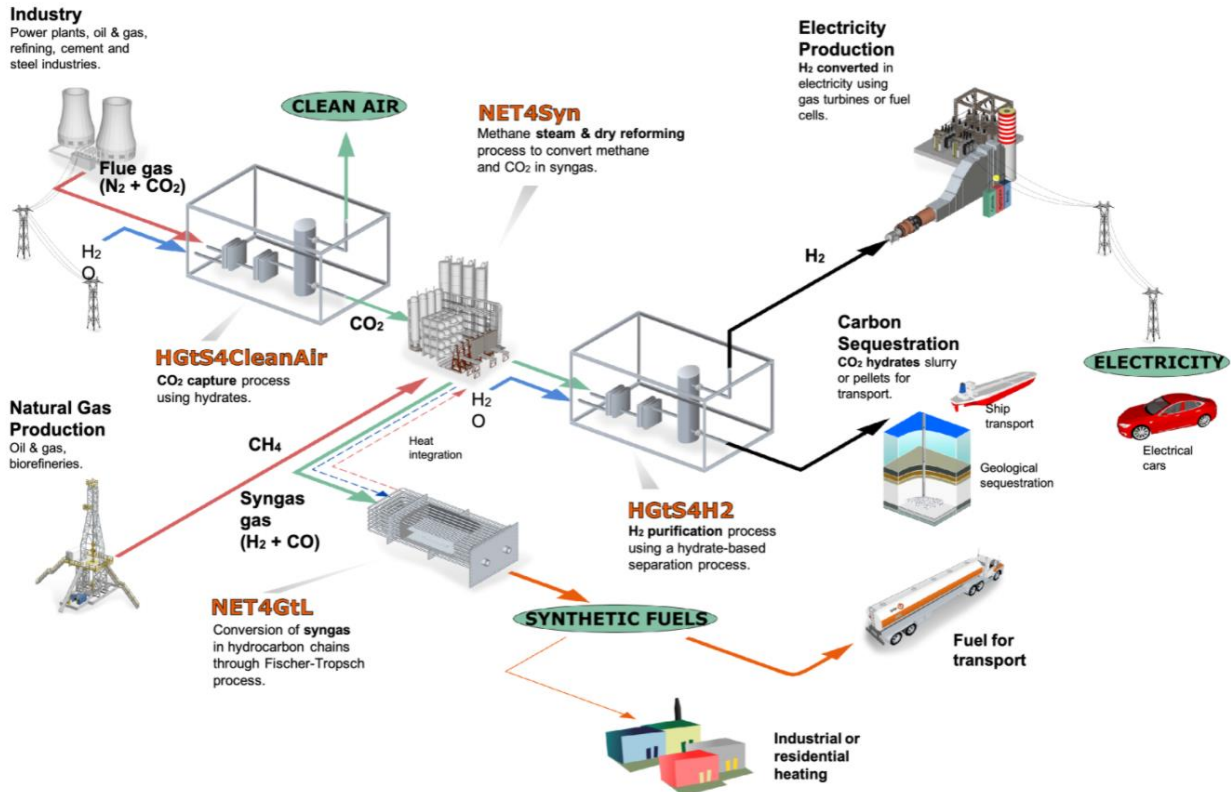


Figure VII.1 NET4CO2 circular economy (NET4CO2 2020).

VII.2 Micro-Scale Analysis

To study the temperature that is attained inside NETmix if heat is released from the unit, the NETmix reactor is considered to be coupled to a heat exchange plate at different temperatures. The resistance of the fluid (heat transfer capacity of NETmix) as well as the resistance of the wall of the reactor (heat transfer capacity of the material) will be included in the simulation model. The resistance of the wall of the heat exchange plates will not be used.

To perform a micro-scale analysis, the NETmix reduced geometric model, ExtendedNUB, will be used in CFD simulations. The heat is transferred through the walls of the ExtendedNUB mesh, represented in black in Figure VII.2a. In Figure VII.2b, the walls are represented schematically. Note that, as the model is 2D, the heat transfer occurs through the side walls of the reactor, i.e., the front and back faces of the 3D reactor are not considered.

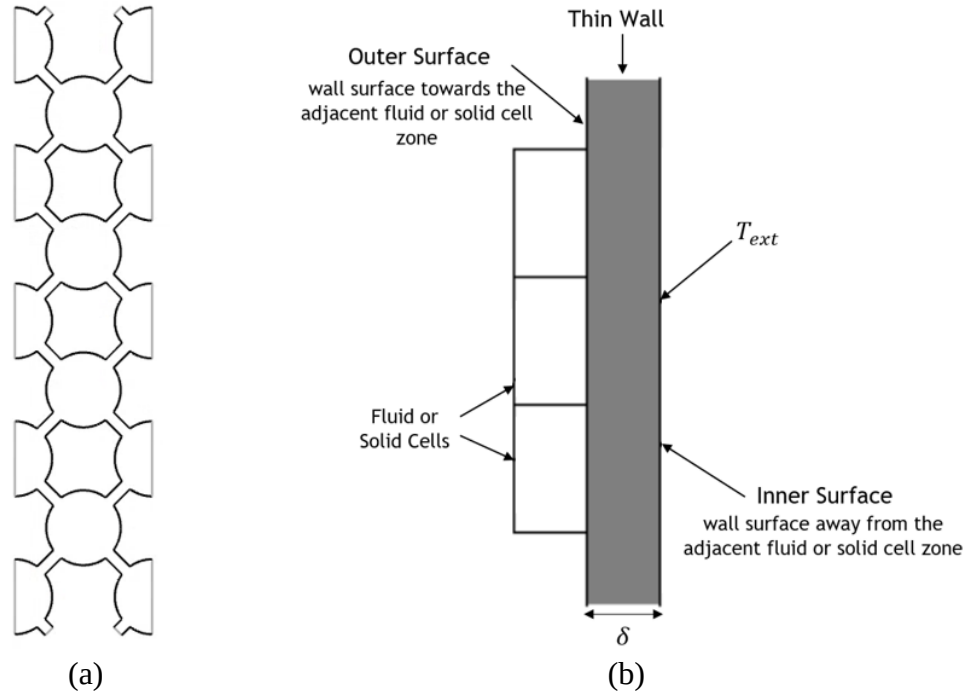


Figure VII.2 (a) ExtendedNUB walls (black). (b) Wall scheme.

In the CFD model of Section V.3.1., *Convective Heat Transfer Boundary Conditions* were used at the walls of the reactor. The heat flux to the wall is calculated as

$$Q_{ext} = h_{ext}(T_{ext} - T_r) \quad (\text{VII.3})$$

in which Q_{ext} is the heat transfer coefficient, T_{ext} is the temperature of the heat exchanger and T_r is the temperature inside the reactor.

The specific heat transfer capacity, $\hat{h}$, of NETmix is between 2.5×10^6 W/(m³ K) and 7.5×10^8 W/(m³ K) for a depth, ω , between 2.5 mm and 0.25 mm, respectively, as shown in Figure VII.3. In this study, $\omega = 1$ mm ($D = 6.65 \times 10^{-3}$ m and $d = 1.00 \times 10^{-3}$ m as in Chapter V) and $\hat{h} = 5 \times 10^7$ W/(m³ K). The heat transfer coefficient, h_{ext} , is

$$h_{ext} = \hat{h} \frac{V}{A} \quad (\text{VII.4})$$

where $h_{ext} = 5 \times 10^4$ W/(m² K), for $A = 3.29 \times 10^{-4}$ m² and $V = 3.49 \times 10^{-7}$ m³, which are the area and volume of NETmix, respectively.

The walls are made of steel and have a thickness $\delta = 2.5 \times 10^{-3}$ m.

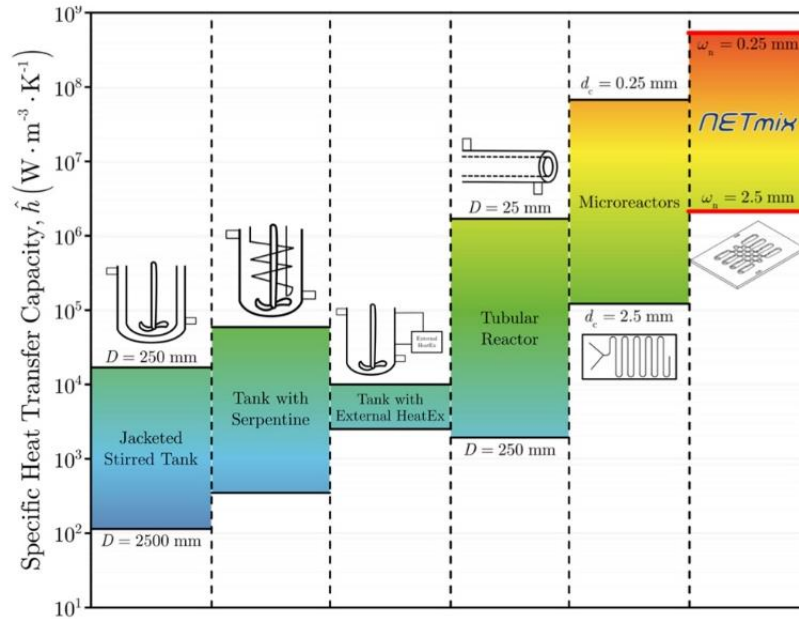


Figure VII.3 Specific heat transfer capacity of NETmix (Costa et al. 2017).

VII.2.1 Global Reaction Scheme

A first study was performed using the global reaction scheme of the hydrogen combustion provided by Ansys (2021) which was used in the previous sections of this work.

The NETmix reactor is considered to exchange heat at different temperatures, $T_{ext} = 25\text{ }^{\circ}\text{C}$, $50\text{ }^{\circ}\text{C}$, $100\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$. Non-premixed combustion using air was considered, in which the fuel stream has 10% of hydrogen.

The results are presented in Table VII.1 and compared with *M4*, which used the same reactive mixture without considering heat transfer to the exterior of the reactor. It is shown that as the external temperature increases, the outlet temperature approaches T_{ext} . In fact, for *Q1* and *Q2*, the difference between T_{C8} and T_{ext} is less than 8%, and for *Q3* and *Q4* the difference is less than 1%.

As shown in Table VII.1, the maximum temperature is lower (28%, 27%, 25% and 23% for each case, respectively) than the original simulation, *M4*, without heat transfer. In this way, it is possible to reduce the temperature of the hotspots that are formed inside the reactor.

Table VII.1 Hydrogen combustion with heat transfer to the exterior, using the global scheme.

Combustion with Q_{ext}								
	Species	$y_{in,left}$	$y_{in,right}$	$\bar{y}_{out}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}\text{C})$	$\bar{T}_{C8}(^{\circ}\text{C})$
Q1 $T_{ext} = 25\text{ }^{\circ}\text{C}$ $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	1600	43
	O ₂	0	0.2	0.11				
	N ₂	0.9	0.8	0.84				
	H ₂ O	0	0	0.042				

Q2 $T_{ext} = 50\text{ }^{\circ}\text{C}$ $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	1610	77
	O ₂	0	0.2	0.075				
	N ₂	0.9	0.8	0.89				
	H ₂ O	0	0	0.053				
Q3 $T_{ext} = 100\text{ }^{\circ}\text{C}$ $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	1680	102
	O ₂	0	0.2	0.075				
	N ₂	0.9	0.8	0.87				
	H ₂ O	0	0	0.053				
Q4 $T_{ext} = 150\text{ }^{\circ}\text{C}$ $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	1730	155
	O ₂	0	0.2	0.079				
	N ₂	0.9	0.8	0.86				
	H ₂ O	0	0	0.054				
M4 $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	2320	445
	O ₂	0	0.2	0.066				
	N ₂	0.9	0.8	0.87				
	H ₂ O	0	0	0.064				

Q1 to Q4 – Non-premixed cases simulated with Maxwell, including heat removal from the walls

M4 – Non-premixed case simulated with Maxwell, adiabatic

The temperature and reaction rate maps are similar for cases Q1 to Q4. An example is shown in Figure VII.4 for Q1 which is compared with M4. It is visible that, if heat is removed from the reactor, the reaction front is already present in the first chamber, while in M4 it was only visible from the third row of chambers. As heat is being removed, the inside of the reactor cools except in the hotspots.

The maximum reaction rate is one order of magnitude lower than M4. As T_{ext} increases, the temperature inside the reactor increases, as well as the maximum reaction rate, which is slightly higher from Q1 to Q4, 6.66×10^{-1} kmol/(m³ s), 6.70×10^{-1} kmol/(m³ s), 6.76×10^{-1} kmol/(m³ s) and 6.77×10^{-1} kmol/(m³ s), respectively.

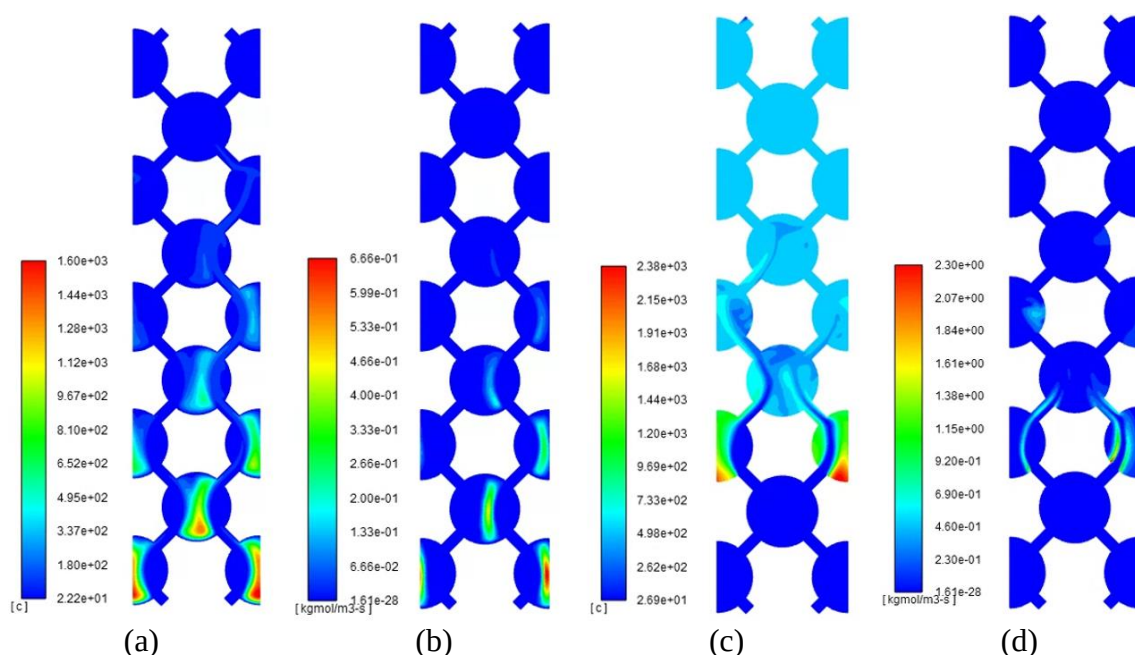


Figure VII.4 ExtendedNUB map of: (a) temperature of $Q1$, (b) reaction rate of $Q1$, (c) temperature of $M4$ and (d) reaction rate of $M4$.

VII.2.2 19-Reactions Scheme

In the previous section it was shown that the outlet temperature of NETmix approaches T_{ext} and the maximum temperature of the hotspots is lower if heat is transferred from the reactor. In this section, $Q1c$ was simulated using the 19-reactions scheme and compared with $Q1$ and $C2$, where Q_{ext} was not considered, as shown in Table VII.2. The results show that if the 19-reactions scheme is used with heat removal, the maximum temperature decreases ca. 10% in relation to $Q1$ (with the global scheme) and decreases approximately 39% in relation to $C2$, in which heat removal was not considered. Comparing with the global scheme, $Q1$, in which the difference between T_{C8} and T_{ext} is ca. 8%, if the 19-reactions scheme is used, the outlet temperature is closer to T_{ext} having ca. 1% difference.

Table VII.2 Hydrogen combustion with heat transfer to the exterior, using the 19-reactions scheme.

Combustion with Q_{ext}								
	Species	$y_{in,left}$	$y_{in,right}$	$\bar{y}_{out}$	X_{H_2}	X_{O_2}	$T_{max}(^{\circ}C)$	$\bar{T}_{C8}(^{\circ}C)$
$Q1c$ $T_{ext} = 25^{\circ}C$ $\theta = 0.27$	H	0.1	0	0	1	0.15	1420	29
	O ₂	0	0.2	0.087				
	N ₂	0.9	0.8	0.89				
	H ₂ O	0	0	0.019				
	H ₂	0	0	0				
	O	0	0	0				
	OH	0	0	0				
	HO ₂	0	0	0				
	H ₂ O ₂	0	0	0				

Q1 $T_{ext} = 25\text{ }^{\circ}\text{C}$ $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	1600	43
	O ₂	0	0.2	0.11				
	N ₂	0.9	0.8	0.84				
	H ₂ O	0	0	0.042				
C2 <i>Adiabatic</i> $\theta = 0.27$	H	0.1	0	0	1	0.15	2520	663
	O ₂	0	0.2	0.086				
	N ₂	0.9	0.8	0.89				
	H ₂ O	0	0	0.029				
	H ₂	0	0	0				
	O	0	0	0				
	OH	0	0	0				
	HO ₂	0	0	0				
	H ₂ O ₂	0	0	0				

Q1c – Simulation with Maxwell, including heat removal from the walls, using the 19-reactions scheme.

Q1 – Simulation with Maxwell, including heat removal from the walls, using the global scheme.

C2 – Simulation with Maxwell, adiabatic, using the global scheme.

The temperature map of Q1c is shown in Figure VII.5a. It is visible that the hotspot has a smaller size when compared to C2 without heat removal (Figure VII.5b). As expected, in Q1c the decrease of temperature after the hotspot is larger since the temperature approaches T_{ext} . In Q1c, the maximum reaction rate of reaction 1 is one order of magnitude lower than C2, as shown in Figure VII.5c and in Figure VII.5d. Comparing with Q1 (global scheme), Figure VII.4a, it is possible to conclude that only one hotspot is formed if the 19-reactions scheme is used (Figure VII.5a).

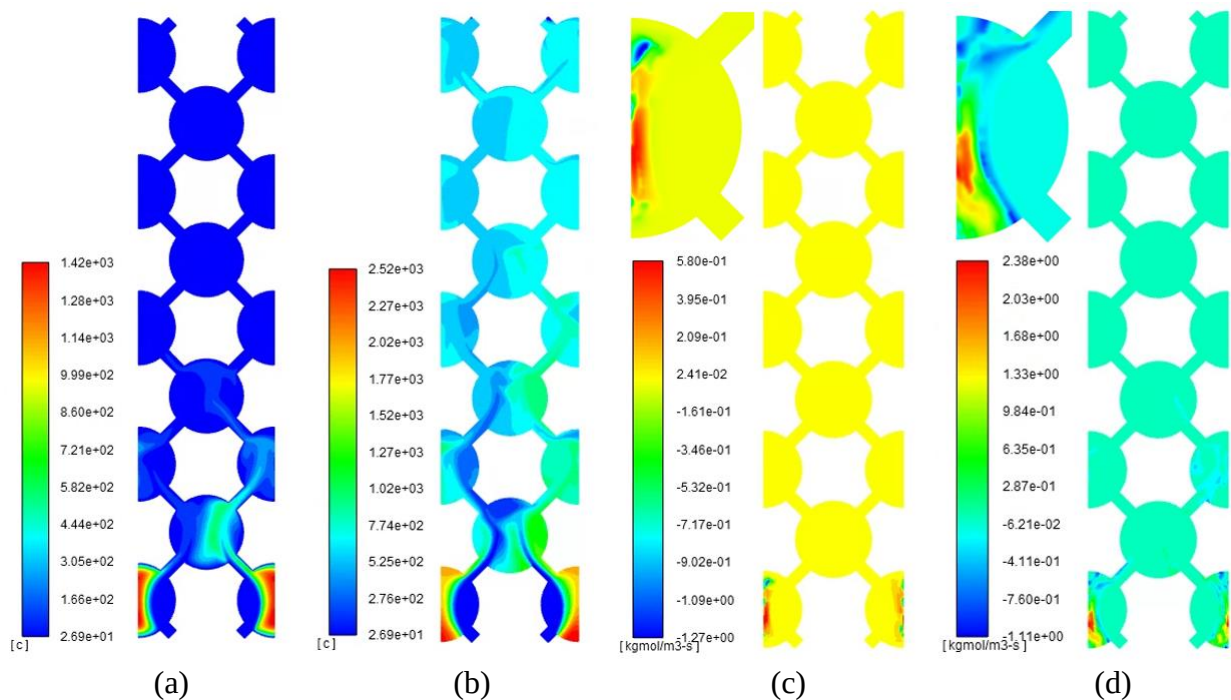


Figure VII.5 Temperature maps of: (a) Q1c and (b) C2. Reaction rate maps of: (c) Q1c and (d) C2.

VII.3 Macro-Scale Analysis

In this section, NETcombustor will be used to simulate combustion in NETmix, including heat transfer to the exterior of the reactor.

To simulate the heat that is removed from the reactor, the energy balance presented in Equation VI.2 of Section VI.2 was changed

$$V \frac{d(\rho_{out} h_{out})}{dt} - V \frac{dp}{dt} = \sum_{j=1}^{nj} F_j h_j - h_{out} \sum_{k=1}^{nk} F_k + Q_{ext} \quad (VII.5)$$

in which Q_{ext} is the heat removed from the system, calculated from

$$Q_{ext} = \hat{h}V(T_r - T_{ext}) \quad (VII.6)$$

where T_{ext} is the temperature of the external stream and T_r is the temperature inside the reactor. The heat transfer capacity of NETmix is $\hat{h} = 5 \times 10^7 \text{ W/(m}^3 \text{ K)}$, considering $\omega = 1 \text{ mm}$ (see Figure VII.3). $D = 10.0 \times 10^{-3} \text{ m}$ and $d = 1.50 \times 10^{-3} \text{ m}$, as in chapter VI.

VII.3.1 Global Reaction Scheme

In this section, the global scheme of hydrogen combustion, presented in VI.2.2, was applied. Previous cases of non-premixed combustion, *R3* and *R5*, were simulated considering heat removal from NETcombustor. For that, the reactor is considered to exchange heat with a fluid at $T_{ext} = 25 \text{ }^\circ\text{C}$, $50 \text{ }^\circ\text{C}$, $100 \text{ }^\circ\text{C}$ and $150 \text{ }^\circ\text{C}$.

The simulations of *R3* with heat removal, *RQ1* to *RQ4* is shown in Table VII.3. The results are compared with the CFD simulations *Q1* to *Q4* and with the original case without heat removal, *R3*.

In Table VII.3 is shown that the heat removed in NETcombustor is sufficient to have an outlet temperature equal to the fluid of the heat exchanger.

As the temperature of the external stream increases, the outlet temperature predicted by NETcombustor approaches the CFD result. In *RQ1* and *RQ2*, the outlet temperature differs less than 8% in relation to the CFD simulations; *RQ3* and *RQ4* differ less than 1%.

Comparing with *R3*, which does not include heat removal, it is visible that as the temperature of the external stream increases, from *RQ1* to *RQ4*, the conversions of oxygen and hydrogen approach the original values.

Table VII.3 Case R3 with heat removal.

Non-premixed Combustion							
	Species	y_{in} (A)	y_{in} (B)	$\overline{y}_{out}$	X_{H_2}	X_{O_2}	$\overline{T}_{out} (^{\circ}C)$
RQ1 $T_{ext} = 25^{\circ}C$ $\theta = 0.27$	H ₂	0.1	0	0.011	0.75	0.21	25
	O ₂	0	0.2	0.066			
	N ₂	0.9	0.8	0.89			
	H ₂ O	0	0	0.034			
ExtendedNUB Q1 $T_{ext} = 25^{\circ}C$ $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	43
	O ₂	0	0.2	0.11			
	N ₂	0.9	0.8	0.84			
	H ₂ O	0	0	0.042			
RQ2 $T_{ext} = 50^{\circ}C$ $\theta = 0.27$	H ₂	0.1	0	0.0027	0.94	0.26	50
	O ₂	0	0.2	0.062			
	N ₂	0.9	0.8	0.89			
	H ₂ O	0	0	0.043			
ExtendedNUB Q2 $T_{ext} = 50^{\circ}C$ $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	77
	O ₂	0	0.2	0.075			
	N ₂	0.9	0.8	0.89			
	H ₂ O	0	0	0.053			
RQ3 $T_{ext} = 100^{\circ}C$ $\theta = 0.27$	H ₂	0.1	0	0	1	0.27	100
	O ₂	0	0.2	0.061			
	N ₂	0.9	0.8	0.89			
	H ₂ O	0	0	0.046			
ExtendedNUB Q3 $T_{ext} = 100^{\circ}C$ $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	102
	O ₂	0	0.2	0.075			
	N ₂	0.9	0.8	0.87			
	H ₂ O	0	0	0.053			
RQ4 $T_{ext} = 150^{\circ}C$ $\theta = 0.27$	H ₂	0.1	0	0	1	0.27	150
	O ₂	0	0.2	0.061			
	N ₂	0.9	0.8	0.89			
	H ₂ O	0	0	0.046			
ExtendedNUB Q4 $T_{ext} = 150^{\circ}C$ $\theta = 0.27$	H ₂	0.1	0	0	1	0.26	155
	O ₂	0	0.2	0.079			
	N ₂	0.9	0.8	0.86			
	H ₂ O	0	0	0.054			
R3 <i>Adiabatic</i> $\theta = 0.27$	H ₂	0.1	0	0	1	0.27	394
	O ₂	0	0.2	0.061			
	N ₂	0.9	0.8	0.89			
	H ₂ O	0	0	0.046			

RQ1 to RQ4 – Simulation in NETcombustor, including heat removal from the walls

Q1 to Q4 – Simulation in CFD with Maxwell, including heat removal from the walls

R3 – Simulation in NETcombustor, adiabatic

As previously stated, the heat that is removed from NETcombustor is sufficient to lower the temperature to the external stream value. As T_{ext} increases, the heat removed, Q_{ext} , decreases. In fact, from $RQ1$ to $RQ4$, the total heat removed is 139 kJ/hr, 125 kJ/hr, 118 kJ/hr and 101 kJ/hr, respectively. As shown in Figure VII.6, for lower T_{ext} , the maximum heat removed is lower. However, the heat is removed until the last row of chambers, increasing the total heat that is removed from the system.

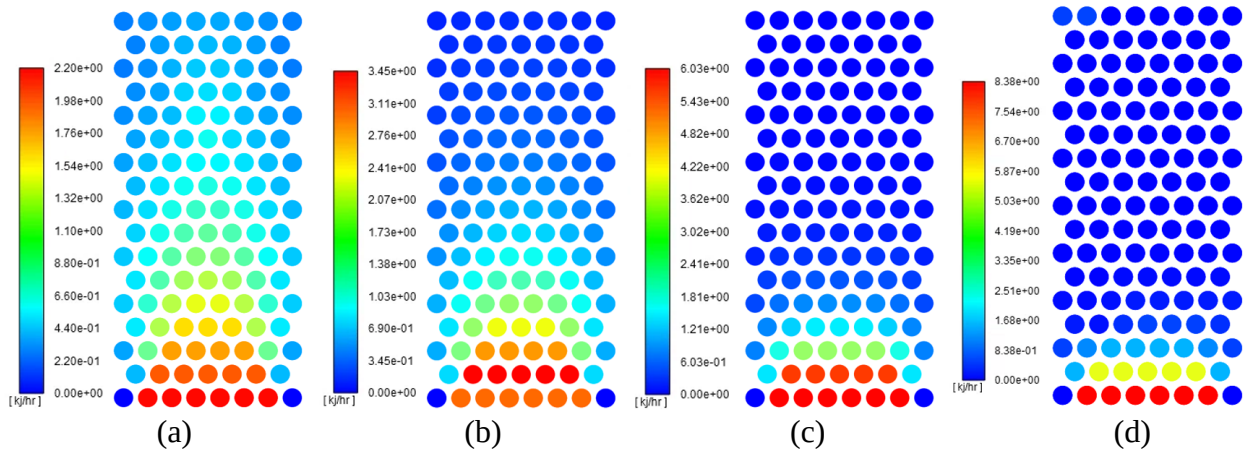


Figure VII.6 NETcombustor map of Q_{ext} of: (a) $RQ1$, (b) $RQ2$, (c) $RQ3$ and (d) $RQ4$.

The temperature inside NETcombustor is close to T_{ext} in all the chambers. For all cases, $RQ1$ to $RQ4$, the temperature in the first rows is slightly lower than T_{ext} due to a large amount of heat removed, as shown in Figure VII.7.

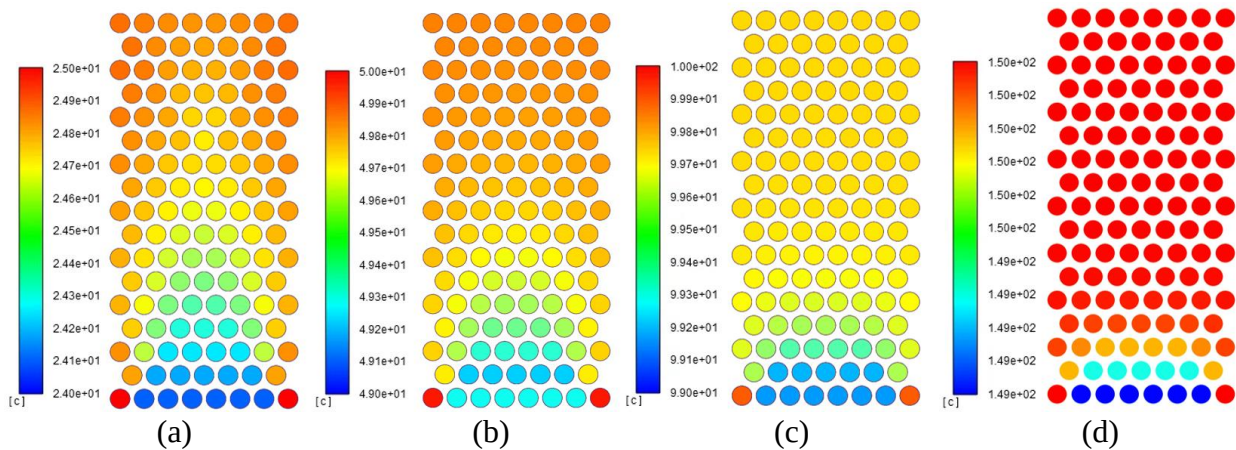


Figure VII.7 NETcombustor map of temperature of: (a) $RQ1$, (b) $RQ2$, (c) $RQ3$ and (d) $RQ4$.

If heat is removed from the reactor, it is possible to extend the reaction to a larger number of rows. As visible in Figure VII.8, the reaction occurs in all chambers in $RQ1$ and $RQ2$. For a lower amount of heat removed, in $RQ3$ and $RQ4$, the reaction has a smaller extension. Note that, if no heat is removed from the system, the reaction only occurs in the first row, as previously shown in

Figure VI.45. As Q_{ext} decreases from $RQ1$ to $RQ4$, the maximum reaction rate increases, approaching the value of $R3$ without heat removal, $2.8 \times 10^{-1} \text{ kmol}/(\text{m}^3 \text{ s})$.

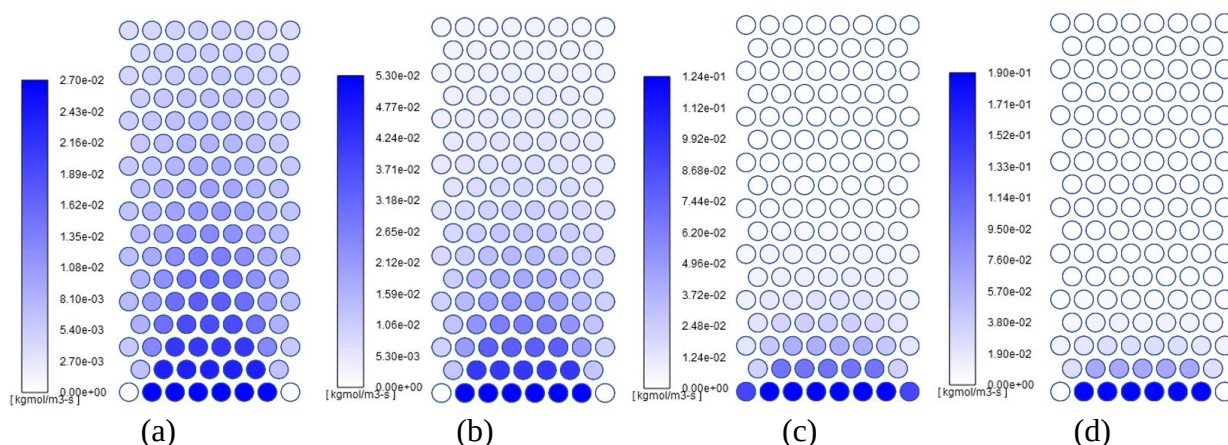


Figure VII.8 NETcombustor map of reaction rate of: (a) $RQ1$, (b) $RQ2$, (c) $RQ3$ and (d) $RQ4$.

As shown in Figure VII.9, the heat is released in the chambers where combustion occurs, i.e., the reaction rate is positive. Thus, the heat of combustion maps have a similar pattern to the reaction rate maps.

As expected, the maximum heat of combustion is lower if heat is removed from the system, since the conversion of the reactants is not complete. From $RQ1$ to $RQ4$, the maximum heat that is released increases, as well as the total heat, 243 kJ/hr, 306 kJ/hr, 335 kJ/hr and 335 kJ/hr, respectively, reaching the same value as $R3$ in the cases where the conversion of hydrogen is complete, $RQ3$ and $RQ4$.

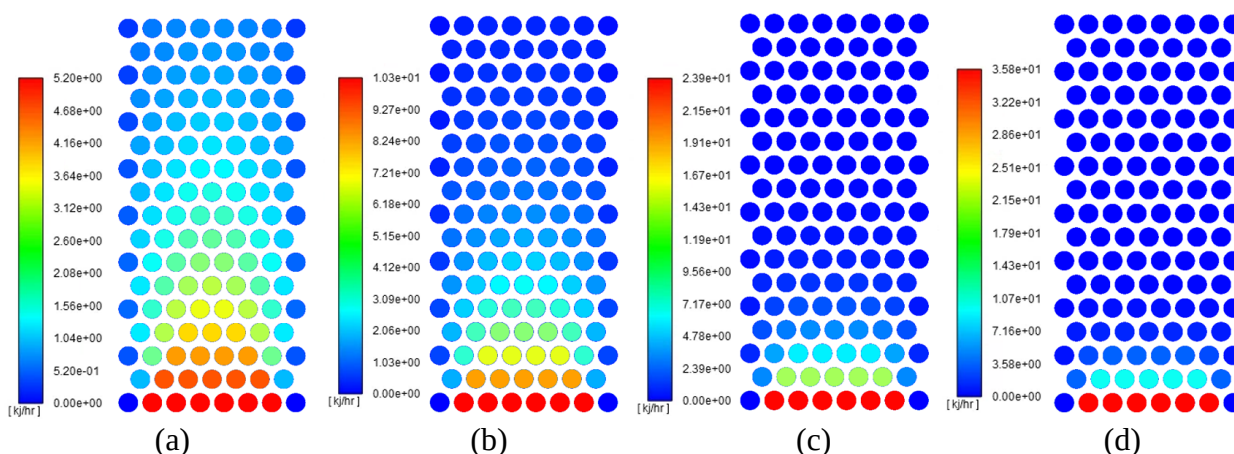


Figure VII.9 NETcombustor map of heat of combustion of: (a) $RQ1$, (b) $RQ2$, (c) $RQ3$ and (d) $RQ4$.

For a larger heat removal, it is possible to extend the reaction to all rows since the fuel is not consumed completely in the first rows, as in $R3$. As visible in Figure VII.10, the amount of fuel that is consumed in the first rows increases as Q_{ext} decreases.

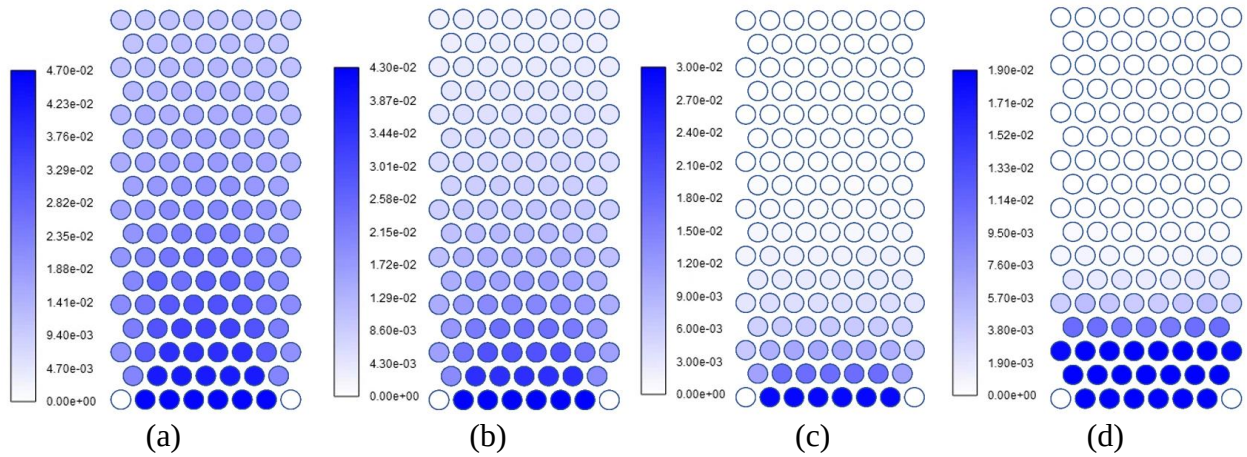


Figure VII.10 NETcombustor map of y_{H_2O} of: (a) RQ1, (b) RQ2, (c) RQ3 and (d) RQ4.

If a larger amount of heat is removed from the system, the maximum production of water is lower. Moreover, the water that is produced in the first rows is in a smaller amount. As the heat removed decreases, the production of water in the first rows approaches the maximum value, as shown in Figure VII.11.

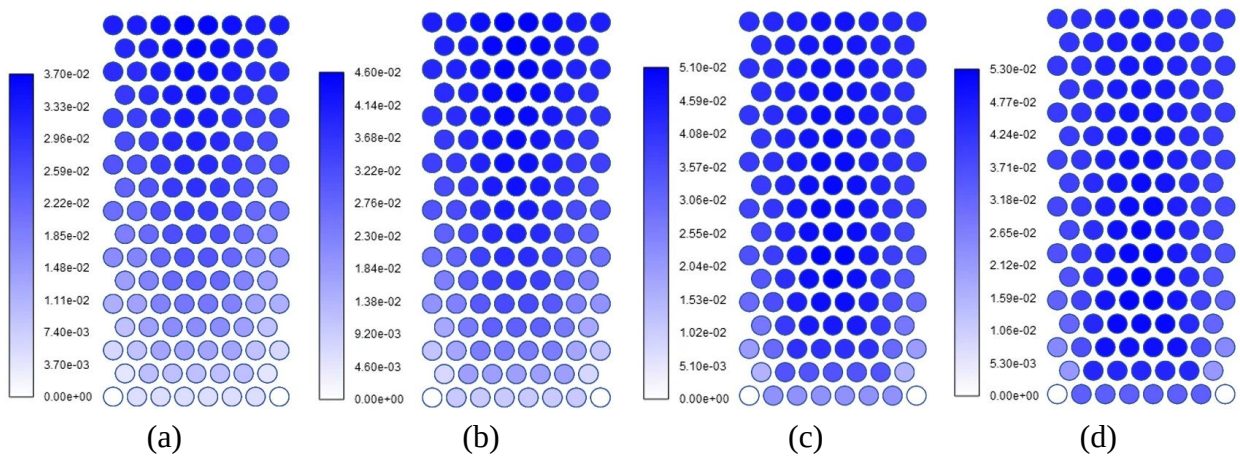


Figure VII.11 NETcombustor map of y_{H_2O} of: (a) RQ1, (b) RQ2, (c) RQ3 and (d) RQ4.

As in the temperature maps (see Figure VII.7), the Re number is similar for all the chambers, as shown in Figure VII.12. The small differences in the Re number form a pattern similar to the maps of y_{H_2O} . As expected, as the temperature of the external stream increases from RQ1 to RQ4, as well as the outlet temperature, the Re number decreases.

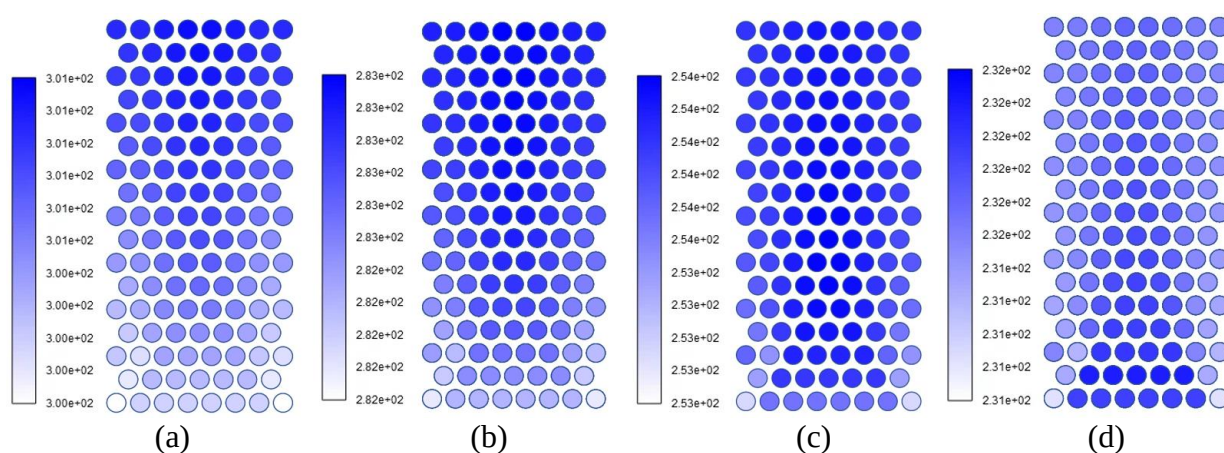


Figure VII.12 NETcombustor map of Re of: (a) RQ1, (b) RQ2, (c) RQ3 and (d) RQ4.

A case with a larger amount of fuel in the reactive mixture was also analysed. The simulation of R5 with heat removal, RQ5 to RQ8, is shown in Table VII.4.

The results are compared with the original case without heat removal, R5. In similarity to the previous case, the removed heat is sufficient to lower the outlet temperature to the external stream that is imposed. For a larger amount of fuel, the difference of temperature of the adiabatic case and the heat removal simulations is larger. As T_{ext} increases, the conversions of oxygen and fuel approach the result without heat removal, R5, where the oxygen is fully consumed. In similarity to RQ1 to RQ4, one of the reactants has complete conversion as T_{ext} increases.

Table VII.4 Case R5 with heat removal.

Non-premixed Combustion							
	Species	y_{in} (A)	y_{in} (B)	$\bar{y}_{out}$	X_{H_2}	X_{O_2}	$\bar{T}_{out}(^{\circ}C)$
RQ5 $T_{ext} = 25^{\circ}C$ $\theta = 8.99$	H ₂	0.9	0	0.62	0.10	0.93	25
	O ₂	0	0.2	0.0026			
	N ₂	0.1	0.8	0.31			
	H ₂ O	0	0	0.072			
RQ6 $T_{ext} = 50^{\circ}C$ $\theta = 8.99$	H ₂	0.9	0	0.62	0.11	1	50
	O ₂	0	0.2	0			
	N ₂	0.1	0.8	0.30			
	H ₂ O	0	0	0.078			
RQ7 $T_{ext} = 100^{\circ}C$ $\theta = 8.99$	H ₂	0.9	0	0.62	0.11	1	100
	O ₂	0	0.2	0			
	N ₂	0.1	0.8	0.30			
	H ₂ O	0	0	0.078			
RQ8 $T_{ext} = 150^{\circ}C$ $\theta = 8.99$	H ₂	0.9	0	0.62	0.11	1	150
	O ₂	0	0.2	0			
	N ₂	0.1	0.8	0.30			
	H ₂ O	0	0	0.078			

R5 <i>Adiabatic</i> $\theta = 8.99$	H ₂	0.9	0	0.62	0.11	1	691
	O ₂	0	0.2	0			
	N ₂	0.1	0.8	0.30			
	H ₂ O	0	0	0.078			

RQ5 to RQ8 – Simulation in NETcombustor, including heat removal from the walls

R5 – Simulation in NETcombustor, adiabatic

In similarity to the previous cases, the total heat that is removed decreases as T_{ext} increases, 536 kJ/hr, 499 kJ/hr, 463 kJ/hr and 425 kJ/hr, respectively. As shown in Figure VII.13, for lower T_{ext} , the maximum Q_{ext} decreases. However, the heat is removed until the last row of chambers, increasing the total heat that is removed from the system. For a larger amount of fuel in the reactive mixture ($y_{H_2} = 0.9$), the maximum heat that is removed is one order of magnitude higher when compared to the previous case ($y_{H_2} = 0.1$). The total removed heat is approximately five times larger.

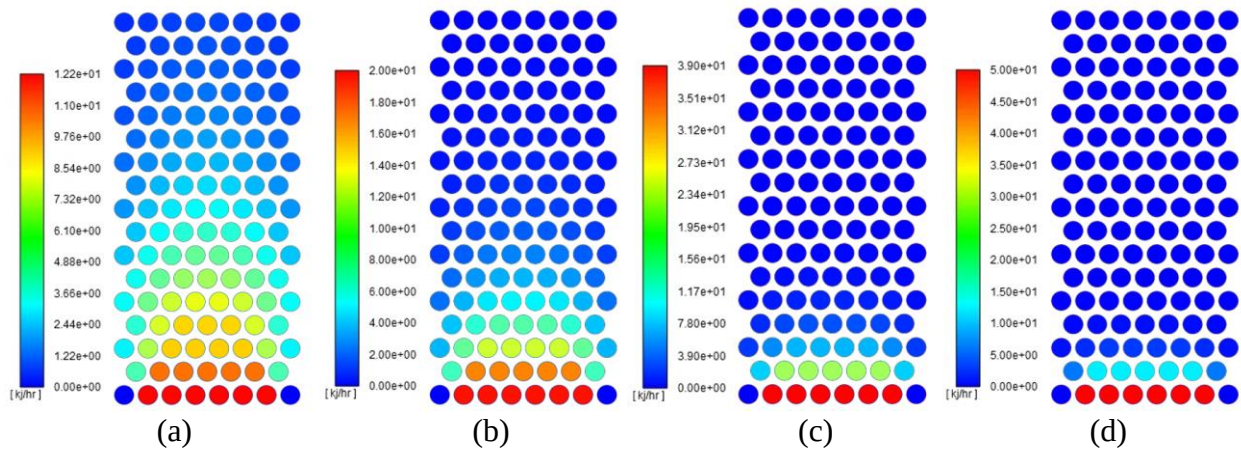


Figure VII.13 NETcombustor map of Q_{ext} of: (a) RQ5, (b) RQ6, (c) RQ7 and (d) RQ8.

In similarity to the previous cases ($y_{H_2} = 0.1$), in RQ5 to RQ8 with $y_{H_2} = 0.9$, the temperature inside NETcombustor is close to T_{ext} in all the chambers. Moreover, the temperature in the first rows is slightly lower than T_{ext} due to a large amount of heat removed, as shown in Figure VII.14.

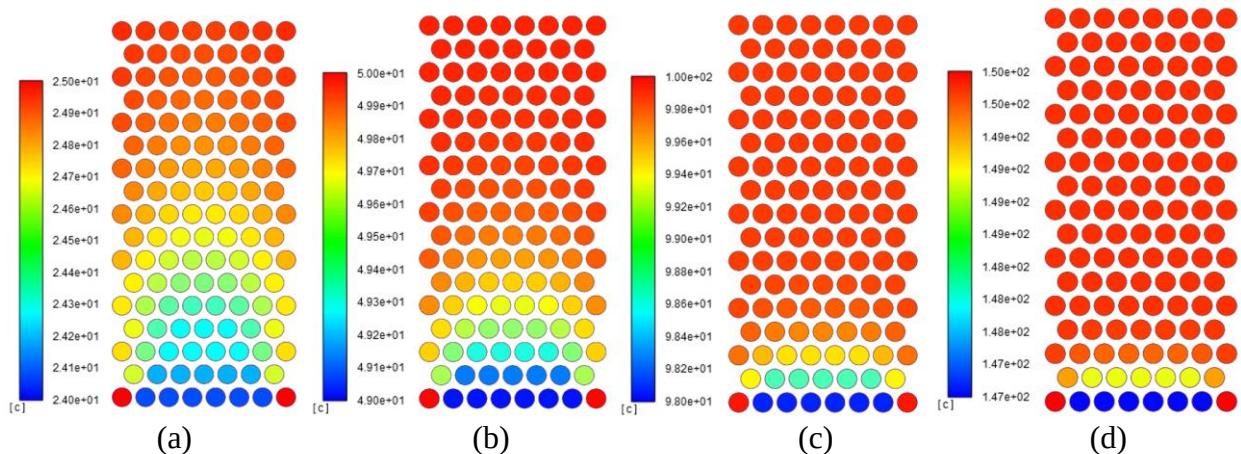


Figure VII.14 NETcombustor map of temperature of: (a) RQ5, (b) RQ6, (c) RQ7 and (d) RQ8.

If heat is removed from the reactor, it is possible to extend the reaction to a larger number of rows. As visible in Figure VII.15, the reaction occurs in all chambers in *RQ5*. For a lower amount of heat removed, the reaction has a smaller extension. When compared to the previous case, it is possible to conclude that if a larger amount of fuel is used in the reactive mixture, the reaction has a smaller extension since the oxygen is consumed faster, even if heat is removed from the system. Note that, if no heat is removed from the system, the reaction only occurs in the first row, as previously shown in Figure VI.45. As Q_{ext} decreases from *RQ5* to *RQ8*, the maximum reaction rate increases, approaching the value of *R5* without heat removal, $1.05 \text{ kmol}/(\text{m}^3 \text{ s})$.

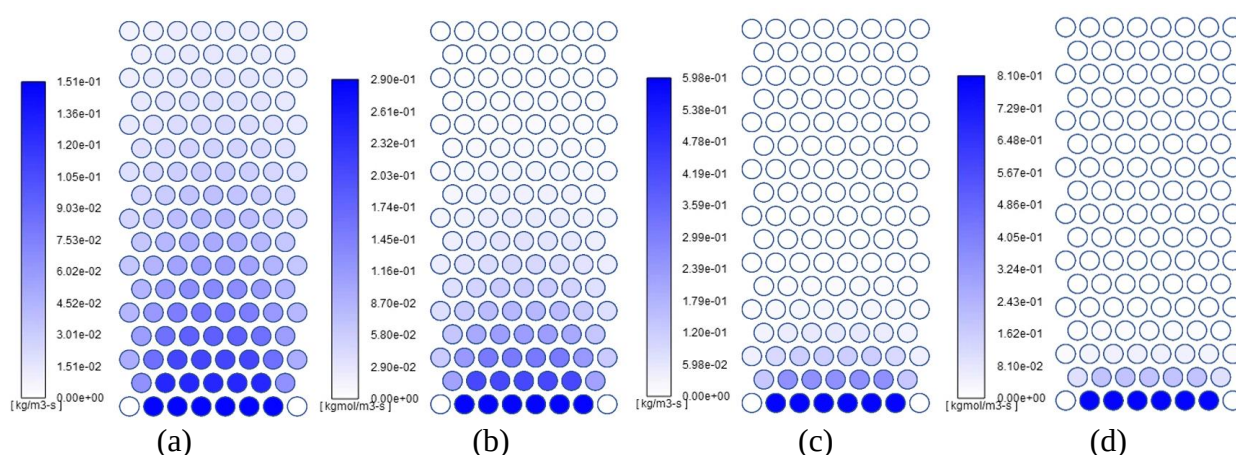


Figure VII.15 NETcombustor map of reaction rate of: (a) *RQ5*, (b) *RQ6*, (c) *RQ7* and (d) *RQ8*.

As for the previous cases, *RQ1* to *RQ4*, the heat of combustion maps have a similar pattern to the reaction rate maps. Moreover, the maximum heat of combustion increases if a smaller amount of energy is removed from the system, as shown in Figure VII.16. From *RQ5* to *RQ8*, the total heat of combustion increases, 1106 kJ/hr, 1196 kJ/hr, 1225 kJ/hr and 1225 kJ/hr, respectively, approaching the value of *R5*, without heat removal.

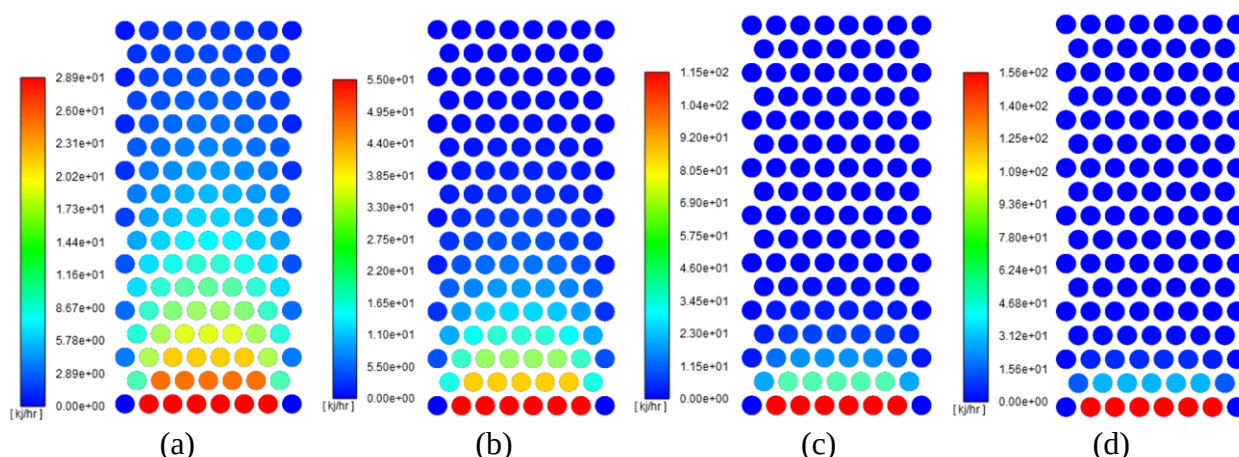


Figure VII.16 NETcombustor map of heat of combustion of: (a) *RQ5*, (b) *RQ6*, (c) *RQ7* and (d) *RQ8*.

For a larger heat removal, it is possible to extend the reaction to all chambers since the oxygen is not consumed completely in the first rows, as in *R5*. As visible in Figure VII.17, the amount of oxygen that is consumed in the first rows increases as Q_{ext} decreases.

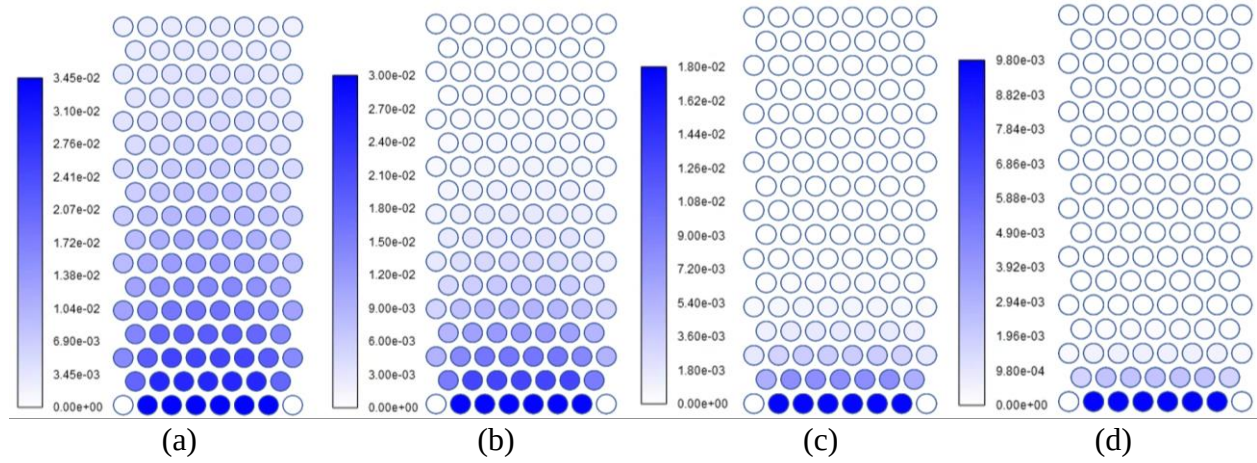


Figure VII.17 NETcombustor map of y_{O_2} of: (a) *RQ5*, (b) *RQ6*, (c) *RQ7* and (d) *RQ8*.

If a larger amount of heat is removed from the system, the water that is produced in the first rows is in a smaller amount. As the removed heat decreases, the production of water approaches the maximum value of case *R5*, 8.34×10^{-2} , as shown in Figure VII.18.

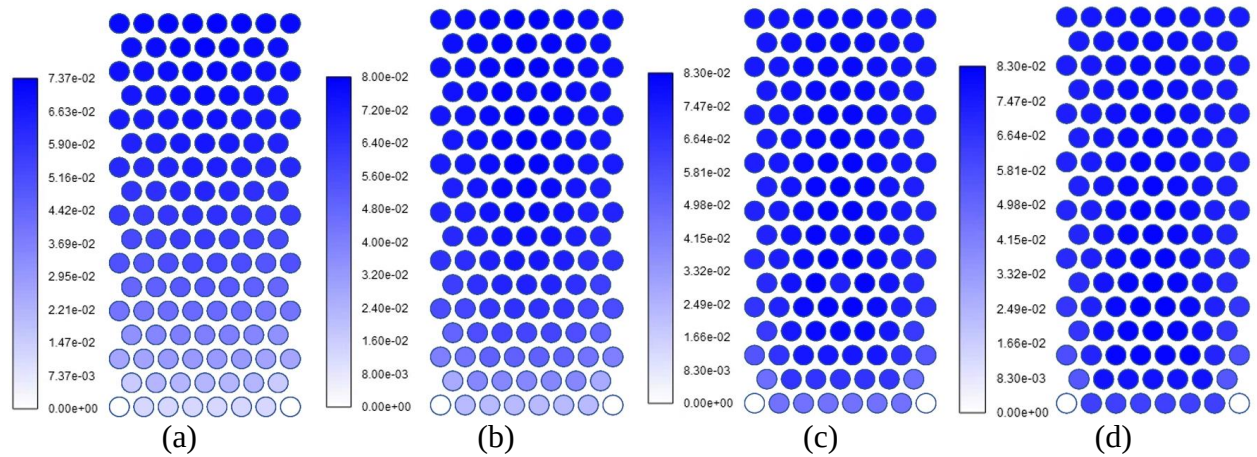


Figure VII.18 NETcombustor map of y_{H_2O} of: (a) *RQ5*, (b) *RQ6*, (c) *RQ7* and (d) *RQ8*.

As expected, as T_{ext} increases from *RQ5* to *RQ8*, the Re number decreases as shown in Figure VII.19. In similarity to the previous cases ($y_{H_2} = 0.1$), in *RQ5* to *RQ8* with $y_{H_2} = 0.9$, the Re number is similar in all the chambers.

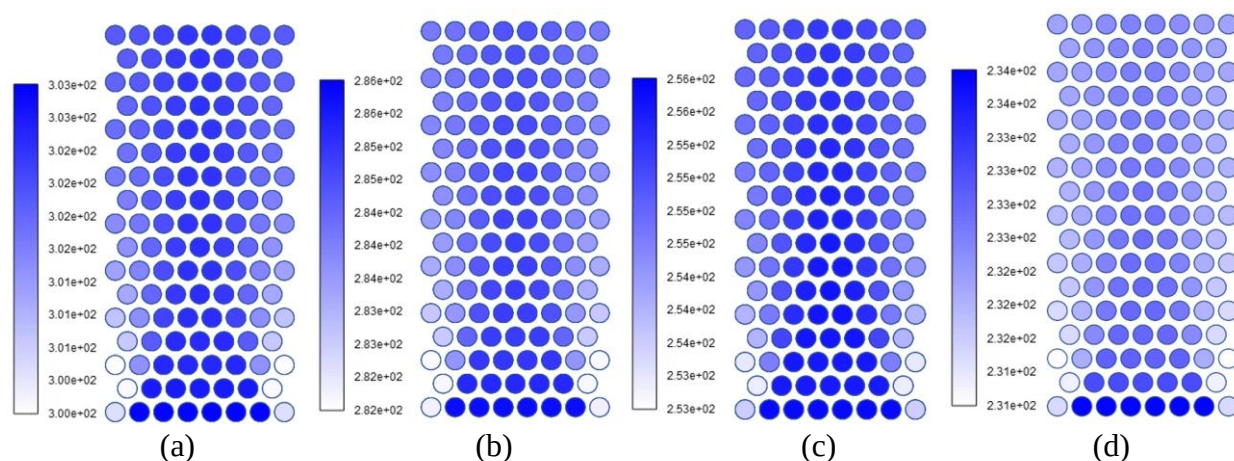


Figure VII.19 NETcombustor map of Re of: (a) RQ5, (b) RQ6, (c) RQ7 and (d) RQ8.

VII.4 Computational Aspects

The 2D ExtendedNUB simulations considering heat transfer with the global scheme of hydrogen were run in 2 nodes of a computational cluster (FEUP) Intel® Xeon® with 16 cores at 2.1 GHz and 64 GB of RAM, and took approximately 15 days to perform 1.5×10^5 time steps. For the case in which the 19-reactions scheme is used, the simulation was run in 8 nodes of the supercomputer BOB (MACC) with an Intel 8-cores "Sandy Bridge" Xeon (2 processors) at 2.7 GHz and 32 GB of RAM, and took ca. 6 days to perform 1.5×10^5 time steps.

The computational aspects of NETcombustor were previously discussed in Section IV.3.

VII.5 Conclusions

To have a closer approach to real cases, combustion in NETmix was simulated including heat transfer to the outside of the reactor. For that, NETmix was considered to contact with heat exchangers at different temperatures.

CFD simulations were performed for both schemes, the global scheme of hydrogen and the 19-reactions scheme. It was shown that removing heat enables to decrease the temperature of the hotspots that are formed inside the reactor. Moreover, the outlet temperature approaches the external temperature that is set. As heat is being removed, the maximum reaction rate decreases.

With NETcombustor, a similar result is obtained, the heat removed in each chamber enables to decrease the temperature to the temperature of the external stream. As a larger amount of heat is removed, the maximum reaction rate decreases, as well as the heat of combustion.

Chapter VIII – Summary and Contributions

The summary of the work that was described in the previous chapters will be assessed, as well as the most relevant scientific contributions. Suggestions for future work will also be made.

VIII.1 Summary and Contributions

In this work, combustion was simulated in the NETmix reactor for the first time. It was shown that from the control of the reactive mixture and using heat transfer, it is possible to perform combustion in NETmix with low temperatures, $T < 1300$ °C, enabling to reduce the emission of pollutants as NO_x compounds.

Prior to the simulation of chemical reactions, the NETmix chaotic system was extensively studied. To start, a 2D reduced geometric model, ExtendedNUB, was developed and numerically validated to represent and simulate the NETmix mixing and hydrodynamics behaviours, reducing the computation time.

To quantify mixing in NETmix, two approaches were used: *micromixing* and *macromixing*.

For the micromixing study, a new Lagrangian algorithm was developed, Lagrangian Mixing Simulation (LMS), which was numerically validated from studies with the Confined Impinging Jets (CIJ) reactor, a simpler and well-known system (Matos et al. 2018, Matos et al. 2020). LMS was then applied to the NETmix chambers which enabled to measure the interfacial area generation and the striation thickness (for which an algorithm was also developed). This analysis has shown an exponential growth of the interfacial area which attains values up to 7×10^4 , typical of chaotic systems. The size of the strias inside NETmix decreases to values lower than 10^{-6} m. A modified version of LMS, Diffusive Lagrangian Mixing Simulation (DLMS), was developed for flows with extreme chaotic behaviour, associated to a larger interfacial area generation. DLMS was applied to combustion in NETmix, and it was shown that the interfacial area attains values up to 1.2×10^6 .

To perform the macromixing study, a modification of LMS was developed, Batch Lagrangian Mixing Simulation (BLMS). This algorithm was applied to the NETmix chambers in order to optimise the network topology in terms of the ratio between the chamber diameter and the channel width, D/d . It was shown that for $6.65 < D/d < 6.85$ mixing inside the NETmix chambers is nearly perfect, having a dilution factor close to 2 (Matos et al. 2021). BLMS was numerically validated

from the comparison with a 2D CFD tracer simulation of ExtendedNUB which showed a tracer molar fraction close to 0.5 inside the NETmix chambers.

In order to extend the knowledge of the *NETmix chaotic system*, 2D CFD simulations with the ExtendedNUB model were performed. From them, hydrodynamics studies of the velocity, vorticity and strain rate were performed. The plot of histories enabled to assess the behaviour of the NETmix oscillations. From the elaboration of phase diagrams, it was possible to conclude that the NETmix system can be represented by strange attractors which are sensitive to the topology of the reactor, as well as to other parameter changes of the system. The NETmix strange attractors were analysed through Poincaré maps and spectral frequencies. It was shown that NETmix presents three different states of chaotic behaviour: *strong-chaotic* (SC), *weak-chaotic* (WC) and *quasi-periodic* (QP) with the scheme SC-WC-QP-WC-QP-WC-SC, which indicates the existence of an *intermittent* bifurcation. Moreover, the best mixing, $6.65 < D/d < 6.85$, occurs at the quasi-periodic regime and presents a strange attractor with a thin *W* shape.

Once the analysis of the NETmix chaotic system was complete, ExtendedNUB was numerically validated for gases and used to simulate the hydrogen combustion. Three H₂-Air reactive schemes were used, the global scheme with and without the reverse rate and the 19-reactions scheme. Combustion was simulated in NETmix following two approaches: a micro-scale analysis and a macro-scale analysis.

To perform the micro-scale analysis, 2D CFD simulations with ExtendedNUB were made. For *premixed* and *non-premixed* combustion, the CFD studies enabled to predict the formation of hotspots inside the reactor. It was shown that the temperature of the hotspots decreases as the fuel in the reactive mixture is diluted, i.e., more nitrogen is added or more oxygen is added. In general, the maximum temperature of non-premixed combustion is higher when compared to the maximum temperature of premixed cases. It was also shown that for a lower amount of fuel in the reactive mixture, the reaction front occurs further in the reactor and the maximum reaction rate decreases.

A comparative analysis between the three reactional schemes has shown that if the reverse rate is included in the global scheme, the maximum temperature is lower for premixed and non-premixed combustion. If the 19-reactions scheme is applied, the temperatures of the hotspots are lower for premixed combustion and higher for non-premixed combustion.

The influence of the mixture properties as well as the diffusion model were studied. It was shown that the physical properties exert a major influence and should be predicted by models that enable

their variation with the temperature. The best diffusion model is the Maxwell diffusion which has shown closer values to at least one of the other two models, Fick and Flame.

Included in the micro-scale analysis, an adaptation of the Lamellar Micromixing Model was developed to simulate combustion in NETmix. A temperature equation was added to the PDE system and the results from LMS were used to represent the flow dynamics of the NETmix system. The difference in the prediction of the temperature between the Lamellar Micromixing Model for Combustion and the CFD simulations is less than 12%.

To perform the macro-scale analysis, a new network model, NETcombustor, was developed to represent the NETmix reactor. In this model, CSTR equations are used to represent the NETmix chambers.

NETcombustor was used to study the hydrogen combustion in NETmix with the global scheme. Both *premixed* and *non-premixed* combustion were simulated. In general, the temperature that is predicted by NETcombustor is lower than the temperature predicted by the CFD simulations. The difference between the two models is less than 15%. In similarity to the CFD results, in NETcombustor, if the backward reaction is considered the temperatures inside the reactor are lower. Moreover, as the amount of fuel of the reactive mixture is reduced, the temperature decreases, as well as the maximum reaction rate and the heat of combustion.

For non-premixed combustion, the injection scheme was studied. It was shown that the distribution of the fuel and oxygen at the inlet exerts a major influence on the temperature of combustion.

The maximum temperature in function of θ (ratio between fuel and oxygen of the initial mixture) was studied and a H₂-Air combustion curve was built for NETmix. The shape of the obtained curve is similar to a typical adiabatic flame temperature H₂-Air curve, measured with conventional experimental tubes.

To conclude the combustion studies in NETmix, the hydrogen combustion was simulated including heat transfer to the outside of the reactor. Two approaches were used: CFD simulations with ExtendedNUB and NETcombustor. It was shown that removing heat enables to decrease the temperature of the hotspots that are formed inside the reactor. Moreover, the removed heat increases as the temperature of the external stream decreases, in order to have a reactor temperature closer to the external temperature. As heat is removed from the system, the maximum reaction rate decreases, as well as the heat of combustion.

VIII.2 Suggestions for Future Work

The study of combustion in NETmix is associated to the environmental issue of reducing the pollutant emissions. If a device with large heat transfer capacity is used, such as NETmix, it is possible to control and improve the performance of combustion, reducing the emission of by-products which are harmful to the environment.

From the CFD simulations of this work it was shown that hotspots are formed inside NETmix, which have a temperature above 1000 °C for most cases. Moreover, the study of the injection scheme in NETcombustor has shown that the configuration of the fuel and oxygen inlet streams exerts a major impact in combustion. In this way, as future work, it is suggested to build a mesh with at least 3 columns of the ExtendedNUB geometry in order to study different injection schemes and understand how the fuel/oxygen streams should be configured to decrease the temperature of the hotspots.

From the study of the inlet Reynolds number, it was possible to conclude that the temperature inside the reactor is dependent on Re . In this way, the analysis of this work should be repeated for different inlet Re to understand how it is possible to control combustion by varying the inlet velocity.

The studies in which heat is removed from NETmix have shown that it is possible to reduce the temperature of the hotspots. However, these studies were performed in 2D, considering heat transfer only from the internal side walls. As future work, a reactive 3D model of ExtendedNUB should be developed to have a more realistic approach of the heat transfer through the walls of NETmix, which includes the front and back faces of the reactor.

In this work, steel was used for the walls of the reactor. Since the heat transfer is dependent on the properties of the material, different temperature resistant materials should be tested to evaluate its impact on the combustion temperature. Moreover, the resistance of the material of the heat exchangers should be included in the heat transfer model.

In the approaches that were used, the pressure was maintained constant at 1 bar. Since the pressure exerts a large influence in chemical reactions, studies should be performed at different pressures to evaluate its effect in combustion.

As a long-term objective, NETmix experiments with combustion should be made in order to compare the simulation results with a real device. Moreover, it would be worth to consider the performance of studies to integrate NETmix combustion plates in units, namely for heat transfer purposes and reuse of by-products.

Literature References

- Abad, A.V., P.E. Dodds, 2017. Production of Hydrogen. *Encyclopedia of Sustainable Technologies*, 293-304.
- Adbulla, A., R. Hanna, k.R. Schell, O. Babacan, D.G. Victor, 2020. Explaining successful and failed investments in U.S. carbon capture and storage using empirical and expert assessments. *Environmental Research Letter*, 16 (1), 014036.
- Alberini, F., M.J.H. Simons, A. Ingram, 2014. Use of an Areal Distribution of Mixing Intensity to Describe Blending of Non-Newtonian Fluids in a Kenics KM Static Mixer Using PLIF. *AIChE J.* 60(1), 332-342.
- AlenTec, 2011. Cited 1 November 2019. Available from: https://www.alentecinc.com/papers/NOx/The%20formation%20of%20NOx_files/The%20formation%20of%20NOx.htm.
- Ali, I., M.A. Basit, 1993. Significance of Hydrogen Content in Fuel Combustion. *Int. J. Hydrogen Energy*, 18(12), 1009-1011.
- Anderson, P.D., H.E.H. Meijer, 2000. Chaotic mixing analysis by distribution matrices. *Applied Rheology* 10(3), 119-133.
- Ansys, Inc. 2016. ANSYS Fluent User's Guide, Release 17.2.
- Ansys, Inc. 2021. Ansys Chemkin-Pro Theory Manual.
- Avci, A.K., D.L. Trimm, M. Karakaya, 2009. Microreactor catalytic combustion for chemicals processing. *Catalysis Today*, 155, 66-74.
- Balakrishnan, G., M.D. Smooke, F.A. Williams, 1995. A Numerical Investigation of Extinction and Ignition Limits in Laminar Nonpremixed Counterflowing Hydrogen-Air Streams for Both Elementary and Reduced Chemistry. *Combustion and Flame*, 102, 329-340.
- Baldyga, J., J.R. Bourne, 1983. Distribution of striation thickness from impingement mixers in reaction injection molding. *Polym. Eng. Sci.* 20(13), 556-559.
- Barths, H. N. Peters, N. Brehm, A. Mack, M. Pfitzner, V. Smiljanovski, 1998. Simulation of Pollutant Formation in a Gas-turbine Combustor using Unsteady Flamelets. *Twenty-Seventh Symposium on Combustion*, 1841-1847.
- Berselli, L.C., W.J. Layton, T. Iliescu, 2006. Scale Similarity Models. In *Mathematics of Large Eddy Simulation of Turbulent Flows*. Scientific Computation. Springer, Berlin, Heidelberg.
- Bird, R.B., W.E. Stewart, E.N. Lightfoot, 2002. *Transport Phenomena*. John Wiley and Sons, Inc.
- Boivin, P. 2011. Reduced-Kinetic Mechanisms for Hydrogen and Syngas Combustion Including Autoignition. Tesis Doctoral del Departamento de Ingeniería Térmica y de Fluidos. Escuela Politécnica Superior. Léguenes.
- Bosch, 2017. Synthetic fuels — The next revolution. Cited 26 December 2021. Available from: <https://www.bosch.com/stories/synthetic-fuels/>.

- Boussinesq, J. 1877. Essai sur la théorie des eaux courantes. Mémoires présentés par divers savants à l'Académie des Sciences XXIII, 1, 1-680.
- Brito, M.S.C.A., L.P. Esteves, C.P. Fonte, M.M. Dias, J.C.B. Lopes, R.J. Santos, 2018. Mixing of fluids with dissimilar viscosities in Confined Impinging Jets. Chem. Eng. Res. Des. 134, 392-404.
- Brito, M.S.C.A., M.M. Dias, R.J. Santos, J.C.B. Lopes, C.P. Fonte, 2020. Fully resolved modelling and simulation of micromixing in confined impinging jets. Chem. Eng. Sci. 211, 115299.
- Brito, M.S.C.A., Matos, J., Torres, M.V.L., Fonte, C.P., Dias, M.M., Lopes, J.C., Santos, R.J. 2022. Rheokinematics for Product Development - Formulation Screening in Rotational Rheometers. AIChE, e17596.
- Carbonell, D., C.D. Perez-Segarra, P.J. Coelho, A. Oliva, 2009. Combustion and Flame 156, 334-347.
- Carrà, S., A. Clô, U. Romano, 2008. Encyclopaedia of Hydrocarbons, Volume V. Istituto della Encuclopedia Italiana fondata da Giovanni Treccani, Roma.
- Çengel, Y.A., Boles, M.A. 2001. Thermodynamics: An Engineering Approach. Mcgraw-Hill College.
- Cerfacs, 2017. Cited 1 November 2019. Available from: <https://www.cerfacs.fr/cantera/mechanisms/hydro.php>.
- Chen, J.Y., W. Kollman, R.W. Dibble, 1989. Pdf Modeling of Turbulent Nonpremixed Methane Jet Flames. Combust. Sci. and Tech. 64, 315-346.
- Chen, J.Y., W. Kollman, 1992. PDF Modeling and Analysis of Thermal NO Formation in Turbulent Nonpremixed Hydrogen-Air Jet Flames. Combustion and Flame, 88, 397-412.
- Chevalier, C. 1993. Dissertation Universitat Stuttgart.
- Choi, K., S. Park, H. Roh, C. Lee, 2019. Combustion and Emission Reduction Characteristics of GTL-Biodiesel Fuel in a Single-Cylinder Diesel Engine. Energies, 12, 2201.
- Conaire, M., H.J. Curran, J.M. Simme, W.J. Pitz, C.K. Westbrook, 2004. A Comprehensive Modeling Study of Hydrogen Oxidation. International Journal of Chemical Kinetics, 36(11), 603 – 622.
- Conant, J.B., 1964. The Overthrow of the phlogiston theory: the chemical revolution of 1775-1789. Cambridge Mass, Harvard University Press.
- Costa, M.F., 2017. The NETmix Technology, Applied to Gas Hydrates Production: A Potential Solution to CCS, PhD Thesis of University of Porto.
- Costa, M.F., C.M., Fonte, M.M. Dias, J.C.B. Lopes, 2017. Heat Transfer Performance of NETmix—A Novel Micro-Meso Structured Mixer and Reactor. AIChE J. 63(6), 2496-2508.
- Cybulski, A., J.A. Moulijn, 2006. Structured Catalysts and Reactors. CRC Press, Taylor & Francis Group. Florida, United States.
- Danckwertz, P.V., 1952. The Definition and Measurement of Some Characters of Mixtures. Appl. Sci. Res. A(3), 279-296.

- Danckwertz, P.V., 1953. Continuous Flow Systems. *Chem. Eng. Sci.* 2(1).
- Das, L.M., 2016. Hydrogen-fueled internal combustion engines. *Compendium of Hydrogen Energy*, 3, 177-217.
- Darwish, M. 2013. Towards Energy Conservation in Qatar. *Open Journal of Energy Efficiency*, 02(04), 176-191.
- Dincer, I., A. Canan, 2015. Review and evaluation of hydrogen production methods for better sustainability. *International Journal of Hydrogen Energy*. 40 (34), 11096.
- DOE Fundamentals Handbook, 1992. Thermodynamics, Heat transfer and Fluid flow. U.S. Department of Energy, Washington, D.C. 20585.
- Drell, I.L., Belles, F.E., 1957. Survey of hydrogen combustion properties. National Advisory Committee for Aeronautics, RM ED57D24.
- Encyclopædia Britannica, Kondratiev, V.N. 2020. Combustion. Cited 1 November 2021. Available from: <https://www.britannica.com/science/combustion>
- Enerdata. Global Energy Statistical Yearbook 2020, cited 12 December 2021. Available from: <https://yearbook.enerdata.net/total-energy/world-energy-production.html>.
- EDP, Serviço Universal, cited 2021, 12 December. Available from: <https://www.edp.pt/origem-energia/>.
- Eckman, J.P., D. Ruelle, 1985. Ergodic theory of chaos and strange attractors. *Reviews of Modern Physics*, 57 (3), Part I, 617-656.
- Emsley, J, 2001. *Nature's Building Blocks: An A–Z Guide to the Elements*. Oxford University Press.
- Erkoç, E.R., R.J. Santos, M.I. Nunes, M.M. Dias, J.C.B. Lopes, 2007. Mixing dynamics control in RIM machines. *Chem. Eng. Sci.* 62(18-20), 5276-5281.
- Erkoç, E.R, C. P. Fonte, M.M. Dias, J. C. B. Lopes, R.J. Santos, 2016. Numerical study of active mixing over a dynamic flow field in a T-jets mixer: induction of resonance. *Chem. Eng. Res. Des.* 106,74-91.
- Evo, 2021. Efuels, sustainability and sports cars – manufacturers weigh in on the issues. Cited 26 December 2021. Available from: <https://www.evo.co.uk/fuels/203323/efuels-sustainability-and-sports-cars-manufacturers-weigh-in-on-the-issues>.
- Falconer, K. 2003. *Fractal Geometry*. John Wiley and Sons.
- Fernandes, I.S., M.S.C.A. Brito, Y.A. Manrique, M.M. Dias, J.C.B. Lopes, R.J. Santos, 2021. Computational Fluid Dynamics Model of Two-Phase Flow in NETmix Reactors. *Chem. Eng. Technol.* 44 (11), 2002-2010.
- Fernández-Galisteo, D., A.L. Sánchez, A. Liñán, F.A. Williams, 2009. One-step reduced kinetics for lean hydrogen–air deflagration. *Combustion and Flame*, 156, 985-996.
- Fernandez-Pello, A.C., 2020. Micropower Generation using combustion: issues and approaches. *Proc. Combust. Inst.* 20, 883-899.

- Filho, B.M.C., A.L.P. Araujo, G.V. Silva b, R.A.R. Boavenura, M.M. Dias, J.C.B. Lopes, V.J.P. Vilar, 2017. Intensification of heterogeneous TiO₂ photocatalysis using an innovative micro-meso-structured-photoreactor for n-decane oxidation at gas phase. *Chem. Eng. J.* 310(2), 331-341.
- Filho, B.M.C., G.V. Silva, R.A.R. Boaventura, M.M. Dias, J.C.B. Lopes, V.J.P. Vilar, 2019. Ozonation and ozone-enhanced photocatalysis for VOC removal from airstreams: Process optimisation, synergy and mechanism assessment. *Science of Total Environment*, 687, 1357-1368.
- Fonte, C.M., 2013. The NETmix Reactor: Application to High Added-Value Products. PhD Thesis of University of Porto.
- Fonte, C.P., 2012. Mixing Studies with Impinging Jets PIV/PLIF Experiments and CFD Simulation. PhD Thesis of University of Porto.
- Fonte, C.M., M.E. Leblebici, M.M. Dias, J.C.B. Lopes, 2013. The NETmix reactor: pressure drop measurements and 3D CFD modeling. *Chem. Eng. Res. Des.* 91(11), 2250–225.
- Fonte, C.P., Santos, R.J., Dias, M.M., Lopes, J.C.B., 2012. Quantification of mixing in RIM using a non-diffusive two-phase flow numerical model. *Int. J. Chem. Reactor Eng.* 9, A114.
- Franjione, J.G., J.M. Ottino, 1987. Feasibility of numerical tracking of material lines and surfaces in chaotic flows. *The Physics of Fluids* 30(12), 3641-3643
- Franzelli, B., E. Riber, M. Sanjosé, T. Poinso, 2010. A two-step chemical scheme for kerosene–air premixed flames. *Combustion and Flame*, 1364-1373.
- Gaba, A., S. F. Irodache. 2019. Reduction of Air Pollution by Combustion Processes. IntechOpen. Available from: <https://www.intechopen.com/books/the-impact-of-air-pollution-on-health-economy-environment-and-agricultural-sources/reduction-of-air-pollution-by-combustion-processes>.
- Galaktionov, O.S., P. D. Anderson, G.W.M. Peters, C. L. Tucker III, 2002. A global, multi-scale simulation of laminar fluid mixing: the extended mapping method. *Int. J. Multiphas Flow* 28, 497–523.
- Germano, M., U. Piomelli, P. Moin, W.H. Cabot, 1991. A Dynamics subgrid-scale eddy viscosity model. *Phys. Fluids*. A3, 1760-1765.
- Gilbert, R.G., K. Luther, J. Troe, 1983. Theory of Thermal Unimolecular Reactions in the Fall-off Range. *Phys. Chem.* 87, 169-177.
- Givi, P., P.A. McMurtry, 1988. Nonpremixed Reaction in Homogeneous Turbulence: Direct Numerical Simulations. *AIChE J.* 34(6), 1039-1042.
- Gomes, P.J., 2011. The NETmix Reactor: strategies for optimising mixing and development of new reactor designs, PhD Thesis of University of Porto.
- Gonçalves, N.D., H. M. Salvador, C. P. Fonte, M. M. Dias, J. C. B. Lopes, R. J. Santos, 2017. On the 2D nature of flow dynamics in opposed jets mixers. *AIChE Journal* 63(6), 2335-2347.
- Göttgens, J., F. Mauss, N. Peters, 1992. Analytic approximations of burning velocities and flame thicknesses of lean hydrogen, methane, ethylene, ethane, acetylene, and propane flames. *Twenty-Fourth Symposium (International) on Combustion/The Combustion Institute*, 129-135.

Gray, P., S.K. Scott, 1994. Chemical oscillations and instabilities: non-linear chemical kinetics. Oxford University Press.

Gregory P. Smith, David M. Golden, Michael Frenklach, Nigel W. Moriarty, Boris Eiteneer, Mikhail Goldenberg, C. Thomas Bowman, Ronald K. Hanson, Soonho Song, William C. Gardiner, Jr., Vitali V. Lissianski, and Zhiwei Qin, . Cited, 1 November 2019. Available from: <https://www.cerfacs.fr/cantera/mechanisms/meth.php>.

Gribble, P., D. Kistemaker, 2012. Cited 1 November, 2019. Available from: https://www.gribblelab.org/compneuro2012/2_Modelling_Dynamical_Systems.html.

Haworth, D.C., M.C. Drake, S.B. Pope, R.J. Blint, 1988. The Importance of Time-dependent Flame Structures in Stretched Laminar Flamelet Models for Turbulent Jet Diffusion Flames. *Twenty-Second on Combustion*, 589-597.

He, L. P. Clavin, 1993. Premixed Hydrogen-Oxygen Flames. Part I: Flame Structure Near the Flammability Limits. *Combustion and Flame*, 93, 391-407.

Hessel, V., C. Knobloch, H. Lowe, 2008. Review on Patents in Microreactor and Micro Process Engineering. *Recent Patents on Chemical Engineering*, 1, 1-16.

Hilborn, R.C. 2001. *Chaos and Nonlinear Dynamics*. Oxford University Press.

Hyman, J.M., 1984. Numerical Methods for Tracking Interfaces. *Physica* 12D 396-407.

Hughes, K.J., T. Turányi, A.R. Clague, M.J. Pilling, 2001. Development and testing of a comprehensive chemical mechanism for the oxidation of methane. *International Journal of Chemical Kinetics*, 33(9), 513-538.

Hydrogen Europe. Cited 1 November, 2019. Available from: <https://hydrogeneurope.eu/hydrogen-industry>.

Industrial Boiler and Mechanical, cited 1 November 2019. Available from: <http://www.industrialboiler.com/Boilers/Firetube-Boilers>.

James, S.R., 1989. Hominid Use of Fire in the Lower and Middle Pleistocene. *Curr. Anthropol.* 30(1), 1-26.

Jenkins, B., P. Mullinger, 2011. *Industrial and Process Furnaces: Principles, Design and Operation*. Butterworth-Heinemann.

Jejurkar, S.Y., D.P. Mishra, 2009. A Review of Recent Patents on Micro-Combustion and Applications. *Recent Patents on Engineering*, 3, 194-209.

Jones, W.P., B.E. Launder, 1972. The prediction of laminarization with a two-equation model of turbulence. *Int. J. Heat Mass Transfer*, 15, 301-314.

Josephine, A.E., R.C. Baliban, C.A. Floudas, 2012. Nationwide Energy Supply Chain Analysis for Hybrid Feedstock Processes with Significant CO₂ Emissions Reduction. *AIChE J.* 58 (7): 2142, 2154.

Junwei, L., Z. Beijing, 2007. Experimental investigation on heat loss and combustion in methane/oxygen micro-tube combustor. *Applied Thermal Engineering*. 28, 707-716.

Kajishima, T., T. Nomachi, 2006. One-Equation Subgrid Scale Model Using Dynamic Procedure for the Energy Production. *J. App. Mech.* 73(3), 368-373.

- Kee, R.J., F. M. Rupley, J. A. Miller, M. E. Coltrin, J. F. Grcar, E. Meeks, H. K. Moffat, A. E. Lutz, G. DixonLewis, M. D. Smooke, J. Warnatz, G. H. Evans, R. S. Larson, R. E. Mitchell, L. R. Petzold, W. C. Reynolds, M. Caracotsios, W. E. Stewart, P. Glarborg, C. Wang, and O. Adigun, 2000. CHEMKIN Collection, Release 3.6, Reaction Design, Inc., San Diego, CA.
- Kengne, J. A. N. Negou, D. Tchiotso, V. K. Tamba, G.H. Kom, 2018. On the Dynamics of Chaotic Systems with Multiple Attractors: A Case Study. In recent Advances in Nonlinear Dynamics and Synchronization. Studies in Systems, Decision and Control, vol 109. Kyamakya K., Mathis W., Stoop R., Chedjou J., Li Z. (eds). Springer, Cham.
- Kenneth, A.B. 1935. Aircraft Spark-Ignition Versus Compression-Ignition Engines. In SAE Transactions, Vol.30, 342-348. SAE International.
- Keuerleber, R., F.W. Pahl, US Patent 3 706 515, 1971.
- Kirkbright, G.F., T.S., West, 1968. The Application of Separated Flames in Analytical Flame Spectroscopy. Applied Optics, 7 (7), 1305-1311.
- Klerk, A. 2011. Fischer-Tropsch Refining. Wiley-VCH Verlag GmbH.
- Klimov, A.M. 1963. Laminar Flame in a Turbulent Flow. Zhur. Prikl. Mekh. i Tekhn. Fiz. 3, 49-58.
- Konnov, A.A. 1996. Detailed reaction mechanism for small hydrocarbons combustion: project-in-progress on the World Wide Web. 15th Journées d'Études of the Belgian Section of the Combustion Institute.
- Konnov, A.A. 2008. Remaining uncertainties in the kinetic mechanism of hydrogen combustion. Combustion and Flame, 152, 507-528.
- Kravtsova, A., P. Ianko, Y. Meshalkin, A. Bilsky, 2018. Influence of external periodic perturbation on the flow in T-microchannel. AIP Conference Proceedings 2027, 040084.
- Kraichnan, R.H., 1967. Inertial Ranges in Two-Dimensional Turbulence. Physics of Fluids, 10, 1417.
- Kukukova, A., J. Aubin, S. Kresta, 2009. A new definition of mixing and segregation: Three dimensions of a key process variable. Chem. Eng. Res. Des. 633-647.
- Lavoisier, A.L., 1789. Traité élémentaire de chimie: présenté dans un ordre nouveau et d'après les découvertes modernes. Cuchet libraire. Paris.
- Laranjeira, P.E., 2005. NETmix Static Mixer, Modelling, CFD Simulation and Experimental Characterization. PhD Thesis of University of Porto.
- Laranjeira, P.E., A.A. Martins, J.C.B. Lopes, M.M. Dias, 2009. NETmix, A New Type of Static Mixer: Modeling, Simulation, Macromixing, and Micromixing Characterization. AIChE J. 55(9), 2226-2243.
- Laranjeira, P.E., A.A. Martins, M.I. Nunes, J.C.B. Lopes, M.M. Dias, 2011. NETmix, a New Type of Static Mixer: Experimental Characterization and Model Validation. AIChE J. 57(4), 1020-1032.
- Launder, B.E., B.I. Sharma, 1974. Application of the energy-dissipation model of turbulence to the calculation of flow near a spinning disc. Lett. Heat Mass Transf. 1, 131-138.

- Law, K., T. Lu, 2007. An Efficient Reduced Mechanism for Methane Oxidation with NO Chemistry. 5th US Combustion Meeting, C17.
- Lee, J.H.S., 2006. Explosion properties of hydrogen-air mixtures. A lecture presented at the First European Summer School on Hydrogen Safety. Cited, 8 July 2021. Available from: <http://www.hysafe.net/wiki/BRHS/LaminarBurningVelocityAndLaminarFlameThickness>.
- Lee, L.J., J.M Ottino, W.E. Ranz, C.W. Macosko, 1980. Impingement mixing in reaction injection molding. *Polym. Eng. Sci.* 20(13), 868-874.
- Li, J., Z. Zhao, A. Kazakov, F.L. Dryer, 2004. An Updated Comprehensive Kinetic Model of Hydrogen Combustion. *International Journal of Chemical Kinetics*, 36(10), 566-575.
- Li, J., H. Huang, N. Kobayashi. 2017. Hydrogen Combustion as a Thermal Source. *Energy Procedia*, 142, 1083-1088.
- Li, W.F., G.F. Huang, G.Y. Tu, H.F. Liu, F.C. Wang, 2013. Experimental study of planar opposed jets with acoustic excitation. *The Physics of Fluids* 25(1), 014108.
- Li, W.F., W.W. Qian, G.S. Yu, H.F. Liu, F.C. Wang, 2015. Experimental study of oscillation behaviors in confined impinging jets reactor under excitation. *AIChE Journal* 61(1), 333-341.
- Li, W.F., G.Y. Tu, Z.H. Shi, H.F. Liu, F.C. Wang, 2016. Experimental study about mixing characteristic and enhancement of T-jet reactor. *Chem. Eng. Sci.* 144, 116-125.
- Lilly, D.K. 1992. A proposed modification of the Germeano subgrid-scale closure method. *Phys. Fluids*, A4, 633-635.
- Lima, M.J., A.M.T. Silva, C.G. Silva, J.L. Faria, J.C.B. Lopes, M.M. Dias, 2016. An innovative static mixer photoreactor: Proof of concept. *Chem. Eng. J.* 287, 419-424.
- Lima, M.J., C.G. Silva, A.M.T. Silva, J.C.B. Lopes, M. M. Dias, J.L. Faria, 2017. Homogeneous and heterogeneous photo-Fenton degradation of antibiotics using an innovative static mixer photoreactor. *Chem. Eng. J.* 310(2), 342-351.
- Lindemann, F. 1922. Discussion on “The radiation theory of chemical action”. *Trans. Faraday Soc.* 7, 598-606.
- Longwell, J.P. 1977. Synthetic fuels and combustion. *Symposium (International) on Combustion*, 16 (1), 1-15.
- Lopes, J.C.B., P.E. Laranjeira, M.M. Dias, A.A. Martins. Network Mixer and Related Mixing Process. PCT/IB2005/000647, February 2005. European Patent EP172643 B1, October 2008. US Patent 8 434 933 B2, May 2013.
- Lopes, J.C.B., M.M.Q. Dias, V.M.T.M. Silva, P.A.Q.O. Santos, F.J.M. Monteiro, P.J.C. Gomes, A.Y.P. Mateus. Método de produção de nanopartículas de fosfatos de cálcio com elevada pureza e respetiva utilização. National Application PT 103528, July 2006. Production Method for Calcium Phosphate Nano-Particles with High Purity and their Use. International Application PCT/PT2007/000031, July 2007.
- Lopes, J.C.B., M.M.G.Q. Dias, M.F.S. Costa, R.J.N. Santos, C.A.M. Teixeira. Network heat exchanger device, method and uses. International Application PCT/IB2018/052463, September 2018. Submitted by PETROGAL, S.A.

- Lopes, J.C.B., M.M.G.Q. Dias, M.F.S. Costa, R.J.N. Santos, C.A.M. Teixeira. Continuous production of clathrate hydrates from aqueous and hydrate-forming streams, methods and uses. Provisional European Patent Application 19220274.5, December 2019. Submitted by PETROGAL, S.A.
- Malguarnera, S.C., N.P. Suh, 1977. Liquid injection molding I. An investigation of impingement mixing. *Polym. Eng. Sci.* 17(2), 111-115.
- Marracino, B., D. Lentini, 1997. Radiation Modelling in Non-Luminous Nonpremixed Turbulent Flames. *Combust. Sci. and Tech.* 128, 23-48.
- Massoudi, A. M.G. Mahjani, M. Jafarian, 2010. Multiple attractors in Koper–Gaspard model of electrochemical periodic and chaotic oscillations. *Journal of Electroanalytical Chemistry*, 647, 74-86.
- Marinho, B.A., R. Djellabi, R.O. Cristóvão, J.M. Loureiro, R.A.R. Boaventura, M.M. Dias, J.C.B. Lopes, V.J.P. Vilar. 2017. Intensification of heterogeneous TiO₂ photocatalysis using an innovative micro–meso-structured-reactor for Cr(VI) reduction under simulated solar light. *Chem. Eng. J.* 318, 76-88. DOI: doi.org/10.1016/j.cej.2016.05.077.
- Matos, J., M.S.C.A. Brito, M.M. Dias, J.C.B. Lopes, R.J. Santos, 2018. Lagrangian Mixing Simulation and Quantification of Scales. *Chem. Eng. Sci.* 192, 199-210.
- Matos, J., Dias, M.M., Lopes, J.C.B., Santos, R.J. 2020. Diffusive Lagrangian Mixing Simulation. *Chemical Engineering Research and Design*, 163, 307-319.
- Matos, J., Dias, M.M., Santos, R.J., Lopes, J.C.B. 2021. Mixing in the NETmix Reactor. *Frontiers in Chemical Engineering*, 3, 771476.
- Mauß, F., D. Keller, N. Peters, 1990. A Lagrangian simulation of flamelet extinction and re-ignition in turbulent jet diffusion flames. *Proc. Combust. Int.* 23, 693-698.
- Meneveau, C. T.S. Lund, W.H. Cabot, 1996. A Lagrangian dynamic subgrid-scale model for turbulence. *J. Fluid Mech.* 319, 353-385.
- Moon, D.J., S.W. Jeon. Microchannel Reactor for Hydrocarbon Reforming. US Patent US 9381488 B2, July 2016.
- Mueller, M.A., T.J. Kim, R.A. Yetter, F.L. Dryer. 1999. Flow Reactor Studies and Kinetic Modeling of the H₂ /O₂ Reaction. *International Journal of Chemical Kinetics*, 31(10), 705-724.
- Moreira, A.C.G., Y.A. Manrique, I.M. Martins, I.P. Fernandes, A.E. Rodrigues, J.C.B. Lopes, M.M. Dias. Continuous Production of Melamine-Formaldehyde Microcapsules Using a Mesostructured Reactor, 2020. *Ind. Eng. Chem. Res.* 59,41,18510-18519. DOI: doi.org/10.1021/acs.iecr.0c02656.
- Muller, C.M., H. Breitbach, N. Peters, 1994. Partially Premixed Turbulent Flame Propagation in Jet Flames. *Twenty-Fifth Symposium on Combustion*, 1099-1106.
- Murthy, S.N.B. 1975. *Turbulent Mixing in Non-reactive and Reactive Flows*. Plenum Press, New York.
- Naik, C.V., E. Meeks, 2009. Detailed Chemical Kinetic Mechanism for Methane and Ethane Combustion including NO_x Emissions for Gas Turbines Applications. Fall Technical Meeting of the Western States Section of the Combustion Institute, Paper 09F-48.

Navier, L.M.H. 1827. *Mémoire sur les lois du Mouvement des Fluides*. Mémoires de l'Académie Royale des Sciences de l'Institut de France, 6, 389-440.

NET4CO₂, 2020. Cited 25 December 2021. Available from <https://www.net4co2.pt/index.php>.

NIST National Institute of Standards and Technology, 2018. U.S. Department of Commerce. Cited, 1 August 2021. Available from: <https://webbook.nist.gov/chemistry/>.

O'Brien, E.E. 1980. The probability density function (pdf) approach to reacting turbulent flows. In *Turbulent Reacting Flows*, Topics in Applied Physics, Volume 44. Springer-Verlag.

Our World in Data, cited 2021, 12 December. Available from: <https://ourworldindata.org/fossil-fuels>.

Ottino, J.M., W.E. Ranz, C.W. Macosko, 1979. A Lamellar Model for Analysis of Liqui-liquid Mixing. *Chem. Eng. Sci.* 34, 877-890.

Ottino, J. M., 1980. Lamellar Mixing Models for Structured Chemical Reactions and Their Relationship to Statistical Models; Macro-and Micromixing and the Problem of Averages. *Chemical Engineering Science* 35, 1377-1391.

Ottino, J. M., 1989. *The kinematic of mixing: stretching, chaos, and transport*. Cambridge University Press, Cambridge, UK.

Ottino, J. M., 1990. Mixing, Chaotic Advection, and Turbulence. *Annual Review of Fluid Mechanics* 22, 207-253.

Ottino, J.M., 1995. Mixing and Chemical Reactors, A Tutorial. *Chemical Engineering Science*, 49 (24A), 4005-4027.

Ottino, J.M., S. Wiggins, 2004. Introduction: mixing in microfluidics. *Philos. Trans. R. Soc. London, Ser. A*, 362, 923-35.

Pearlman, H., R.M. Chapek, 1999. Cool Flames and Autoignition: Thermal-Ignition Theory of Combustion Experimentally Validated in Microgravity. *Research and Technology, NASA*.

Perry, R.H. and Green, D.W. 1997. *Perry's Chemical Engineering Handbook*. McGraw-Hill.

Peters, N., 1984. Laminar Diffusion Flamelet Models in Non-premixed Turbulent Combustion. *Prog. Energy Combust. Sci.* 10, 319-339.

Peters, N., 1986. Laminar Flamelet Concepts in Turbulent Combustion. *Twenty-first Symposium on Combustion*, 1231-1250.

Peters, N. 2000. *Turbulent Combustion*. Cambridge University Press. Cambridge, UK.

Peters, N., R.J. Kee, 1987. The Computation of Stretched Laminar Methane-Air Diffusion Flames Using a Reduced Four-Step Mechanism. *Combustion and Flame*, 68, 17-29.

Pierce, C.D., P. Moin, 2004. Progress-variable approach for large-eddy simulation of non-premixed turbulent combustion. *J. Fluid Mech.* 504, 73-97.

Pitsch, H. Y.P. Wan, N. Peters, 1995. Numerical Investigation of Soot Formation and Oxidation Under Diesel Engine Conditions. *Journal of Fuels and Lubricants*, 104(4), 938-949.

- Pitsch, H., M. Chen, N. Peters, 1998. Unsteady Flamelet Modeling of Turbulent Hydrogen-air Diffusion Flames. Twenty-Seventh Symposium on Combustion, 1057-1064.
- Poinsot, T., D. Veynante, 2005. Theoretical and Numerical Combustion. R.T. Edwards, Inc., Philadelphia.
- Pope, S.B. 1976. The Probability Approach to the Modelling of Turbulent Reacting Flows. Combustion and Flame, 27, 299-312.
- Pope, S.B. 1983b. A Lagrangian twotime probability density function equation for inhomogeneous turbulent flows. Phys. Fluids 26, 3448-3450.
- Pope, S.B. 1985. PDF Methods for Turbulent Reactive Flows. Prog. Energy Combust. Sci. 11, 119-192.
- Pope, S.B. 1990. Computations of Turbulent Combustion Progress and Challenges. Twenty-Third Symposium on Combustion, 591-612.
- Pope, S.B. 2000. Turbulent Flows. Cambridge University Pres.
- Pupo, R. 2011. Adiabatic Flame Temperature for Combustion of Methane. Undergraduate Journal of Mathematical Modelling: One + Two, 2(6).
- Press, R.J., K.S.V. Santhanam, M.J. Miri, A.V. Bailey, G.A. Takacs, 2008. Introduction to hydrogen Technology. John Wiley & Sons.
- Priyank, S, F.A. Williams, 2006. Testing a small detailed chemical-kinetic mechanism for the combustion of hydrogen and carbon monoxide. Combustion and Flame, 145, 316-323.
- San Diego Mechanism Web Page, 2012. Cited 1 November 2019. Available from: <https://web.eng.ucsd.edu/mae/groups/combustion/mechanism.html>.
- Santos, R.J., A.M. Teixeira, J.C.B. Lopes, 2005. Study of Mixing and Chemical Reaction in RIM. Chem. Eng. Sci. 60 (8-9), 2381-2398.
- Santos, R.J., E. Erkoc, M. Sultan, M. M. Dias, J. C. B. Lopes, 2009. Dynamic behavior of the flow field in a RIM machine mixing chamber. AIChE Journal 55(6), 1338-1351.
- Santos, R.J., A. M. Teixeira, E. Erkoc, M. Sultan, A. M. Karpinska, M. M. Dias, J. C. B. Lopes, 2010. Validation of a 2D CFD Model for Hydrodynamics' Studies in CIJ Mixers. Int. J. Chem. React. Eng. 8, A32.
- Santos, R.J., M.M. Dias, J.C.B. Lopes, 2012. Mixing through half a century of chemical engineering. In Single and Two-Phase Flows on Chemical and Biomedical Engineering, 79-112. R. Dias, A. Martins, T. Mata, R. Lima, T. Yaginuma (Eds), Bentham Science Publishers.
- Santos, R.J., M.A. Sultan, 2013. State of the Art of Mini/Micro Jet Reactors. Chem. Eng. Technol. 36(6), 937-949.
- Santos, R.J., E. Erkoc, M. Sultan, M. M. Dias, J. C. B. Lopes, 2009. Dynamic behavior of the flow field in a RIM machine mixing chamber. AIChE Journal 55(6), 1338-1351.
- Santos, S.G.S. Santos, L.O. Paulista, T.F.C.V. Silva, M.M. Dias, J.C.B. Lopes, R.A.R. Boaventura, V.J.P. Vilar. 2019. Intensifying heterogeneous TiO₂ photocatalysis for bromate reduction using the NETmix photoreactor. Science of Total Environment, 664, 805-816.

- Santos, S.G.S. Santos, L.O. Paulista, B.A. Marinho, C. Passalía, M. Flores, M.D. Labas, R.J. Brandi, V.J.P. Vilar. 2021. A step forward on NETmix reactor for heterogeneous photocatalysis: Kinetic modeling of As(III) oxidation. *Chem. Eng. J.* 405, 126612.
- Saxena, P., F.A. Williams, 2006. Testing a small detailed chemical-kinetic mechanism for the combustion of hydrogen and carbon monoxide. *Combustion and Flame*, 145, 316-323.
- Schlick, C.P., I.C. Christov, P.B. Umbanhowar, J. M. Ottino, R.M. Lueptow, 2013. A mapping method for distributive mixing with diffusion: Interplay between chaos and diffusion in time-periodic sine flow. *Phys. Fluids* 25, 052102.
- Schobeiri, M.T. 2018. *Gas Turbine Design, Components and System Design Integration*. Springer.
- Silva, V., P.A. Quadros, P.E. Laranjeira, M.M. Dias, J.C.B. Lopes, 2008. J. A Novel Continuous Industrial Process for Producing Hydroxyapatite Nanoparticles. *Disper. Sci. Technol.* 29, 542-547.
- Singh, M.K., O. S. Galaktionov, H. E. H. Meijer, P. D. Anderson, 2009a. A simplified approach to compute distribution matrices for the mapping method. *Comput. Chem. Eng.* 33 (8), 1354-1362.
- Smagorinsky, J. 1963. General Circulation Experiments with the Primitive Equations. *Monthly Weather Review*, 91(3), 99-164.
- Snow, D. 2002. *Plant Engineer's Reference Book*. Butterworth-Heinemann. Oxford.
- SND, 2015. Predicting Pressure-Dependent Combustion Chemical Reactions. Cited 2021, 8 October. Available from: <https://energy.sandia.gov/predicting-pressure-dependent-combustion-chemical-reactions-2/>.
- Speight, J.G. 2020. *Handbook of industrial hydrocarbon processes*. Cambridge, MA. ISBN 9780128099230.
- Spalart, P.R., S.R. Allmaras, 1994. A one-equation turbulence model for aerodynamic flows. *Recherche aéronautique* 1, 5-21.
- Spangenburg R. and Moser, D.K., 1993. *The Birth of Science: Ancient Times to 1699*. Facts on File, Inc. New York.
- Steward, P.H., C.W. Larson, D. Golden, 1989. Pressure and Temperature Dependence of Reactions Proceeding Via A Bound Complex. *Combustion and Flame*, 75, 25-31.
- Stokes, G.G. 1845. On the Theories of the Internal Friction of Fluids in Motion and of the Equilibrium and Motion of Elastic Solids. *Proc. Cambridge Phil. Soc.* 8, 287-319.
- Sullivan, J. Princeton University, 2012. Synthetic fuels could eliminate entire U.S. need for crude oil, create 'new economy'. Cited 26 December 2021. Available from: <https://www.princeton.edu/news/2012/11/27/synthetic-fuels-could-eliminate-entire-us-need-crude-oil-create-new-economy>.
- Sultan, M.A., C.P. Fonte, M.M. Dias, J.C.B. Lopes, R.J. Santos, 2012. Experimental study of flow regime and mixing in T-jets mixers. *Chem. Eng. Sci.* 73, 388-399.

- Sultan, M.A., S.L., Pardilhó, M.S.C.A, Brito, C.P. Fonte, M.M. Dias, J.C.B. Lopes, R.J. Santos, 2019. 3D Mixing Dynamics in T-jet Mixers. *Chem. Eng. Technol.* 42 (1), 119-128.
- Rankin, D. T. Peter, 2008. *Lean combustion : technology and control*. Academic Press, Elsevier. London, UK.
- Ranz, W.E. 1979. Applications of a Stretch Model Diffusion, and Reaction in Laminar and Turbulent Flows. *AIChE J.* 25(1), 41-47.
- Ranz, W.E. 1986. Analysis of Reaction Processes in Which Microscopic Heterogeneities Appear: Scale-Up and Scale-Down of Polymerization Reactions. *Ind. Eng. Chem. Fundam.* 25(4), 561-565.
- Reimert, R., M., Friedemann, R. Hans-Joachim, B. Walter, S. Emil, B. Miron, L. Waldemar, S. Georg, 2011. Gas Production, 2. Processes. *Ullmann's Encyclopedia of Industrial Chemistry*. DOI:10.1002/14356007.o12_o01. ISBN 978-3-527-30673-2.
- Ribeiro, A., Y.A. Manrique, F. Barreiro, J.C.B. Lopes, M.M. Dias. 2021. Continuous production of hydroxyapatite Pickering emulsions using a mesostructured reactor. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 615, 12365.
- Rotta, J.C. 1951. Statistische Theorie nichthomogener Turbulenz. *Z. Phys.* 129, 547-572.
- Ruelle, D., F. Takens, 1971. On the Nature of Turbulence. *Commun. Math. Phys.* 20, 167-192.
- Tadmor, Z., C. G. Gogos, 2009. *Principles of Polymer Processing*. John Wiley & Sons. New Jersey.
- Torres, J.P. 2017. Proper Orthogonal Decomposition of Turbulent Flows, MSc Thesis of University of Porto.
- Tu, G.Y., W.F. Li, W.W. Qian, Z.H. Shi, H.F. Liu, F.C. Wang, 2015. Experimental study on oscillation behaviors in T-jets reactor with excitation. *Chem. Eng. Sci.* 34, 67-75
- Tuckerman, M.E. 2010. *Statistical Mechanics: Theory and Molecular Simulation*. Oxford University Press.
- Turns, S.R. 2000. *An Introduction to Combustion, Concepts and Applications*. McGraw Hill. New York.
- Vaccaro, S., L. Malangone, P. Ciambelli, 2010. Modelling of a Catalytic Micro-Reactor Coupling Endothermic Methane Reforming and Combustion. *Int. J. Chem. React. Eng.* 8, A51.
- Vassilatos, G., H.L. Toor, 1965. Second-Order Chemical Reactions in a Nonhomogeneous Turbulent Fluid. *AIChE J.* 11(4), 666-673.
- Veloudis, I., Z. Yang, J.J McGuirk, 2008. LES of Wall-Bounded Flows Using a New Subgrid Scale Model Based on Energy Spectrum Dissipation. *J. App. Mech.* 75, 021005-1-11.
- Vicsek, T. 1992. *Fractal growth phenomena*. World Scientific.
- Villermaux, E., P. Meunier, 2010. The diffusive strip method for scalar mixing in two dimensions. *J. Fluid Mech.* 66, 134-172.
- White, C.M., R.R. Steeper, A.E. Lutz, 2006. The hydrogen-fueled internal combustion engine: a technical review, *International Journal of Hydrogen Energy*, 31, 1292-1305.

- Wilcox, D.C. 1993. Turbulence modeling for CFD. La Canãda, CA: DCW Industries.
- William, M.H. 2015. CRC Handbook of Chemistry and Physics, 96th Edition. CRC Press.
- Williams, F.A. 1974. Recent Advances in Theoretical Descriptions of Turbulent Diffusion Flames. In Turbulent Mixing in Nonreactive and Reactive Flows. S.N.B. Murthy. Springer.
- Williams, F.A. 2008. Detailed and reduced chemistry for hydrogen autoignition. Journal of Loss Prevention in the Process Industries, 21, 131-135.
- Wirth, M. N. Peters, 1992. Turbulent Premixed Combustion: A Flamelet Formulation and Spectral Analysis in Theory and IC-engine Experiments. Twenty-Fourth Symposium on Combustion, 493-501.
- Wood, P., A.N. Hrymak, R. Yeo, D.A Johnson, A. Tyagi, 1991. Experimental and computational studies of the fluid mechanics in an opposed jet mixing head. Physics of Fluids A 3(5), 1362-1368.
- Wu, M., Y. Wang, V. Yang, R.A. Yetter, 2007. Combustion in meso-scale vortex chambers. Proc. Comb. Inst. 31, 3235-3242.

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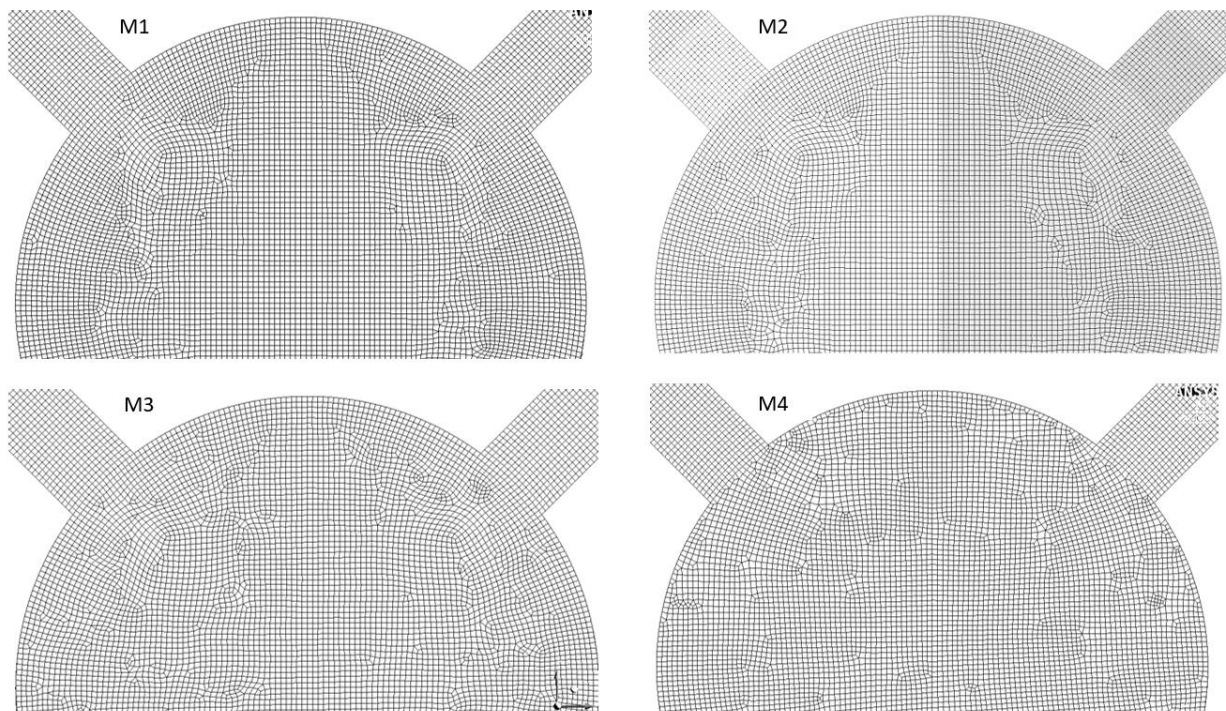
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Appendix A – Sensitivity Analysis of Chaos

As stated in Section IV.3.3, the strange attractors of NETmix change their shape if the simulation parameters are varied. In this appendix, different meshes will be shown as well as the strange attractors that are obtained. The variation of several simulation parameters will also be assessed.

A.1 Asymmetrical Meshes Study

In this Section, asymmetrical meshes will be used to simulate the hydrodynamics in NETmix, using the ExtendedNUB geometry. Twelve different meshes will be used, seven quadrilateral based meshes, M1 to M7, and five triangular based meshes, M8 to M12. A portion of the meshes is shown in Figure A.1.



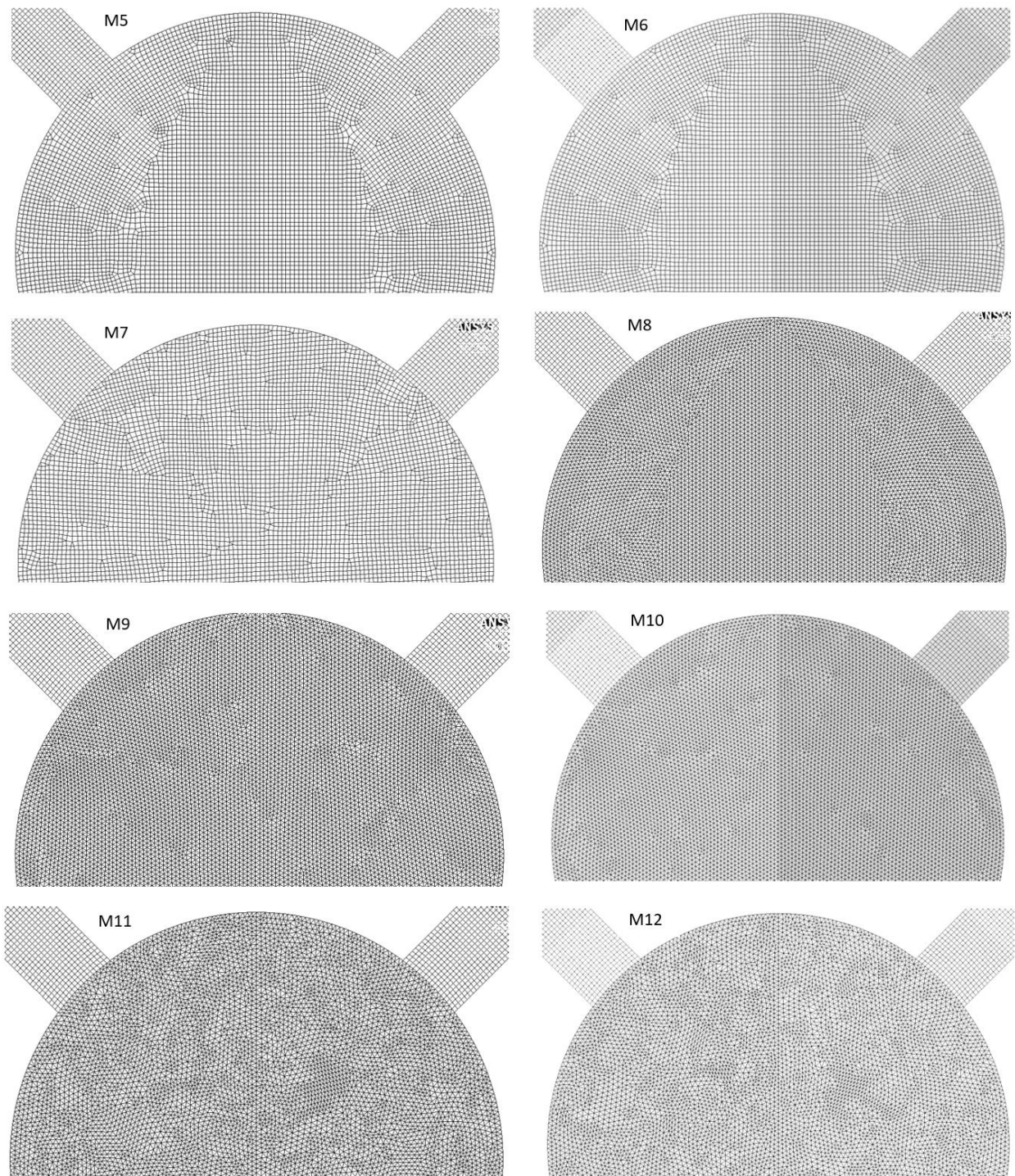
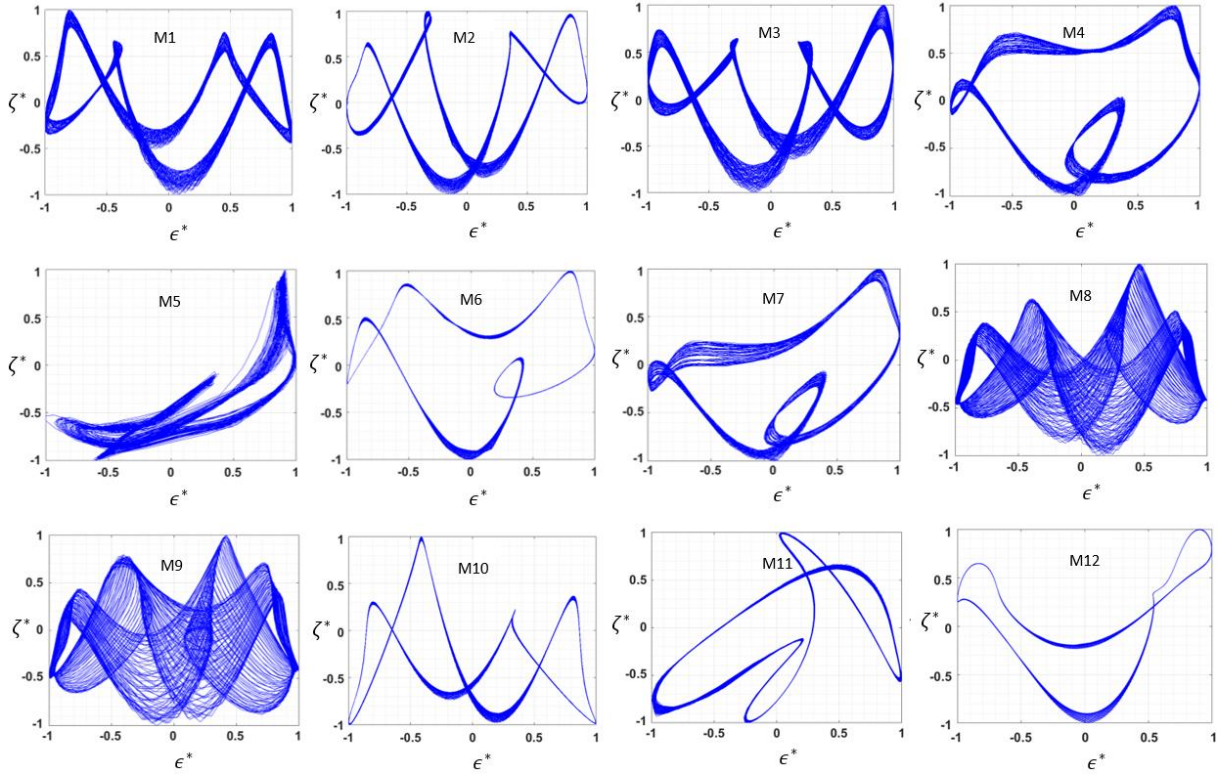
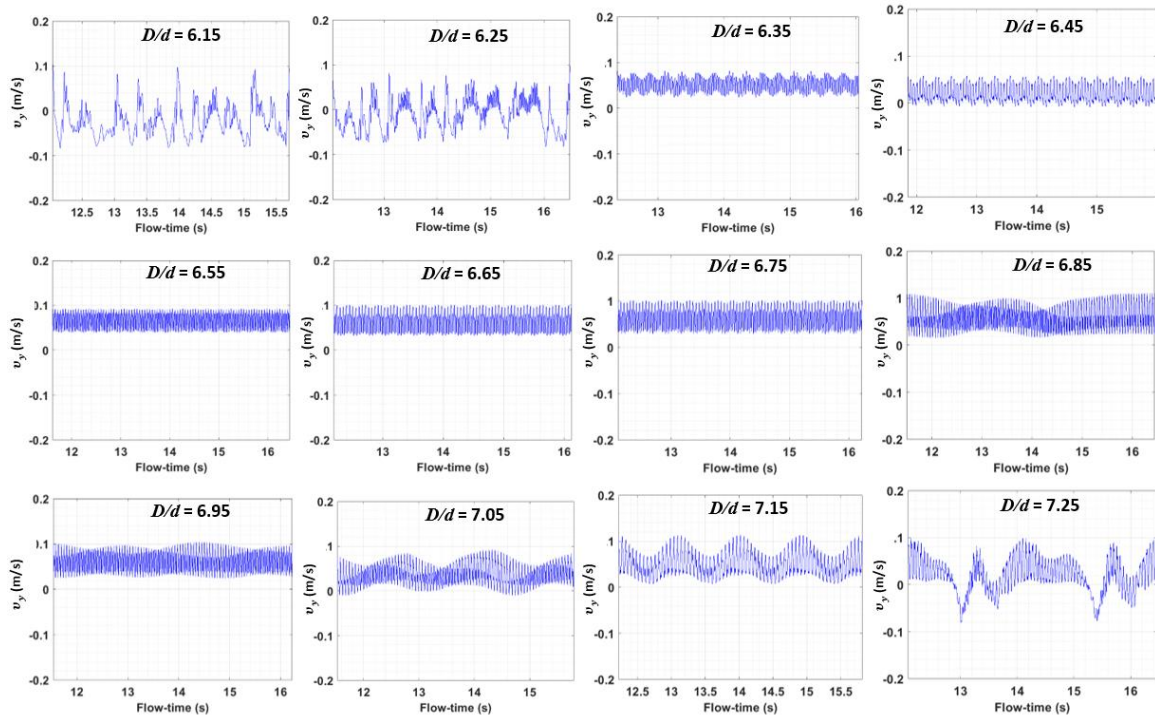


Figure A.1 Quadrilateral based mesh grids, M1 to M7. Triangular based mesh grids, M8 to M12.

The CFD model and boundary conditions are the same as Section II.3.2. For $D/d = 6.77$, the strange attractors are shown in Figure A.2.


 Figure A.2 Strange attractors in the centre of C6 for $D/d = 6.77$.

For M2, several ratios, $6.15 < D/d < 7.25$, were simulated. The histories of the y -velocity are shown in Figure A.3. It is visible that the oscillations are more irregular if a asymmetrical mesh is used (see Section IV.3.3). As expected, a symmetrical mesh enables to reduce the numerical residuals.


 Figure A.3 y -velocity histories with M2 for $6.15 < D/d < 7.25$.

The strange attractors are in Figure A.4, Figure A.5 and Figure A.6. The spectral analysis for all the ratios is shown in Figure A.7 and Figure A.8.

As expected, it is visible that with a assymetrical mesh the number of interferent frequencies is larger. To conclude, symmetrical meshes should be used to avoid numerical residuals and increase the stability of the NETmix oscillations.

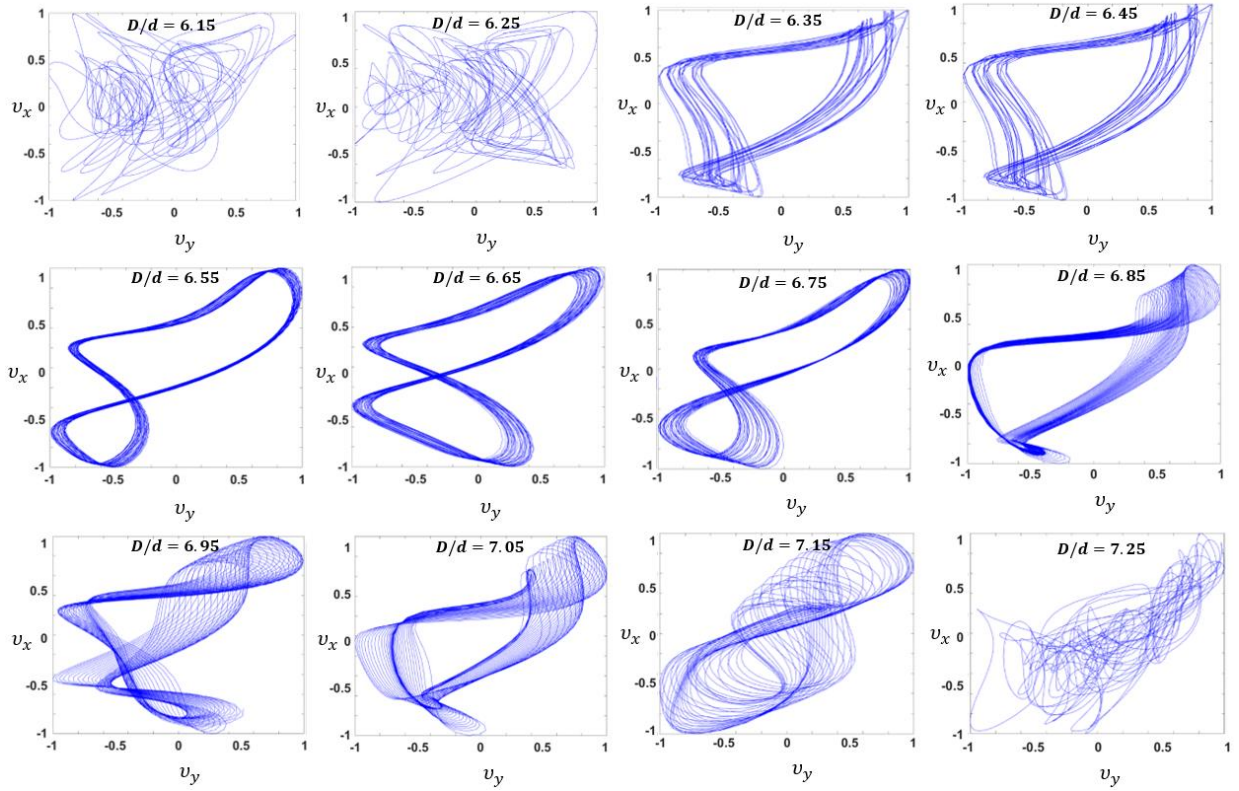
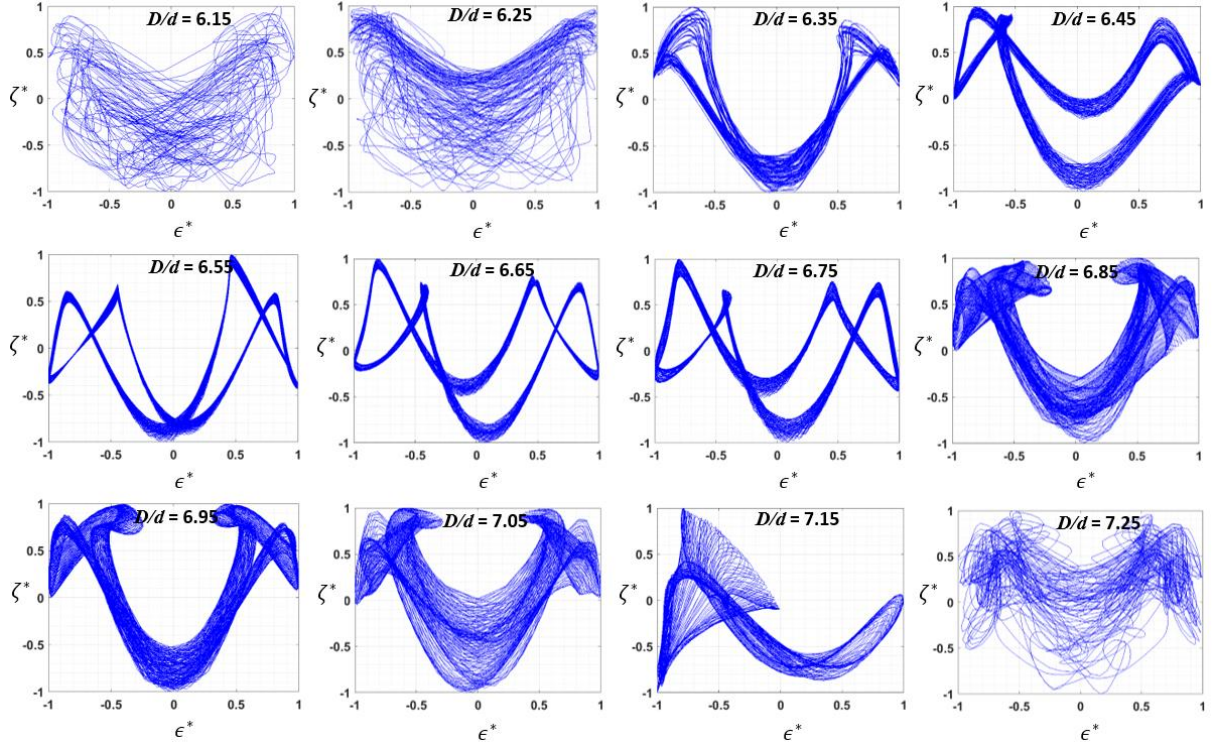
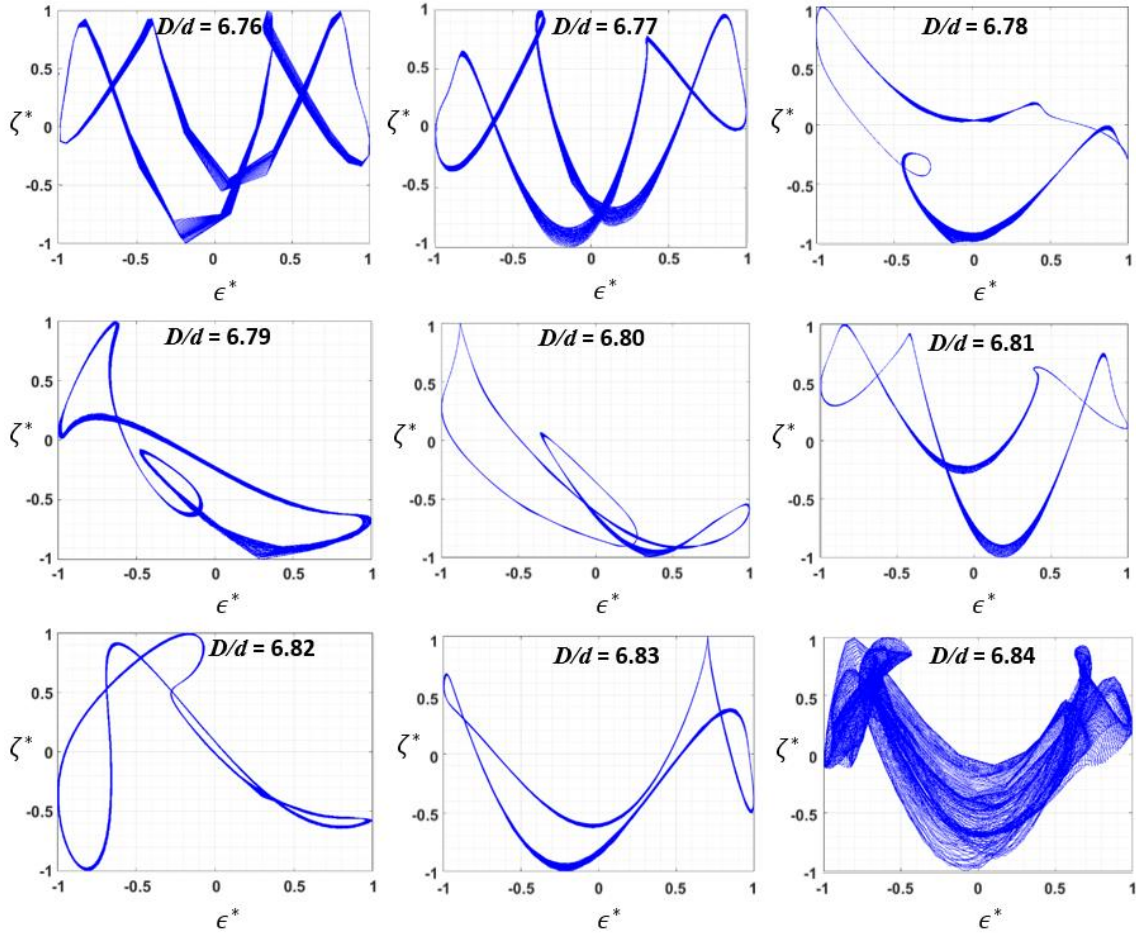
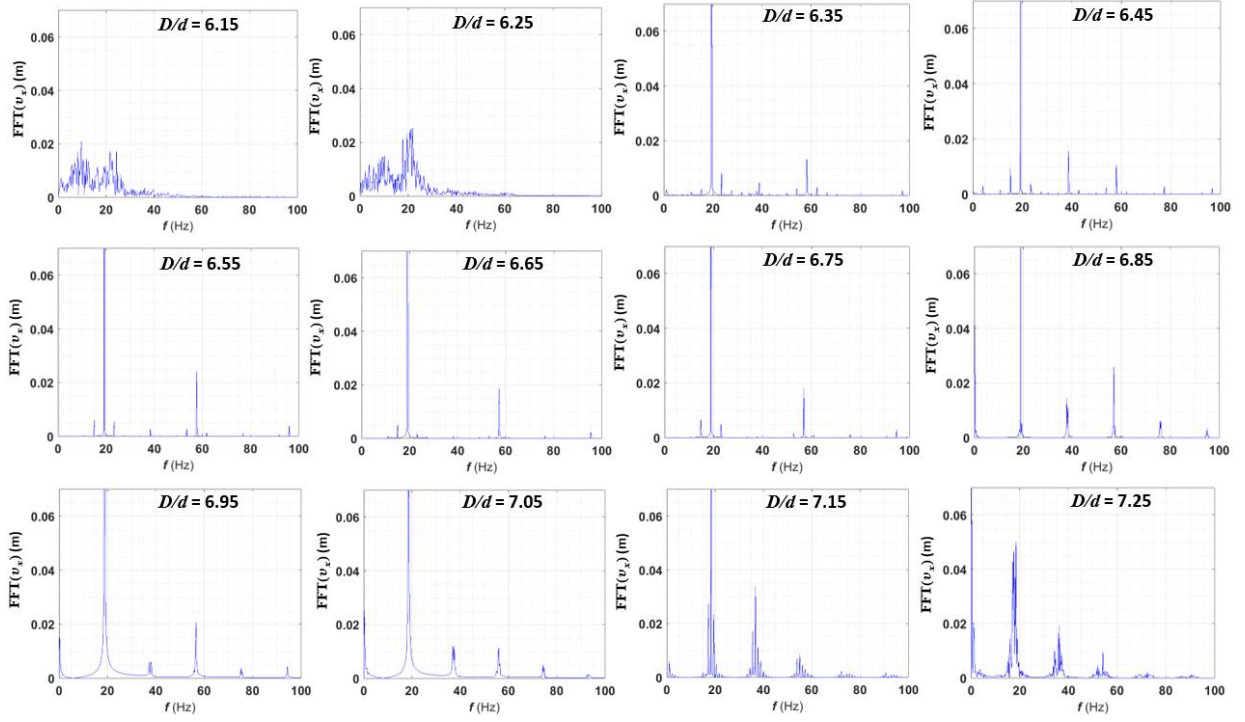
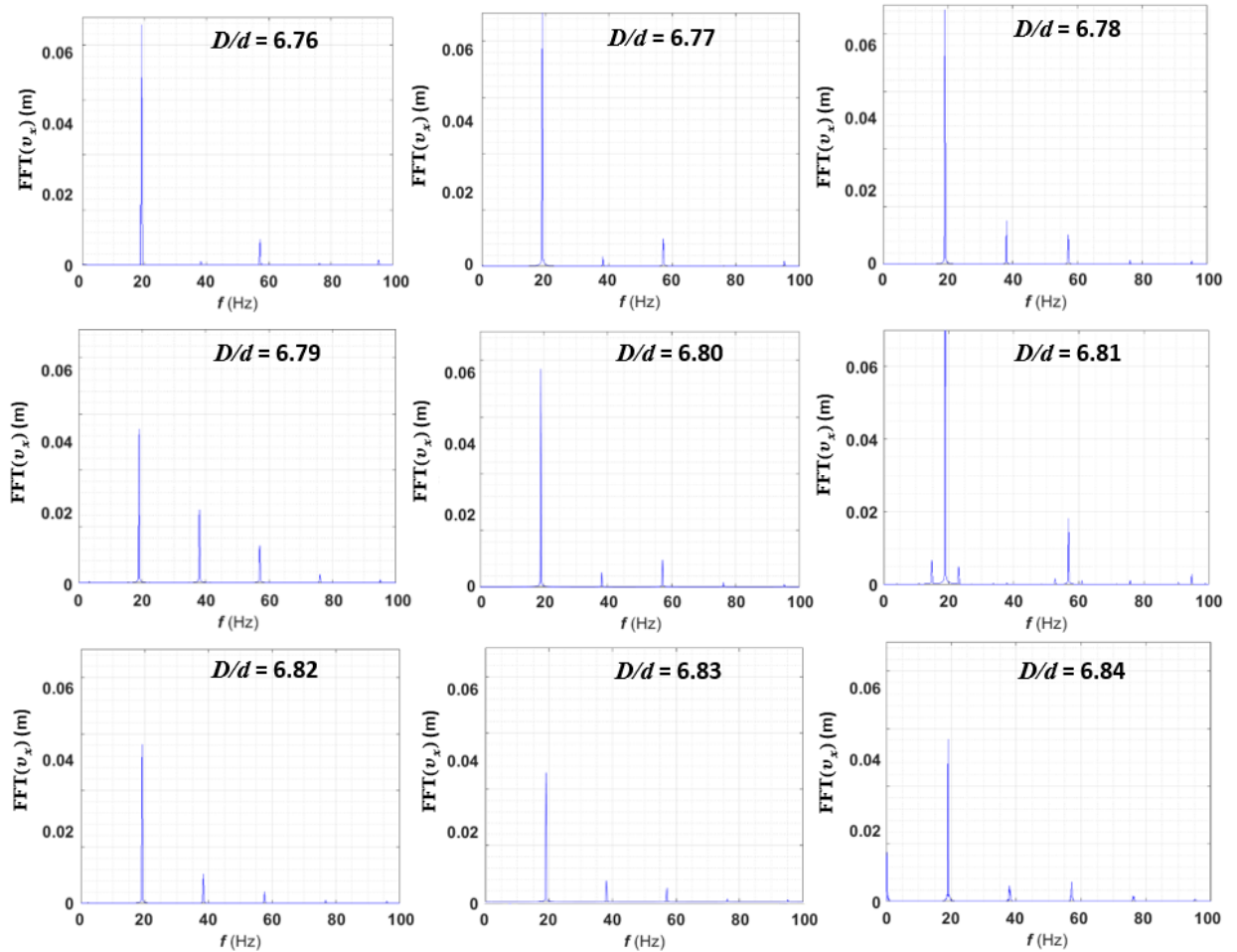


Figure A.4 Strange attractors v_x vs v_y with M2 for $6.15 < D/d < 7.25$.


 Figure A.5 Strange attractors ζ^* vs ϵ^* with M2 for $6.15 < D/d < 7.25$.

 Figure A.6 Strange attractors with M2 for $6.76 < D/d < 6.84$.

Figure A.7 Spectral analysis with M2 for $6.15 < D/d < 7.25$.Figure A.8 Spectral analysis with M2 for $6.76 < D/d < 6.84$.

A.2 Initial Condition Study

In the cases that were presented previously in this work, the initial solution of the transient CFD simulations was obtained by setting all variables to zero. To understand the influence of the initialization in the NETmix oscillations, different initial solutions, provided by ANSYS® FLUENT™, were applied: standard with all variables to zero, *st0*, standard computed from the right inlet, *stR*, standard computed from the left inlet, *stL*, and Hybrid, *Hy*.

The ExtendedNUB model with $D/d = 6.77$ was used and the CFD model and boundary conditions are the same as Section II.3.2.

The strange attractors in the centre of chamber C6 are shown in Figure A.9. It is visible that the initializations *Hy* and *st0* are the methods that result in a thinner attractor which indicates a higher regularity in the NETmix oscillations.

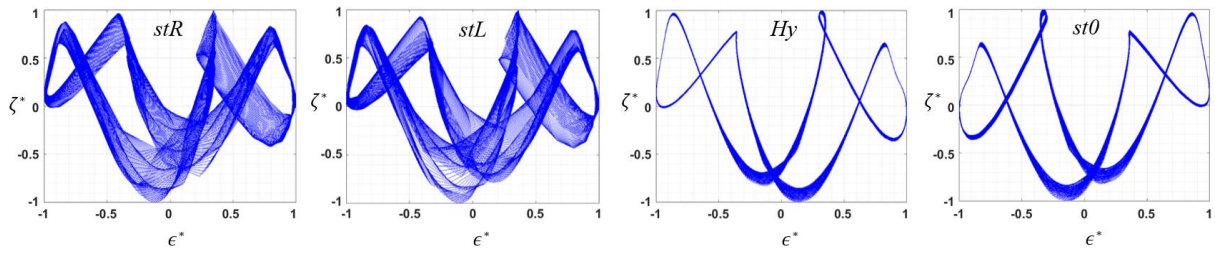


Figure A.9 Strain rate vs vorticity in chamber C6 of ExtendedNUB with $D/d = 6.77$ for $Re = 300$, starting from different initializations.

A.3 Inlet Reynolds study

In this section, the influence of the inlet Reynolds number in the NETmix chaotic system will be studied. The case that was previously presented with M2 for $D/d = 6.55$ will be used to analyse the influence of Re in the oscillations of NEMix. To vary the inlet Re , the inlet velocity was changed according to Eq. II.24, as well as the time step size which was recalculated to maintain the Courant number at $C = 1$. The CFD model and boundary conditions are the same as Section II.3.2.

The strange attractor in the centre of chamber C6 of the ExtendedNUB model is shown in Figure A.10. As expected, it is visible that small differences in the inlet Re are noticeable in the NETmix system. For $Re = 303$, the oscillations are more regular, i.e., the amplitude of the oscillations vary in a straiter range, since the attractor is thinner. For $Re = 315$, the oscillations are more irregular, since the attractor is thicker.

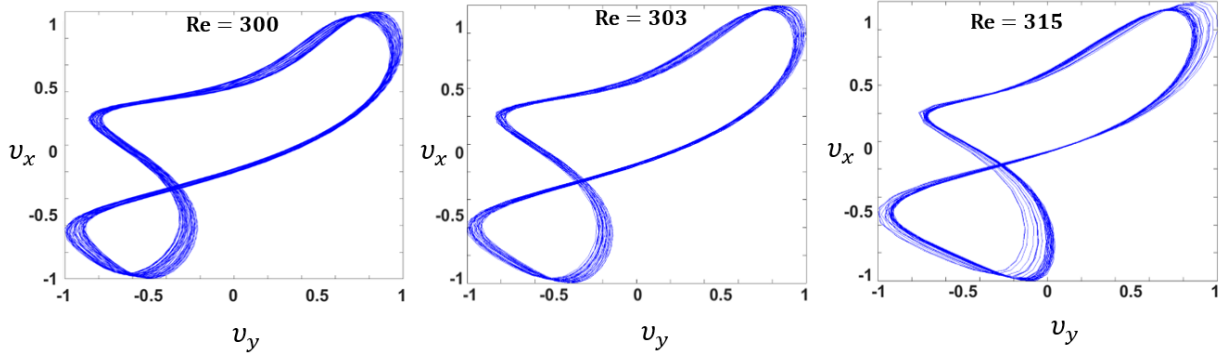


Figure A.10 Strange attractors for $D/d = 6.55$ at different injection Re .

A.4 Courant Number and Residuals Study

As stated in previous chapters, the Courant number was set to 1 and the CFD maximum residuals of continuity and momentum were 10^{-5} . In this section, the Courant number was decreased to 0.1 and the residuals to 10^{-6} to assess the influence of these parameters in the chaoticity of NETmix. To vary the Courant number, the time step size was decreased one order of magnitude. The CFD model and boundary conditions are the same as Section II.3.2.

The strange attractor in the centre of chamber C6 of the ExtendedNUB model for $D/d = 6.55$ is shown in Figure A.11. It is visible that reducing the residuals 10 times does not have a major influence in the attractor thickness, as visible when comparing Figure A.11a to Figure A.11b, and Figure A.11c to Figure A.11d. In contrast, if the Courant number is decreased from 1 to 0.1, the attractor is thicker. Thus, the oscillations are less regular, as visible in the comparison between Figure A.11c and Figure A.11d.

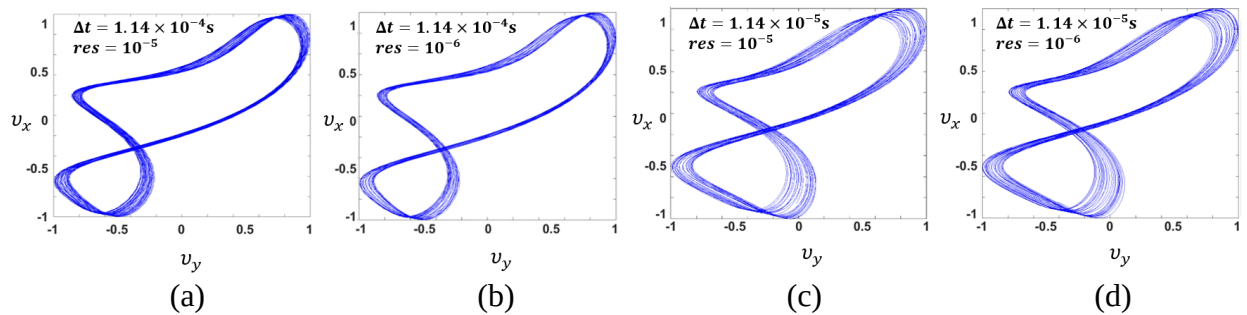


Figure A.11 Strange attractors for $D/d = 6.55$ with different time step size and residuals.

Appendix B – ExpandedNUB

Using a variation of meshing M1, presented in the previous Appendix, the ExpandedNUB mesh was built. While the ExtendedNUB geometry has four full chambers and five half chambers, the ExpandedNUB comprises six full chambers, C2, C4, C6, C8, C10 and C12, and seven half chambers. The ExpandedNUB geometry is shown in Figure B.1.

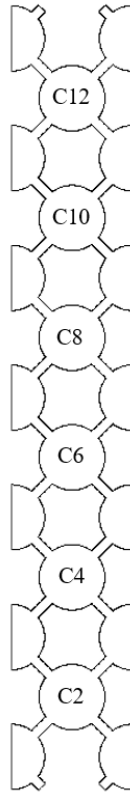
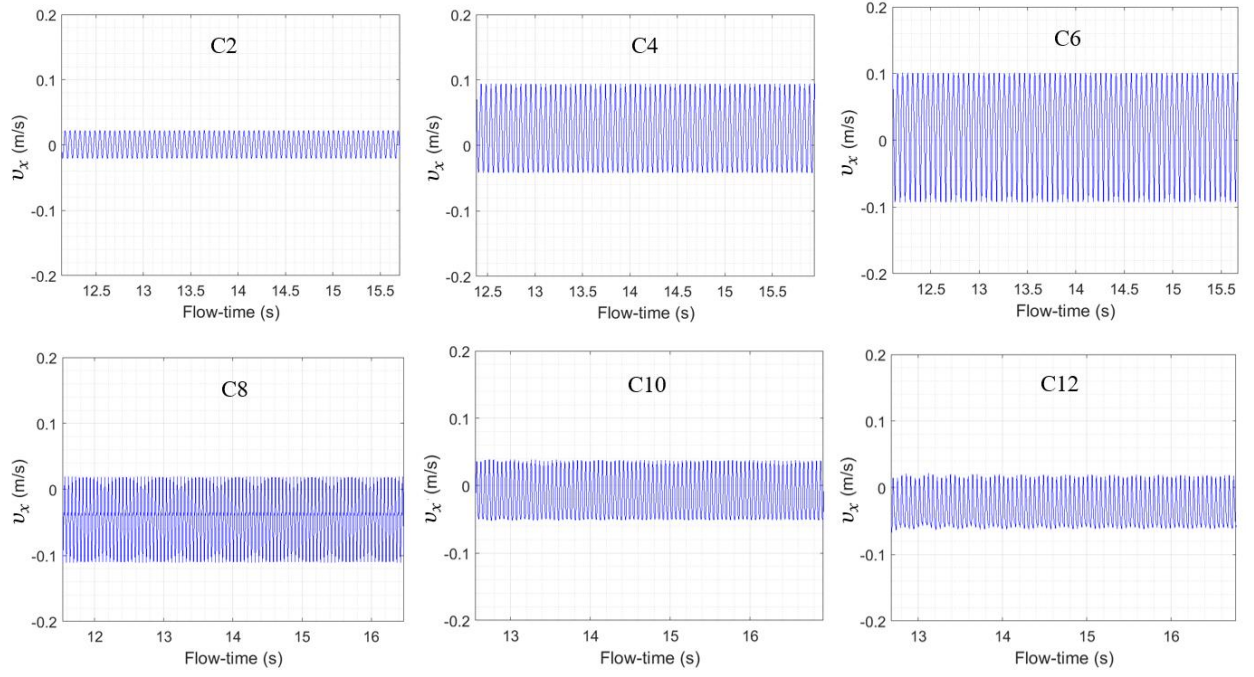
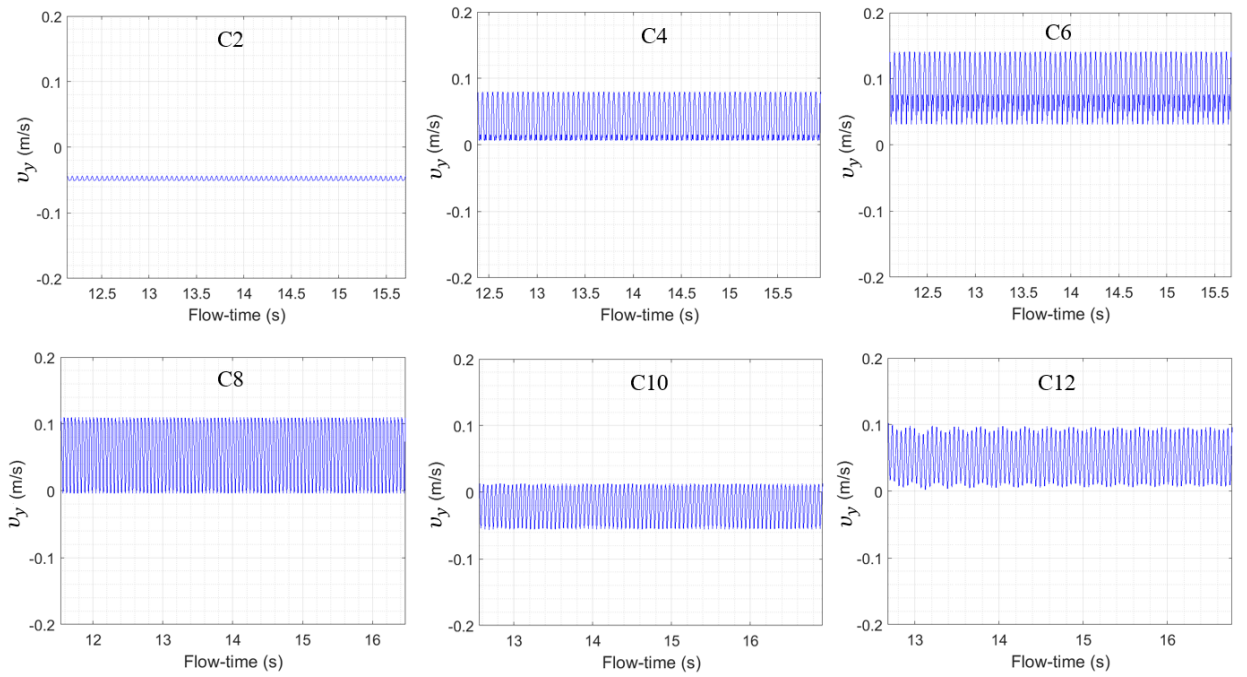


Figure B.1 ExpandedNUB geometry.

The ExpandedNUB geometry was designed to show that if additional rows of chambers are added to the geometry, chamber C6 remains the zone of the reactor with the largest turbulence intensity, for $Re = 300$, as shown in Section II.3.3. As visible in Section V.2., the highest turbulence intensity coincides with a larger amplitude of the x -velocity.

The simulation was run using the CFD model of Section II.3.2. The histories of x -velocity and y -velocity were plotted in the centre of each chamber of ExpandedNUB, for $D/d = 6.75$.

In Figure B.2 and in Figure B.3, is visible that the amplitude of the oscillations increases from C2 to C6 and then decreases from C8 to C12, as expected. The strange attractors are shown in Figure B.4.


 Figure B.2 x-velocity in the centre of chambers for $D/d = 6.75$, at $Re = 300$.

 Figure B.3 y-velocity in the centre of chambers for $D/d = 6.75$, at $Re = 300$.

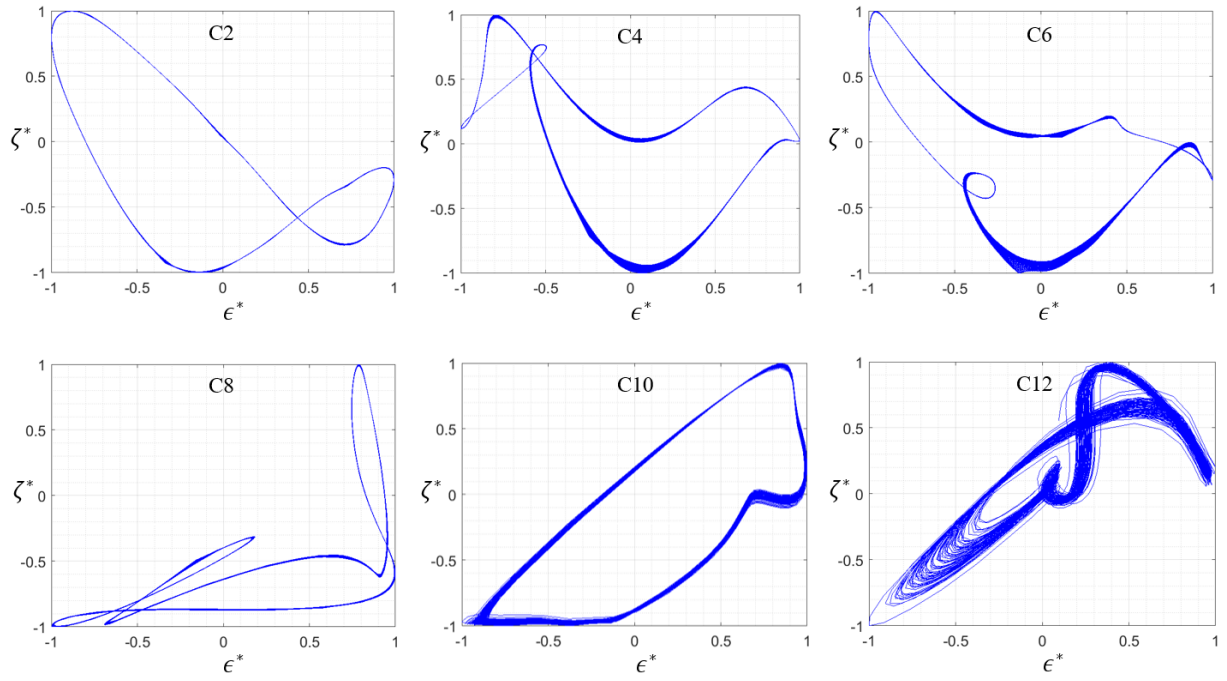


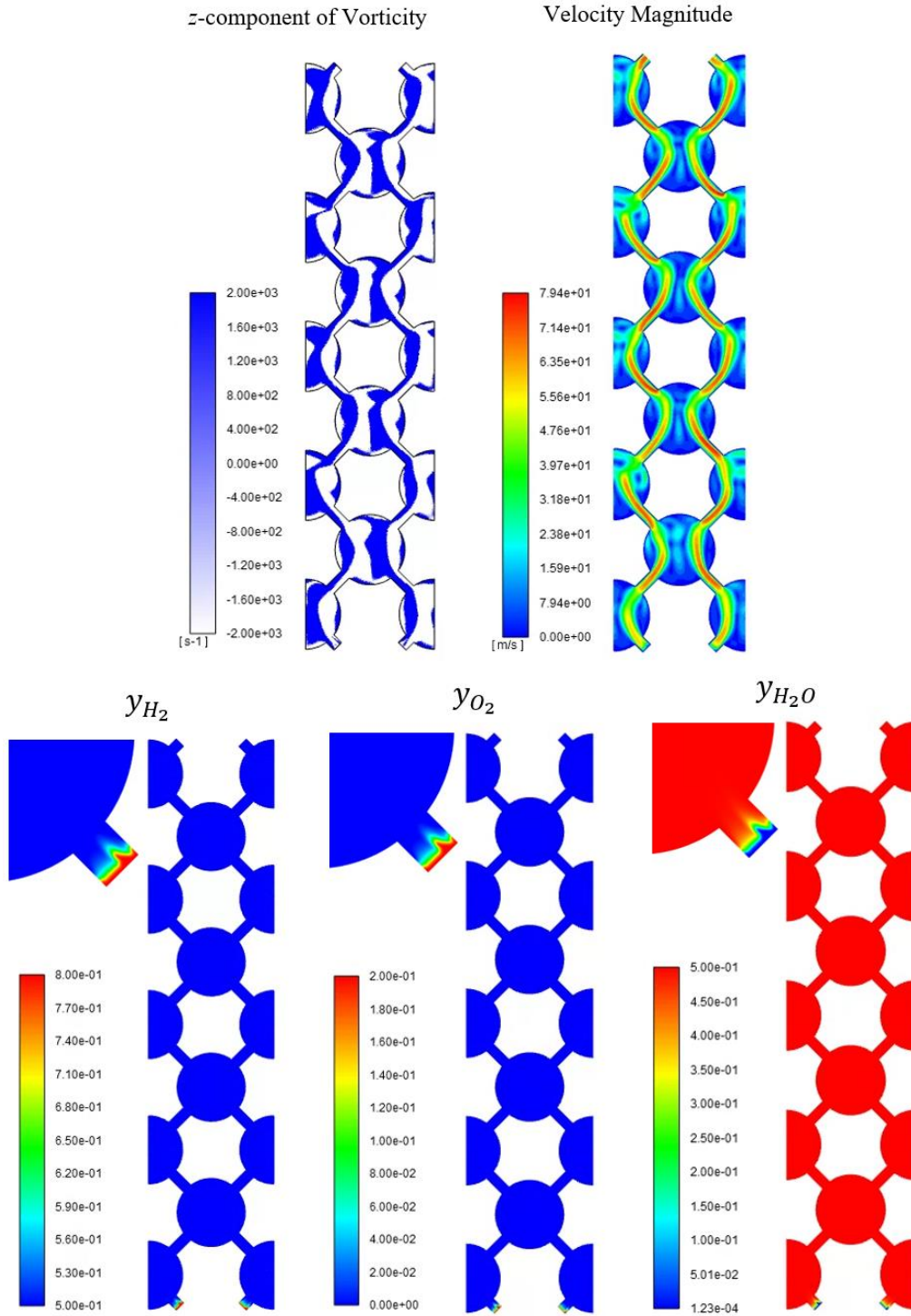
Figure B.4 Strange attractors in the centre of chambers for $D/d = 6.75$, at $Re = 300$.

Appendix C – Combustion NETmix Flow

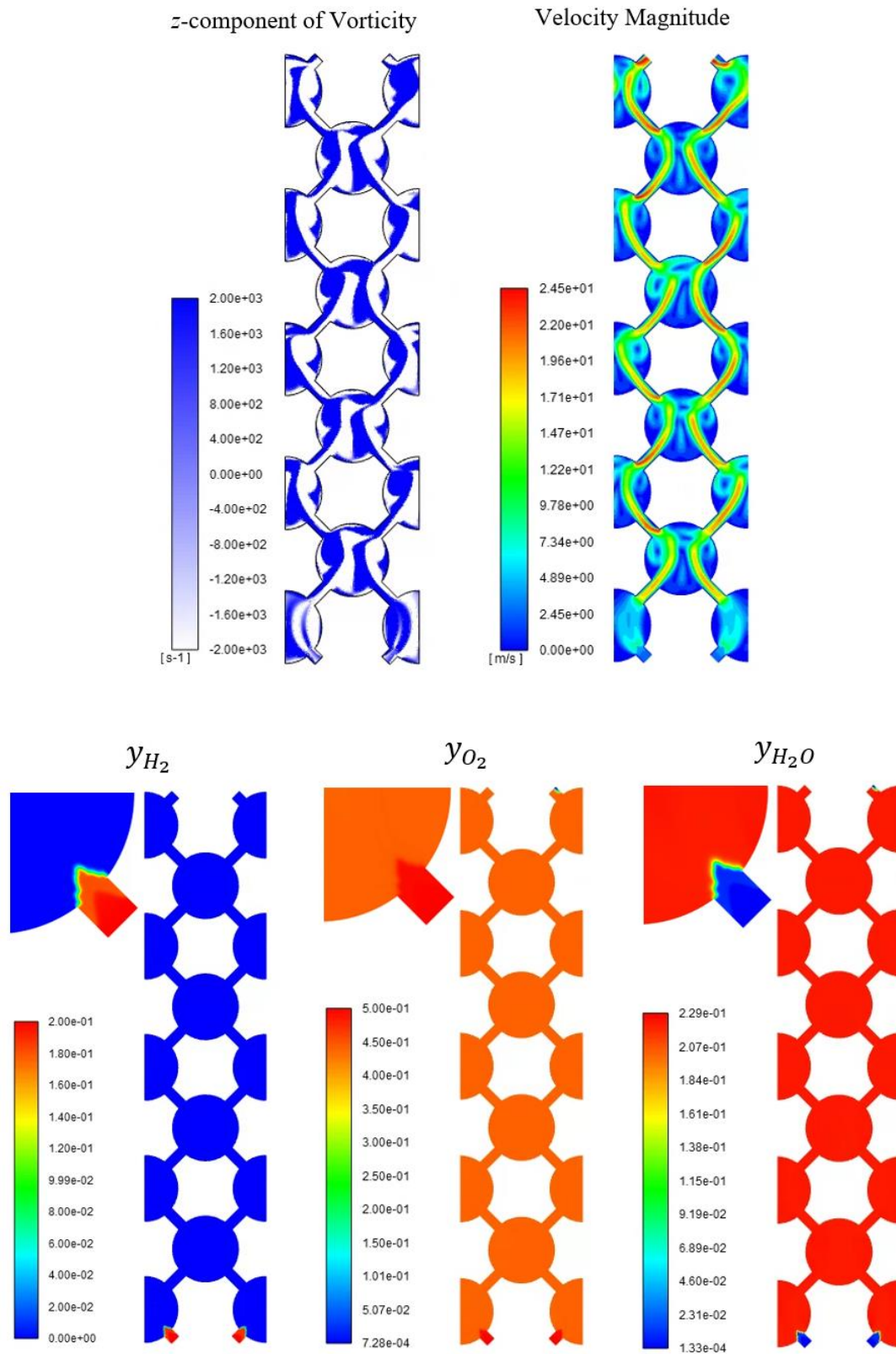
The vorticity and velocity maps, as well as the maps of the molar fraction of the reactants and products, will be shown next for the simulations of this work, in order of appearance in the text.

Table C.1 Combustion Maps in ExtendedNUB.

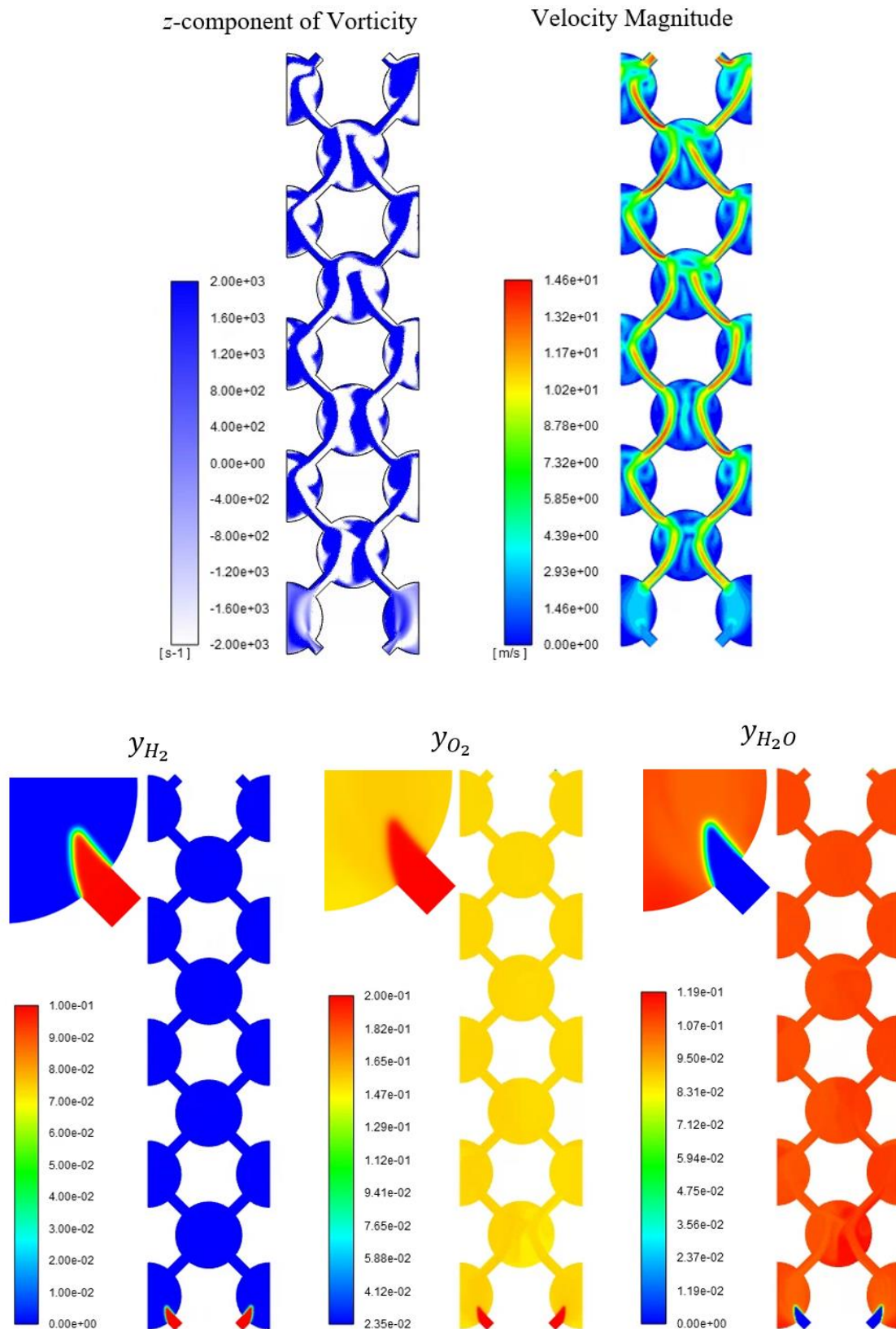
S1 – V.3.2.3



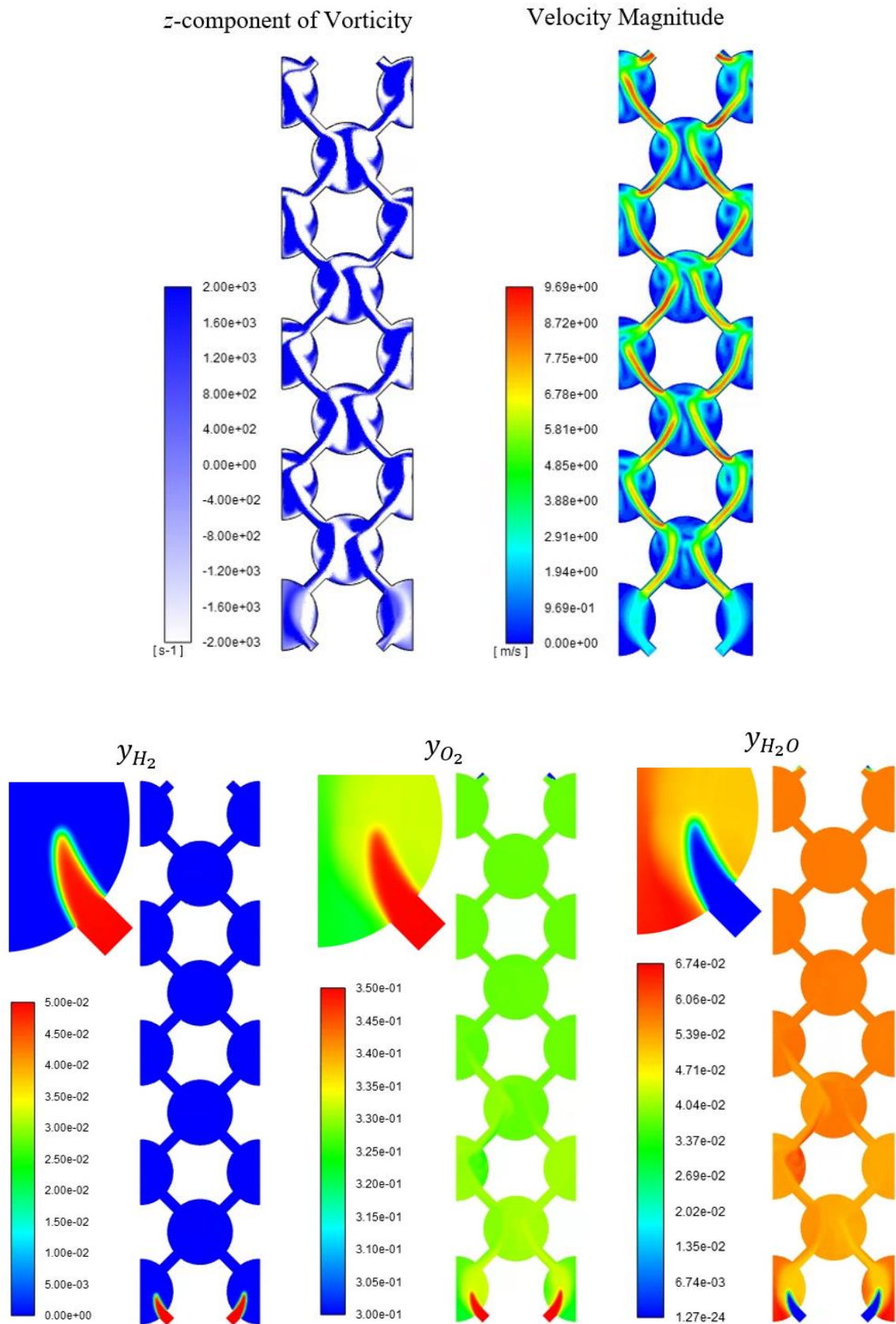
S4 – V.3.2.3

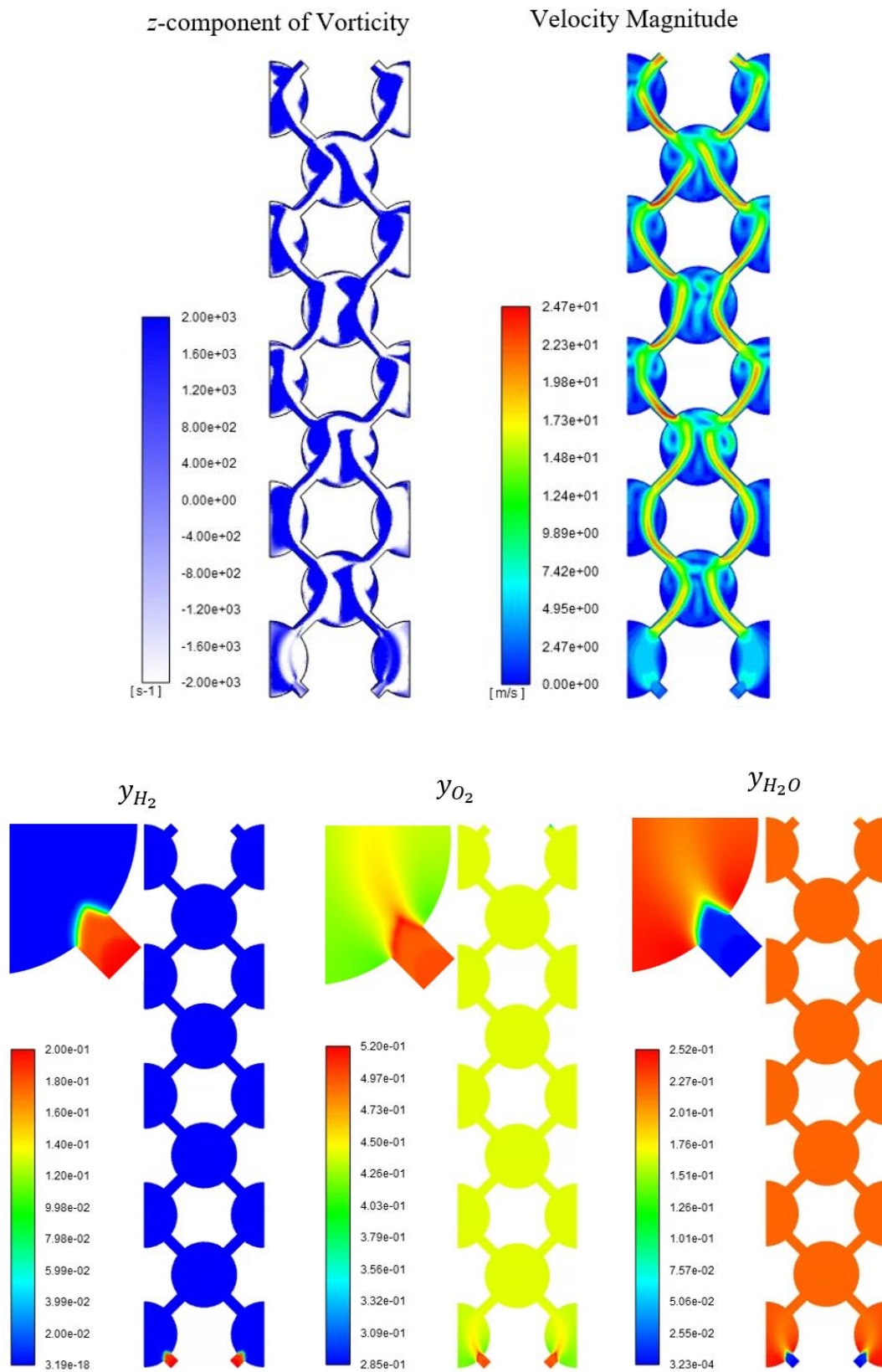


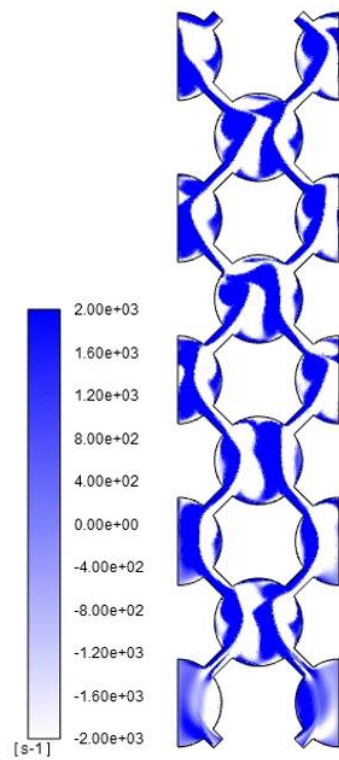
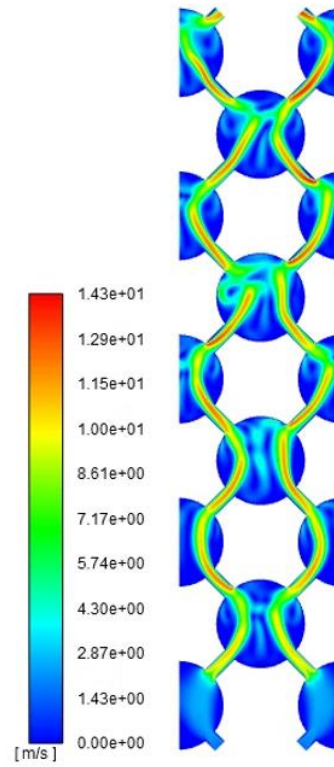
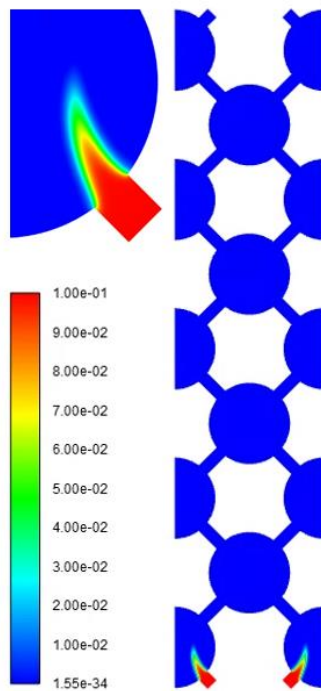
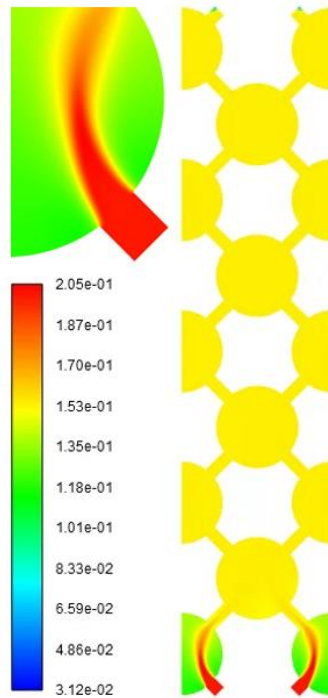
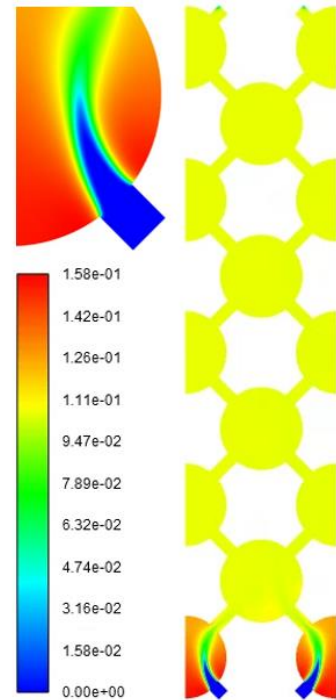
S7 – V.3.2.3

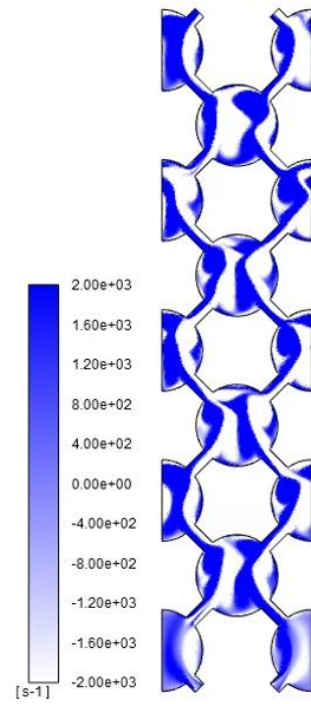


S9 – V.3.2.3

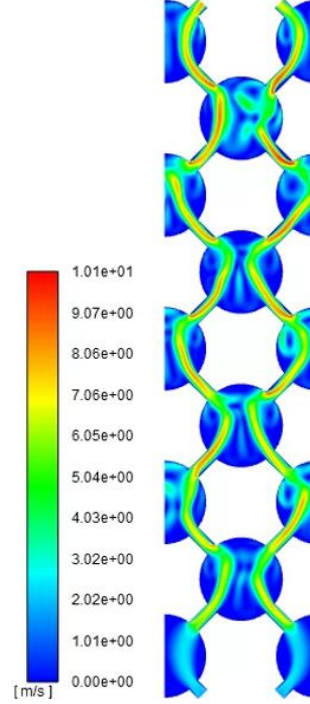
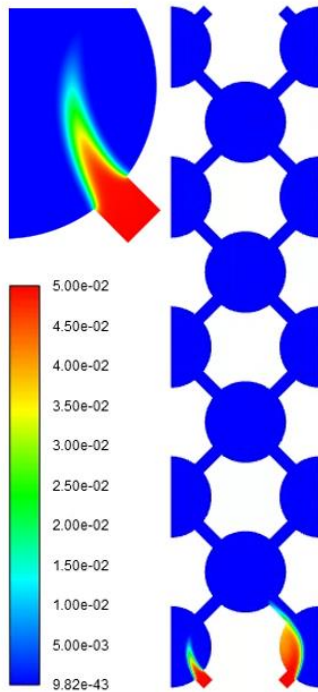
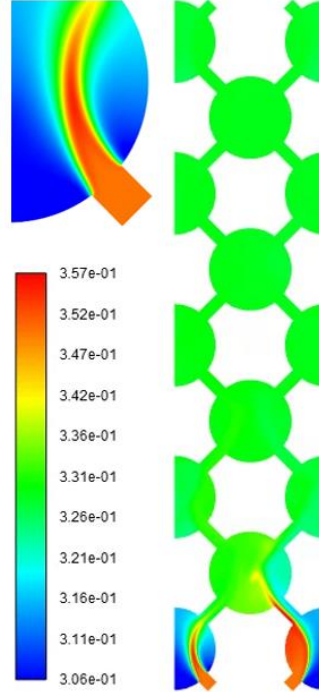
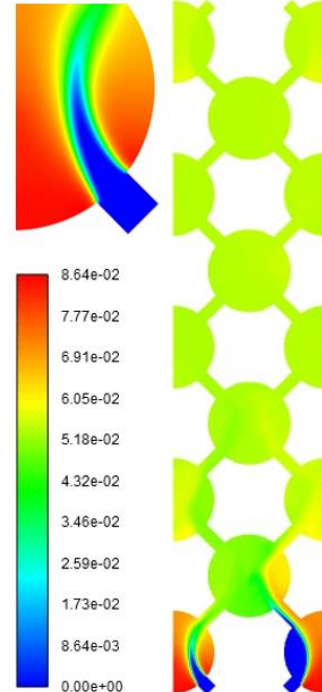


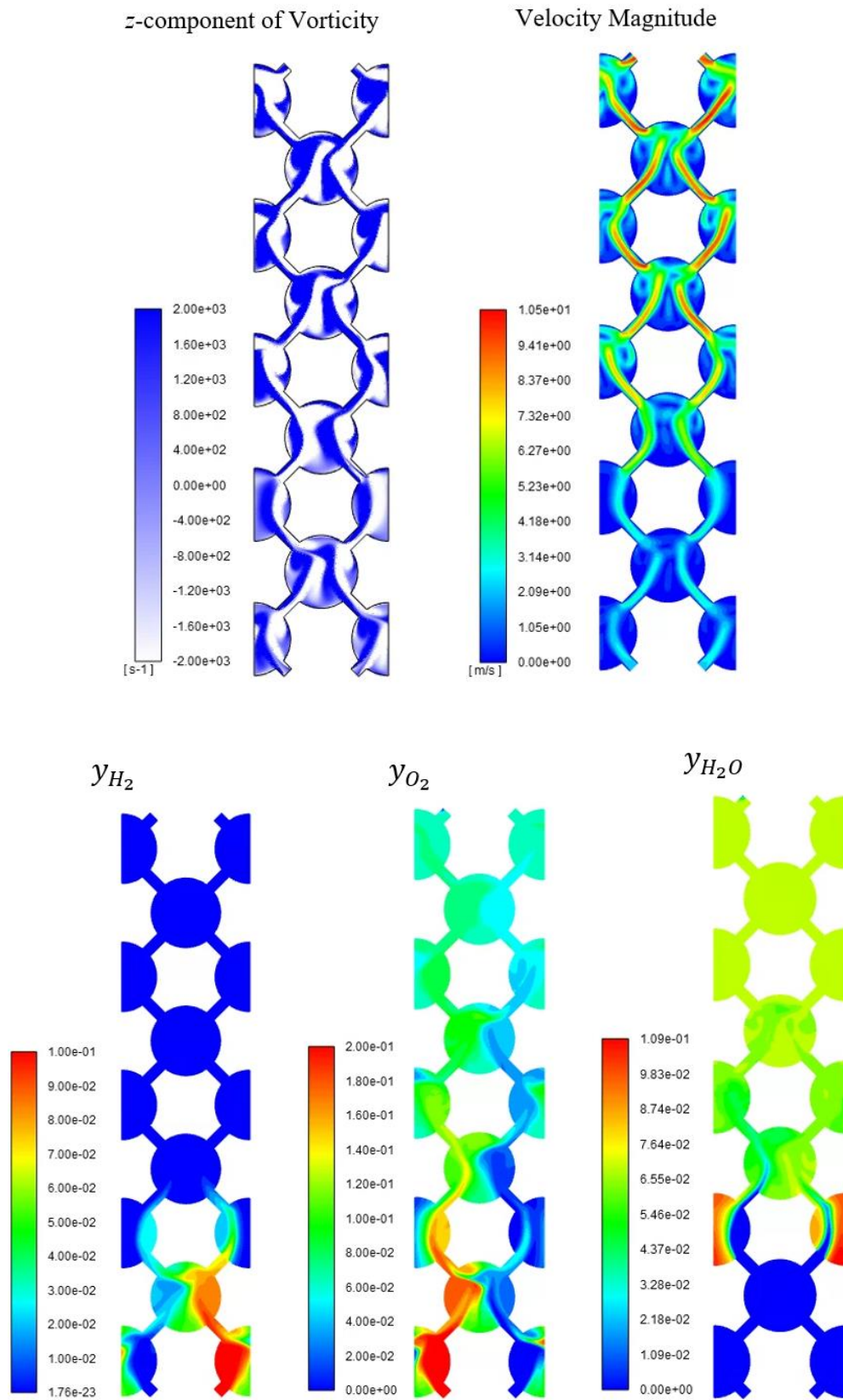
S4p – V.3.2.3

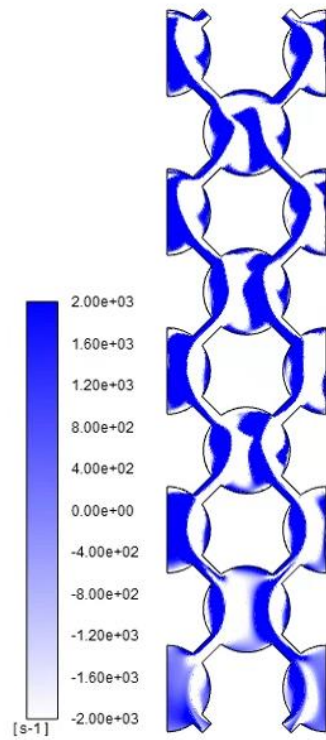
S7p – V.3.2.3 **z -component of Vorticity****Velocity Magnitude** **y_{H_2}**  **y_{O_2}**  **y_{H_2O}** 

S9p – V.3.2.3 z -component of Vorticity

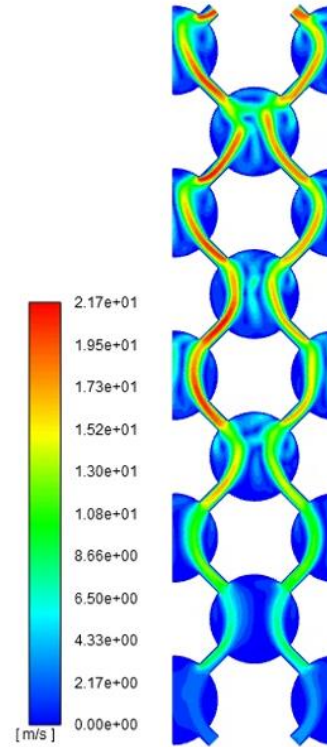
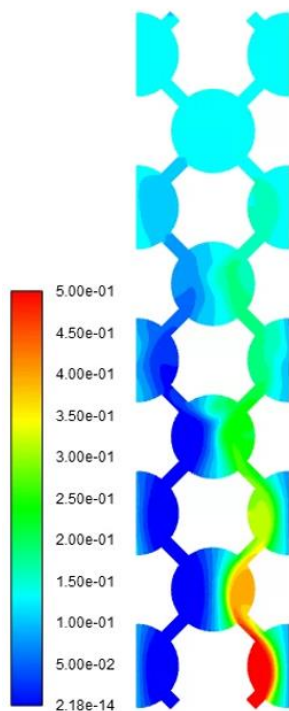
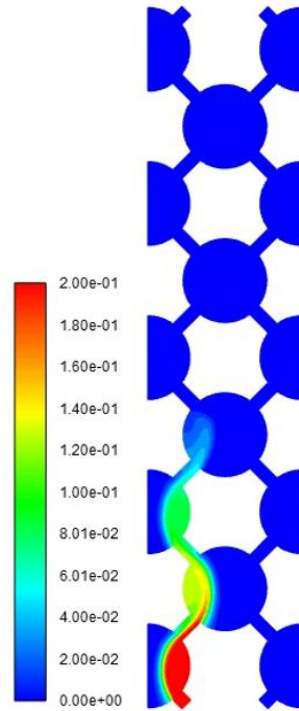
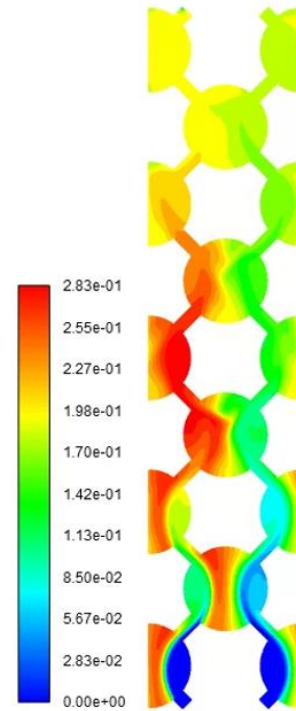
Velocity Magnitude

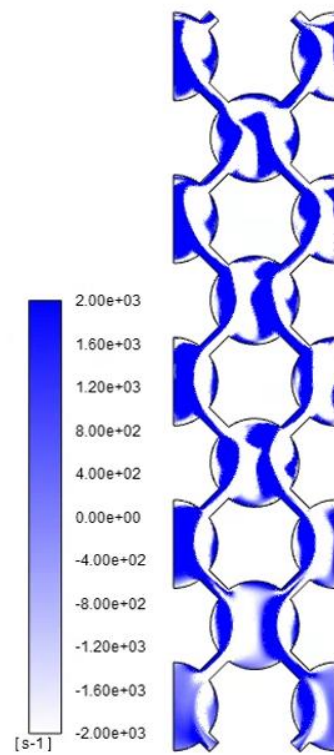
 y_{H_2}  y_{O_2}  y_{H_2O} 

S10p – V.3.2.4

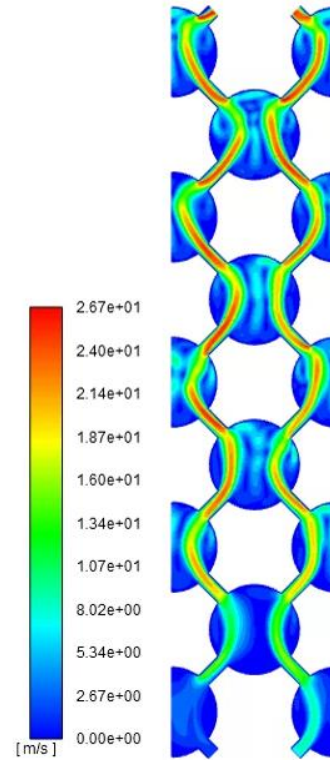
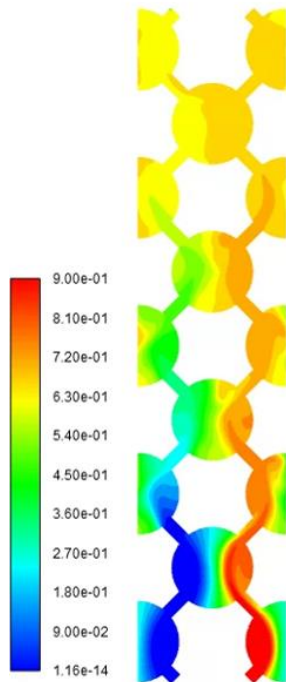
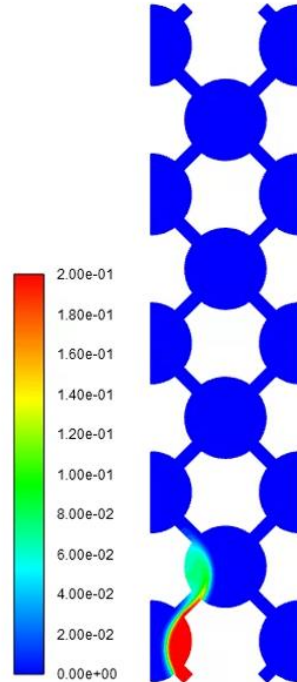
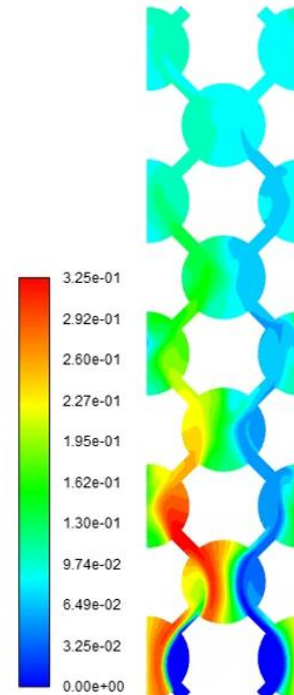
S11p – V.3.2.4 z -component of Vorticity

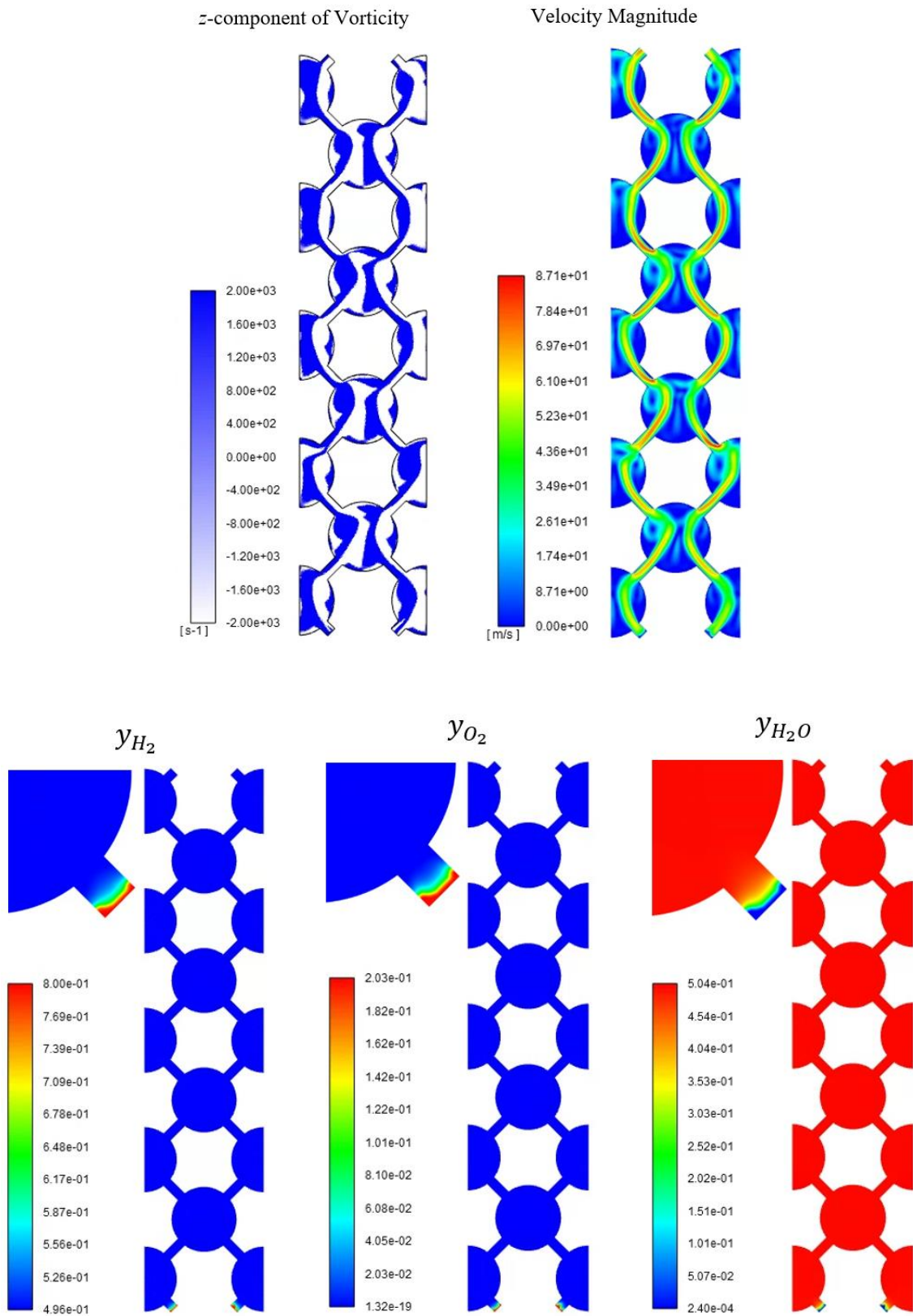
Velocity Magnitude

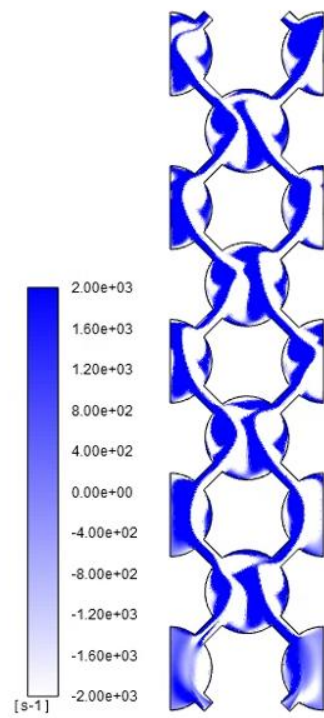
 y_{H_2}  y_{O_2}  y_{H_2O} 

S12p – V.3.2.4 z -component of Vorticity

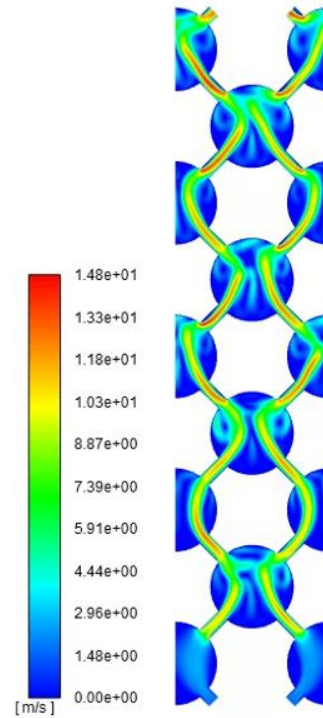
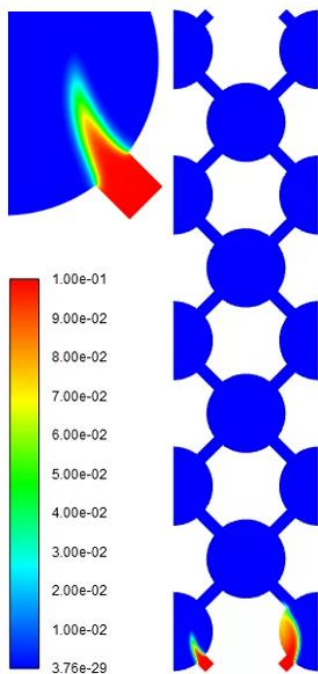
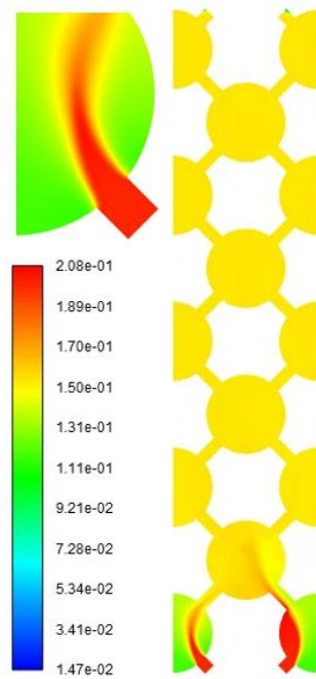
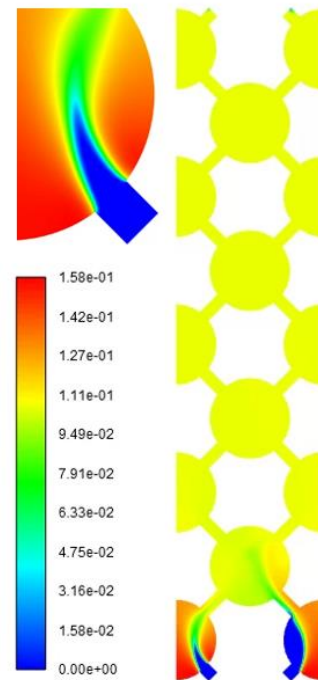
Velocity Magnitude

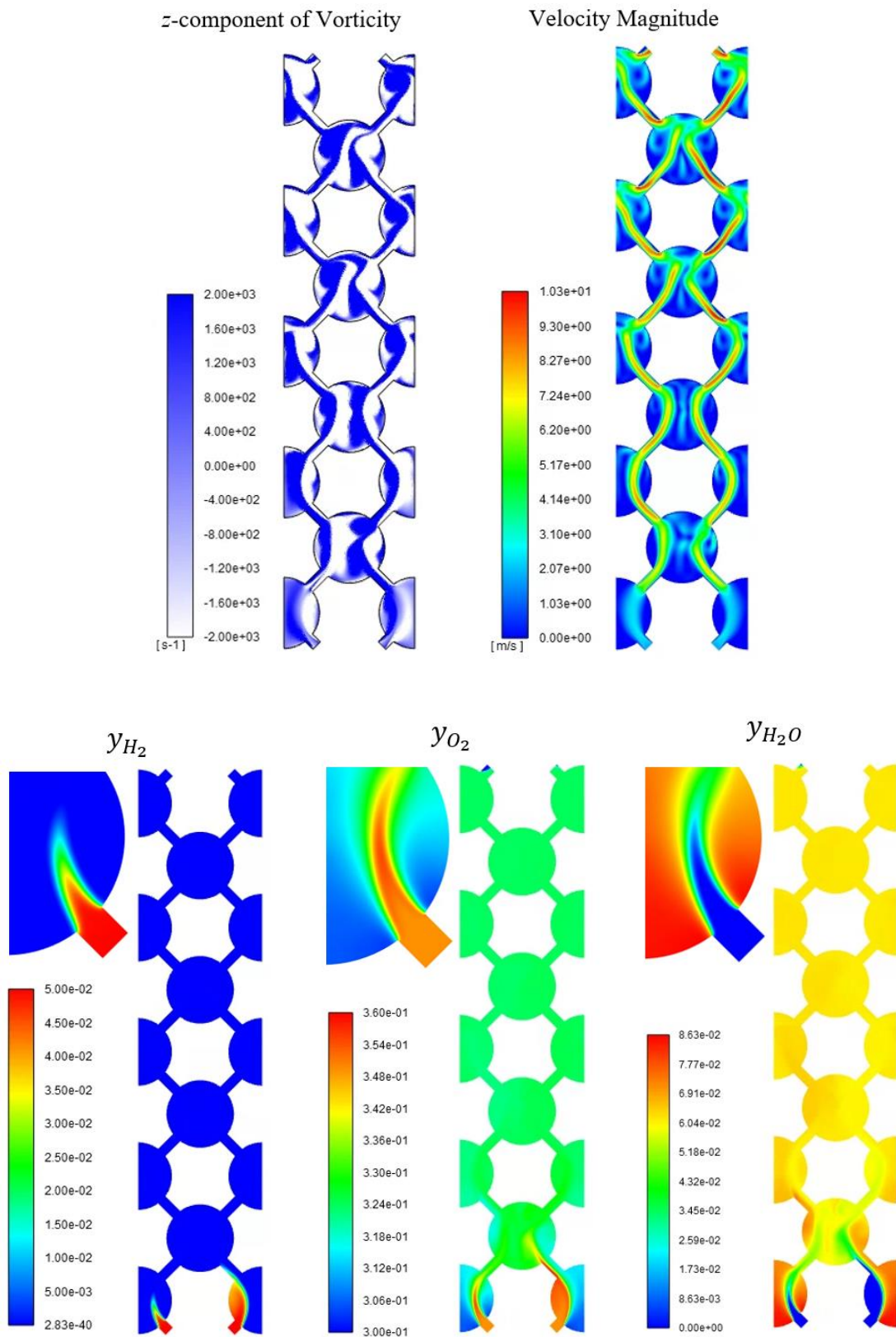
 y_{H_2}  y_{O_2}  y_{H_2O} 

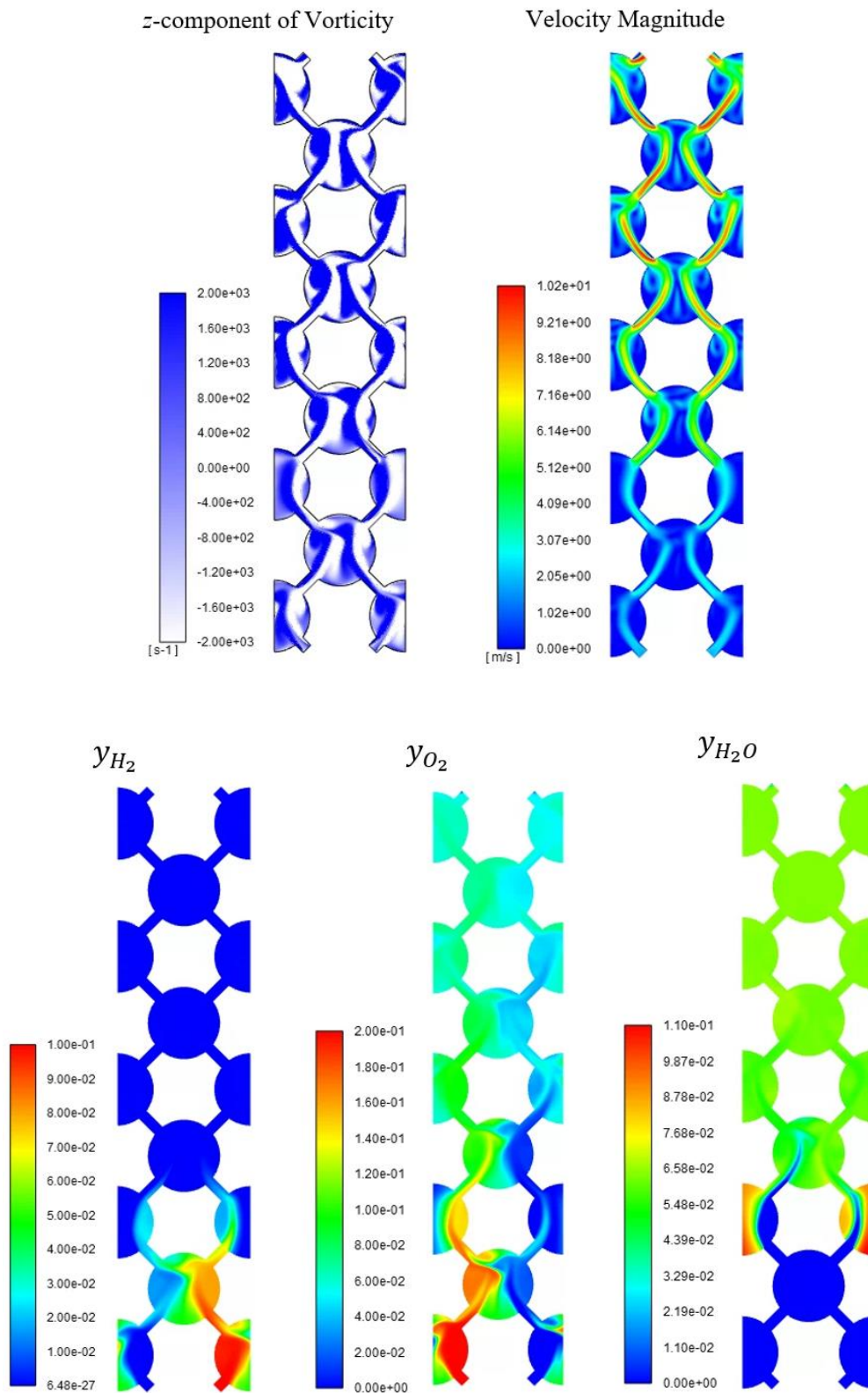
M1 – V.3.2.5

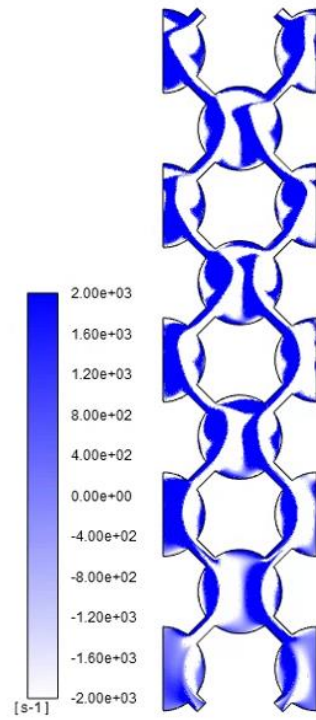
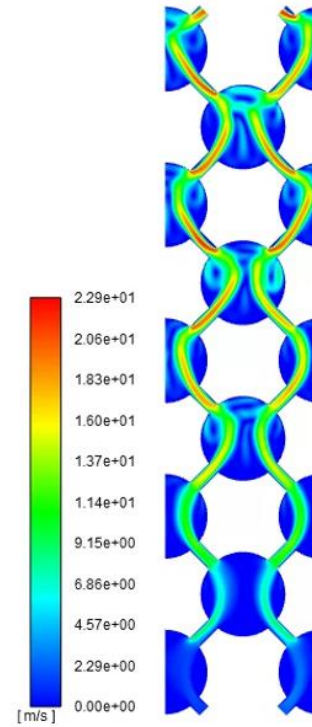
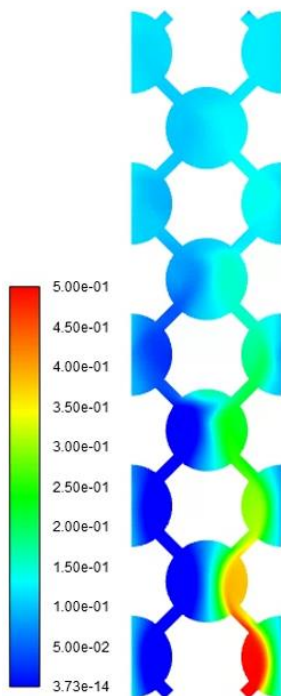
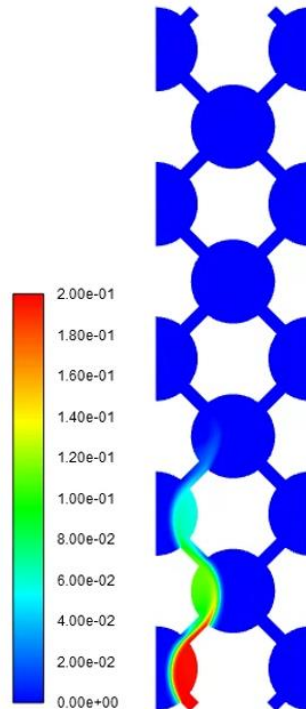
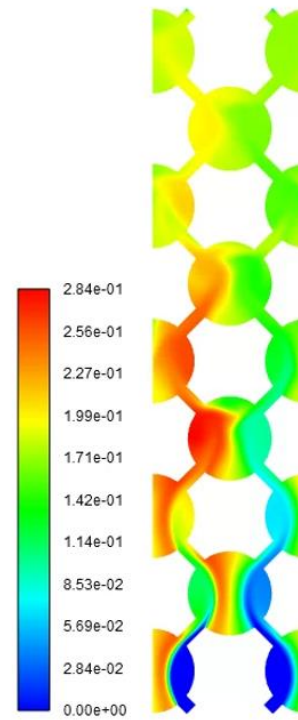
M2 – V.3.2.5 z -component of Vorticity

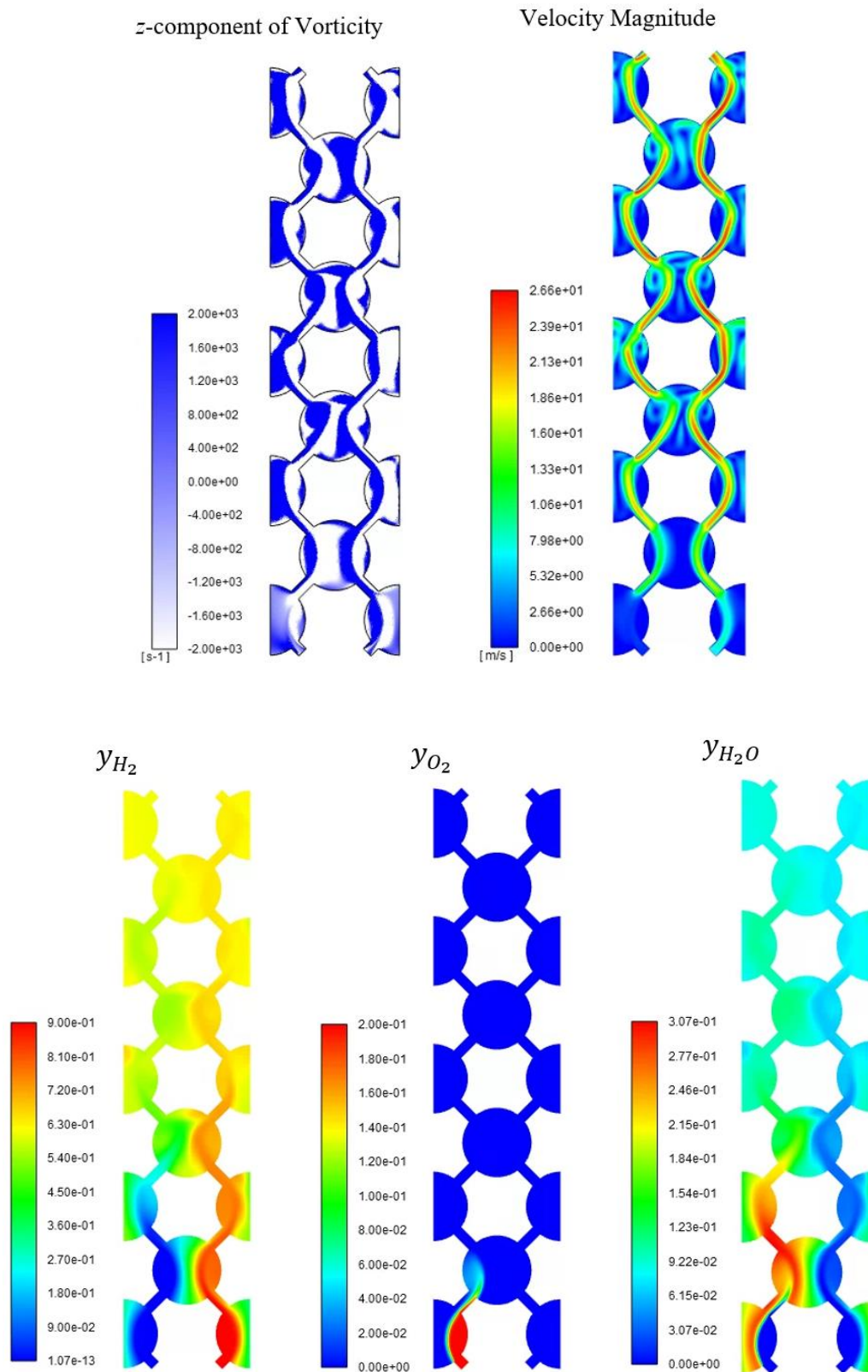
Velocity Magnitude

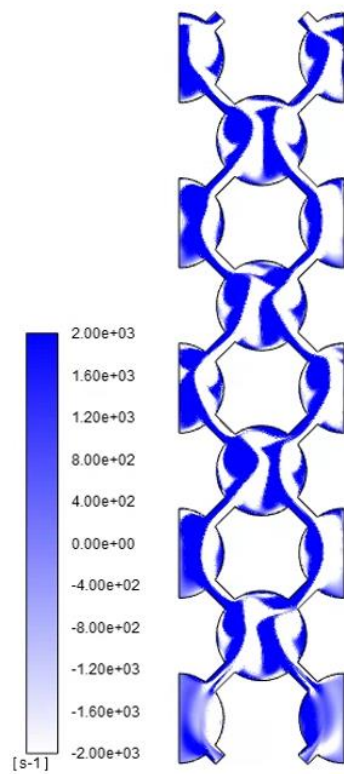
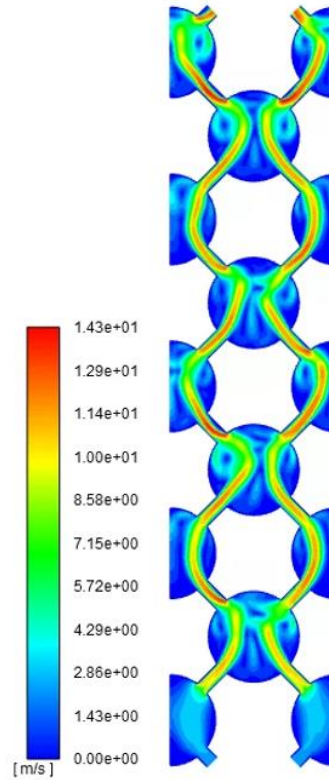
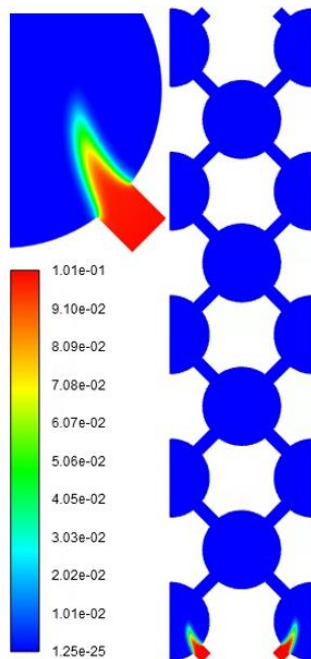
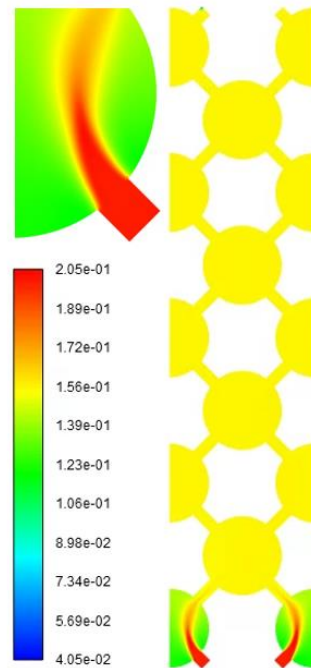
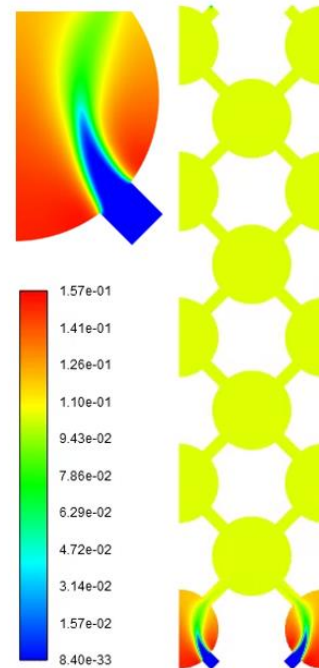
 y_{H_2}  y_{O_2}  y_{H_2O} 

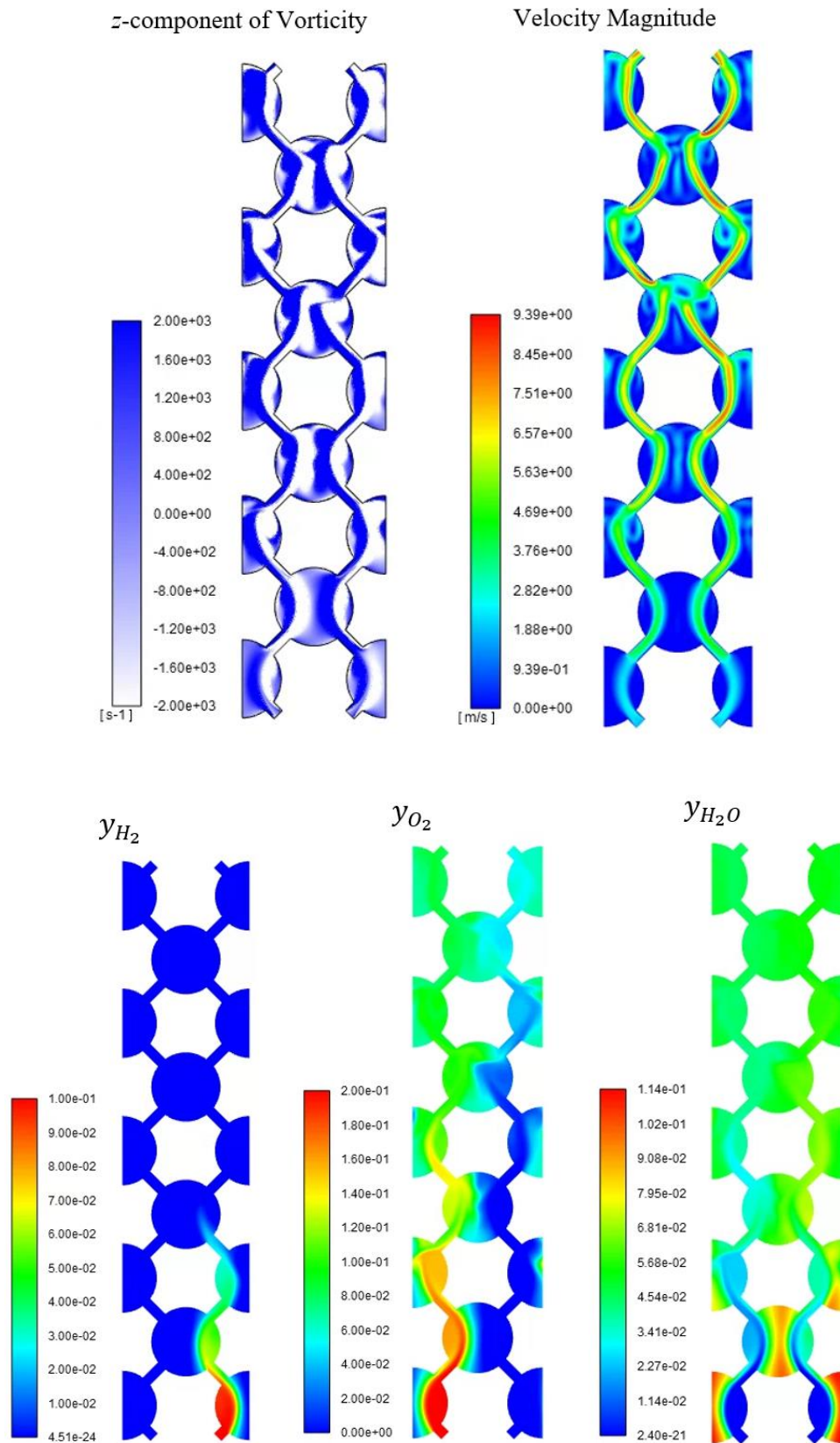
M3 – V.3.2.5

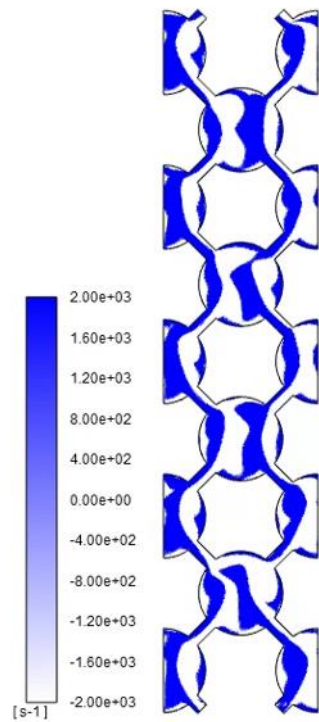
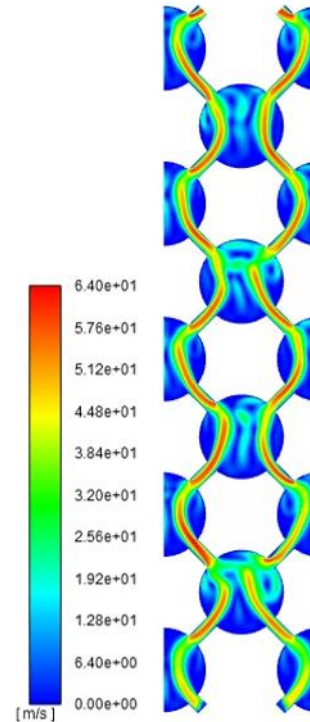
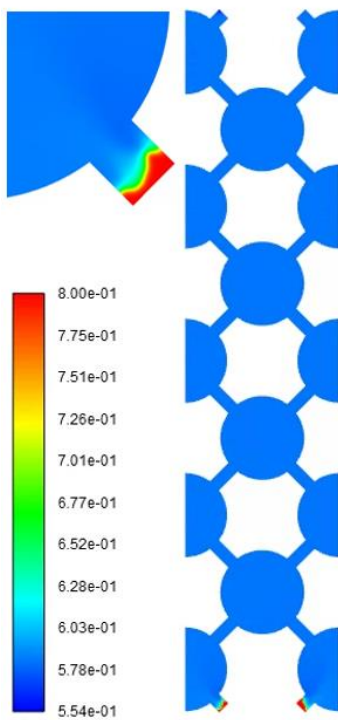
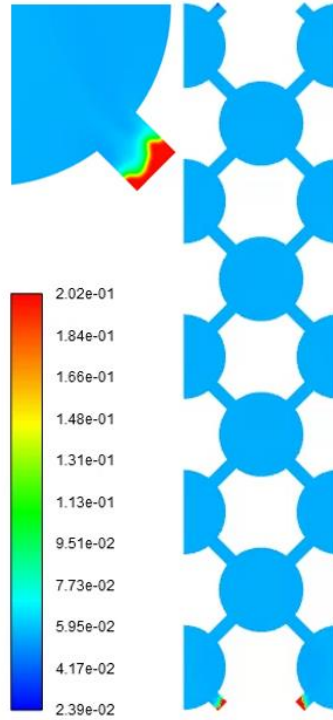
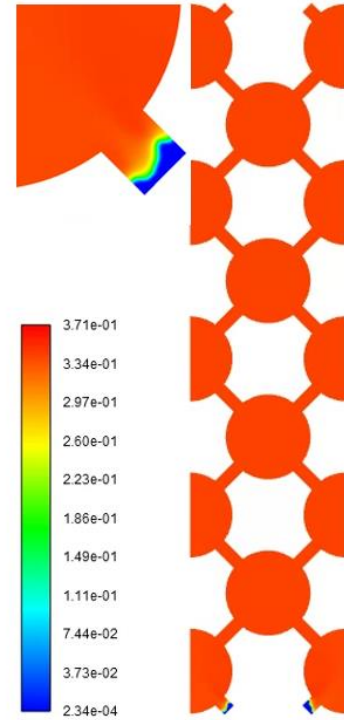
M4 – V.3.2.5

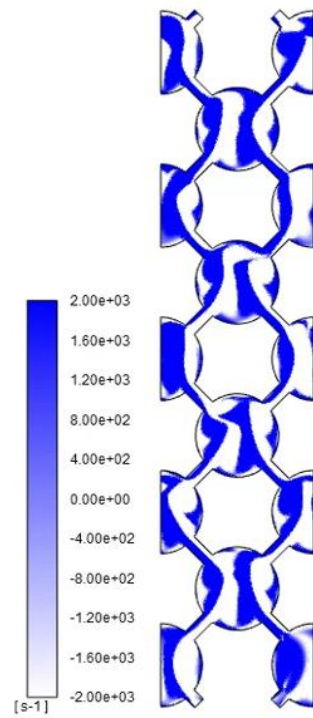
M5 – V.3.2.5 **z -component of Vorticity****Velocity Magnitude** **y_{H_2}**  **y_{O_2}**  **y_{H_2O}** 

M6 – V.3.2.5

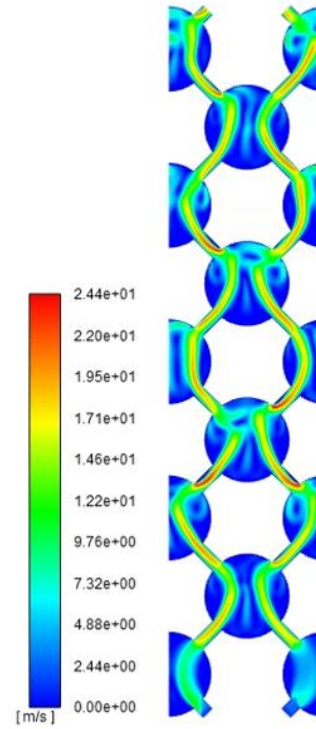
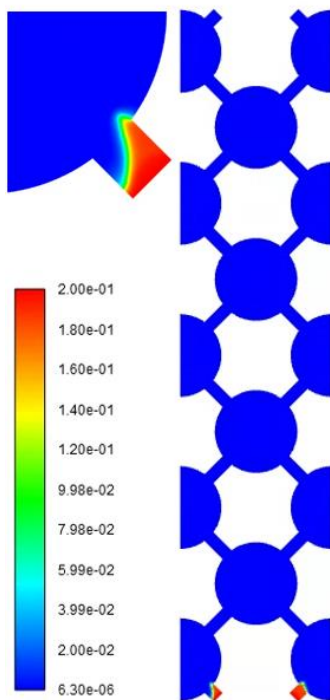
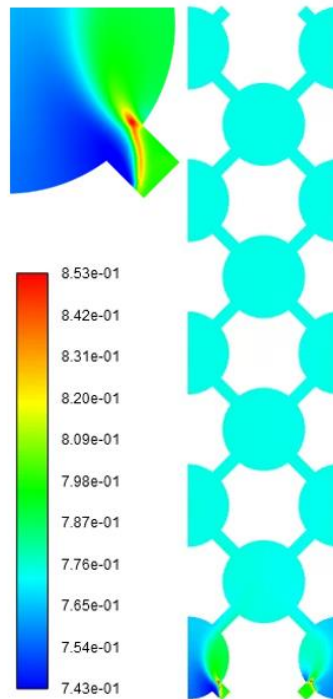
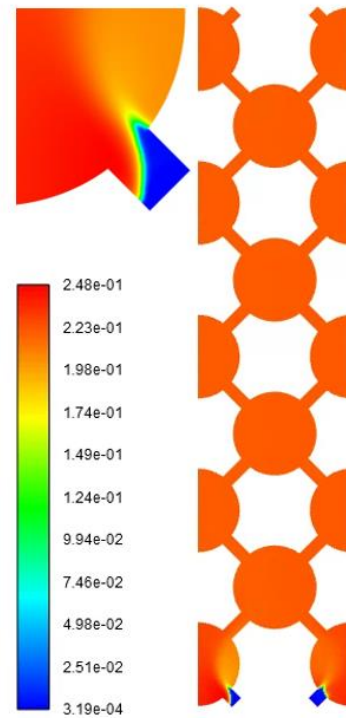
F2u – V.3.2.5**z-component of Vorticity****Velocity Magnitude** **y_{H_2}**  **y_{O_2}**  **y_{H_2O}** 

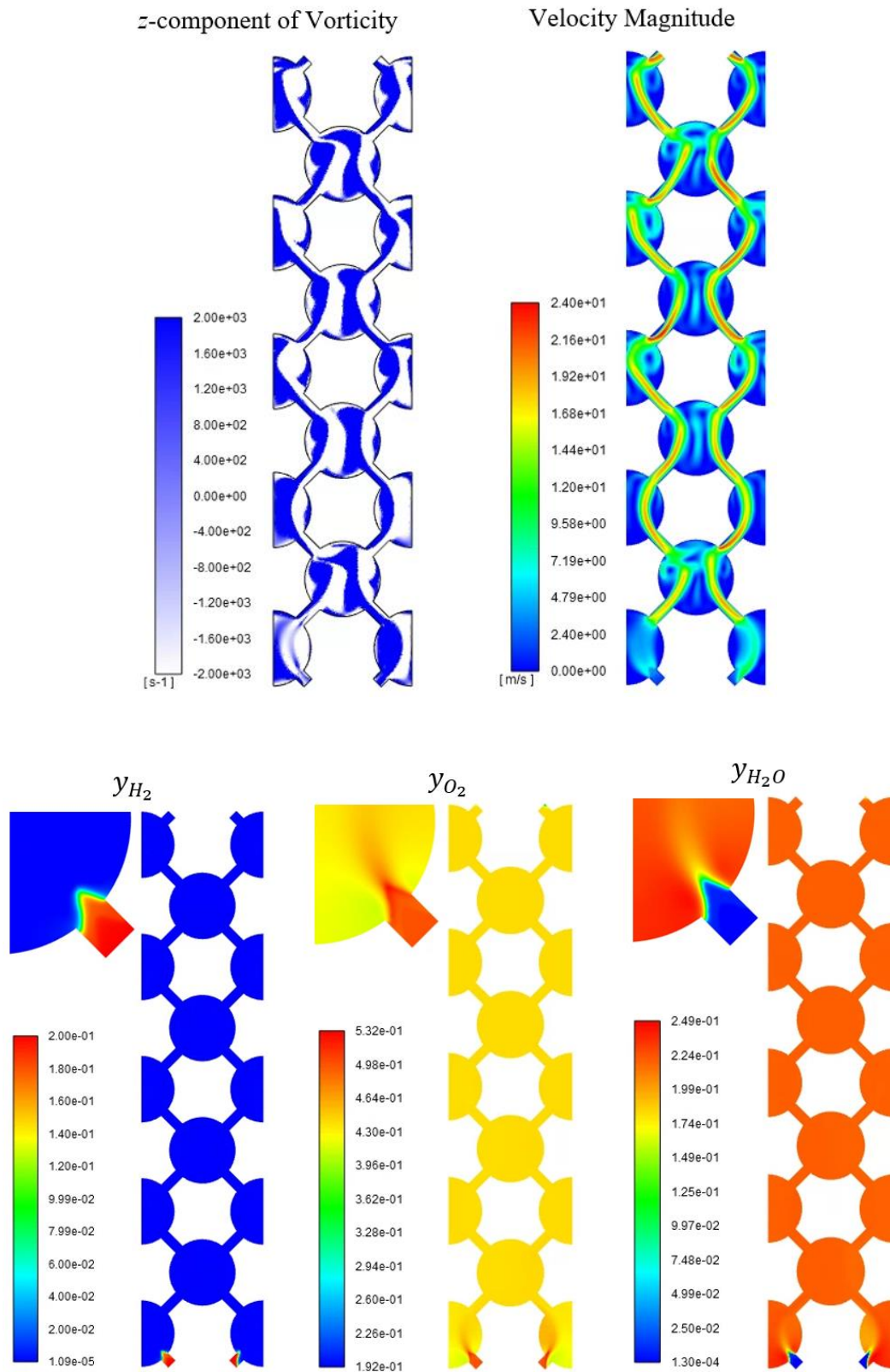
F4u – V.3.2.5

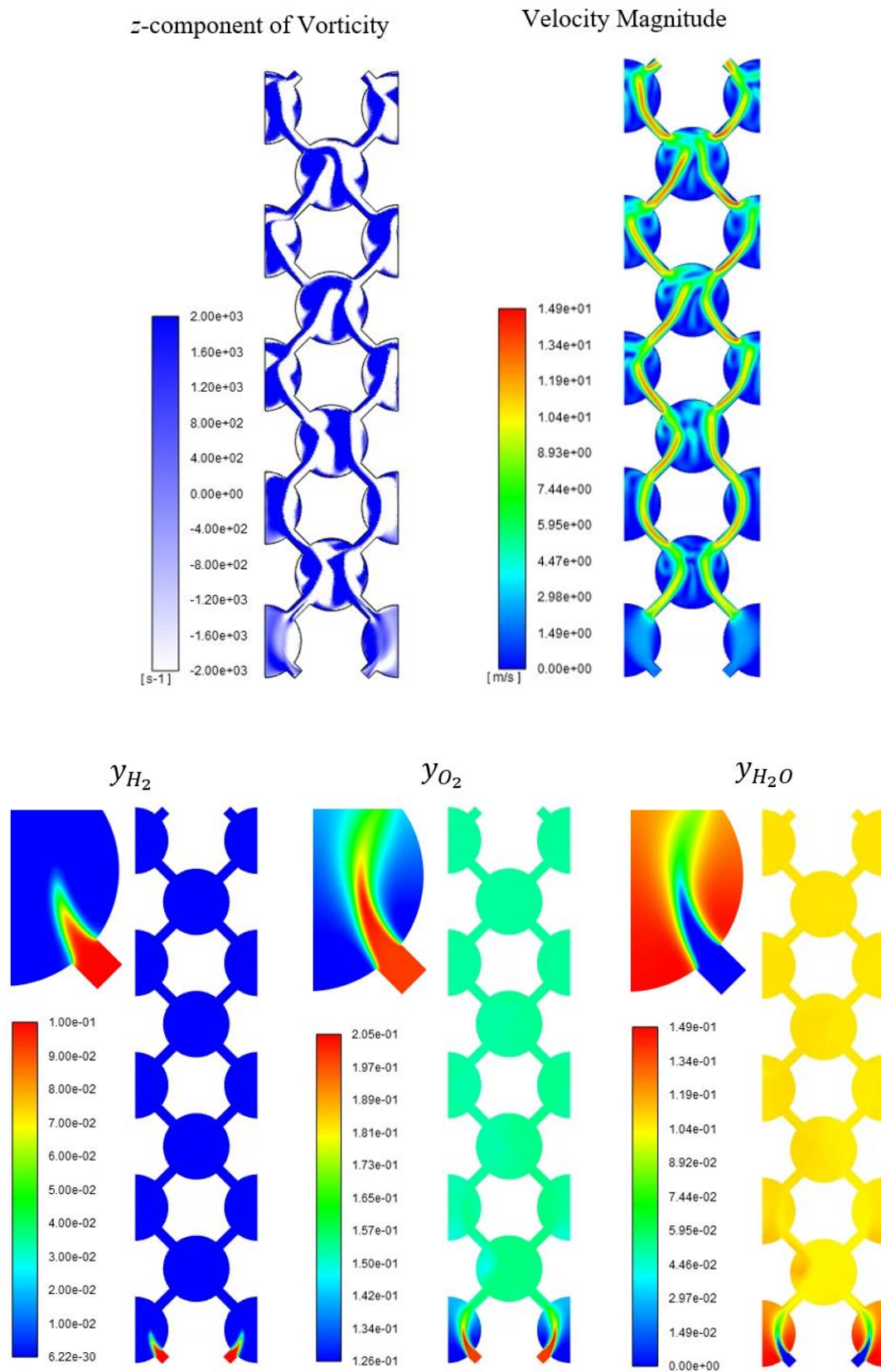
B1 – V.3.2.6 **z -component of Vorticity****Velocity Magnitude** **y_{H_2}**  **y_{O_2}**  **y_{H_2O}** 

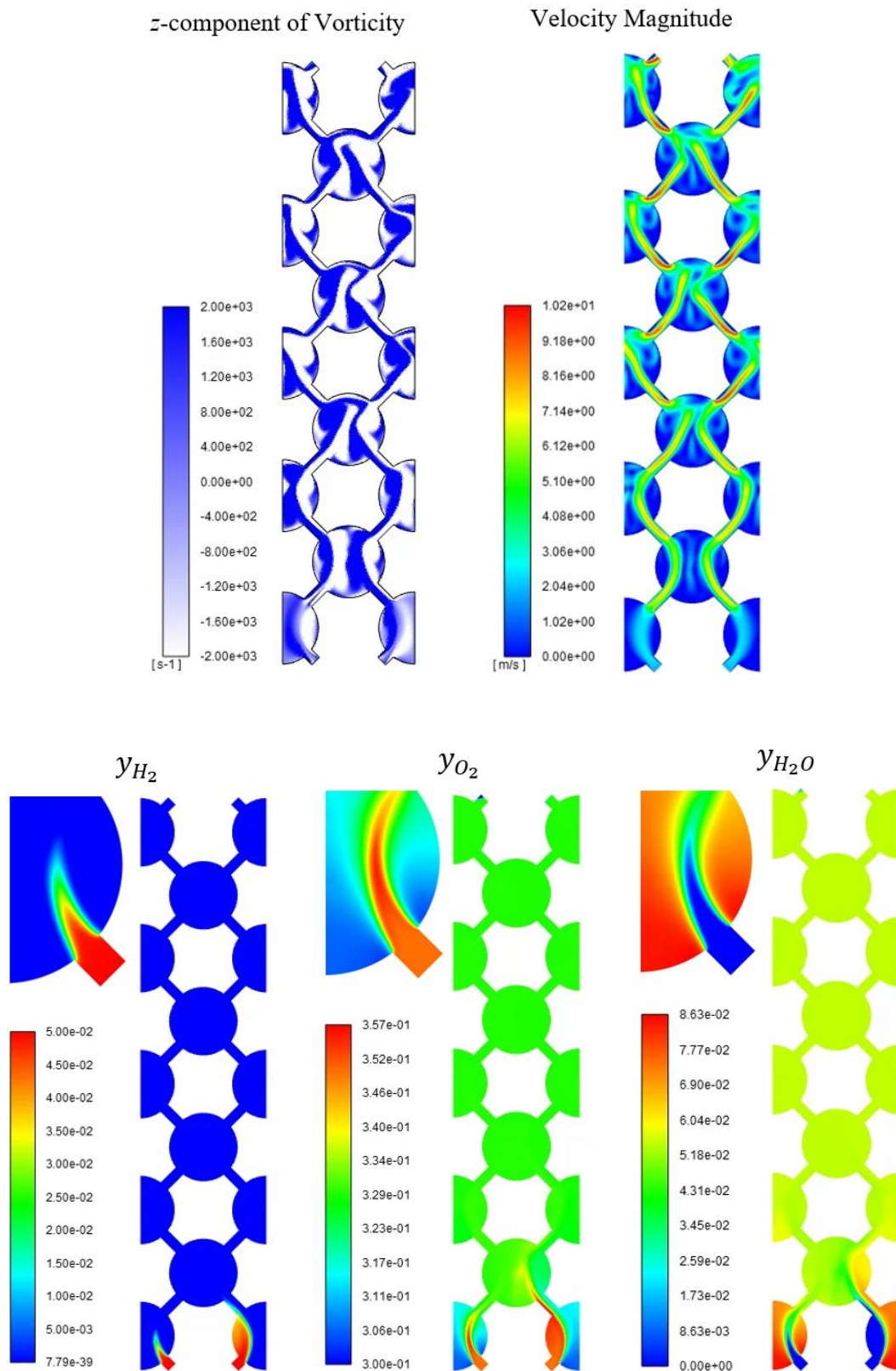
B3 – V.3.2.6 z -component of Vorticity

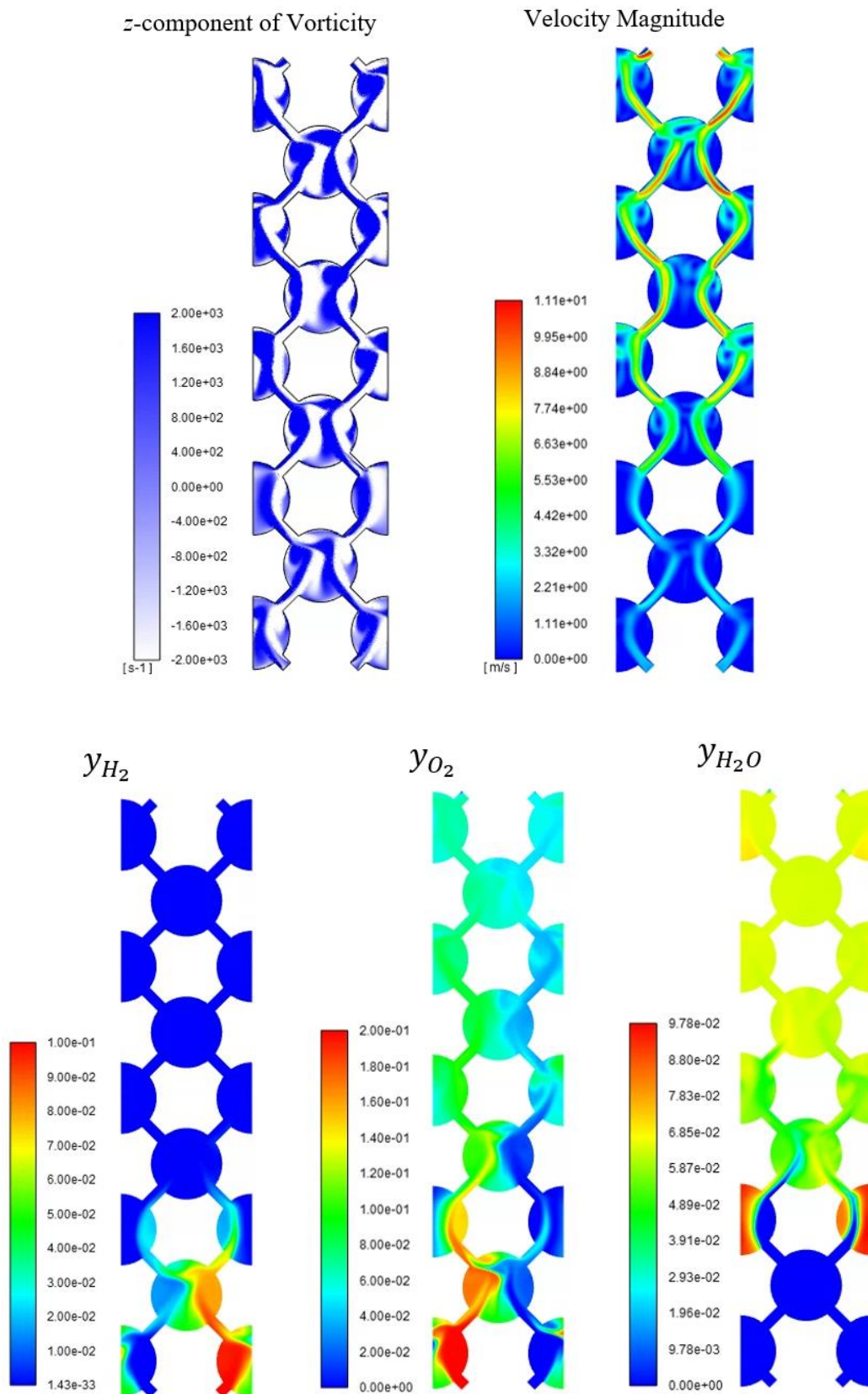
Velocity Magnitude

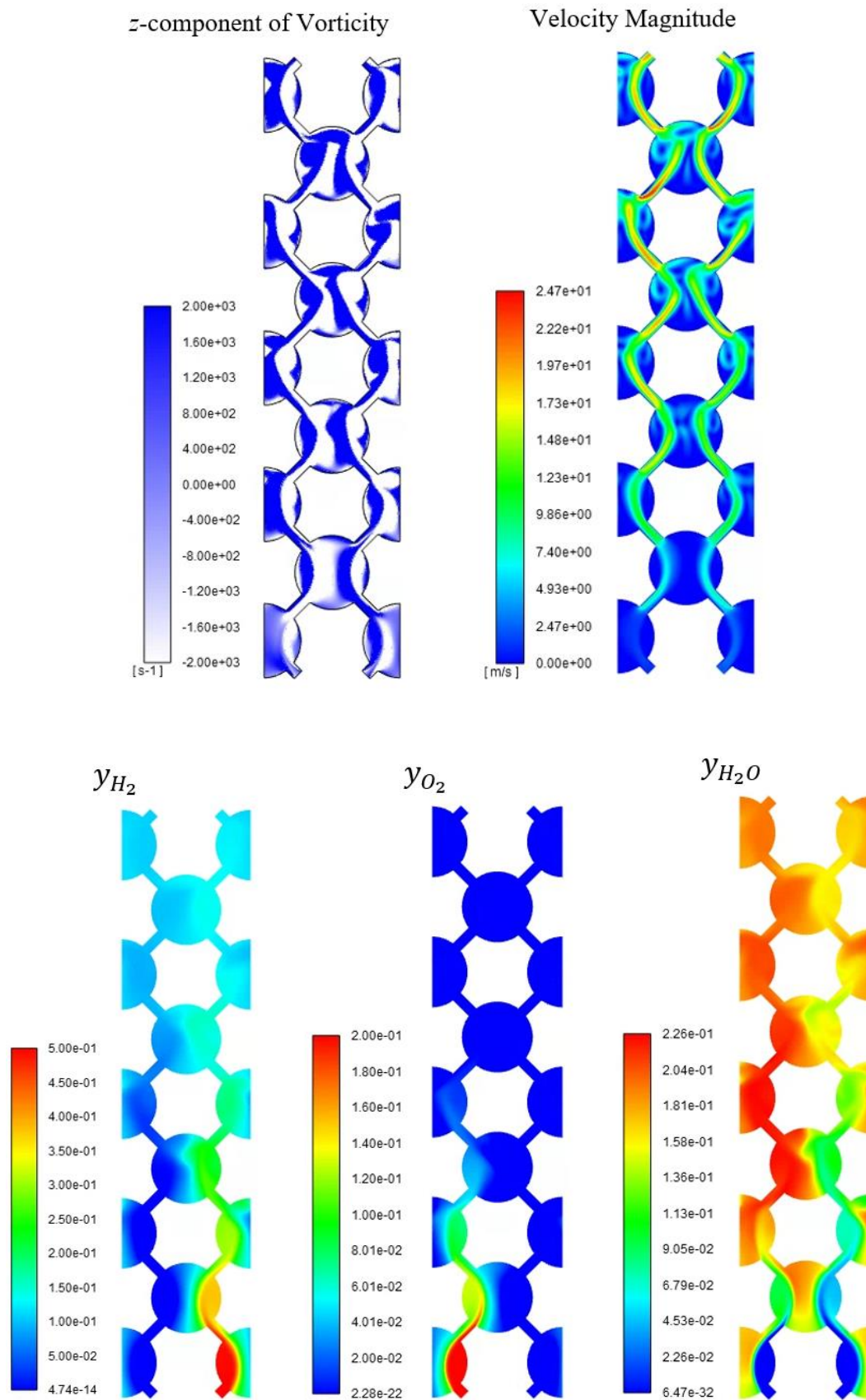
 y_{H_2}  y_{O_2}  y_{H_2O} 

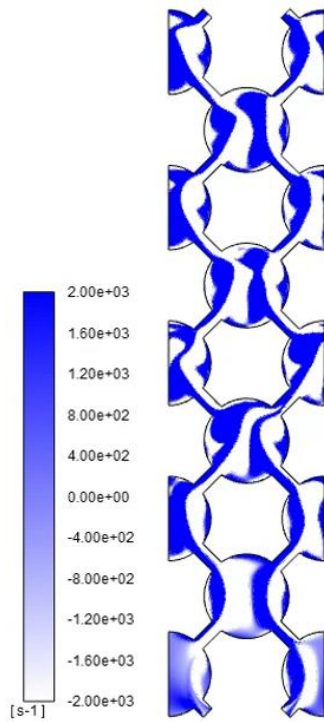
B4 – V.3.2.6

B7 – V.3.2.6

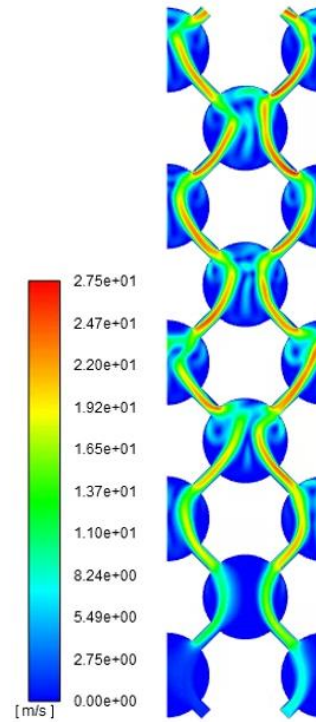
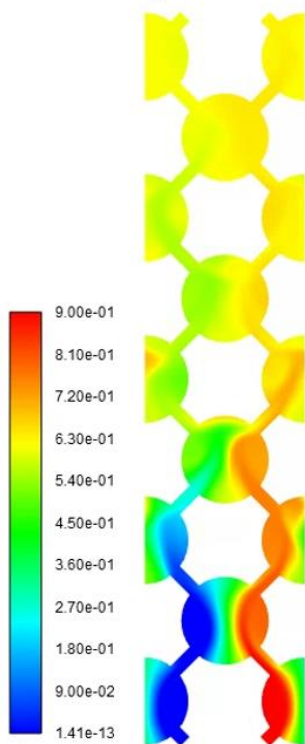
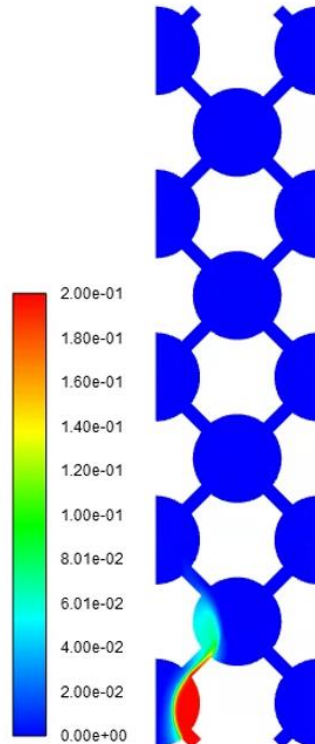
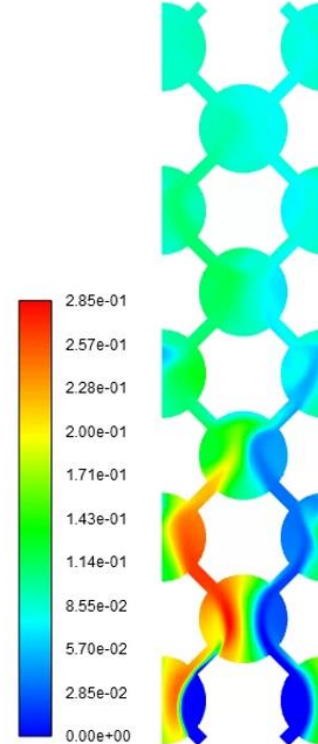
B9 – V.3.2.6

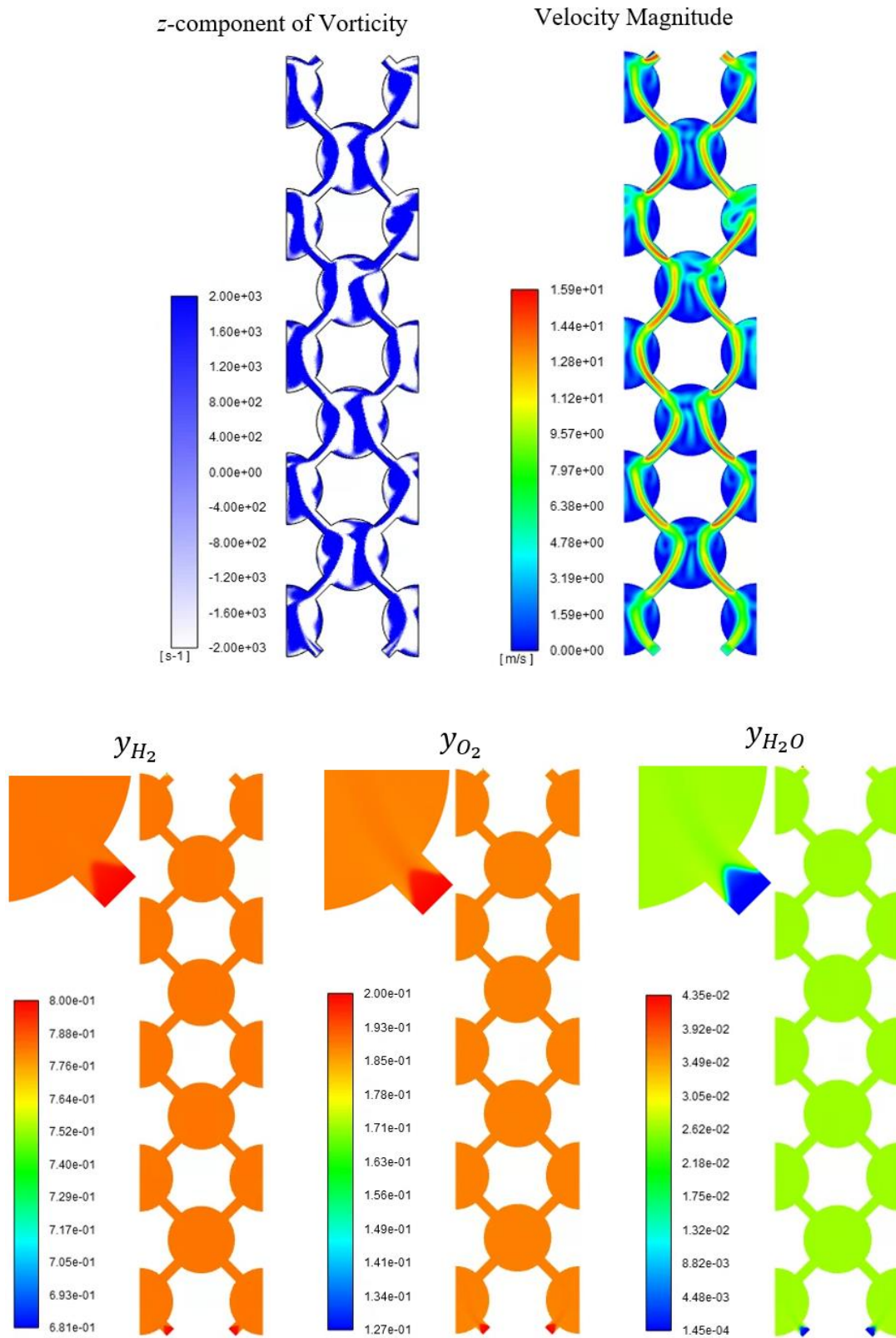
B10 – V.3.2.6

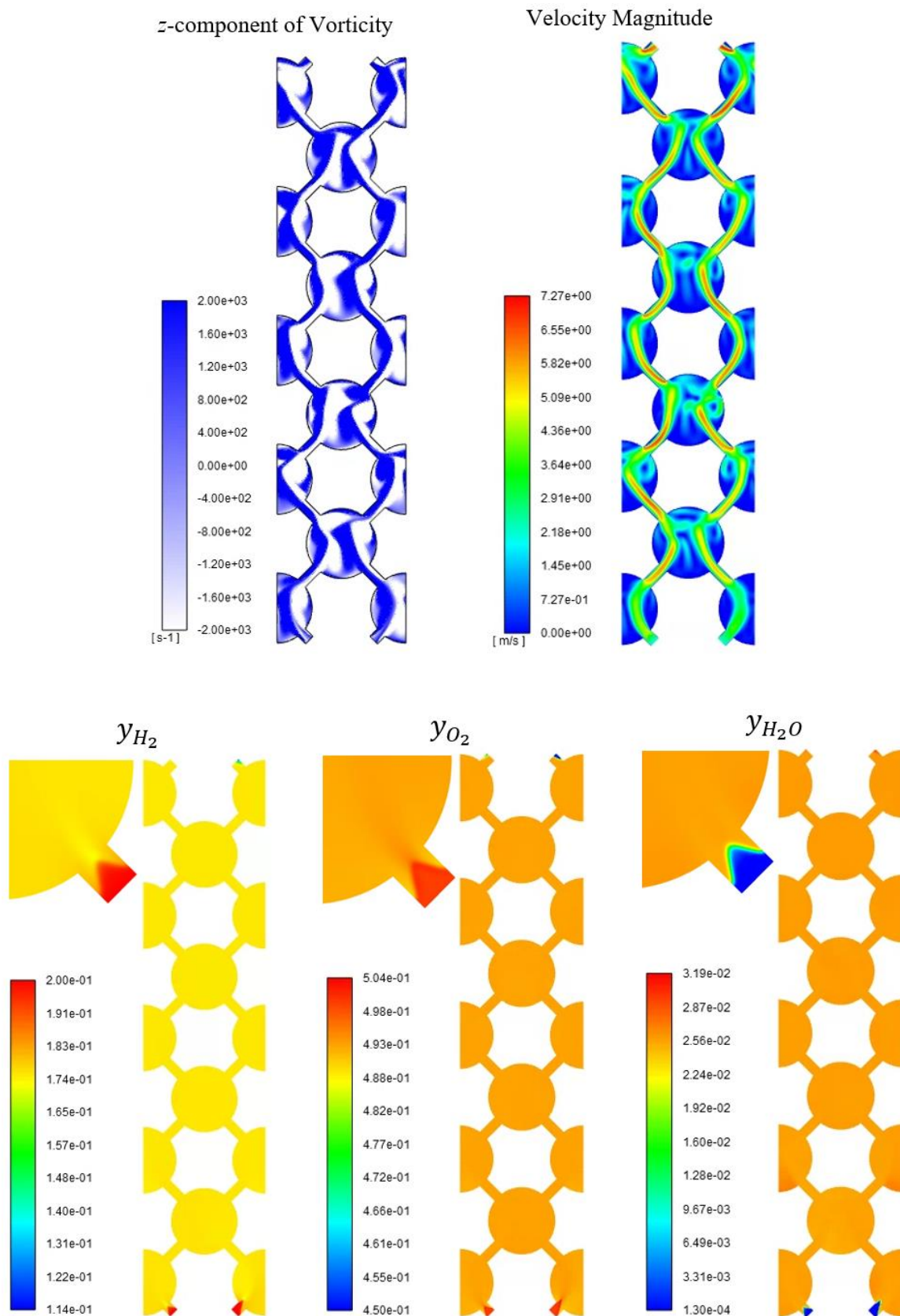
B11 – V.3.2.6


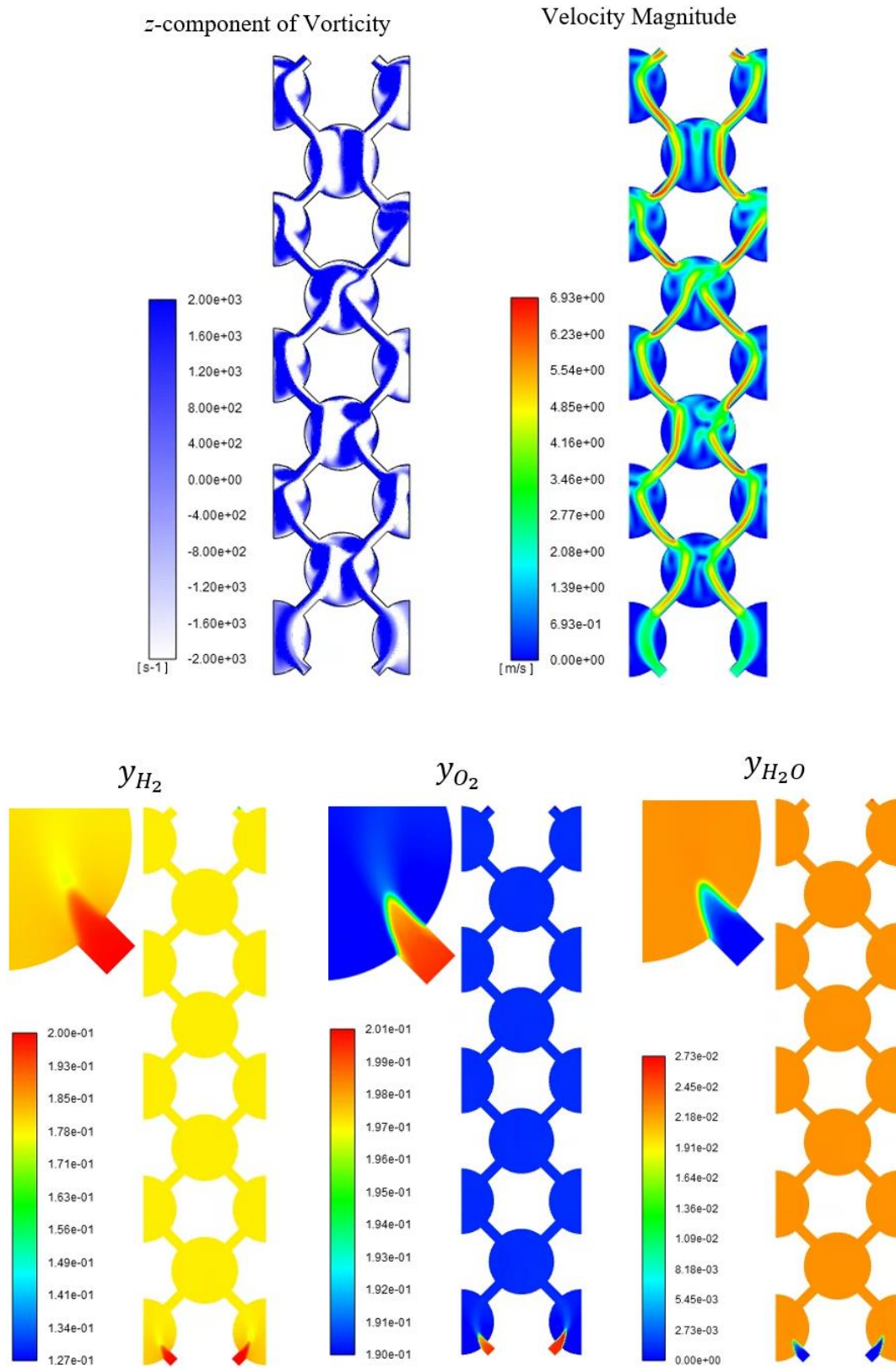
B12 – V.3.2.6 z -component of Vorticity

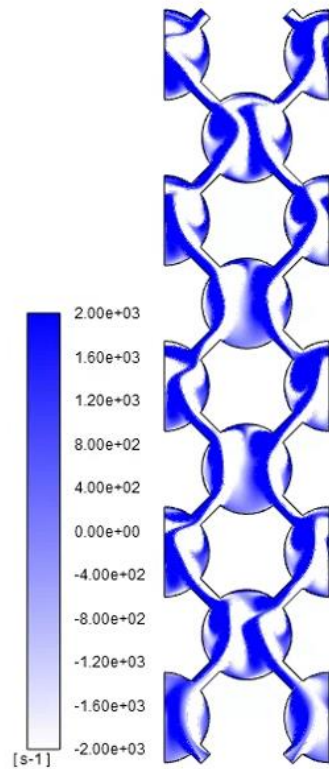
Velocity Magnitude

 y_{H_2}  y_{O_2}  y_{H_2O} 

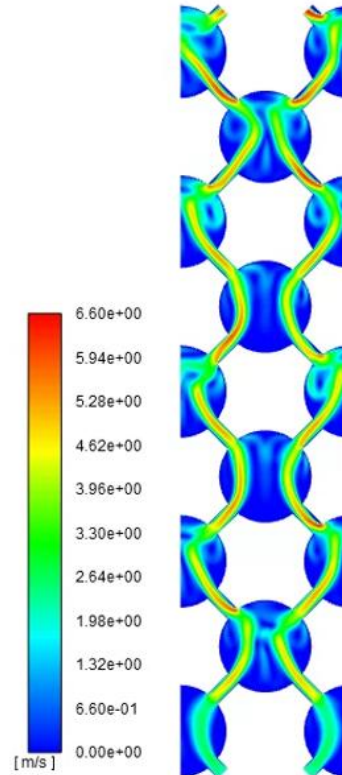
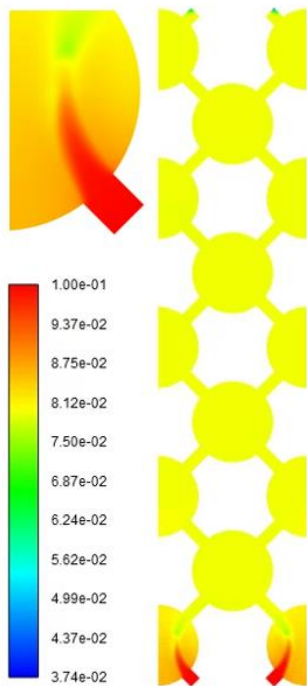
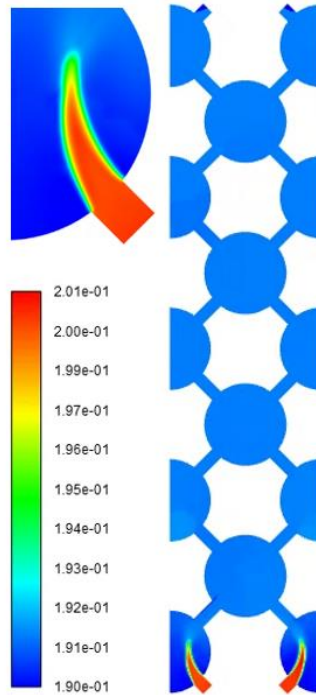
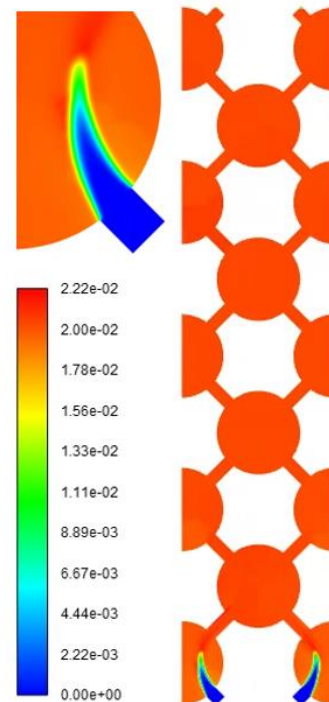
B1' – V.3.2.6

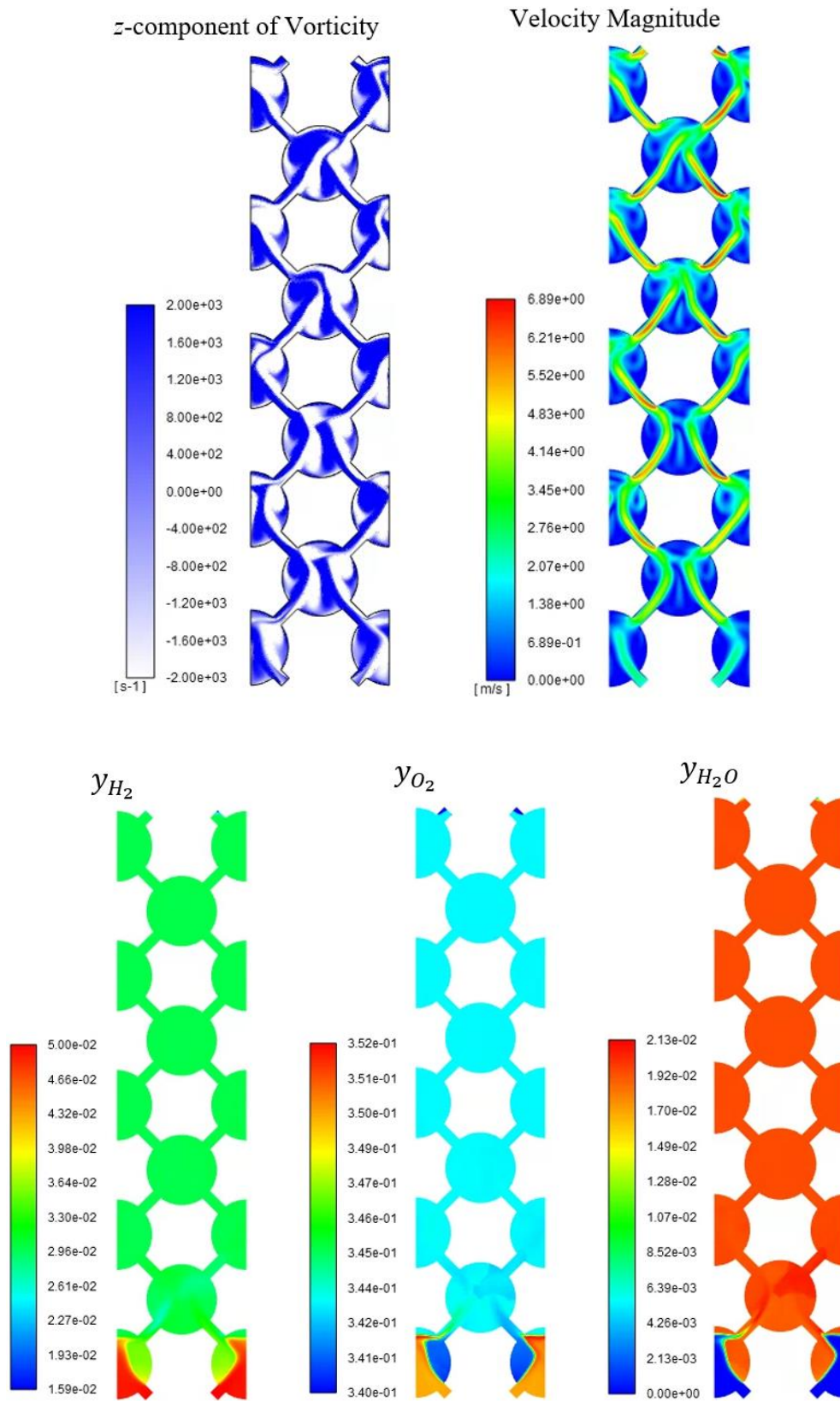
B4' – V.3.2.6

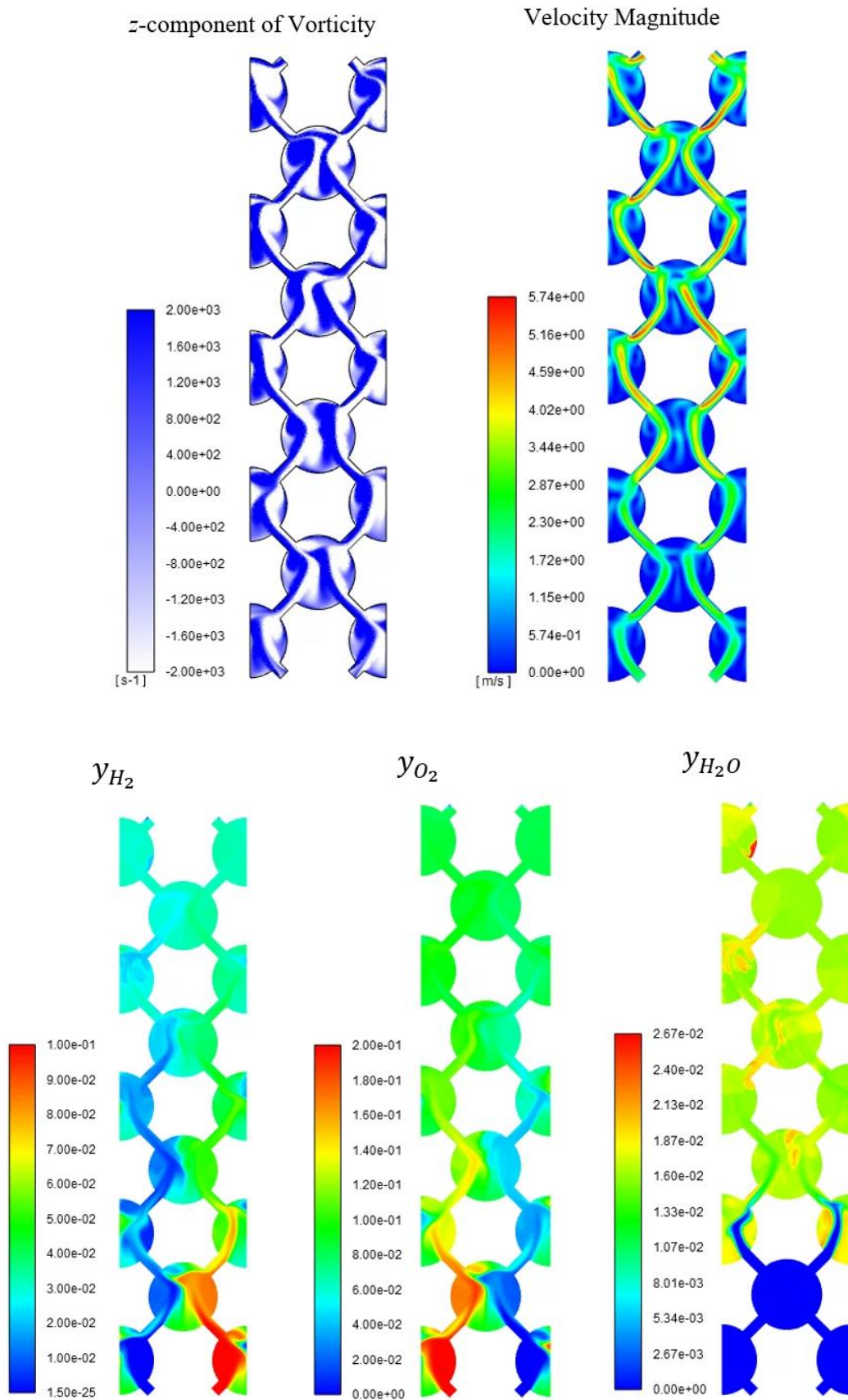
B5' – V.3.2.6

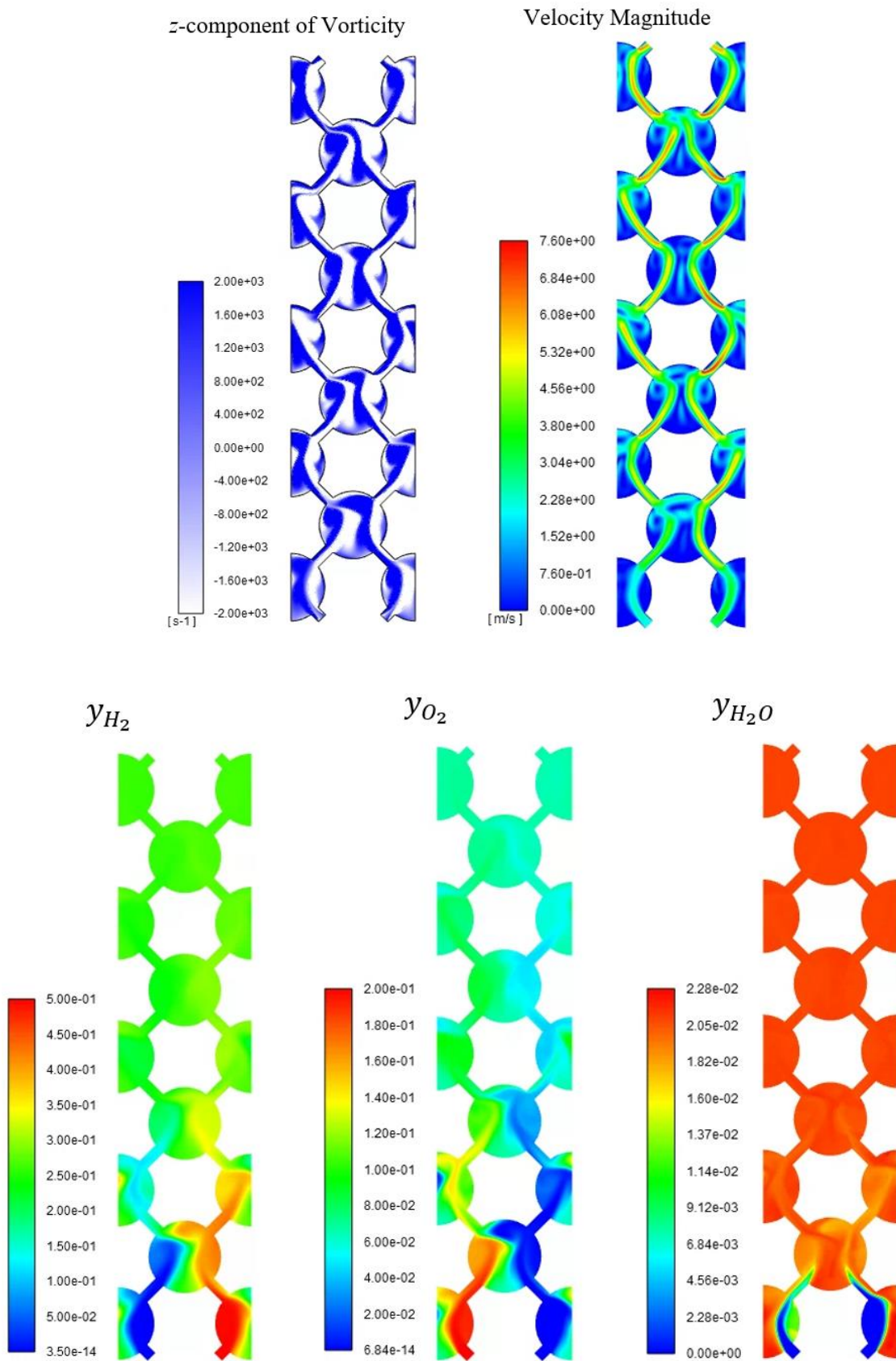
B7' – V.3.2.6 z -component of Vorticity

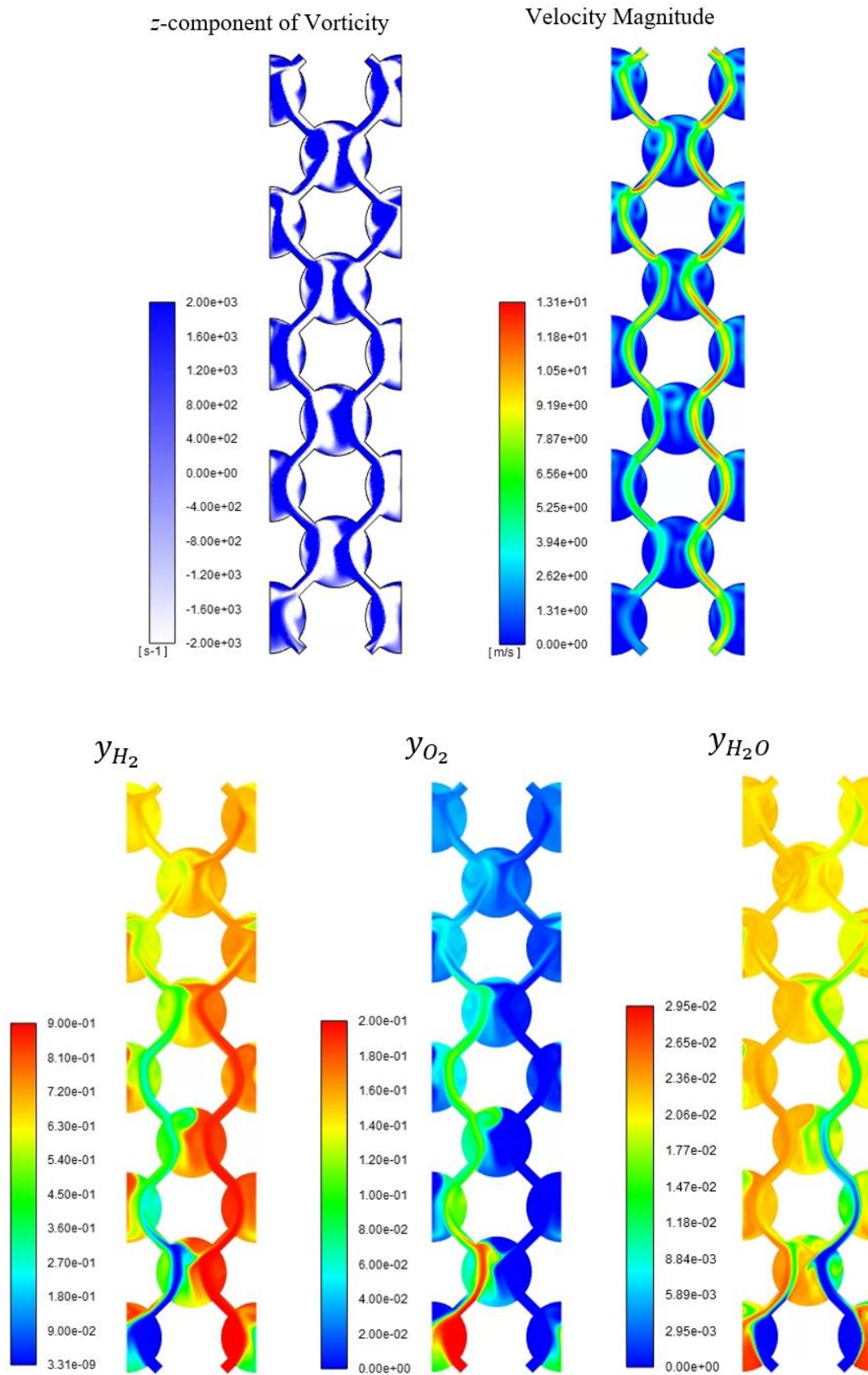
Velocity Magnitude

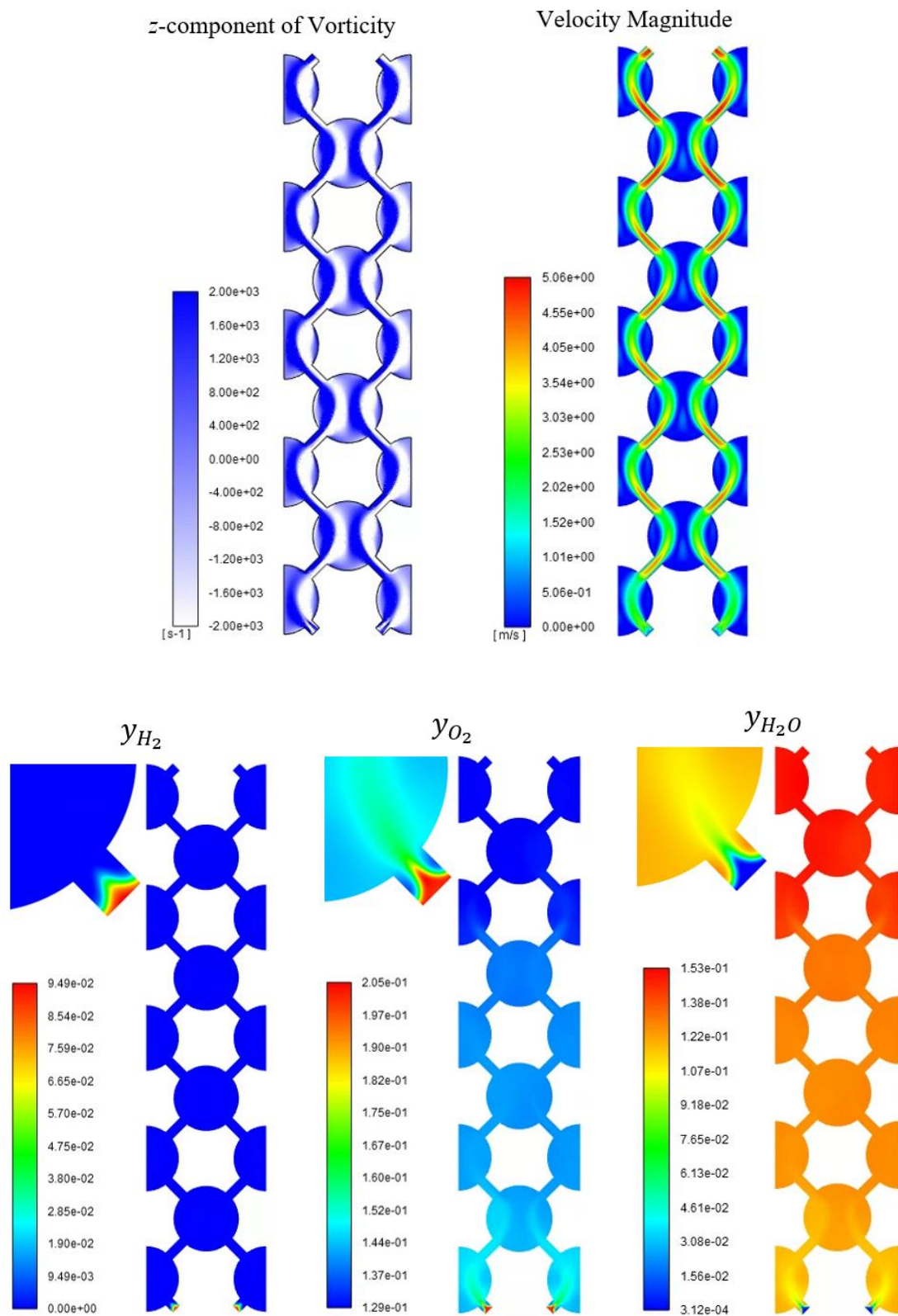
 y_{H_2}  y_{O_2}  y_{H_2O} 

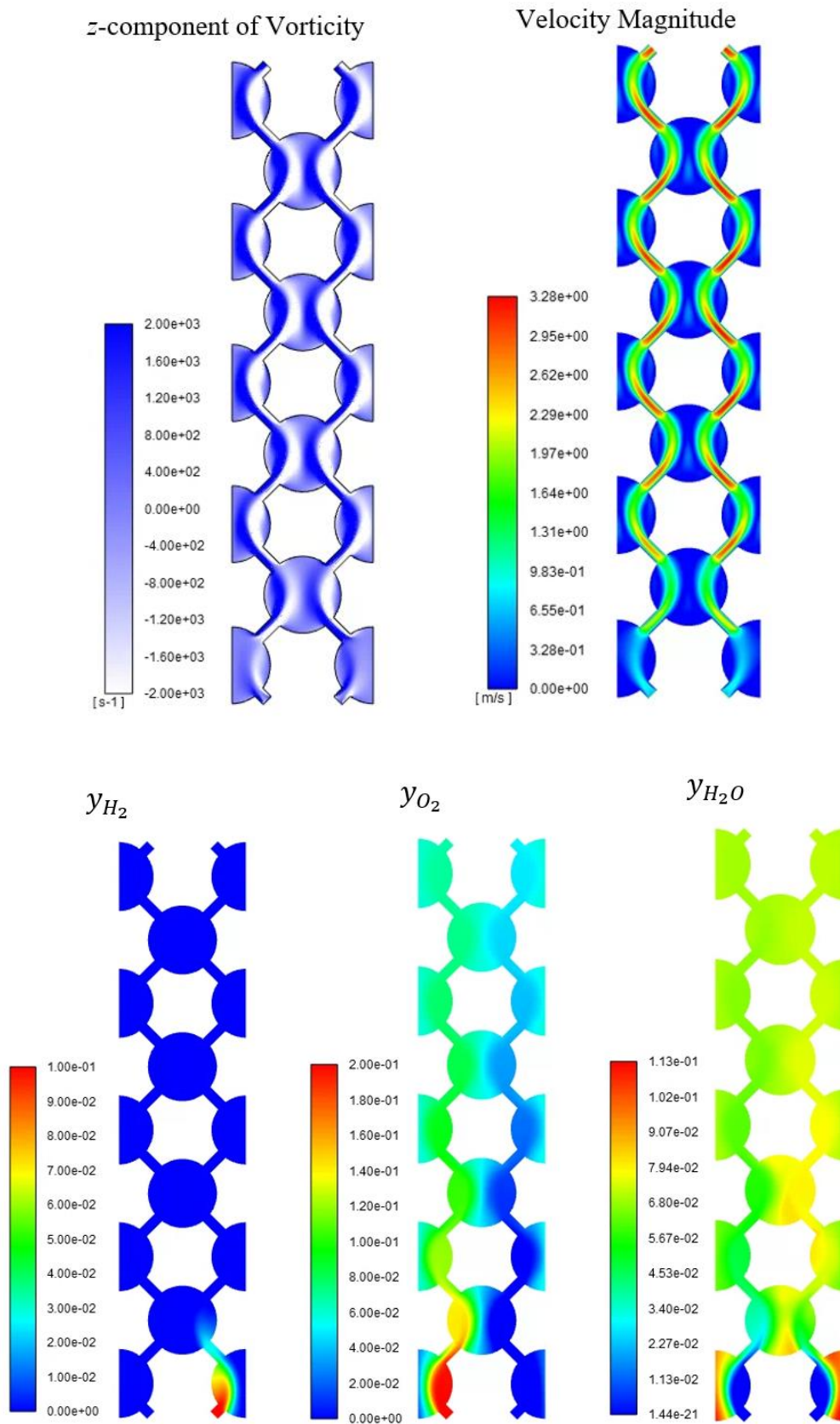
B9' – V.3.2.6

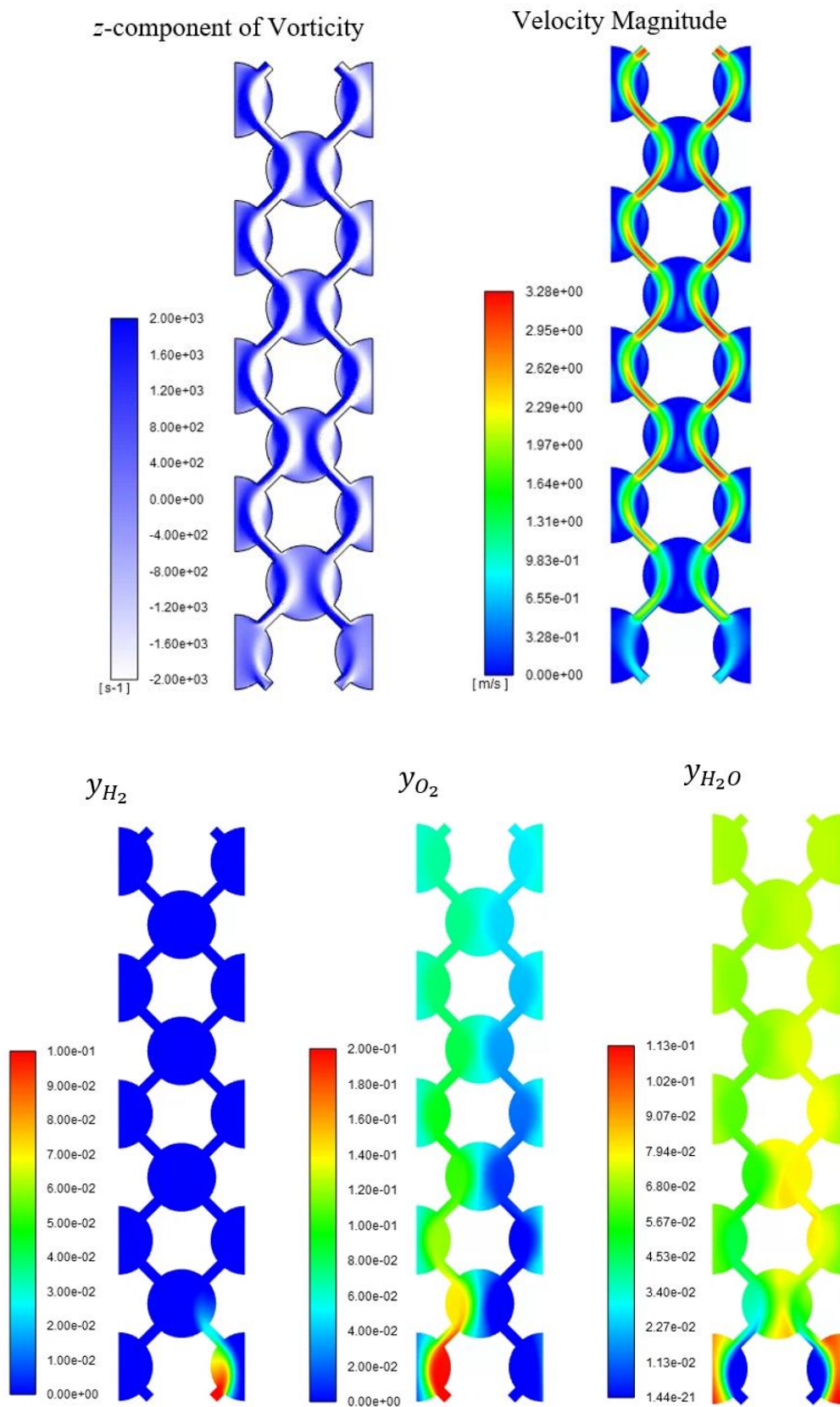
B10' – V.3.2.6


BII' – V.3.2.6

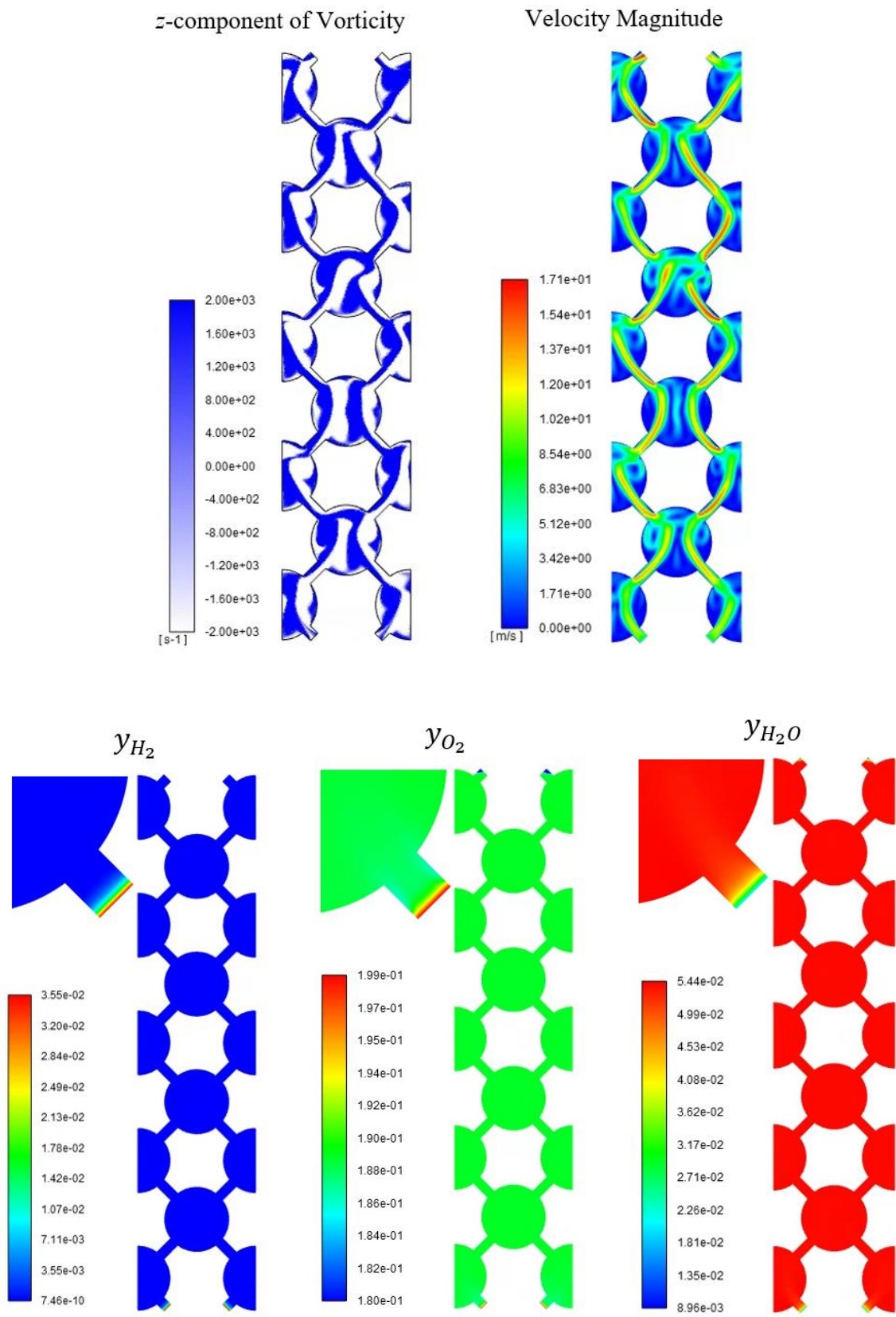
B12' – V.3.2.6

M2s – V.3.2.7


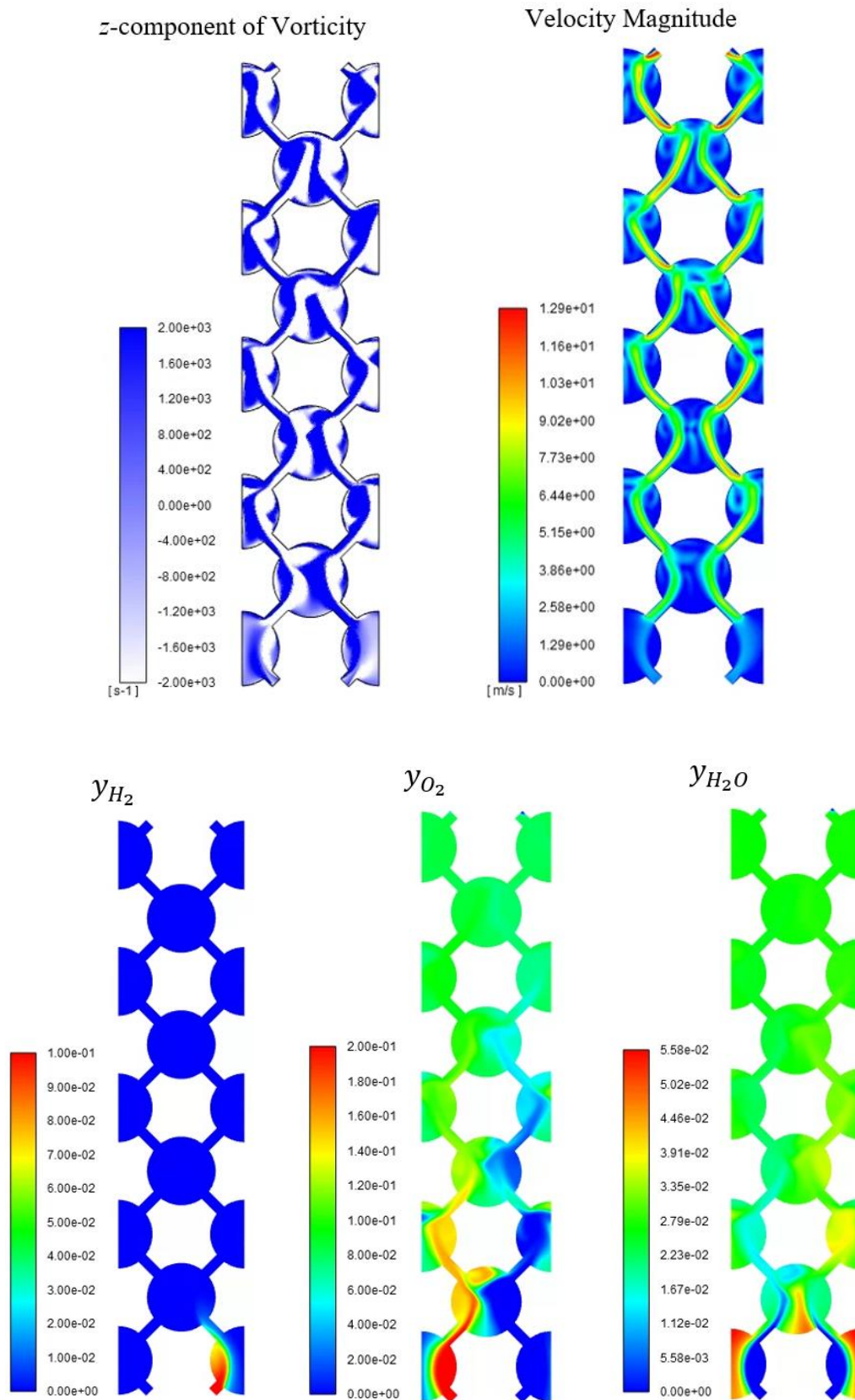
M4s – V.3.2.7

M4s – V.3.2.7

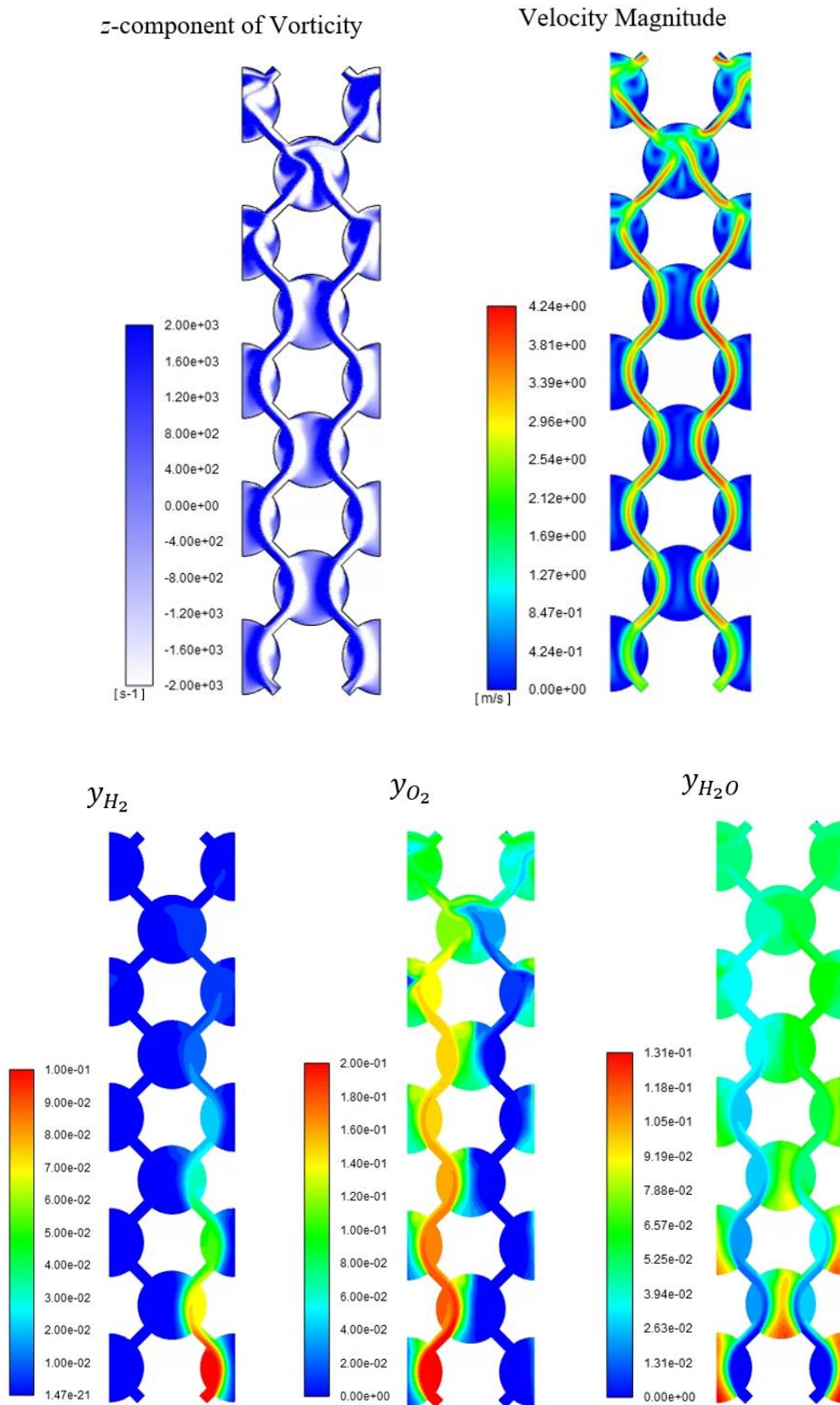
C1 – V.3.3

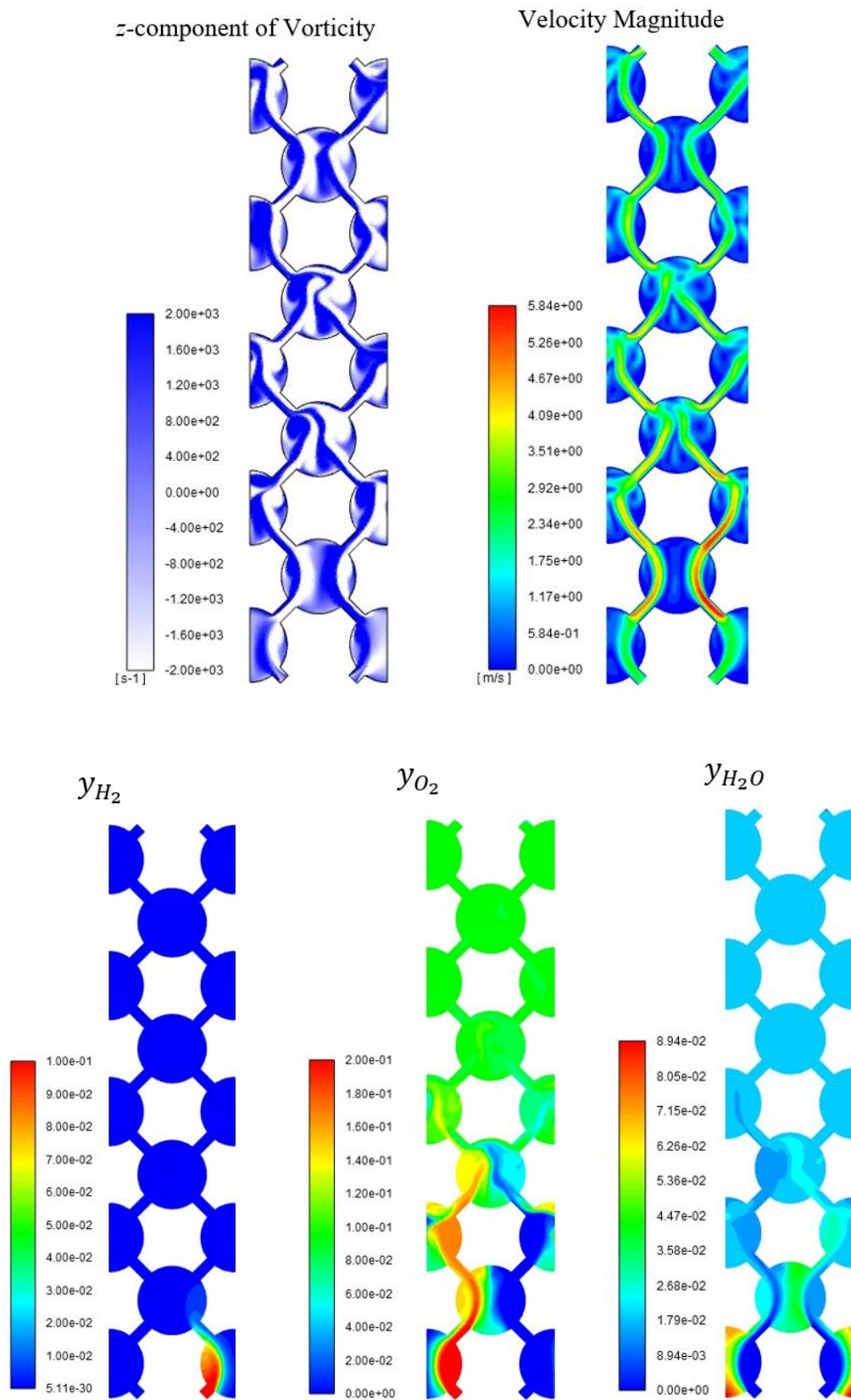


C2 – V.3.3



Q1 – VII.2.1



Q1c – VII.2.2


Appendix D – Listings of Computer Codes

D.1 CIJ Inlet Velocity Profile UDF

```
#include "udf.h"

DEFINE_PROFILE(v_in_yn,thread,index)
{
    real x[ND_ND] /*hold the position vector */
    face_t f;
    real t = CURRENT_TIME;

    /* Parameters
    real d      = 1.5E-3;
    real vmed = 4.0;
    real amp   = 0.5;
    real freq  = 83;
    real pi    = 3.1415926535897932385;
    real tau = (10.0E-3 * 50.0E-3) / (vmed * 2.0 * d);
    real a = 0.1; /* a - maximum amplitude: 10% of 1*/
    real b = 0.1; /* b - perturbation time: 10% of tau */

    begin_f_loop(f,thread)
    {
        F_CENTROID(x,f,thread);
        F_PROFILE(f,thread, index) = 1.5*vmed*(1.0- (x[0]/(d/2.0))
                                                *(x[0]/(d/2.0)));

        if(t/tau < b)
            F_PROFILE(f,thread, index) *= 1.0+a/2.0*(1.0-cos(t/(b*tau) *
                                                    2.0*pi));
        else
            F_PROFILE(f,thread, index) *= 1.0+amp*sin(2.0*pi*freq*t);
    }
    end_f_loop(f,thread)
}

DEFINE_PROFILE(v_in_yp,thread,index)
{
    real x[ND_ND];
    face_t f;
    real t = CURRENT_TIME;

    /* Parameters */
    real d      = 1.5E-3;
    real vmed = 4.0;
    real amp   = 0.5;
    real freq  = 83;
    real pi    = 3.1415926535897932385;
    real fi    = pi;
    real tau = (10.0E-3 * 50.0E-3) / (vmed * 2.0 * d);
```



```

real a = 0.1;
real b = 0.1;

begin_f_loop(f,thread)
{
    F_CENTROID(x,f,thread);
    F_PROFILE(f,thread, index) = 1.5*vmed*(1.0- (x[0]/(d/2.0))
                                                *(x[0]/(d/2.0)));

    if(t/tau > b)
        F_PROFILE(f,thread, index) *= 1.0+amp*sin(2.0*pi*freq*t+fi);
}
end_f_loop(f,thread)
}

```

D.2 Transform ASCII into Matlab Format

D.2.1 Transform a Set of Points at Each Iteration

```

%% Input variables
%nit - number of files to transform (iterations)
%nn - name of the first ASCII file to transform minus 10, e.g., "data-
40000-10"
%% Input files: ASCII files from CFD simulation

nit=200;
nn=40000-10;

cd('C:\Users\Admin\Documents');
folderName=strcat('data_matlab');
mkdir (folderName)

for i=1:nit
    i
    % Read ASCII file
    cd('C:\Users\Admin\Documents');
    fileName = strcat('data-',int2str(nn+10*i));
    A = dlmread(fileName, ',', 1, 1);
    xmin=min(A(:,1));
    xmax=max(A(:,1));
    ymin=min(A(:,2));
    ymax=max(A(:,2));

    %create vectors
    xa=A(:,1);
    ya=A(:,2);
    u=A(:,3);
    v=A(:,4);

    %create matrix
    dx = 0.0001; %tamanho da celula
    [x,y]=meshgrid(min(xa):dx:max(xa), min(ya):dx:max(ya));
    vx = griddata(xa,ya,u,x,y);
    vy = griddata(xa,ya,v,x,y);

    %Save .mat file

```

```

cd('C:\Users\Admin\Documents\data_matlab');
fileName = strcat('data-',int2str(i),'.mat');

save(fileName, 'x', 'y', 'vx', 'vy')
end

```

D.2.2 Plot of Histories

```

%% Input variables
%delat -time step size from CFD
%nit - number of files to transform (iterations)
%nn - name of the first ASCII file to transform minus 10, e.g., "data-
1000-10"
%% Input files: ASCII files from CFD simulation

delat=1.14e-4;
nit=15000-100;
nn=1000-10;
cd('C:\Users\Admin\Documents');

for i=1:nit
    i
    %Read ASCII file
    cd('C:\Users\Admin\Documents');
    fileName = strcat('data-',int2str(nn+10*i));
    A = dlmread(fileName, ',', 1, 1);

    %Create matrix for 3D simulation
    %x=A(1);a
    %y=A(2);
    %z=A(3);
    %vx(i)=A(4);
    %vy(i)=A(5);

    % Create matrix for 2D simulation
    %x=A(1);
    %y=A(2);
    vx(i)=A(3);
    vy(i)=A(4);
    vorticity(i)=A(5);
    strain(i)=A(6);

    t(i)=(nn+10)+(i-1)*10)*delat;
end

%Save file .mat with the history
cd('C:\Users\Admin\Documents');
save('data4', 't', 'vx', 'vy', 'vorticity', 'strain')

```

D.3 Transform Text into Excel Format

D.3.1 Change the Format of a Series of Data Points

'Example for temperature in chambers C2 C4 C6 C8

```

'Input Files: .out from Fluent

Sub data2()

'Directory to Save file
Dim pasta As String

pasta = "G:\combustao\NUB_combustion\H2_8_MULTI_NEW_Re100_steady"

'Open .out and save in .xlsx
'C2
Workbooks.OpenText Filename:=pasta & "\t_2.out" _
, Origin:=xlMSDOS, StartRow:=1, DataType:=xlDelimited,
TextQualifier:= _
xlDoubleQuote, ConsecutiveDelimiter:=True, Tab:=False,
Semicolon:=False, _
Comma:=False, Space:=True, Other:=False,
FieldInfo:=Array(Array(1, 1), _Array(2, 1), Array(3, 1)
, Array(4, 1)), TrailingMinusNumbers:=True
ActiveWorkbook.SaveAs Filename:=pasta & "\t_2.xlsx" _
, FileFormat:=xlOpenXMLWorkbook, CreateBackup:=False
ActiveWorkbook.Close SaveChanges:=False

'C4
Workbooks.OpenText Filename:=pasta & "\t_4.out" _
, Origin:=xlMSDOS, StartRow:=1, DataType:=xlDelimited,
TextQualifier:= _
xlDoubleQuote, ConsecutiveDelimiter:=True, Tab:=False,
Semicolon:=False, _
Comma:=False, Space:=True, Other:=False,
FieldInfo:=Array(Array(1, 1), _Array(2, 1), Array(3, 1)
, Array(4, 1)), TrailingMinusNumbers:=True
ActiveWorkbook.SaveAs Filename:=pasta & "\t_4.xlsx" _
, FileFormat:=xlOpenXMLWorkbook, CreateBackup:=False
ActiveWorkbook.Close SaveChanges:=False

'C6
Workbooks.OpenText Filename:=pasta & "\t_6.out" _
, Origin:=xlMSDOS, StartRow:=1, DataType:=xlDelimited,
TextQualifier:= _
xlDoubleQuote, ConsecutiveDelimiter:=True, Tab:=False,
Semicolon:=False, _
Comma:=False, Space:=True, Other:=False,
FieldInfo:=Array(Array(1, 1), _Array(2, 1), Array(3, 1)
, Array(4, 1)), TrailingMinusNumbers:=True
ActiveWorkbook.SaveAs Filename:=pasta & "\t_6.xlsx" _
, FileFormat:=xlOpenXMLWorkbook, CreateBackup:=False
ActiveWorkbook.Close SaveChanges:=False

'C8
Workbooks.OpenText Filename:=pasta & "\t_8.out" _
, Origin:=xlMSDOS, StartRow:=1, DataType:=xlDelimited,
TextQualifier:= _
xlDoubleQuote, ConsecutiveDelimiter:=True, Tab:=False,
Semicolon:=False, _
Comma:=False, Space:=True, Other:=False,
FieldInfo:=Array(Array(1, 1), _Array(2, 1), Array(3, 1)

```

```

        , Array(4, 1)), TrailingMinusNumbers:=True
ActiveWorkbook.SaveAs Filename:=pasta & "\t_8.xlsx" _
    , FileFormat:=xlOpenXMLWorkbook, CreateBackup:=False
ActiveWorkbook.Close SaveChanges:=False
End Sub

```

D.3.2 Plot of Histories

```

%Input Files: .xlsx from VBA

close all
clear all
clc

cd('C:\Users\Joana Matos\Documents\NUB_Combustion\H2_8_BACK')

deltat=7.45681e-06;

ii=1
tt=xlsread(' vx2', ' vx2', 'A4:A600000');
t=tt*deltat;

%Read Excel files
vx2=xlsread('vx2', 'vx2', 'B4:B600000');
vy2=xlsread('vy2', 'vy2', 'B4:B600000');
strain2=xlsread('strain2', 'strain2', 'B4:B600000');
vorticity2=xlsread('vorticity2', 'vorticity2', 'B4:B600000');

vx4=xlsread('vx4', 'vx4', 'B4:B600000');
vy4=xlsread('vy4', 'vy4', 'B4:B600000');
strain4=xlsread('strain4', 'strain4', 'B4:B600000');
vorticity4=xlsread('vorticity4', 'vorticity4', 'B4:B600000');

vx6=xlsread('vx6', 'vx', 'B4:B600000');
vy6=xlsread('vy6', 'v', 'B4:B600000');
strain6=xlsread('strain6', 'strain', 'B4:B600000');
vorticity6=xlsread('vorticity6', 'vorticity', 'B4:B600000');

vx8=xlsread('vx8', 'vx8', 'B4:B600000');
vy8=xlsread('vy8', 'vy8', 'B4:B600000');
strain8=xlsread('strain8', 'strain8', 'B4:B600000');
vorticity8=xlsread('vorticity8', 'vorticity8', 'B4:B600000');

ii=2
vx_r1=xlsread('vx_r1', 'vx_r1', 'B4:B600000');
vx_r2=xlsread('vx_r2', 'vx_r2', 'B4:B600000');
vx_r3=xlsread('vx_r3', 'vx_r3', 'B4:B600000');
vx_r4=xlsread('vx_r4', 'vx_r4', 'B4:B600000');
vx_r5=xlsread('vx_r5', 'vx_r5', 'B4:B600000');
vx_r6=xlsread('vx_r6', 'vx_r6', 'B4:B600000');
vx_r7=xlsread('vx_r7', 'vx_r7', 'B4:B600000');
vx_r8=xlsread('vx_r8', 'vx_r8', 'B4:B600000');

vx_l1=xlsread('vx_l1', 'vx_l1', 'B4:B600000');

```

```

vx_12=xlsread('vx_12','vx_12','B4:B600000');
vx_13=xlsread('vx_13','vx_13','B4:B600000');
vx_14=xlsread('vx_14','vx_14','B4:B600000');
vx_15=xlsread('vx_15','vx_15','B4:B600000');
vx_16=xlsread('vx_16','vx_16','B4:B600000');
vx_17=xlsread('vx_17','vx_17','B4:B600000');
vx_18=xlsread('vx_18','vx_18','B4:B600000');

ii=3
vy_r1=xlsread('vy_r1','vy_r1','B4:B600000');
vy_r2=xlsread('vy_r2','vy_r2','B4:B600000');
vy_r3=xlsread('vy_r3','vy_r3','B4:B600000');
vy_r4=xlsread('vy_r4','vy_r4','B4:B600000');
vy_r5=xlsread('vy_r5','vy_r5','B4:B600000');
vy_r6=xlsread('vy_r6','vy_r6','B4:B600000');
vy_r7=xlsread('vy_r7','vy_r7','B4:B600000');
vy_r8=xlsread('vy_r8','vy_r8','B4:B600000');

vy_l1=xlsread('vy_l1','vy_l1','B4:B600000');
vy_l2=xlsread('vy_l2','vy_l2','B4:B600000');
vy_l3=xlsread('vy_l3','vy_l3','B4:B600000');
vy_l4=xlsread('vy_l4','vy_l4','B4:B600000');
vy_l5=xlsread('vy_l5','vy_l5','B4:B600000');
vy_l6=xlsread('vy_l6','vy_l6','B4:B600000');
vy_l7=xlsread('vy_l7','vy_l7','B4:B600000');
vy_l8=xlsread('vy_l8','vy_l8','B4:B600000');

ii=4
strain_r1=xlsread('strain_r1','strain_r1','B4:B600000');
strain_r2=xlsread('strain_r2','strain_r2','B4:B600000');
strain_r3=xlsread('strain_r3','strain_r3','B4:B600000');
strain_r4=xlsread('strain_r4','strain_r4','B4:B600000');
strain_r5=xlsread('strain_r5','strain_r5','B4:B600000');
strain_r6=xlsread('strain_r6','strain_r6','B4:B600000');
strain_r7=xlsread('strain_r7','strain_r7','B4:B600000');
strain_r8=xlsread('strain_r8','strain_r8','B4:B600000');

strain_l1=xlsread('strain_l1','strain_l1','B4:B600000');
strain_l2=xlsread('strain_l2','strain_l2','B4:B600000');
strain_l3=xlsread('strain_l3','strain_l3','B4:B600000');
strain_l4=xlsread('strain_l4','strain_l4','B4:B600000');
strain_l5=xlsread('strain_l5','strain_l5','B4:B600000');
strain_l6=xlsread('strain_l6','strain_l6','B4:B600000');
strain_l7=xlsread('strain_l7','strain_l7','B4:B600000');
strain_l8=xlsread('strain_l8','strain_l8','B4:B600000');

ii=5
vorticity_r1=xlsread('vorticity_r1','vorticity_r1','B4:B600000');
vorticity_r2=xlsread('vorticity_r2','vorticity_r2','B4:B600000');
vorticity_r3=xlsread('vorticity_r3','vorticity_r3','B4:B600000');
vorticity_r4=xlsread('vorticity_r4','vorticity_r4','B4:B600000');
vorticity_r5=xlsread('vorticity_r5','vorticity_r5','B4:B600000');
vorticity_r6=xlsread('vorticity_r6','vorticity_r6','B4:B600000');
vorticity_r7=xlsread('vorticity_r7','vorticity_r7','B4:B600000');
vorticity_r8=xlsread('vorticity_r8','vorticity_r8','B4:B600000');

vorticity_l1=xlsread('vorticity_l1','vorticity_l1','B4:B600000');

```

```

vorticity_l2=xlsread('vorticity_l2','vorticity_l2','B4:B600000');
vorticity_l3=xlsread('vorticity_l3','vorticity_l3','B4:B600000');
vorticity_l4=xlsread('vorticity_l4','vorticity_l4','B4:B600000');
vorticity_l5=xlsread('vorticity_l5','vorticity_l5','B4:B600000');
vorticity_l6=xlsread('vorticity_l6','vorticity_l6','B4:B600000');
vorticity_l7=xlsread('vorticity_l7','vorticity_l7','B4:B600000');
vorticity_l8=xlsread('vorticity_l8','vorticity_l8','B4:B600000');

ii=6
T_2=xlsread('t_2','t_2_1_1','B4:B600000');
T_4=xlsread('t_4','t_4_1_1','B4:B600000');
T_6=xlsread('t_6','t_6_1_1','B4:B600000');
T_8=xlsread('t_8','t_8_1_1','B4:B600000');

T_r1=xlsread('t_r1','t_r1','B4:B600000');
T_r2=xlsread('t_r2','t_r2','B4:B600000');
T_r3=xlsread('t_r3','t_r3','B4:B600000');
T_r4=xlsread('t_r4','t_r4','B4:B600000');
T_r5=xlsread('t_r5','t_r5','B4:B600000');
T_r6=xlsread('t_r6','t_r6','B4:B600000');
T_r7=xlsread('t_r7','t_r7','B4:B600000');
T_r8=xlsread('t_r8','t_r8','B4:B600000');

T_l1=xlsread('t_l1','t_l1','B4:B600000');
T_l2=xlsread('t_l2','t_l2','B4:B600000');
T_l3=xlsread('t_l3','t_l3','B4:B600000');
T_l4=xlsread('t_l4','t_l4','B4:B600000');
T_l5=xlsread('t_l5','t_l5','B4:B600000');
T_l6=xlsread('t_l6','t_l6','B4:B600000');
T_l7=xlsread('t_l7','t_l7','B4:B600000');
T_l8=xlsread('t_l8','t_l8','B4:B600000');

i=7
xh2_2=xlsread('xh2_2','xh2_2','B4:B600000');
xh2_4=xlsread('xh2_4','xh2_4','B4:B600000');
xh2_6=xlsread('xh2_6','xh2_6','B4:B600000');
xh2_8=xlsread('xh2_8','xh2_8','B4:B600000');

xh2_r1=xlsread('xh2_r1','xh2_r1','B4:B600000');
xh2_r2=xlsread('xh2_r2','xh2_r2','B4:B600000');
xh2_r3=xlsread('xh2_r3','xh2_r3','B4:B600000');
xh2_r4=xlsread('xh2_r4','xh2_r4','B4:B600000');
xh2_r5=xlsread('xh2_r5','xh2_r5','B4:B600000');
xh2_r6=xlsread('xh2_r6','xh2_r6','B4:B600000');
xh2_r7=xlsread('xh2_r7','xh2_r7','B4:B600000');
xh2_r8=xlsread('xh2_r8','xh2_r8','B4:B600000');

xh2_l1=xlsread('xh2_l1','xh2_l1','B4:B600000');
xh2_l2=xlsread('xh2_l2','xh2_l2','B4:B600000');
xh2_l3=xlsread('xh2_l3','xh2_l3','B4:B600000');
xh2_l4=xlsread('xh2_l4','xh2_l4','B4:B600000');
xh2_l5=xlsread('xh2_l5','xh2_l5','B4:B600000');
xh2_l6=xlsread('xh2_l6','xh2_l6','B4:B600000');
xh2_l7=xlsread('xh2_l7','xh2_l7','B4:B600000');
xh2_l8=xlsread('xh2_l8','xh2_l8','B4:B600000');

```



```

i=8
xo2_2=xlsread('xo2_2','xo2_2','B4:B600000');
xo2_4=xlsread('xo2_4','xo2_4','B4:B600000');
xo2_6=xlsread('xo2_6','xo2_6','B4:B600000');
xo2_8=xlsread('xo2_8','xo2_8','B4:B600000');

xo2_r1=xlsread('xo2_r1','xo2_r1','B4:B600000');
xo2_r2=xlsread('xo2_r2','xo2_r2','B4:B600000');
xo2_r3=xlsread('xo2_r3','xo2_r3','B4:B600000');
xo2_r4=xlsread('xo2_r4','xo2_r4','B4:B600000');
xo2_r5=xlsread('xo2_r5','xo2_r5','B4:B600000');
xo2_r6=xlsread('xo2_r6','xo2_r6','B4:B600000');
xo2_r7=xlsread('xo2_r7','xo2_r7','B4:B600000');
xo2_r8=xlsread('xo2_r8','xo2_r8','B4:B600000');

xo2_l1=xlsread('xo2_l1','xo2_l1','B4:B600000');
xo2_l2=xlsread('xo2_l2','xo2_l2','B4:B600000');
xo2_l3=xlsread('xo2_l3','xo2_l3','B4:B600000');
xo2_l4=xlsread('xo2_l4','xo2_l4','B4:B600000');
xo2_l5=xlsread('xo2_l5','xo2_l5','B4:B600000');
xo2_l6=xlsread('xo2_l6','xo2_l6','B4:B600000');
xo2_l7=xlsread('xo2_l7','xo2_l7','B4:B600000');
xo2_l8=xlsread('xo2_l8','xo2_l8','B4:B600000');

ii=9
xn2_2=xlsread('xn2_2','xn2_2','B4:B600000');
xn2_4=xlsread('xn2_4','xn2_4','B4:B600000');
xn2_6=xlsread('xn2_6','xn2_6','B4:B600000');
xn2_8=xlsread('xn2_8','xn2_8','B4:B600000');

xn2_r1=xlsread('xn2_r1','xn2_r1','B4:B600000');
xn2_r2=xlsread('xn2_r2','xn2_r2','B4:B600000');
xn2_r3=xlsread('xn2_r3','xn2_r3','B4:B600000');
xn2_r4=xlsread('xn2_r4','xn2_r4','B4:B600000');
xn2_r5=xlsread('xn2_r5','xn2_r5','B4:B600000');
xn2_r6=xlsread('xn2_r6','xn2_r6','B4:B600000');
xn2_r7=xlsread('xn2_r7','xn2_r7','B4:B600000');
xn2_r8=xlsread('xn2_r8','xn2_r8','B4:B600000');

xn2_l1=xlsread('xn2_l1','xn2_l1','B4:B600000');
xn2_l2=xlsread('xn2_l2','xn2_l2','B4:B600000');
xn2_l3=xlsread('xn2_l3','xn2_l3','B4:B600000');
xn2_l4=xlsread('xn2_l4','xn2_l4','B4:B600000');
xn2_l5=xlsread('xn2_l5','xn2_l5','B4:B600000');
xn2_l6=xlsread('xn2_l6','xn2_l6','B4:B600000');
xn2_l7=xlsread('xn2_l7','xn2_l7','B4:B600000');
xn2_l8=xlsread('xn2_l8','xn2_l8','B4:B600000');
ii=10
xh2o_2=xlsread('xh2o_2','xh2o_2','B4:B600000');
xh2o_4=xlsread('xh2o_4','xh2o_4','B4:B600000');
xh2o_6=xlsread('xh2o_6','xh2o_6','B4:B600000');
xh2o_8=xlsread('xh2o_8','xh2o_8','B4:B600000');

xh2o_r1=xlsread('xh2o_r1','xh2o_r1','B4:B600000');
xh2o_r2=xlsread('xh2o_r2','xh2o_r2','B4:B600000');
xh2o_r3=xlsread('xh2o_r3','xh2o_r3','B4:B600000');
xh2o_r4=xlsread('xh2o_r4','xh2o_r4','B4:B600000');

```

```

xh2o_r5=xlsread('xh2o_r5','xh2o_r5','B4:B600000');
xh2o_r6=xlsread('xh2o_r6','xh2o_r6','B4:B600000');
xh2o_r7=xlsread('xh2o_r7','xh2o_r7','B4:B600000');
xh2o_r8=xlsread('xh2o_r8','xh2o_r8','B4:B600000');

xh2o_l1=xlsread('xh2o_l1','xh2o_l1','B4:B600000');
xh2o_l2=xlsread('xh2o_l2','xh2o_l2','B4:B600000');
xh2o_l3=xlsread('xh2o_l3','xh2o_l3','B4:B600000');
xh2o_l4=xlsread('xh2o_l4','xh2o_l4','B4:B600000');
xh2o_l5=xlsread('xh2o_l5','xh2o_l5','B4:B600000');
xh2o_l6=xlsread('xh2o_l6','xh2o_l6','B4:B600000');
xh2o_l7=xlsread('xh2o_l7','xh2o_l7','B4:B600000');
xh2o_l8=xlsread('xh2o_l8','xh2o_l8','B4:B600000');

save('data1')

%Plot in centre of C2 C4 C6 and C8
for i=2:2:8
    i
    vx=eval(['vx' num2str(i)]);
    vy=eval(['vy' num2str(i)]);
    strain=eval(['strain' num2str(i)]);
    vorticity=eval(['vorticity' num2str(i)]);
    T=eval(['T' num2str(i)]);
    xh2o=eval(['xh2o_' num2str(i)]);
    xo2=eval(['xo2_' num2str(i)]);
    xn2=eval(['xn2_' num2str(i)]);
    xh2=eval(['xh2_' num2str(i)]);

    figure1=figure
    axes1 = axes('Parent',figure1,'FontSize',17);
    box(axes1,'on');
    hold(axes1,'all');
    plot(t(1:length(vx2)),vx(1:length(vx2)),'b')
    grid on
    grid minor
    xlabel('\it iteration','LineWidth',2,'FontSize',19);
    ylabel('\itv_x \rm(m/s)','LineWidth',2,'FontSize',19);

    saveas(gcf,['vx_',num2str(i)],'tif')

    figure1=figure
    axes1 = axes('Parent',figure1,'FontSize',17);
    box(axes1,'on');
    hold(axes1,'all');
    plot(t(1:length(vx2)),vy(1:length(vx2)),'b')
    curtick = get(gca, 'XTick');
    set(gca, 'XTick', unique(round(curtick)))
    grid on
    grid minor
    xlabel('\it iteration','LineWidth',2,'FontSize',19);
    ylabel('\itv_y \rm(m/s)','LineWidth',2,'FontSize',19);

    saveas(gcf,['vy_',num2str(i)],'tif')

```

```

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(1:length(vx2)),vorticity(1:length(vx2)),'b')
grid on
grid minor
xlabel('\it t \rm (s)','LineWidth',2,'FontSize',19);
ylabel('\it vorticity \rm (s^{-1})','LineWidth',2,'FontSize',19);

saveas(gcf,['vorticity_',num2str(i)],'tif')

```

```

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(1:length(vx2)),strain(1:length(vx2)),'b')
grid on
grid minor
xlabel('\it t \rm (s)','LineWidth',2,'FontSize',19);
ylabel('\it strain \rm (s^{-1})','LineWidth',2,'FontSize',19);

saveas(gcf,['strain_',num2str(i)],'tif')

```

```

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(1:length(xh2)),xh2o(1:length(xh2)),'b')
grid on
grid minor
xlabel('\it t \rm (s)','LineWidth',2,'FontSize',19);
ylabel('\it x_{H_2}_O','LineWidth',2,'FontSize',19);
ylim([0 1])

saveas(gcf,['xh2o_',num2str(i)],'tif')

```

```

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(1:length(xh2)),xo2(1:length(xh2)),'b')
grid on
grid minor
xlabel('\it t \rm (s)','LineWidth',2,'FontSize',19);
ylabel('\it x_{O_2}','LineWidth',2,'FontSize',19);
ylim([0 1])

saveas(gcf,['xo2_',num2str(i)],'tif')

```

```

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');

```

```

hold(axes1,'all');
plot(t(1:length(xh2)),xn2(1:length(xh2)),'b')
grid on
grid minor
xlabel('\it t \rm (s)','LineWidth',2,'FontSize',19);
ylabel('\it x_{N_2}','LineWidth',2,'FontSize',19);
ylim([0 1])

saveas(gcf,['xn2_',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(1:length(xh2)),xh2(1:length(xh2)),'b')
grid on
grid minor
xlabel('\it t \rm (s)','LineWidth',2,'FontSize',19);
ylabel('\it x_{H_2}','LineWidth',2,'FontSize',19);
ylim([0 1])

saveas(gcf,['xh2_',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(1:length(vx2)),T(1:length(vx2)),'b')
grid on
grid minor
xlabel('\it t \rm (s)','LineWidth',2,'FontSize',19);
ylabel('\it T \rm (K)','LineWidth',2,'FontSize',19);

saveas(gcf,['T_',num2str(i)],'tif')

clear vx vy vorticity strain xch4 xco xco2 xh2o xn2 xo2 T
end

save('data2')

close all

%Plot in left channels
for i=1:8
    i
    vx=eval(['vx_1' num2str(i)]);
    vy=eval(['vy_1' num2str(i)]);
    strain=eval(['strain_1' num2str(i)]);
    vorticity=eval(['vorticity_1' num2str(i)]);
    T=eval(['T_1' num2str(i)]);
    xh2o=eval(['xh2o_1' num2str(i)]);
    xo2=eval(['xo2_1' num2str(i)]);
    xn2=eval(['xn2_1' num2str(i)]);
    xh2=eval(['xh2_1' num2str(i)]);

```

```

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(1:length(vx2)),vx(1:length(vx2)),'b')
grid on
grid minor
xlabel('\it t \rm (s)','LineWidth',2,'FontSize',19);
ylabel('\itv_x \rm(m/s)','LineWidth',2,'FontSize',19);

saveas(gcf,['vx_1',num2str(i)],'tif')
figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(1:length(vx2)),vy(1:length(vx2)),'b')
grid on
grid minor
xlabel('\it t \rm (s)','LineWidth',2,'FontSize',19);
ylabel('\itv_y \rm(m/s)','LineWidth',2,'FontSize',19);

saveas(gcf,['vy_1',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(1:length(vx2)),vorticity(1:length(vx2)),'b')
grid on
grid minor
xlabel('\it t \rm (s)','LineWidth',2,'FontSize',19);
ylabel('\it vorticity \rm(s^-1)','LineWidth',2,'FontSize',19);

saveas(gcf,['vorticity_1',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(1:length(vx2)),strain(1:length(vx2)),'b')
grid on
grid minor
xlabel('\it t \rm (s)','LineWidth',2,'FontSize',19);
ylabel('\it strain \rm (s^-1)','LineWidth',2,'FontSize',19);

saveas(gcf,['strain_1',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(1:length(vx2)),xh2o(1:length(vx2)),'b')
grid on
grid minor

```

```

xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\it x_{H_2}_O', 'LineWidth', 2, 'FontSize', 19);
ylim([0 1])

saveas(gcf, ['xh2o_1', num2str(i)], 'tif')

figure1=figure
axes1 = axes('Parent', figure1, 'FontSize', 17);
box(axes1, 'on');
hold(axes1, 'all');
plot(t(1:length(vx2)), xo2(1:length(vx2)), 'b')
grid on
grid minor
xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\it x_{O_2}', 'LineWidth', 2, 'FontSize', 19);
ylim([0 1])

saveas(gcf, ['xo2_1', num2str(i)], 'tif')

figure1=figure
axes1 = axes('Parent', figure1, 'FontSize', 17);
box(axes1, 'on');
hold(axes1, 'all');
plot(t(1:length(vx2)), xn2(1:length(vx2)), 'b')
grid on
grid minor
xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\it x_{N_2}', 'LineWidth', 2, 'FontSize', 19);
ylim([0 1])

saveas(gcf, ['xn2_1', num2str(i)], 'tif')

figure1=figure
axes1 = axes('Parent', figure1, 'FontSize', 17);
box(axes1, 'on');
hold(axes1, 'all');
plot(t(1:length(vx2)), xh2(1:length(vx2)), 'b')
grid on
grid minor
xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\it x_{H_2}', 'LineWidth', 2, 'FontSize', 19);
ylim([0 1])

saveas(gcf, ['xh2_1', num2str(i)], 'tif')

figure1=figure
axes1 = axes('Parent', figure1, 'FontSize', 17);
box(axes1, 'on');
hold(axes1, 'all');
plot(t(1:length(vx2)), T(1:length(vx2)), 'b')
grid on
grid minor
xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);

```



```

ylabel('\it T \rm(K)', 'LineWidth', 2, 'FontSize', 19);
%ylim([0 1])

saveas(gcf, ['T_1', num2str(i)], 'tif')

clear vx vy vorticity strain xch4 xco xco2 xh2o xn2 xo2 T
end

save('data3')

close all

% Plot in the right channels
for i=1:8
    i
    vx=eval(['vx_r' num2str(i)]);
    vy=eval(['vy_r' num2str(i)]);
    strain=eval(['strain_r' num2str(i)]);
    vorticity=eval(['vorticity_r' num2str(i)]);
    T=eval(['T_r' num2str(i)]);
    xh2o=eval(['xh2o_r' num2str(i)]);
    xo2=eval(['xo2_r' num2str(i)]);
    xn2=eval(['xn2_r' num2str(i)]);
    xh2=eval(['xh2_r' num2str(i)]);

    figure1=figure
    axes1 = axes('Parent',figure1,'FontSize',17);
    box(axes1,'on');
    hold(axes1,'all');
    plot(t(1:length(vx2)),vx(1:length(vx2)),'b')
    grid on
    grid minor
    xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
    ylabel('\itv_x \rm(m/s)', 'LineWidth', 2, 'FontSize', 19);

    saveas(gcf, ['vx_r', num2str(i)], 'tif')

    figure1=figure
    axes1 = axes('Parent',figure1,'FontSize',17);
    box(axes1,'on');
    hold(axes1,'all');
    plot(t(1:length(vx2)),vy(1:length(vx2)),'b')
    grid on
    grid minor
    xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
    ylabel('\itv_y \rm(m/s)', 'LineWidth', 2, 'FontSize', 19);

    saveas(gcf, ['vy_r', num2str(i)], 'tif')

    figure1=figure
    axes1 = axes('Parent',figure1,'FontSize',17);
    box(axes1,'on');
    hold(axes1,'all');
    plot(t(1:length(vx2)),vorticity(1:length(vx2)),'b')

```

```

grid on
grid minor
xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\it vorticity \rm (s^{-1})', 'LineWidth', 2, 'FontSize', 19);

saveas(gcf, ['vorticity_r', num2str(i)], 'tif')

figure1=figure
axes1 = axes('Parent', figure1, 'FontSize', 17);
box(axes1, 'on');
hold(axes1, 'all');
plot(t(1:length(vx2)), strain(1:length(vx2)), 'b')
grid on
grid minor
xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\it strain \rm (s^{-1})', 'LineWidth', 2, 'FontSize', 19);

saveas(gcf, ['strain_r', num2str(i)], 'tif')

figure1=figure
axes1 = axes('Parent', figure1, 'FontSize', 17);
box(axes1, 'on');
hold(axes1, 'all');
plot(t(1:length(vx2)), xh2o(1:length(vx2)), 'b')
grid on
grid minor
xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\it x_{H_2}_O', 'LineWidth', 2, 'FontSize', 19);
ylim([0 1])

saveas(gcf, ['xh2o_r', num2str(i)], 'tif')

figure1=figure
axes1 = axes('Parent', figure1, 'FontSize', 17);
box(axes1, 'on');
hold(axes1, 'all');
plot(t(1:length(vx2)), xo2(1:length(vx2)), 'b')
grid on
grid minor
xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\it x_{O_2}', 'LineWidth', 2, 'FontSize', 19);
ylim([0 1])

saveas(gcf, ['xo2_r', num2str(i)], 'tif')

figure1=figure
axes1 = axes('Parent', figure1, 'FontSize', 17);
box(axes1, 'on');
hold(axes1, 'all');
plot(t(1:length(vx2)), xn2(1:length(vx2)), 'b')
grid on
grid minor

```

```

xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\it x_{N_2}', 'LineWidth', 2, 'FontSize', 19);
ylim([0 1])

saveas(gcf, ['xn2_r', num2str(i)], 'tif')

figure1=figure
axes1 = axes('Parent', figure1, 'FontSize', 17);
box(axes1, 'on');
hold(axes1, 'all');
plot(t(1:length(vx2)), xh2(1:length(vx2)), 'b')
grid on
grid minor
xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\it x_{H_2}', 'LineWidth', 2, 'FontSize', 19);
ylim([0 1])

saveas(gcf, ['xh2_r', num2str(i)], 'tif')

figure1=figure
axes1 = axes('Parent', figure1, 'FontSize', 17);
box(axes1, 'on');
hold(axes1, 'all');
plot(t(1:length(vx2)), T(1:length(vx2)), 'b')
grid on
grid minor
xlabel('\it t \rm (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\it T \rm (K)', 'LineWidth', 2, 'FontSize', 19);
%ylim([0 1])

saveas(gcf, ['T_r', num2str(i)], 'tif')
clear vx vy vorticity strain xch4 xco xco2 xh2o xn2 xo2 T
end

save('data4')
close all

```

D.4 Lagrangian Mixing Simulation (LMS) Algorithm

D.4.1 LMS with One Series Applied to the Confined Impinging Jets (CIJ) Reactor

```

%% Input Files: velocity fields .mat from CFD simulation (see C.2.1)
%% Input variables
%ddxdy - maximum distance between two consecutive particles
%dt     - CFD time step size multiplied by 10
%np     - initial number of particles
%s0     - length of the inlet
%ti     - initial time (iteration)
%tmax   - maximum number of iterations

ddxdy=0.0001;
dt=8.3e-6*10;
np=18;

```

```

s0=1.5e-3;
ti=1;
tmax=192;

%Start program
t=ti;

%load the first file from CFD simulation
cd('C:\Users\Admin\Documents');
file=strcat('data-', num2str(t), '.mat');
load(file)

%load the first velocity field
vx(isnan(vx))=0;
vy(isnan(vy))=0;

%% Particle Injection
% TOP inlet
xpp(1)=min(x(1,:))+0.01/2-1.5e-3/2;
xpp(np)=xpp(1)+1.5e-3;

ypp(1)=max(y(:,1))-0.00001;
ypp(np)=ypp(1);

dd=(xpp(np)-xpp(1))/np;
for i=2:np-1
    xpp(i)=xpp(i-1)+dd;
    ypp(i)=ypp(1);
end

%% Plot the first figure
figure1 = figure();%'visible','off');
axes1 = axes('Parent',figure1,...
    'Position',[0.05 0.4 0.9 0.25]);
box(axes1,'on');
hold(axes1,'all');
quiver(x,y,vx,vy,'color','white','AutoScaleFactor',1)
%set(gca,'TickLength',[0 0])
set(gca,'xtick',[])
xlim([-5e-3 4.5e-2])
%set(gca,'TickLength',[0 0])
set(gca,'ytick',[])
ylim([-5e-3 5e-3])
hold on
plot(xpp,ypp,'b-')
hold off

saveas(gcf,['t_',num2str(t)], 'tif')

%% Run iterations 2 to tmax
clear d dd e ee

for t=ti+1:tmax
    t
    xppold=xpp;
    yppold=ypp;

```

```

%insert new particles
dx2=abs(xpp(1:np-1)-xpp(2:np));
dy2=abs(ypp(1:np-1)-ypp(2:np));
dxdy2=sqrt(dx2.^2+dy2.^2);
A=find(dxdy2>ddxdy);
if A~=0
    AA=length(A);
    xxpp=(xpp(A)+xpp(A+1))/2;
    yypp=(ypp(A)+ypp(A+1))/2;
    for i=AA:-1:1
        if i==AA
            xppnew_rjs=
                =[xpp(1:A(i)),xxpp(i),xpp(A(i)+1:length(xpp))];

            yppnew_rjs=
                =[ypp(1:A(i)),yypp(i),ypp(A(i)+1:length(ypp))];
        else
            xppnew_rjs=[xppnew_rjs(1:A(i)),xxpp(i),...
                ... xppnew_rjs(A(i)+1:length(xppnew_rjs))];
            yppnew_rjs=[yppnew_rjs(1:A(i)),yypp(i),...
                ... yppnew_rjs(A(i)+1:length(yppnew_rjs))];
        end
    end
end

if A~=0
    np=length(xppnew_rjs);
    xpp=xppnew_rjs;
    ypp=yppnew_rjs;
    xppold=xpp;
    yppold=ypp;
end

%load new velocity field
cd('C:\Users\matos\Documents');
file=strcat('data-', num2str(t), '.mat');
load(file)
vx(isnan(vx))=0;
vy(isnan(vy))=0;

%recalculate particle's positions with interp2
vxpp(2:np-1)=interp2(x,y,vx,xpp(2:np-1),ypp(2:np-1),'spline');
vypp(2:np-1)=interp2(x,y,vy,xpp(2:np-1),ypp(2:np-1),'spline');
xpp(2:np-1)=xppold(2:np-1)+vxpp(2:np-1)*dt;
ypp(2:np-1)=yppold(2:np-1)+vypp(2:np-1)*dt;

%Keep position at the wall
B=find(xpp>max(x(1,:)));
C=find(xpp<min(x(1,:)));
D=find(ypp>max(y(:,1)));
E=find(ypp<min(y(:,1)));
if B~=0
    xpp(B)=max(x(1,:));
end
if C~=0

```

```

        xpp(C)=min(x(1,:));
    end
    if D~=0
        ypp(D)=max(y(:,1));
    end
    if E~=0
        ypp(E)=min(y(:,1));
    end

    % calculate interfacial area generation: s/s0
    dx=abs(xpp(1:np-1)-xpp(2:np));
    dy=abs(ypp(1:np-1)-ypp(2:np));
    dxdy=sqrt(dx.^2+dy.^2);
    s(t)=sum(dxdy);
    timee(t)=t*dt;
    alfa(t)=s(t)/s0;

    %% plot figure
    quiver(x,y,vx,vy,'color','white','AutoScaleFactor',1)
    set(gca,'xtick',[])
    %set(gca,'TickLength',[0 0])
    xlim([-5e-3 4.5e-2])
    set(gca,'ytick',[])
    %set(gca,'TickLength',[0 0])
    ylim([-5e-3 5e-3])
    hold on
    plot(xpp,ypp,'b-')
    hold off
    saveas(gcf,['t_',num2str(t)],'tif')
end

```

D.4.2 LMS with Two Series Applied to One Chamber of the NETmix Reactor

```

%% Input Files: Velocity fields .mat from CFD simulation (see C.2.1)
%% Input variables
%ddxdy - maximum distance between two consecutive particles
%dt      - CFD time step size multiplied by 10
%np      - initial number of particles at the left inlet
%np3     - initial number of particles at the right inlet
%s0      - length of the inlet
%ti      - initial time (iteration)
%tmax    - maximum number of iterations

ddxdy=0.0001;
dt=1.14e-4*10;
np=18;
np3=18;
s0=0.001;
ti=1;
tmax=500;

%Start program
t=ti;

%load first file

```



```

cd('C:\Users\Admin\Desktop');
file=strcat('data-',num2str(t),'.mat');
load(file)

%load first velocity field
vx(isnan(vx))==0;
vy(isnan(vy))==0;

%% Particle Injection
% left side
xpp(1)=0.003653575;
xpp(np)= 0.004177331;
ddx=abs(xpp(np)-xpp(1))/np;

ypp(1)=0.02900029;
ypp(np)=0.02848549;
ddy=abs(ypp(np)-ypp(1))/np;

for i=2:np-1
    xpp(i)=xpp(i-1)+ddx;
    ypp(i)=ypp(i-1)-ddy;
end

%right side
xpp3(1)=0.008241201;
xpp3(np3)=0.00877391;
ddx3=abs(xpp3(np3)-xpp3(1))/np3;

ypp3(1)=0.02848995;
ypp3(np3)=0.02901371;
ddy3=abs(ypp3(np3)-ypp3(1))/np3;

for i=2:np3-1
    xpp3(i)=xpp3(i-1)+ddx3;
    ypp3(i)=ypp3(i-1)+ddy3;
end

%% Plot first figure
figure1 = figure();
axes1 = axes('Parent',figure1,...
    'Position',[0.257601351351351 0.126385809312639 0.581047804370981
0.793154420572418]);
hold(axes1,'all');
quiver(x,y,vx,vy,'color','white','AutoScaleFactor',1)
xlim([0.002 0.01])
ylim([0.027 0.035])
hold on
plot(xpp,ypp,'b-')
hold on
plot(xpp3,ypp3,'r-')
hold off

cd('C:\Users\Admin\Desktop');
cd(folderName)
saveas(gcf,['t_',num2str(t)],'tif')

```

```

%% Run iterations 2 to tmax
clear d dd e ee

for t=ti+1:tmax
    t

    xppold=xpp;
    yppold=ypp;
    xppold3=xpp3;
    yppold3=ypp3;

    %insert new particles
    %left
    dx2=abs(xpp(1:np-1)-xpp(2:np));
    dy2=abs(ypp(1:np-1)-ypp(2:np));
    dxdy2=sqrt(dx2.^2+dy2.^2);
    A=find(dxdy2>ddxdy);
    if A~=0
        AA=length(A);
        xxpp=(xpp(A)+xpp(A+1))/2;
        yypp=(ypp(A)+ypp(A+1))/2;
        for i=AA:-1:1
            if i==AA
                xppnew_rjs=
                    [xpp(1:A(i)),xxpp(i),xpp(A(i)+1:length(xpp))];
                yppnew_rjs=
                    [ypp(1:A(i)),yypp(i),ypp(A(i)+1:length(ypp))];
            else
                xppnew_rjs=[xppnew_rjs(1:A(i)),xxpp(i), ...
                    ... xppnew_rjs(A(i)+1:length(xppnew_rjs))];
                yppnew_rjs=[yppnew_rjs(1:A(i)),yypp(i), ...
                    ... yppnew_rjs(A(i)+1:length(yppnew_rjs))];
            end
        end
    end
end

if A~=0
    np=length(xppnew_rjs);
    xpp=xppnew_rjs;
    ypp=yppnew_rjs;
    xppold=xpp;
    yppold=ypp;
end

clear dx2 dy2 dxdy2 A AA xxpp yypp xppnew_rjs yppnew_rjs

%right
dx2=abs(xpp3(1:np3-1)-xpp3(2:np3));
dy2=abs(ypp3(1:np3-1)-ypp3(2:np3));
dxdy2=sqrt(dx2.^2+dy2.^2);
A=find(dxdy2>ddxdy);
if A~=0
    AA=length(A);
    xxpp=(xpp3(A)+xpp3(A+1))/2;
    yypp=(ypp3(A)+ypp3(A+1))/2;
end

```

```

for i=AA:-1:1
    if i==AA
        xppnew_rjs=[xpp3(1:A(i))
                    ,xxpp(i),xpp3(A(i)+1:length(xpp3))];
        yppnew_rjs=[ypp3(1:A(i))
                    ,yypp(i),ypp3(A(i)+1:length(ypp3))];
    else
        xppnew_rjs=[xppnew_rjs(1:A(i)),xxpp(i), ...
                    ... xppnew_rjs(A(i)+1:length(xppnew_rjs))];
        yppnew_rjs=[yppnew_rjs(1:A(i)),yypp(i), ...
                    ... yppnew_rjs(A(i)+1:length(yppnew_rjs))];
    end
end
end

if A~=0
    np3=length(xppnew_rjs);
    xpp3=xppnew_rjs;
    ypp3=yppnew_rjs;
    xppold3=xpp3;
    yppold3=ypp3;
end

clear dx2 dy2 dxdy2 A AA xxpp yypp xppnew_rjs yppnew_rjs

%load new file
tolddd=t;
cd('C:\Users\Admin\Desktop\data_sym6_all\data_matlab');
file=strcat('data-',num2str(t),'.mat');
load(file)%,'-mat')
vx(isnan(vx))=0;
vy(isnan(vy))=0;
clear t
t=tolddd;

%recalculate particle's positions with interp2
%left
vxpp(2:np-1)=interp2(x,y,vx,xpp(2:np-1),ypp(2:np-1),'spline');
vypp(2:np-1)=interp2(x,y,vy,xpp(2:np-1),ypp(2:np-1),'spline');
xpp(2:np-1)=xppold(2:np-1)+vxpp(2:np-1)*dt;
ypp(2:np-1)=yppold(2:np-1)+vypp(2:np-1)*dt;

%right
vxpp3(2:np3-1)=interp2(x,y,vx,xpp3(2:np3-1),ypp3(2:np3-1),
                        'spline');
vypp3(2:np3-1)=interp2(x,y,vy,xpp3(2:np3-1),ypp3(2:np3-1),
                        'spline');
xpp3(2:np3-1)=xppold3(2:np3-1)+vxpp3(2:np3-1)*dt;
ypp3(2:np3-1)=yppold3(2:np3-1)+vypp3(2:np3-1)*dt;

%Keep position at the walls
%left
B=find(xpp>max(x(1,:)));
C=find(xpp<min(x(1,:)));
D=find(ypp>max(y(:,1)));
E=find(ypp<min(y(:,1)));
if B~=0

```

```

        xpp(B)=max(x(1,:));
    end
    if C~=0
        xpp(C)=min(x(1,:));
    end
    if D~=0
        ypp(D)=max(y(:,1));
    end
    if E~=0
        ypp(E)=min(y(:,1));
    end

    clear B C D E

    %right
    B=find(xpp3>max(x(1,:)));
    C=find(xpp3<min(x(1,:)));
    D=find(ypp3>max(y(:,1)));
    E=find(ypp3<min(y(:,1)));
    if B~=0
        xpp3(B)=max(x(1,:));
    end
    if C~=0
        xpp3(C)=min(x(1,:));
    end
    if D~=0
        ypp3(D)=max(y(:,1));
    end
    if E~=0
        ypp3(E)=min(y(:,1));
    end

    clear B C D E

    %calculate interfacial area generation: s/s0
    %left
    dx=abs(xpp(1:np-1)-xpp(2:np));
    dy=abs(ypp(1:np-1)-ypp(2:np));
    dxdy=sqrt(dx.^2+dy.^2);
    s(t)=sum(dxdy);
    timee(t)=t*dt;
    alfa(t)=s(t)/s0;

    clear dx dy dxdy

    %right
    dx=abs(xpp3(1:np3-1)-xpp3(2:np3));
    dy=abs(ypp3(1:np3-1)-ypp3(2:np3));
    dxdy=sqrt(dx.^2+dy.^2);
    s3(t)=sum(dxdy);
    timee(t)=t*dt;
    alfa3(t)=s3(t)/s0;

    clear dx dy dxdy

```

```

%% Plot figure

quiver(x,y,vx,vy,'color','white','AutoScaleFactor',1)
set(gca,'xtick',[])
xlim([0.002 0.01])
set(gca,'ytick',[])
ylim([0.027 0.035])
hold on
plot(xpp,ypp,'b-')
hold on
plot(xpp3,ypp3,'r-')
hold off
cd('C:\Users\Admin\Desktop\data_sym6_all\data_matlab');

cd(folderName)
saveas(gcf,['t_',num2str(t)],'tif')
end

```

D.5 Diffusive Lagrangian Mixing Simulation (DLMS) Algorithm

```

%% Input Files: velocity fields .mat from CFD simulation (see C.2.1)
%% Input variables
%distancia - radius of the circle within which the striation thickness
              is calculated
%distancia2 - striation thickness value below which the particles are
              deleted
%distancia3 - maximum distance between consecutive particles in each
              series
%ddxdy - maximum distance between two consecutive particles
%dt - CFD time step size multiplied by 10
%fatorcanto - minimum number of particles at the tips to have blob
              formation
%fatormd - minimum number of particles between consecutive blob
%mdgap - number of particles below/above which the blobs are
          joined
%np - initial number of particles
%s0 - length of the inlet
%ti - initial time (iteration)
%tmax - maximum number of iterations

distancia=1e-4;
distancia2=1e-6;
distancia3=1.5e-3;
ddxdy=0.0001
dt=8.3e-5;
fatorcanto=20;
fatormd=500;
mdgap=6;
ndgap=mdgap;
np=18;
s0=1.5e-3;
ti=1;
tmax=200;

```

```

%Start program
ti=1;
pathname='C:\Users\Admin\Desktop';
cd (pathname);
folderName=strcat('DLMS',num2str(ti));
mkdir (folderName)

%load first velocity field
cd (pathname);
file=strcat('data-',num2str(t),'.mat');
load(file)
vx(isnan(vx))=0;
vy(isnan(vy))=0;

%% Particle Injection
%Top inlet
xpp(1)=min(x(1,:))+0.01/2-1.5e-3/2;
xpp(np)=xpp(1)+1.5e-3;

ypp(1)=max(y(:,1))-0.00001;
ypp(np)=ypp(1);

dd=(xpp(np)-xpp(1))/np;
for i=2:np-1
    xpp(i)=xpp(i-1)+dd;
    ypp(i)=ypp(1);
end

%% Placement of Particles over the node values;

for i=1:np
    a(:,i)=abs(x(1,:)-xpp(i)); %finds all the distances between xpp and
                                the nodes
    [d(i),dd(i)]=min(a(:,i)); %finds the closest node to position xpp
    b(:,i)=abs(y(:,1)-ypp(i)); %finds all the distances between ypp and
                                the nodes
    [e(i),ee(i)]=min(b(:,i)); %finds the closest node to position ypp
    vxpp(i)=vx(ee(i),dd(i)); %calculates the initial vector of
                              x-velocity
    vypp(i)=vy(ee(i),dd(i)); %calculates the initial vector of
                              y-velocity
end

%%
%Plot first figure
figure1 = figure();
axes1 = axes('Parent',figure1,...
    'Position',[0.05 0.4 0.9 0.25]);
box(axes1,'on');
hold(axes1,'all');
quiver(x,y,vx,vy,'color','white','AutoScaleFactor',1)
set(gca,'xtick',[])
xlim([-5e-3 4.5e-2])
set(gca,'ytick',[])
ylim([-5e-3 5e-3])
hold on

```



```

plot(xpp,ypp,'b-')
hold off

cd (pathname);
cd(folderName)

saveas(gcf,['t_',num2str(t)],'tif')

%% Run for iteration 2 to tmax
clear d dd e ee

AVISOXpp1=0; % no series yet

for t=ti+1:tmax
    t
    time(t)=t*dt; %calculates flow time

    if AVISOXpp1==0
        xppold=xpp;
        yppold=ypp;
        vxppold=vxpp;
        vyppold=vypp;

        %insert new particles
        dx2=abs(xpp(1:np-1)-xpp(2:np));
        dy2=abs(ypp(1:np-1)-ypp(2:np));
        dxdy2=sqrt(dx2.^2+dy2.^2);
        A=find(dxdy2>ddxdy);
        if A~=0
            AA=length(A);
            xxpp=(xpp(A)+xpp(A+1))/2;
            yypp=(ypp(A)+ypp(A+1))/2;
            vvxxpp=vxpp(A)-(xpp(A)-xxpp).*(vxpp(A)-vxpp(A+1))/(xpp(A)-xpp(A+1));
            vvyypp=vypp(A)-(ypp(A)-yypp).*(vypp(A)-vypp(A+1))/(ypp(A)-ypp(A+1));
            for i=AA:-1:1
                if i==AA
                    xppnew_rjs=[xpp(1:A(i)),
                                xxpp(i),xpp(A(i)+1:length(xpp))];
                    yppnew_rjs=[ypp(1:A(i)),
                                yypp(i),ypp(A(i)+1:length(ypp))];
                    vyppnew_rjs=[vypp(1:A(i)),
                                vvyypp(i),vypp(A(i)+1:length(vypp))];
                    vxppnew_rjs=[vxpp(1:A(i)),
                                vvxxpp(i),vxpp(A(i)+1:length(vxpp))];
                else
                    xppnew_rjs=[xppnew_rjs(1:A(i)),xxpp(i), ...
                                ... xppnew_rjs(A(i)+1:length(xppnew_rjs))];
                    yppnew_rjs=[yppnew_rjs(1:A(i)),yypp(i), ...
                                ... yppnew_rjs(A(i)+1:length(yppnew_rjs))];
                    vyppnew_rjs=[vyppnew_rjs(1:A(i)),vvyypp(i), ...
                                ... vyppnew_rjs(A(i)+1:length(vyppnew_rjs))];
                    vxppnew_rjs=[vxppnew_rjs(1:A(i)),vvxxpp(i), ...
                                ... vxppnew_rjs(A(i)+1:length(vxppnew_rjs))];
                end
            end
        end
    end
end

```

```

end

if A~=0
    np=length(xppnew_rjs);
    xpp=xppnew_rjs;
    ypp=yppnew_rjs;
    vxpp=vxppnew_rjs;
    vypp=vyppnew_rjs;
    xppold=xpp;
    yppold=ypp;
    vxppold=vxpp;
    vyppold=vypp;
end

else % AVISOxpp1 = 1 if there are series
    xppold1=xpp1;
    yppold1=ypp1;
    vxppold1=vxpp1;
    vyppold1=vypp1;

clear xpp ypp xppnew_rjs yppnew_rjs dx2 dy2 dxdy2 A AA xxpp yypp

for jj=1:length(xpp1)
    xpp=[xpp1{jj}];
    ypp=[ypp1{jj}];
    vxpp=[vxpp1{jj}];
    vypp=[vypp1{jj}];
    np=length(xpp);
    dx2=abs(xpp(1:np-1)-xpp(2:np));
    dy2=abs(ypp(1:np-1)-ypp(2:np));
    dxdy2=sqrt(dx2.^2+dy2.^2);
    A=find(dxdy2>ddxdy);
    if A~=0
        AA=length(A);
        xxpp=(xpp(A)+xpp(A+1))/2;
        yypp=(ypp(A)+ypp(A+1))/2;
        vxpp=(vxpp(A)+vxpp(A+1))/2;
        vypp=(vypp(A)+vypp(A+1))/2;

        for i=AA:-1:1
            if i==AA
                xppnew_rjs=[xpp(1:A(i)),
                             xxpp(i),xpp(A(i)+1:length(xpp))];
                yppnew_rjs=[ypp(1:A(i)),
                             yypp(i),ypp(A(i)+1:length(ypp))];
                vyppnew_rjs=[vypp(1:A(i)),
                             vvypp(i),vypp(A(i)+1:length(vypp))];
                vxppnew_rjs=[vxpp(1:A(i)),
                             vvxxpp(i),vxpp(A(i)+1:length(vxpp))];
            else
                xppnew_rjs=[xppnew_rjs(1:A(i)),xxpp(i), ...
                             ... xppnew_rjs(A(i)+1:length(xppnew_rjs))];
                yppnew_rjs=[yppnew_rjs(1:A(i)),yypp(i), ...
                             ... yppnew_rjs(A(i)+1:length(yppnew_rjs))];
                vyppnew_rjs=[vyppnew_rjs(1:A(i)),vvypp(i), ...
                             ... vyppnew_rjs(A(i)+1:length(vyppnew_rjs))];
                vxppnew_rjs=[vxppnew_rjs(1:A(i)),vvxxpp(i), ...

```

```

        ... vxppnew_rjs(A(i)+1:length(vxppnew_rjs))] ;
    end
end
end

if A~=0
    xpp1{jj}=[];
    ypp1{jj}=[];
    vxpp1{jj}=[];
    vypp1{jj}=[];
    xppold1{jj}=[];
    yppold1{jj}=[];
    vxppold1{jj}=[];
    vyppold1{jj}=[];
    np1{jj}=[];
    np1{jj}=length(xppnew_rjs);
    xpp=xppnew_rjs;
    ypp=yppnew_rjs;
    vxpp=vxppnew_rjs;
    vypp=vyppnew_rjs;
    xpp1{jj}=xpp;
    ypp1{jj}=ypp;
    vxpp1{jj}=vxpp;
    vypp1{jj}=vypp;
    xppold=xpp;
    yppold=ypp;
    vxppold=vxpp;
    vyppold=vypp;
    xppold1{jj}=xppold;
    yppold1{jj}=yppold;
    vxppold1{jj}=vxppold;
    vyppold1{jj}=vyppold;

else
    xpp1{jj}=xpp1{jj};
    ypp1{jj}=ypp1{jj};
    vxpp1{jj}=vxpp1{jj};
    vypp1{jj}=vypp1{jj};
    xppold1{jj}=xppold1{jj};
    yppold1{jj}=yppold1{jj};
    vxppold1{jj}=vxppold1{jj};
    vyppold1{jj}=vyppold1{jj};
    np1{jj}=np1{jj};
end
clear xpp ypp xppnew_rjs yppnew_rjs dx2 dy2 dxdy2 A AA xxpp
      yypp xppold yppold
end
clear xpp ypp xppold yppold np vxppold vyppold

xpp=[xpp1{1:end}];
ypp=[ypp1{1:end}];
xppold=[xppold1{1:end}];
yppold=[yppold1{1:end}];
vxppold=[vxppold1{1:end}];
vyppold=[vyppold1{1:end}];
npj=[np1{1:end}];
np=sum(npj);

```

```

end

%load new velocity field
cd (pathname);
file=strcat('data-',num2str(t),'.mat')
load(file)
vx(isnan(vx))=0;
vy(isnan(vy))=0;
clear t

%recalculate particle's positions with first order interpolation
if AVISOxpp1==0
    for i=2:np-1
        xpp(i)=xppold(i)+vxpold(i)*dt;
        a=abs(x(1,:)-xpp(i));
        for j=1:2
            [d(j),dd(j)] = min(a);
            if j==2
                break
            end
            a(dd) = [];
        end
        if dd(1)==dd(2);
            dd(1)=dd(1)+1;
        end

        ypp(i)=yppold(i)+vypold(i)*dt;
        b=abs(y(:,1)-ypp(i));
        for j=1:2
            [e(j),ee(j)] = min(b);
            if j==2
                break
            end
            b(ee) = [];
        end
        if ee(1)==ee(2)
            ee(1)=ee(1)+1;
        end

        vxp(1)=vx(max(ee),min(dd));
        vxp(2)=vx(min(ee),max(dd));
        vxp(3)=vx(max(ee),max(dd));
        vxp(4)=vx(min(ee),min(dd));
        vyp(1)=vy(max(ee),min(dd));
        vyp(2)=vy(min(ee),max(dd));
        vyp(3)=vy(max(ee),max(dd));
        vyp(4)=vy(min(ee),min(dd));

        ux=vxp(4)-(vxp(4)-vxp(1))*(y(min(ee),1)-ypp(i))/(y(min(ee),1)-
            y(max(ee),1));
        uxx=vxp(2)-(vxp(2)-vxp(3))*(y(min(ee),1)-
            ypp(i))/(y(min(ee),1)-y(max(ee),1));
        vxpp(i)=ux-(ux-uxx)*(x(1,min(dd))-xpp(i))/(x(1,min(dd))-
            x(1,max(dd)));
        uy=vyp(4)-(vyp(4)-vyp(1))*(y(min(ee),1)-ypp(i))/(y(min(ee),1)-
            y(max(ee),1));
        uyy=vyp(2)-(vyp(2)-vyp(3))*(y(min(ee),1)-

```

```

        ypp(i)/(y(min(ee),1)-y(max(ee),1));
        vypp(i)=uy-(uy-uyy)*(x(1,min(dd))-xpp(i))/(x(1,min(dd))-
            x(1,max(dd)));
    end

else
    for jj=1:length(xpp1)
        clear xpp ypp xppold yppold vxpp vypp vxppold yppold
        xpp=[xpp1{jj}];
        ypp=[ypp1{jj}];
        vxpp=[vxpp1{jj}];
        vypp=[vypp1{jj}];
        xppold=[xppold1{jj}];
        yppold=[yppold1{jj}];
        vxppold=[vxppold1{jj}];
        vyppold=[vyppold1{jj}];

        clear np
        np=[np1{jj}];

        if jj==1
            xppp1=xpp(1);
            xpppn=xpp(np);
            yppp1=ypp(1);
            ypppn=ypp(np);
            vxppp1=vxpp(1);
            vxpppn=vxpp(np);
            vyppp1=vypp(1);
            vypppn=vypp(np);

            clear vxpp vypp xpp ypp

            for i=2:np-1
                xpp(i)=xppold(i)+vxppold(i)*dt;
                a=abs(x(1,:)-xpp(i));
                for j=1:2
                    [d(j),dd(j)] = min(a);
                    if j==2
                        break
                    end
                    a(dd) = [];
                end
                if dd(1)==dd(2);
                    dd(1)=dd(1)+1;
                end

                ypp(i)=yppold(i)+vyppold(i)*dt;
                b=abs(y(:,1)-ypp(i));
                for j=1:2
                    [e(j),ee(j)] = min(b);
                    if j==2
                        break
                    end
                    b(ee) = [];
                end
                if ee(1)==ee(2)
                    ee(1)=ee(1)+1;

```

```

end

vxp(1)=vx(max(ee),min(dd));
vxp(2)=vx(min(ee),max(dd));
vxp(3)=vx(max(ee),max(dd));
vxp(4)=vx(min(ee),min(dd));
vyp(1)=vy(max(ee),min(dd));
vyp(2)=vy(min(ee),max(dd));
vyp(3)=vy(max(ee),max(dd));
vyp(4)=vy(min(ee),min(dd));

ux=vxp(4)-(vxp(4)-vxp(1))*(y(min(ee),1)-ypp(i)) ...
.../(y(min(ee),1)-y(max(ee),1));
uxx=vxp(2)-(vxp(2)-vxp(3))*(y(min(ee),1)-ypp(i)) ...
.../(y(min(ee),1)-y(max(ee),1));
vxpp(i)=ux-(ux-uxx)*(x(1,min(dd))-xpp(i)) ...
.../(x(1,min(dd))-x(1,max(dd)));
uy=vyp(4)-(vyp(4)-vyp(1))*(y(min(ee),1)-ypp(i)) ...
.../(y(min(ee),1)-y(max(ee),1));
uyy=vyp(2)-(vyp(2)-vyp(3))*(y(min(ee),1)-ypp(i)) ...
.../(y(min(ee),1)-y(max(ee),1));
vypp(i)=uy-(uy-uyy)*(x(1,min(dd))-xpp(i)) ...
.../(x(1,min(dd))-x(1,max(dd)));
end

xpp(1)=xppp1;
ypp(1)=yppp1;
vxpp(1)=vxppp1;
vypp(1)=vyppp1;
xpp=[xpp,xpppn];
ypp=[ypp,ypppn];
vxpp=[vxpp,vxpppn];
vypp=[vypp,vypppn];

else
for i=1:np
xpp(i)=xppold(i)+vxppold(i)*dt;
a=abs(x(1,:)-xpp(i));
for j=1:2
[d(j),dd(j)] = min(a);
if j==2
break
end
a(dd) = [];
end
if dd(1)==dd(2);
dd(1)=dd(1)+1;
end

ypp(i)=yppold(i)+vyppold(i)*dt;
b=abs(y(:,1)-ypp(i));
for j=1:2
[e(j),ee(j)] = min(b);
if j==2
break
end
b(ee) = [];

```



```

        end
        if ee(1)==ee(2)
            ee(1)=ee(1)+1;
        end

        vxp(1)=vx(max(ee),min(dd));
        vxp(2)=vx(min(ee),max(dd));
        vxp(3)=vx(max(ee),max(dd));
        vxp(4)=vx(min(ee),min(dd));
        vyp(1)=vy(max(ee),min(dd));
        vyp(2)=vy(min(ee),max(dd));
        vyp(3)=vy(max(ee),max(dd));
        vyp(4)=vy(min(ee),min(dd));

        ux=vxp(4)-(vxp(4)-vxp(1))*(y(min(ee),1)-ypp(i)) ...
            .../(y(min(ee),1)-y(max(ee),1));
        uxx=vxp(2)-(vxp(2)-vxp(3))*(y(min(ee),1)-ypp(i)) ...
            .../(y(min(ee),1)-y(max(ee),1));
        vxpp(i)=ux-(ux-uxx)*(x(1,min(dd))-xpp(i)) ...
            .../(x(1,min(dd))-x(1,max(dd)));
        uy=vyp(4)-(vyp(4)-vyp(1))*(y(min(ee),1)-ypp(i)) ...
            .../(y(min(ee),1)-y(max(ee),1));
        uyy=vyp(2)-(vyp(2)-vyp(3))*(y(min(ee),1)-ypp(i)) ...
            .../(y(min(ee),1)-y(max(ee),1));
        vypp(i)=uy-(uy-uyy)*(x(1,min(dd))-xpp(i)) ...
            .../(x(1,min(dd))-x(1,max(dd)));
    end

end

xpp1{jj}=[];
ypp1{jj}=[];
vxpp1{jj}=[];
vypp1{jj}=[];

xpp1{jj}=xpp;
ypp1{jj}=ypp;
vxpp1{jj}=vxpp;
vypp1{jj}=vypp;
clear xpp ypp vxpp vypp np
end
xpp=[xpp1{1:end}];
ypp=[ypp1{1:end}];
vxpp=[vxpp1{1:end}];
vypp=[vypp1{1:end}];
np=length(xpp);
end

%delete particles
tic
clear md nd that dif mc mc1 bc1 mc2 bc2 xc yx ddfic um dois xppi
    yppi

if AVISOxpp1==0
    md=0;
    nd=0;
    for i=3:np-2

```

```

AVISOmd=0;
mc(i)=(ypp(i-1)-ypp(i+1))/(xpp(i-1)-xpp(i+1));
mc1(i)=-1/mc(i);
bc1(i)=ypp(i)-mc1(i)*xpp(i);
%Draw circle
dif=sqrt((xpp-xpp(i)).^2+(ypp-ypp(i)).^2);
that=find(dif<distancia);
if length(that)>=3
    for j=2:length(that)-1
        if that(j)~=i
            mc2(j)=(ypp(that(j)-1)-ypp(that(j)+1)) ...
                .../(xpp(that(j)-1)-xpp(that(j)+1));
            bc2(j)=ypp(that(j))-mc2(j)*xpp(that(j));
            if mc2(j)*mc1(i)<0
                xc(j)=-(bc1(i)-bc2(j))/(mc1(i)-mc2(j));
                yc(j)=-mc1(i)*(bc1(i)-bc2(j))/(mc1(i)-
                    mc2(j))+bc1(i);
                x1=min(xpp(that(j)-1),xpp(that(j)+1));
                x2=max(xpp(that(j)-1),xpp(that(j)+1));
                y1=min(ypp(that(j)-1),ypp(that(j)+1));
                y2=max(ypp(that(j)-1),ypp(that(j)+1));

                if xc(j)>x1 && xc(j)<x2 && yc(j)>y1 && yc(j)<y2
                    xc(j)=xc(j);
                    yc(j)=yc(j);
                else
                    xc(j)=0;
                    yc(j)=0;
                end
            else
                xc(j)=0;
                yc(j)=0;
            end
        else
            mc2(j)=0;
            bc2(j)=0;
            xc(j)=0;
            yc(j)=0;
        end
    end
end

yc(isnan(xc))=1000000;
xc(isnan(xc))=1000000;

xc(isnan(yc))=1000000;
yc(isnan(yc))=1000000;

that(xc==0) = 1000000;

yc(xc==0) = 1000000;
xc(xc==0) = 1000000;

xc(yc==0) = 1000000;
yc(yc==0) = 1000000;

ggg=any(xc~=1000000);

```

```

if ggg ==1
    if xc~=0
        for j=1:length(xc)
            if xc(j)~=0
                ddfic(j)=sqrt((xc(j)-xpp(i)).^2+(yc(j)-ypp(i)).^2);
            else
                ddfic(j)=1000000;
            end
        end

        [mmd,ndd]=min(ddfic);
        [h,hh]=min(sqrt((xc(ndd)-xpp).^2+(yc(ndd)-ypp).^2));
        difc(i)=mmd;
        if mmd < distancia2
            if md<hh
                difc(i)=mmd;
                md=[md,i];
                nd=[nd,hh];
                AVISOmd=1;
            else
                difc(i)=0;
                md=md;
                nd=nd;
            end
        end
    end
else
    difc(i)=0;
end

end
end

clear dif that mmd hh h ggg

end

nd(md==0)=[ ];
md(md==0)=[ ];

if md~=0

    if length(md)==1

        xpp1{1} = [xpp(1:md-mdgap),xpp(nd+ndgap:end)];
        ypp1{1} = [ypp(1:md-mdgap),ypp(nd+ndgap:end)];
        vxpp1{1} = [vxpp(1:md-mdgap),vxpp(nd+ndgap:end)];
        vypp1{1} = [vypp(1:md-mdgap),vypp(nd+ndgap:end)];
        np1{1}= length(xpp1{1,1}(1,:));

        xpp1{2} = [xpp(md+mdgap:nd-ndgap),xpp(md+mdgap)];
        ypp1{2} = [ypp(md+mdgap:nd-ndgap),ypp(md+mdgap)];
        vxpp1{2} = [vxpp(md+mdgap:nd-ndgap),vxpp(md+mdgap)];
        vypp1{2} = [vypp(md+mdgap:nd-ndgap),vypp(md+mdgap)];
    end
end

```

```

    np1{2}=length(xpp1{1,2}(1,:));
    AVISOxpp1=1;
else
    xpp1{1} = [xpp(1:md(1)-mdgap),xpp(nd(1)+ndgap:end)];
    ypp1{1} = [ypp(1:md(1)-mdgap),ypp(nd(1)+ndgap:end)];
    vxpp1{1} = [vxpp(1:md(1)-mdgap),vxpp(nd(1)+ndgap:end)];
    vypp1{1} = [vypp(1:md(1)-mdgap),vypp(nd(1)+ndgap:end)];
    np1{1}= length(xpp1{1,1}(1,:));

    fatorii=0;

    for ii=2:length(md)

        if abs(md(ii-1)-md(ii))>fatormd
            iii=ii-fatorii;
            xpp1{iii} = [xpp(md(ii-1)+mdgap:md(ii)-mdgap) ...
                ...,xpp(nd(ii)+ndgap:nd(ii-1)-
                ndgap),xpp(md(ii-1)+mdgap)];
            ypp1{iii} = [ypp(md(ii-1)+mdgap:md(ii)-mdgap) ...
                ...,ypp(nd(ii)+ndgap:nd(ii-1)-
                ndgap),ypp(md(ii-1)+mdgap)];
            vxpp1{iii} =[vxpp(md(ii-1)+mdgap:md(ii)-mdgap)
                ...,vxpp(nd(ii)+ndgap:nd(ii-1)-
                ndgap),vxpp(md(ii-1)+mdgap)];
            vypp1{iii} =[vypp(md(ii-1)+mdgap:md(ii)-mdgap),
                ...,vypp(nd(ii)+ndgap:nd(ii-1)-
                ndgap),vypp(md(ii-1)+mdgap)];
            np1{iii}= length(xpp1{1,iii}(1,:));
        else
            fatorii=fatorii+1;
            iii=1;
        end
    end

    xpp1{iii+1} = [xpp(md(length(md))+ndgap:nd(length(md))-
        ndgap) ...
        ...,xpp(md(length(md))+ndgap)];
    ypp1{iii+1} = [ypp(md(length(md))+ndgap:nd(length(md))-
        ndgap) ...
        ...,ypp(md(length(md))+ndgap)];
    vxpp1{iii+1} =[vxpp(md(length(md))+ndgap:nd(length(md))-
        ndgap) ...
        ...,vxpp(md(length(md))+ndgap)];
    vypp1{iii+1} =[vypp(md(length(md))+ndgap:nd(length(md))-
        ndgap) ...
        ...,vypp(md(length(md))+ndgap)];

    np1{iii+1}=length(xpp1{1,iii+1}(1,:));
    AVISOxpp1=1;
end

clear xpp ypp vxpp vypp np xppnd1 yppnd1 vxppnd1 vyppnd1
      xppnd2 yppnd2 vxppnd2 vyppnd2

xpp=[xpp1{1:end}];
ypp=[ypp1{1:end}];

```

```

vxpp=[vxpp1{1:end}];
vypp=[vypp1{1:end}];
np=length(xpp);
end

else
mdold=1;
for jj=1:length(xpp1)
xpp=[xpp1{jj}];
ypp=[ypp1{jj}];
np=[np1{jj}];
md=0;
nd=0;
if np>=5
for i=3:np-2
AVISOMd=0;
mc(i)=(ypp(i-1)-ypp(i+1))/(xpp(i-1)-xpp(i+1));
mc1(i)=-1/mc(i);
bc1(i)=ypp(i)-mc1(i)*xpp(i);

dif=sqrt((xpp-xpp(i)).^2+(ypp-ypp(i)).^2);
that=find(dif<distancia);

if length(that)>=3
for j=2:length(that)-1
if that(j)~=i
mc2(j)=(ypp(that(j)-1)-ypp(that(j)+1))
.../(xpp(that(j)-1)-
xpp(that(j)+1));
bc2(j)=ypp(that(j))-mc2(j)*xpp(that(j));
if mc2(j)*mc1(i)<0
xc(j)=-(bc1(i)-bc2(j))/(mc1(i)-
mc2(j));
yc(j)=-mc1(i)*(bc1(i)-bc2(j))/(mc1(i)-
mc2(j))+bc1(i);
x1=min(xpp(that(j)-1),xpp(that(j)+1));
x2=max(xpp(that(j)-1),xpp(that(j)+1));
y1=min(ypp(that(j)-1),ypp(that(j)+1));
y2=max(ypp(that(j)-1),ypp(that(j)+1));

if xc(j)>x1 && xc(j)<x2 && yc(j)>y1 &&
yc(j)<y2
xc(j)=xc(j);
yc(j)=yc(j);
else
xc(j)=0;
yc(j)=0;
end
else
xc(j)=0;
yc(j)=0;
end
else
mc2(j)=0;
bc2(j)=0;
xc(j)=0;
yc(j)=0;
end
end
end

```

```

        end
    end

    yc(isnan(xc))=1000000;
    xc(isnan(xc))=1000000;

    xc(isnan(yc))=1000000;
    yc(isnan(yc))=1000000;

    that(xc==0) = 1000000;

    yc(xc==0) = 1000000;
    xc(xc==0) = 1000000;

    xc(yc==0) = 1000000;
    yc(yc==0) = 1000000;

    ggg=any(xc~=1000000);
    if ggg ==1
        if xc~=0
            for j=1:length(xc)
                if xc(j)~=0
                    ddfic(j)=sqrt((xc(j)-xpp(i)).^2+(yc(j)-ypp(i)).^2);
                else
                    ddfic(j)=1000000;
                end
            end
        end

        [mmd, ndd]=min(ddfic);

        [h, hh]=min(sqrt((xc(ndd)-xpp).^2+(yc(ndd)-ypp).^2));
        if mmd < distancia2
            if md<hh
                difc(i)=mmd;
                md=[md, i];
                nd=[nd, hh];
                AVISOmd=1;
            else
                difc(i)=0;
                md=md;
                nd=nd;
            end
        end
    end
    else
        difc(i)=0;
    end
end
clear dif that mmd hh h ggg
end
else
    md=md;
    nd=nd;
end
nd(md==0)=[ ];

```



```

md(md==0)=[ ];

canto=find(abs(md-nd)<fatorcanto);
if canto~=0
    md(canto)=[ ];
    nd(canto)=[ ];
end

[xpp1{jj}]=xpp;
[ypp1{jj}]=ypp;
[np1{jj}]=np;

%create the blobs
if md~=0
    mdgap=3;
    ndgap=3;
    if length(md)==1
        if md+mdgap<=length(vxpp1{jj})
            mdgap=3;
            ndgap=3;
        else
            mdgap=length(vxpp1{jj})-md;
            ndgap=mdgap;
        end

        xpp2{mdold} = [xpp1{jj}(1:md-
                        mdgap),xpp1{jj}(nd+ndgap:end)];
        ypp2{mdold} = [ypp1{jj}(1:md-
                        mdgap),ypp1{jj}(nd+ndgap:end)];
        vxpp2{mdold} = [vxpp1{jj}(1:md-
                        mdgap),vxpp1{jj}(nd+ndgap:end)];
        vypp2{mdold} = [vypp1{jj}(1:md-
                        mdgap),vypp1{jj}(nd+ndgap:end)];
        np2{mdold}= length(xpp2{1,mdold}(1,:));

        xpp2{mdold+1} = [xpp1{jj}(md+mdgap:nd-
                        ndgap),xpp1{jj}(md+mdgap)];
        ypp2{mdold+1} = [ypp1{jj}(md+mdgap:nd-
                        ndgap),ypp1{jj}(md+mdgap)];
        vxpp2{mdold+1} = [vxpp1{jj}(md+mdgap:nd-
                        ndgap),vxpp1{jj}(md+mdgap)];
        vypp2{mdold+1} = [vypp1{jj}(md+mdgap:nd-
                        ndgap),vypp1{jj}(md+mdgap)];
        np2{mdold+1}=length(xpp2{1,mdold+1}(1,:));

        mdold=mdold+length(md)+1;
    else
        mdgap=3;
        ndgap=3;
        if md(1)+mdgap<=length(vxpp1{jj})
            mdgap=3;
            ndgap=3;
        else
            mdgap=length(vxpp1{jj})-md(1);
            ndgap=mdgap;
        end
        xpp2{mdold} = [xpp1{jj}(1:md(1)-

```

```

        mdgap), xpp1{jj}(nd(1)+ndgap:end)];
ypp2{mdold} = [ypp1{jj}(1:md(1)-
        mdgap), ypp1{jj}(nd(1)+ndgap:end)];
vxpp2{mdold} = [vxpp1{jj}(1:md(1)-mdgap), ...
        ...vxpp1{jj}(nd(1)+ndgap:end)];
vypp2{mdold} = [vypp1{jj}(1:md(1)-mdgap), ...
        ...vypp1{jj}(nd(1)+ndgap:end)];
np2{mdold}= length(xpp2{1,mdold}(1,:));

fatorii=0;
for ii=2:length(md)
    mdgap=3;
    ndgap=3;
    if md(ii)+mdgap<=length(vxpp1{jj})
        mdgap=3;
        ndgap=3;
    else
        mdgap=length(vxpp1{jj})-md(ii);
        ndgap=mdgap;
    end

    if abs(md(ii-1)-md(ii))>fatormd
        iii=ii-fatorii;
        xpp2{mdold+iii-1} = [xpp1{jj}(md(ii)-
                                1)+mdgap:md(ii)-mdgap) ...
        ...,xpp1{jj}(nd(ii)+ndgap:nd(ii-1)-
        ndgap), xpp1{jj}(md(ii-1)+mdgap)];

        ypp2{mdold+iii-1} = [ypp1{jj}(md(ii)-
                                1)+mdgap:md(ii)-mdgap) ...
        ...,ypp1{jj}(nd(ii)+ndgap:nd(ii-1)-
        ndgap), ypp1{jj}(md(ii-1)+mdgap)];
        vxpp2{mdold+iii-1} = [vxpp1{jj}(md(ii)-
                                1)+mdgap:md(ii)-mdgap) ...
        ...,vxpp1{jj}(nd(ii)+ndgap:nd(ii-1)-
        ndgap), vxpp1{jj}(md(ii-1)+mdgap)];
        vypp2{mdold+iii-1} =[vypp1{jj}(md(ii)-
                                1)+mdgap:md(ii)-mdgap) ...
        ...,vypp1{jj}(nd(ii)+ndgap:nd(ii-1)-
        ndgap), vypp1{jj}(md(ii-1)+mdgap)];
        np2{mdold+iii-1}= length(xpp2{1,mdold+iii-
                                1}(1,:));

    else
        fatorii=fatorii+1;
        iii=1;
    end
end

xpp2{mdold+iii} = [xpp1{jj}(md(length(md))
        +ndgap:nd(length(md))-ndgap),
        xpp1{jj}(md(length(md))+ndgap)];
ypp2{mdold+iii} = [ypp1{jj}(md(length(md))
        )+ndgap:nd(length(md))-ndgap),
        ypp1{jj}(md(length(md))+ndgap)];
vxpp2{mdold+iii} =[vxpp1{jj}(md(length(md))
        )+ndgap:nd(length(md))- ndgap),
        vxpp1{jj}(md(length(md))+ndgap)];

```

```

        vypp2{mdold+iii} =[vypp1{jj} (md(length(md))
                           )+ndgap:nd(length(md))- ndgap),
                           vypp1{jj} (md(length(md))+ndgap)];
        np2{mdold+iii}=length(xpp2{1,mdold+iii}(1,:));

        mdold=mdold+iii+1;
    end

    clear md nd xppnd1 yppnd1 vxppnd1 vyppnd1 xppnd2 yppnd2
           vxppnd2 vyppnd2 xppi yppi

    else
        xpp2{mdold} =xpp1{jj};
        ypp2{mdold} =ypp1{jj};
        vxpp2{mdold} =vxpp1{jj};
        vypp2{mdold} =vypp1{jj};
        np2{mdold}=length(xpp2{1,mdold}(1,:));
        mdold=mdold+1;
    end
end

xpp2=xpp2(~cellfun('isempty',xpp2));
ypp2=ypp2(~cellfun('isempty',ypp2));
vxpp2=vxpp2(~cellfun('isempty',vxpp2));
vypp2=vypp2(~cellfun('isempty',vypp2));

np2([np2{:}]==0)={[]};
np2=np2(~cellfun('isempty',np2));

clear xpp1 ypp1 vxpp1 vypp1 np1
xpp1=xpp2;
ypp1=ypp2;
vxpp1=vxpp2;
vypp1=vypp2;
np1=np2;
xpp=[xpp1{1:end}];
ypp=[ypp1{1:end}];
vxpp=[vxpp1{1:end}];
vypp=[vypp1{1:end}];
np=length(xpp);
clear xpp2 ypp2 vxpp2 vypp2 np2
end

%check distance between particles in consecutive series
if AVISOxpp1==1
    mdold=1;
    for jj=1:length(xpp1)
        xpp=[xpp1{jj}];
        ypp=[ypp1{jj}];
        np=[np1{jj}];
        dx2=abs(xpp(1:np-1)-xpp(2:np));
        dy2=abs(ypp(1:np-1)-ypp(2:np));
        dxdy2=sqrt(dx2.^2+dy2.^2);
        A=find(dxdy2>distancia3);
        [xpp1{jj}]=xpp;
        [ypp1{jj}]=ypp;
    end
end

```

```

    [np1{jj}]=np;

    if A~=0
        AA=length(A);
        for i=1:AA
            xpp2{mdold} = [xpp1{jj}(1:A(1))];
            xpp2{mdold+1} = [xpp1{jj}(A(1)+1:end)];
            ypp2{mdold} = [ypp1{jj}(1:A(1))];
            ypp2{mdold+1} = [ypp1{jj}(A(1)+1:end)];
            vxpp2{mdold} = [vxpp1{jj}(1:A(1))];
            vxpp2{mdold+1} = [vxpp1{jj}(A(1)+1:end)];
            vypp2{mdold} = [vypp1{jj}(1:A(1))];
            vypp2{mdold+1} = [vypp1{jj}(A(1)+1:end)];

            np2{mdold}= length(xpp2{1,mdold}(1,:));
            np2{mdold+1}= length(xpp2{1,mdold+1}(1,:));

            mdold=mdold+2;
        end
    else
        xpp2{mdold}=xpp1{jj};
        ypp2{mdold}=ypp1{jj};
        vxpp2{mdold}=vxpp1{jj};
        vypp2{mdold}=vypp1{jj};
        np2{mdold}=np1{jj};

        mdold=mdold+1;
    end
end

xpp2=xpp2(~cellfun('isempty',xpp2));
ypp2=ypp2(~cellfun('isempty',ypp2));
vxpp2=vxpp2(~cellfun('isempty',vxpp2));
vypp2=vypp2(~cellfun('isempty',vypp2));

np2([np2{:}]==0)={[]};
np2=np2(~cellfun('isempty',np2));

clear xpp1 ypp1 vxpp1 vypp1 np1
xpp1=xpp2;
ypp1=ypp2;
vxpp1=vxpp2;
vypp1=vypp2;
np1=np2;
xpp=[xpp1{1:end}];
ypp=[ypp1{1:end}];
vxpp=[vxpp1{1:end}];
vypp=[vypp1{1:end}];
np=length(xpp);
clear xpp2 ypp2 vxpp2 vypp2 np2
end

if AVISOxpp1==1
    vetor=0;
    for jj=1:length(xpp1)
        xpp=[xpp1{jj}];
        ypp=[ypp1{jj}];
        np=[np1{jj}];
    end
end

```

```

        if length(xpp)<5
            vetor=[vetor, jj];
        end
    end
    vetor(vetor==0)=[];
    xpp1(vetor)=[];
    ypp1(vetor)=[];
    vxpp1(vetor)=[];
    vypp1(vetor)=[];
    np1(vetor)=[];

    xpp=[xpp1{1:end}];
    ypp=[ypp1{1:end}];
    vxpp=[vxpp1{1:end}];
    vypp=[vypp1{1:end}];
    np=length(xpp);
end

%keep position at the wall
if AVISOxpp1==0
    B=find(xpp>max(x(1,:)));
    C=find(xpp<min(x(1,:)));
    D=find(ypp>max(y(:,1)));
    E=find(ypp<min(y(:,1)));
    if B~=0
        xpp(B)=max(x(1,:));
    end
    if C~=0
        xpp(C)=min(x(1,:));
    end
    if D~=0
        ypp(D)=max(y(:,1));
    end
    if E~=0
        ypp(E)=min(y(:,1));
    end
else
    for ii=1:length(np1)
        xpp=[xpp1{ii}];
        ypp=[ypp1{ii}];
        B=find(xpp>max(x(1,:)));
        C=find(xpp<min(x(1,:)));
        D=find(ypp>max(y(:,1)));
        E=find(ypp<min(y(:,1)));
        if B~=0
            xpp(B)=max(x(1,:));
        end
        if C~=0
            xpp(C)=min(x(1,:));
        end
        if D~=0
            ypp(D)=max(y(:,1));
        end
        if E~=0
            ypp(E)=min(y(:,1));
        end
    end
end

```

```

        xpp1{ii}=xpp;
        ypp1{ii}=ypp;
    end
    clear xpp ypp
    xpp=[xpp1{1:end}];
    ypp=[ypp1{1:end}];
end

%calculate the interfacial area generation: s/s0
if AVISOxpp1==0
    dx=abs(xpp(1:np-1)-xpp(2:np));
    dy=abs(ypp(1:np-1)-ypp(2:np));
    dxdy=sqrt(dx.^2+dy.^2);
    s(t)=sum(dxdy);
    timee(t)=t*dt;
    alfa(t)=s(t)/s0;
else
    for ii=1:length(np1)
        xpp=[xpp1{ii}];
        ypp=[ypp1{ii}];
        np=[np1{ii}];
        dx=abs(xpp(1:np-1)-xpp(2:np));
        dy=abs(ypp(1:np-1)-ypp(2:np));
        dxdy=sqrt(dx.^2+dy.^2);
        sii(ii)=sum(dxdy);

        clear dx dy dxdy xpp ypp np
    end

    s(t)=sum(sii);
    timee(t)=t*dt;
    alfa(t)=s(t)/s0;

    clear xpp ypp np
    xpp=[xpp1{1:end}];
    ypp=[ypp1{1:end}];
    np=[np1{1:end}];
end

%% plot figure
quiver(x,y,vx,vy,'color','white','AutoScaleFactor',1)
set(gca,'xtick',[])
xlim([-5e-3 4.5e-2])
set(gca,'ytick',[])
ylim([-5e-3 5e-3])
hold on
if AVISOxpp1~=0
    for i=1:length(np1)
        plot(xpp1{i},ypp1{i},'-b')
    end
    hold on
else
    plot(xpp,ypp,'-b')
    hold off
end

cd (pathname);

```



```

cd(folderName)
saveas(gcf,['t_',num2str(t)],'tif')
end

```

D.6 Batch Lagrangian Mixing Simulation (BLMS) Algorithm

```

% Required Programs: BLMS_vmed; BLMS_dx
% Required Files: velocity fields .mat from CFD simulation (see C.2.1)

clearvars -except deltaa a1 a2 %Medvx1
ti=a1;
tr=1;

cd('C:\Users\Admin\Documents\ICM_particulas\7_25\data\data_matlab1');
folderName=strcat('particulas_injection_1');
mkdir (folderName)

%%
for iii=1:a2
    is=iii;
    ti=1;

    % Definition of program variables
    np=length(deltaa);
    np3=length(deltaa);
    s0=0.001;
    dt=1.14e-3;
    delta=dt/(1.14e-3);
    ddx=dy=0.0001;
    distancia=1e-8;
    tmax=ti+510;
    t=ti;

    %load files
    file=strcat('data-',num2str(t),'.mat');
    load(file)
    vx(isnan(vx))=0;
    vy(isnan(vy))=0;

    %% Particle Injection
    xmin=0.0103; %+0.0001;
    xmax=0.0109; %-0.0001;
    xmin3=0.0153; %-0.00015;
    xmax3=0.0159; %-0.00015;
    ymin=0.0495+0.0001;
    ymax=0.0501+0.0001;

    bout6x=0.0544-xmin; %b=y-x
    bout6x3=0.0552+xmin3; %b=y+x

    xmin1=xmin;%-0.00005;
    xmax1=xmax;%+0.0001;
    xmin31=xmin3-0.0001;
    xmax31=xmax3-0.0001; %+0.0003;

    x1out=xmin1;

```

```

x2out=xmax1;

x3out=xmin31;
x4out=xmax31;

%left side
%calculate xpp e ypp
xpp(1)=xmin;
xpp(np)=xmax;
for i=2:np-1
    xpp(i)=xpp(i-1)+deltaa(i-1);
end

ypp(1)=ymax;
ypp(np)=ymin;
for i=2:np-1
    ypp(i)=ypp(i-1)-deltaa(i-1);
end

%righth side
xpp3(1)=xmin3;
xpp3(np)=xmax3;
for i=2:np-1
    xpp3(i)=xpp3(i-1)+deltaa(i-1);
end

ypp3(1)=ymin;
ypp3(np)=ymax;
for i=2:np-1
    ypp3(i)=ypp3(i-1)+deltaa(i-1);
end

% figure1 = figure();
% axes1 = axes('Parent',figure1,...
%             'Position',[0.164196123147092 0.137767220902613
%                         0.603636044685076 0.88]);
% hold(axes1,'all');
% quiver(x,y,vx,vy,'color','blue','AutoScaleFactor',1)
% xlim([0.009 0.017])
% ylim([0.048 0.056])
% hold on
% plot(xpp,ypp,'b.')
% hold on
% plot(xpp3,ypp3,'r.')
% hold off
% pbaspect([1 1 1])
% %
%
cd('C:\Users\Admin\Documents\ICM_particulas\7_25\data\data_matlab1');
% cd(folderName)
% if is==1
%     saveas(gcf,['t_',num2str(t)],'tif')
% elseif is==2
%     ty=(t-1)+510*(is-1)+1;
%     saveas(gcf,['t_',num2str(ty)],'tif')
% else

```

```

%      ty=(t-1)+510*(is-1)+(is-2);
%      saveas(gcf,['t_',num2str(ty)],'tif')
%  end
%%

poutbl=0;
toutbl=0;
poutbr=0;
toutbr=0;
poutrl=0;
toutrl=0;
poutrr=0;
toutrr=0;
xtapar=0;
ytapar=0;

for t=ti+1:tmax
    t
    %load new file
    tolddd=t;
    file=strcat('data-',num2str((t-1)*delta),'.mat');
    load(file)
    vx(isnan(vx))==0;
    vy(isnan(vy))==0;
    clear t
    t=tolddd;

    xppold=xpp;
    yppold=ypp;
    xppold3=xpp3;
    yppold3=ypp3;

    %recalculate particle's positions with interp2
    %serie 1
    vxpp=interp2(x,y,vx,xpp,ypp,'spline');
    vypp=interp2(x,y,vy,xpp,ypp,'spline');
    xpp=xppold+vxpp(1:np)*dt;
    ypp=yppold+vypp(1:np)*dt;

    %serie 2
    vxpp3=interp2(x,y,vx,xpp3,ypp3,'spline');
    vypp3=interp2(x,y,vy,xpp3,ypp3,'spline');
    xpp3=xppold3+vxpp3*dt;
    ypp3=yppold3+vypp3*dt;

    %Keep position at wall
    %serie 1
    B=find(xpp>max(x(1,:)));
    C=find(xpp<min(x(1,:)));
    D=find(ypp>max(y(:,1)));
    E=find(ypp<min(y(:,1)));
    if B~=0
        xpp(B)=max(x(1,:));
    end
    if C~=0
        xpp(C)=min(x(1,:));
    end
end

```

```

end
if D~=0
    ypp(D)=max(y(:,1));
end
if E~=0
    ypp(E)=min(y(:,1));
end

%Particles out
%left
xlout=xmin1;
x2out=xmax1;
mout=1.0;
bout2=0.004393;
bout4=0.01656;
bout6=bout6x;
bout8=0.040572;
for ii=1:length(xpp)
    if xpp(ii)>xlout & xpp(ii)<x2out
        yout=mout*xpp(ii)+bout6+0.0002;
        if ypp(ii)>=yout
            poutbl=[poutbl;ii];
            toutbl=[toutbl;t*dt];
            xtapar=[xtapar;xpp(ii)];
            ytapar=[ytapar;ypp(ii)];
        end
    end
    clear yout
end

%righth
x3out=xmin31;
x4out=xmax31;
mout=-1.00;
bout2=0.01653;
bout4=0.02854;
bout6=bout6x3;
bout8=0.0526;
for ii=1:length(xpp)
    if xpp(ii)>x3out & xpp(ii)<x4out
        yout=mout*xpp(ii)+bout6-0.00005;
        if ypp(ii)>=yout
            poutbr=[poutbr;ii];
            toutbr=[toutbr;t*dt];
            xtapar=[xtapar;xpp(ii)];
            ytapar=[ytapar;ypp(ii)];
        end
    end
    clear yout
end

%serie 2
B=find(xpp3>max(x(1,:)));
C=find(xpp3<min(x(1,:)));
D=find(ypp3>max(y(:,1)));
E=find(ypp3<min(y(:,1)));
if B~=0

```

```

        xpp3(B)=max(x(1,:));
    end
    if C~=0
        xpp3(C)=min(x(1,:));
    end
    if D~=0
        ypp3(D)=max(y(:,1));
    end
    if E~=0
        ypp3(E)=min(y(:,1));
    end

    %Particles out
    %left
    xlout=xmin1;
    x2out=xmax1;
    mout=1.0;
    bout2=0.004393;
    bout4=0.01656;
    bout6=bout6x;
    bout8=0.040572;
    for ii=1:length(xpp3)
        if xpp3(ii)>xlout & xpp3(ii)<x2out
            yout=mout*xpp3(ii)+bout6+0.0002;
            if ypp3(ii)>=yout
                poutrl=[poutrl;ii];
                toutrl=[toutrl;t*dt];
                xtapar=[xtapar;xpp(ii)];
                ytapar=[ytapar;ypp(ii)];
            end
        end
        clear yout
    end

    %righth
    x3out=xmin31;
    x4out=xmax31;
    mout=-1.00;
    bout2=0.01653;
    bout4=0.02854;
    bout6=bout6x3;
    bout8=0.0526;

    for ii=1:length(xpp3)
        if xpp3(ii)>x3out & xpp3(ii)<x4out
            yout=mout*xpp3(ii)+bout6-0.00005;
            if ypp3(ii)>=yout
                poutrr=[poutrr;ii];
                toutrr=[toutrr;t*dt];
                xtapar=[xtapar;xpp3(ii)];
                ytapar=[ytapar;ypp3(ii)];
            end
        end
        clear yout
    end

    %
    %plot

```

```

%     quiver(x,y,vx,vy,'color','blue','AutoScaleFactor',1)
%     set(gca,'xtick',[])
%     xlim([0.009 0.017])
%     ylim([0.048 0.056])
%     set(gca,'ytick',[])
%     hold on
%     plot(xpp,ypp,'.b')
%     hold on
%     plot(xpp3,ypp3,'.r')
%     hold on
%     plot(xtapar,ytapar,'.w','MarkerSize',8)
%     hold off
%     pbaspect([1 1 1])
%
%     cd('C:\Users\Admin\Documents\ICM_particulas\7_25\data
%         \data_matlab1');
%     cd(folderName)
%     if is==1
%         saveas(gcf,['t_',num2str(t)],'tif')
%     elseif is==2
%         ty=(t-1)+510*(is-1)+1;
%         saveas(gcf,['t_',num2str(ty)],'tif')
%     else
%         ty=(t-1)+510*(is-1)+(is-2);
%         saveas(gcf,['t_',num2str(ty)],'tif')
%     end
% %

%calculate nout
%bl
bhbh= horzcat(poutbl,toutbl);
bjbj=unique(bhbh,'rows');
bj=bjbj(:,1);
bjj=bjbj(:,2);
bla=[1;diff(bj)];
bjj(bla==0)=[];
bj(bla==0)=[];
out=horzcat(bj, bjj);
outbl=sortrows(horzcat(bjj, bj));
nbl=length(bj)-1;

clear bhbh bjbj bj bjj bla out

%br
bhbh= horzcat(poutbr,toutbr);
bjbj=unique(bhbh,'rows');
bj=bjbj(:,1);
bjj=bjbj(:,2);
bla=[1;diff(bj)];
bjj(bla==0)=[];
bj(bla==0)=[];
out=horzcat(bj, bjj);
outbr=sortrows(horzcat(bjj, bj));
nbr=length(bj)-1;

clear bhbh bjbj bj bjj bla out

```



```

%rl
bhbh= horzcat(poutrl,toutrl);
bjbj=unique(bhbh,'rows');
bj=bjbj(:,1);
bjj=bjbj(:,2);
bla=[1;diff(bj)];
bjj(bla==0)=[];
bj(bla==0)=[];
out=horzcat(bj, bjj);
outrl=sortrows(horzcat(bjj, bj));
nrl=length(bj)-1;

clear bhbh bjbj bj bjj bla out

%rr
bhbh= horzcat(poutrr,toutrr);
bjbj=unique(bhbh,'rows');
bj=bjbj(:,1);
bjj=bjbj(:,2);
bla=[1;diff(bj)];
bjj(bla==0)=[];
bj(bla==0)=[];
out=horzcat(bj, bjj);
outrr=sortrows(horzcat(bjj, bj));
nrr=length(bj)-1;

clear bhbh bjbj bj bjj bla out

%save
RANGE=['A',num2str(tr)];
WRITE={ti,nbl,nbr,nrl,nrr};
xlswrite('n_out2.xlsx',WRITE,'sheet1',RANGE);

close all
clearvars -except ti tr folderName deltaa

ti=ti+1;
tr=tr+1;
end

%%
%Set outlet line
xmin1=xmin;%-0.00005;
xmax1=xmax;%+0.0001;
xmin31=xmin3-0.0001;
xmax31=xmax3-0.0001;

x1out=xmin1;
x2out=xmax1;

x3out=xmin31;
x4out=xmax31;

bout6=bout6x3;
mout=-1;
bla(1)=x3out;

```

```

for i=2:20
    bla(i)=bla(i-1)+(x4out-x3out)/20;
end
blaa=mout*bla+bout6-0.00005;

bout6=bout6x;
mout=1;

bla1(1)=x1out;
for i=2:20
    bla1(i)=bla1(i-1)+(x2out-x1out)/20;
end
blaa1=mout*bla1+bout6+0.0002;

figure1 = figure();
axes1 = axes('Parent',figure1,...
    'Position',[0.257601351351351 0.126385809312639 0.581047804370981
0.793154420572418]);
hold(axes1,'all');
quiver(x,y,vx,vy,'color','blue','AutoScaleFactor',1)
xlim([0.009 0.017])
ylim([0.048 0.056])
hold on
% plot(xpp,ypp,'b.')
% hold on
% plot(xpp3,ypp3,'r.')
hold on
plot(bla,blaa,'r')
% plot(xpp3,ypp3,'r.')
hold on
plot(bla1,blaa1,'r')
pbaspect([1 1 1])

```

D.6.1 BLMS Inlet Velocity Profile

```

%% nub r=6.5 (diametro original)
i=1;
ti=856;
tmax=856+5000

for t=ti:tmax
    i
    cd('C:\Users\Joana Matos\Documents\nub\300_sym6\data_matlab')
    file=strcat('data-',num2str(t),'.mat');
    load(file)
    vx(isnan(vx))=0;
    vy(isnan(vy))=0;
    v(i,1)=vx(16,7);
    v(i,2)=vx(15,8);
    v(i,3)=vx(14,9);
    v(i,4)=vx(13,10);
    v(i,5)=vx(12,11);
    v(i,6)=vx(11,12);
    v(i,7)=vx(10,13);
    v(i,8)=vx(9,14);

```

```

u(i,1)=vy(16,7);
u(i,2)=vy(15,8);
u(i,3)=vy(14,9);
u(i,4)=vy(13,10);
u(i,5)=vy(12,11);
u(i,6)=vy(11,12);
u(i,7)=vy(10,13);
u(i,8)=vy(9,14);

cd('C:\Users\Joana Matos\Documents\nub\300_sym6\data_matlab\vmcd')
%fileName=strcat('data_',num2str(i));
if i==1
    save('vmcd.mat','v','u')
else
    save('vmcd.mat','v','u','-append')
end

i=i+1;
end
for i=1:8
    Medvx(i)=mean(v(:,i));
    Medvy(i)=mean(u(:,i));
end
Medvx1=Medvx';
Medvy1=Medvy';

```

D.6.2 BLMS Particles Distribution Over the Inlet

```

clearvars -except Medvx1 a1 a2

%r=5.75 to 6.05
%x00=[0.0033 0.0034 0.0035 0.0036 0.0037 0.0038 0.0039];

%r=6.15
%x00=[0.0039 0.0040 0.0041 0.0042 0.0043 0.0044 0.0045];

%6.78
%x00=[0.0036 0.0037 0.0038 0.0039 0.0040 0.0041 0.0042];

%6.65 ICM
x00=[0.0103 0.0104 0.0105 0.0106 0.0107 0.0108 0.0109];
v00=Medvx1(1:end);

x(1)=x00(1);
%dx(1)=3.5e-5; %r=6.5
%dx(1)=2.5e-5; %r=8.5
%dx(1)=2.5e-5; %r=4.5
dx(1)=3.5e-5; %r=2.5e-5
x(2)=x(1)+dx(1);
vx=interp1(x00,v00,x(2));
area(1)=(vx+v00(1))/2*dx(1);

i=3;
dx1=dx(1);
dx(2)=dx(1);

```

```

while i<=13
    i
    x(i)=x(i-1)+dx(i-1);
    vx=interp1(x00,v00,x(i));
    area(i-1)=(vx+v00(1))/2*dx(i-1);
    while abs(area(i-1)-area(1))>=1e-8
        dx1=dx1-1e-7;
        x(i)=x(i-1)+dx1;
        vx=interp1(x00,v00,x(i));
        area(i-1)=(vx+v00(1))/2*dx1;
    end
    dx(i-1)=dx1;
    i=i+1;
    dx(i-1)=dx(i-2);
end

dx2=fliplr(dx);
deltaa=[dx dx2];
%deltaa=[dx dx(13) dx(13) dx2]; %5_75

save('deltaa_particulas.mat','deltaa','a1','a2')

```

D.7 Striation Thickness Algorithm

% Input Files: velocity fields .mat from CFD simulation (see C.2.1)

```

ypp=[ypp, ypp3];
xpp=[xpp, xpp3];
np=np+np3;

clearvars -except ypp xpp np

xpp=xpp(60:60+10000);
ypp=ypp(60:60+10000);
np=length(xpp);

%figure
%plot(xpp,ypp,'.b')

for i=3:np-2
    i
    %line in i
    mc(i)=(ypp(i-1)-ypp(i+1))/(xpp(i-1)-xpp(i+1));
    mc1(i)=-1/mc(i);
    bc1(i)=ypp(i)-mc1(i)*xpp(i);
    %Set circle
    dif=sqrt((xpp-xpp(i)).^2+(ypp-ypp(i)).^2);
    that=find(dif<1.5e-3);
    %slope at j from circle and intercept with tangent in i
    if length(that)>=3
        for j=2:length(that)-1
            %j
            if that(j)~=i
                mc2(j)=(ypp(that(j)-1)-ypp(that(j)+1))/(xpp(that(j)-1)-

```

```

        xpp(that(j)+1));
bc2(j)=ypp(that(j))-mc2(j)*xpp(that(j));

if mc2(j)*mc1(i)<0
    xc(j)=-(bc1(i)-bc2(j))/(mc1(i)-mc2(j));
    yc(j)=-mc1(i)*(bc1(i)-bc2(j))/(mc1(i)-mc2(j))+bc1(i);
    x1=min(xpp(that(j)-1),xpp(that(j)+1));
    x2=max(xpp(that(j)-1),xpp(that(j)+1));
    y1=min(ypp(that(j)-1),ypp(that(j)+1));
    y2=max(ypp(that(j)-1),ypp(that(j)+1));

    if xc(j)>x1 && xc(j)<x2 && yc(j)>y1 && yc(j)<y2
        xc(j)=xc(j);
        yc(j)=yc(j);
    else
        xc(j)=0;
        yc(j)=0;
    end
else
    xc(j)=0;
    yc(j)=0;
end
else
    mc2(j)=0;
    bc2(j)=0;
    xc(j)=0;
    yc(j)=0;
end
end

yc(isnan(xc))=1000000;
xc(isnan(xc))=1000000;

xc(isnan(yc))=1000000;
yc(isnan(yc))=1000000;

that(xc==0) = 1000000;

yc(xc==0) = 1000000;
xc(xc==0) = 1000000;

xc(yc==0) = 1000000;
yc(yc==0) = 1000000;

el=0;
for j=1:length(xc)
    difx=sqrt((xc(j)-xpp(i)).^2+(yc(j)-ypp(i)).^2);
    if difx>1.5e-3
        el=[el,j];
    end
end

if el~=0
    yc(el)=1000000;
    xc(el)=1000000;
end
ggg=any(xc~=1000000);

```

```

if ggg ==1
    if xc~=0
        for j=1:length(xc)
            if xc(j)~=0
                ddfic(j)=sqrt((xc(j)-xpp(i)).^2+(yc(j)-ypp(i)).^2);
            else
                ddfic(j)=1000000;
            end
        end

        [mmd, ndd]=min(ddfic);
        %closeste particle to xc
        [h, hh]=min(sqrt((xc(ndd)-xpp).^2+(yc(ndd)-ypp).^2));
        nd=hh;
        difc(i)=mmd;

        if nd>i
            difc(i)=mmd;
        else
            difc(i)=0;
        end
    end
else
    difc(i)=0;
end
end
end
%%

% Plot histogram
cd('C:\Users\Joana Matos\Documents\6_85_st');
save('data_hist_8')

lx=sqrt((xpp(1:np-2)-xpp(3:np)).^2+(ypp(1:np-2)-ypp(3:np)).^2);
sx=difc(2:end);
lx(sx==0) = [];
sx(sx==0) = [];

nx=50;
s1=1e-16;
ss=find(sx<=s1);
llx(1)=sum(lx(ss));

for i=2:nx
    ss=find(sx>s1 & sx<=s1*2);
    llx(i)=sum(lx(ss));
    s1=s1*2;
end

xb(1)=1e-16;
for i=2:50
    xb(i)=xb(i-1)*2;
end

xb1=[xb1,xb];
llx1=[llx1,llx];
figure2=figure();

```



```

axes2 = axes('Parent',figure2,'XScale','log', 'XMinorTick','on');
box(axes2,'on');
hold(axes2,'all');
bar(xb,llx,'BarWidth',1)
hold on
plot(xb,llx)
hold off
xlabel('\itS \rm(m)')
ylabel('\Sigma\it\alpha^\bullet \rm(m)')

close all
clear all

```

D.8 Strange Attractor Phase Diagram and Spectral Analysis

%Input Files : CFD data in format .xlsx (see Section C.3)

```

cd('C:\Users\Admin\Documents\7_25_ICM_mais_tempo')

ii=1
tt=xlsread('vx2','vx2_1_1','A4:A800000');
t=tt*deltat;

vx2=xlsread('vx2','vx2_1_1','B4:B600000');
vy2=xlsread('vy2','vy2_1_1','B4:B600000');
strain2=xlsread('strain2','strain2','B4:B600000');
vorticity2=xlsread('vorticity2','vorticity2','B4:B600000');

vx4=xlsread('vx4','vx4_1_1','B4:B600000');
vy4=xlsread('vy4','vy4_1_1','B4:B600000');
strain4=xlsread('strain4','strain4','B4:B600000');
vorticity4=xlsread('vorticity4','vorticity4','B4:B600000');

vx6=xlsread('vx6','vx_1_1','B4:B600000');
vy6=xlsread('vy6','vy_1_1','B4:B600000');
strain6=xlsread('strain6','strain','B4:B600000');
vorticity6=xlsread('vorticity6','vorticity','B4:B600000');

vx8=xlsread('vx8','vx8_1_1','B4:B600000');
vy8=xlsread('vy8','vy8_1_1','B4:B600000');
strain8=xlsread('strain8','strain8','B4:B600000');
vorticity8=xlsread('vorticity8','vorticity8','B4:B600000');

ii=2
vx_r1=xlsread('vx_r1','vx_r1','B4:B600000');
vx_r2=xlsread('vx_r2','vx_r2','B4:B600000');
vx_r3=xlsread('vx_r3','vx_r3','B4:B600000');
vx_r4=xlsread('vx_r4','vx_r4','B4:B600000');
vx_r5=xlsread('vx_r5','vx_r5','B4:B600000');
vx_r6=xlsread('vx_r6','vx_r6','B4:B600000');
vx_r7=xlsread('vx_r7','vx_r7','B4:B600000');
vx_r8=xlsread('vx_r8','vx_r8','B4:B600000');

vx_l1=xlsread('vx_l1','vx_l1','B4:B600000');
vx_l2=xlsread('vx_l2','vx_l2','B4:B600000');

```

```

vx_13=xlsread('vx_13','vx_13','B4:B600000');
vx_14=xlsread('vx_14','vx_14','B4:B600000');
vx_15=xlsread('vx_15','vx_15','B4:B600000');
vx_16=xlsread('vx_16','vx_16','B4:B600000');
vx_17=xlsread('vx_17','vx_17','B4:B600000');
vx_18=xlsread('vx_18','vx_18','B4:B600000');

ii=3
vy_r1=xlsread('vy_r1','vy_r1','B4:B600000');
vy_r2=xlsread('vy_r2','vy_r2','B4:B600000');
vy_r3=xlsread('vy_r3','vy_r3','B4:B600000');
vy_r4=xlsread('vy_r4','vy_r4','B4:B600000');
vy_r5=xlsread('vy_r5','vy_r5','B4:B600000');
vy_r6=xlsread('vy_r6','vy_r6','B4:B600000');
vy_r7=xlsread('vy_r7','vy_r7','B4:B600000');
vy_r8=xlsread('vy_r8','vy_r8','B4:B600000');

vy_l1=xlsread('vy_l1','vy_l1','B4:B600000');
vy_l2=xlsread('vy_l2','vy_l2','B4:B600000');
vy_l3=xlsread('vy_l3','vy_l3','B4:B600000');
vy_l4=xlsread('vy_l4','vy_l4','B4:B600000');
vy_l5=xlsread('vy_l5','vy_l5','B4:B600000');
vy_l6=xlsread('vy_l6','vy_l6','B4:B600000');
vy_l7=xlsread('vy_l7','vy_l7','B4:B600000');
vy_l8=xlsread('vy_l8','vy_l8','B4:B600000');

ii=4
strain_r1=xlsread('strain_r1','strain_r1','B4:B600000');
strain_r2=xlsread('strain_r2','strain_r2','B4:B600000');
strain_r3=xlsread('strain_r3','strain_r3','B4:B600000');
strain_r4=xlsread('strain_r4','strain_r4','B4:B600000');
strain_r5=xlsread('strain_r5','strain_r5','B4:B600000');
strain_r6=xlsread('strain_r6','strain_r6','B4:B600000');
strain_r7=xlsread('strain_r7','strain_r7','B4:B600000');
strain_r8=xlsread('strain_r8','strain_r8','B4:B600000');

strain_l1=xlsread('strain_l1','strain_l1','B4:B600000');
strain_l2=xlsread('strain_l2','strain_l2','B4:B600000');
strain_l3=xlsread('strain_l3','strain_l3','B4:B600000');
strain_l4=xlsread('strain_l4','strain_l4','B4:B600000');
strain_l5=xlsread('strain_l5','strain_l5','B4:B600000');
strain_l6=xlsread('strain_l6','strain_l6','B4:B600000');
strain_l7=xlsread('strain_l7','strain_l7','B4:B600000');
strain_l8=xlsread('strain_l8','strain_l8','B4:B600000');

ii=5
vorticity_r1=xlsread('vorticity_r1','vorticity_r1','B4:B600000');
vorticity_r2=xlsread('vorticity_r2','vorticity_r2','B4:B600000');
vorticity_r3=xlsread('vorticity_r3','vorticity_r3','B4:B600000');
vorticity_r4=xlsread('vorticity_r4','vorticity_r4','B4:B600000');
vorticity_r5=xlsread('vorticity_r5','vorticity_r5','B4:B600000');
vorticity_r6=xlsread('vorticity_r6','vorticity_r6','B4:B600000');
vorticity_r7=xlsread('vorticity_r7','vorticity_r7','B4:B600000');
vorticity_r8=xlsread('vorticity_r8','vorticity_r8','B4:B600000');

vorticity_l1=xlsread('vorticity_l1','vorticity_l1','B4:B600000');
vorticity_l2=xlsread('vorticity_l2','vorticity_l2','B4:B600000');

```

```

vorticity_13=xlsread('vorticity_13','vorticity_13','B4:B600000');
vorticity_14=xlsread('vorticity_14','vorticity_14','B4:B600000');
vorticity_15=xlsread('vorticity_15','vorticity_15','B4:B600000');
vorticity_16=xlsread('vorticity_16','vorticity_16','B4:B600000');
vorticity_17=xlsread('vorticity_17','vorticity_17','B4:B600000');
vorticity_18=xlsread('vorticity_18','vorticity_18','B4:B600000');

%Centre of chambers C2, C4, C6 and C8

for i=2:2:8
    i
    vx=eval(['vx' num2str(i)]);
    vy=eval(['vy' num2str(i)]);
    strain=eval(['strain' num2str(i)]);
    vorticity=eval(['vorticity' num2str(i)]);

    t1=108;
    t2=109;
    [A,B]=min(abs(t-t1));
    [AA,BB]=min(abs(t-t2));

    [C,CC]=max(vorticity(B:BB));
    CC=CC+B;

    t11=117;
    t21=118;
    [A1,B1]=min(abs(t-t11));
    [AA1,BB1]=min(abs(t-t21));

    [C1,CC1]=max(vorticity(B1:BB1));
    CC1=CC1+B1;

    CC=1;
    CC1=length(vx);
    save('data7')

    figure1=figure
    axes1 = axes('Parent',figure1,'FontSize',17);
    box(axes1,'on');
    hold(axes1,'all');
    plot(t(CC:CC1),vx(CC:CC1),'b')
    grid on
    grid minor
    xlabel('\it t \rm (s)','LineWidth',2,'FontWeight','normal','FontSize',19);
    ylabel('\itv_x \rm(m/s)','LineWidth',2,'FontWeight','normal','FontSize',19);
    xlim(axes1,[t(CC) t(CC1)]);
    ylim(axes1,[-0.2 0.2]);
    box(axes1,'on');

    saveas(gcf,['vx',num2str(i)],'tif')

    figure1=figure

```

```

axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(CC:CC1),vy(CC:CC1),'b')
grid on
grid minor
xlabel('\it t\rm (s)',
      'LineWidth',2,'FontWeight','normal','FontSize',19);
ylabel('\itv_y \rm(m/s)',
      'LineWidth',2,'FontWeight','normal','FontSize',19);
xlim(axes1,[t(CC) t(CC1)]);
ylim(axes1,[-0.1 0.15]);
box(axes1,'on');

saveas(gcf,['vy',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all')
plot(t(CC:CC1),vorticity(CC:CC1),'b')
grid on
grid minor
xlabel('Flow time (s)', 'LineWidth',2,'FontSize',19);
ylabel('\itvorticity \rm(s^-^1)', 'LineWidth',2,'FontSize',19);
xlim(axes1,[t(CC) t(CC1)]);
box(axes1,'on');

saveas(gcf,['vorticity',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all')
plot(t(CC:CC1),strain(CC:CC1),'b')
grid on
grid minor
xlabel('Flow time (s)', 'LineWidth',2,'FontSize',19);
ylabel('\itstrain rate \rm(s^-^1)', 'LineWidth',2,'FontSize',19);
xlim(axes1,[t(CC) t(CC1)]);
box(axes1,'on');

saveas(gcf,['strain',num2str(i)],'tif')

%Attractor -1 to 1

% normalize between [a, b]
% x=(b-a)*(x-min(x))/(max(x)-min(x))+a

vvx1=2*(vx(CC:CC1)-min(vx(CC:CC1)))/(max(vx(CC:CC1))-
    min(vx(CC:CC1)))-1;
vvy1=2*(vy(CC:CC1)-min(vy(CC:CC1)))/(max(vy(CC:CC1))-
    min(vy(CC:CC1)))-1;
vorticity1=2*(vorticity(CC:CC1)-

```

```

        min(vorticity(CC:CC1)))/(max(vorticity(CC:CC1))-
        min(vorticity(CC:CC1)))-1;
strain1=2*(strain(CC:CC1)-
        min(strain(CC:CC1)))/(max(strain(CC:CC1))-
        min(strain(CC:CC1)))-1;

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(vorticity1,strain1,'b');
box(axes1,'on');
hold(axes1,'all')
pbaspect([1 1 1])
grid on
grid minor
xlabel('\it \zeta^*',
        'LineWidth',2,'FontWeight','normal','FontSize',24);
ylabel('\it \epsilon^*'
        , 'LineWidth',2,'FontWeight','normal','FontSize',24);

saveas(gcf,['attractor',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(vvy1,vvx1,'b')
grid on
grid minor
xlabel('\it vy','LineWidth',2,'FontSize',16);
ylabel('\it vx','LineWidth',2,'FontSize',16);

saveas(gcf,['attractor_1',num2str(i)],'tif')

clear all
close all

% Spectral Analysis vx
cd('C:\Users\Admin\Documents\7_25_ICM_mais_tempo')

load('data8')

nt = length(t(CC:CC1));
tau_max = max(t(CC:CC1))-min(t(CC:CC1));

% subtracts the average component to the data
xmed=mean(vx(CC:CC1));
x=vx(CC:CC1)-xmed;

%time to frequency
f_min = 1/tau_max; % minimum detectable frequency [s^-1]
dt = tau_max/(nt-1); % time step [s]
tau_min =2*dt; % minimum detectable period [s]
f_max = 1/tau_min; % maximim detectable frequency [s^-1]
f = [0:nt-1]*f_min;

```

```

%abs(Fourrier transform)
y = fft(x)*dt;
E = abs(y);

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(f(1:nt/2), E(1:nt/2), 'b-');
grid on
grid minor
xlim([0 100])
ylim([0 0.3])
xlabel('\itf \rm (Hz)','LineWidth',2,'FontSize',19);
ylabel('\rm FFT(\it v_x\rm) \rm(m)','LineWidth',2,'FontSize',19);

saveas(gcf,['vx_spectrum',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
set(gca,'yscale','log')
semilogy(f(1:nt/2), E(1:nt/2), 'b-');
grid on
grid minor
xlim([0 100])
ylim([1e-8 1])
xlabel('\itf \rm (Hz)','LineWidth',2,'FontSize',19);
ylabel('\rm FFT(\it v_x\rm) \rm(m)','LineWidth',2,'FontSize',19);

saveas(gcf,['vx_log_',num2str(i)],'tif')

%Spectral Analysis vy
nt = length(t(CC:CC1));
tau_max = max(t(CC:CC1))-min(t(CC:CC1));

% subtracts the average component to the data
ymed=mean(vy(CC:CC1));
x=vy(CC:CC1)-ymed;

%time to frequency
f_min = 1/tau_max; % minimum detectable frequency [s^-1]
dt = tau_max/(nt-1); % time step [s]
tau_min = 2*dt; % minimum detectable period [s]
f_max = 1/tau_min; % maximim detectable frequency [s^-1]
f = [0:nt-1]*f_min;

%abs(Fourrier transform)
y = fft(x)*dt;
E = abs(y);

figure1=figure

```



```

axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(f(1:nt/2), E(1:nt/2), 'b-');
grid on
grid minor
xlim([0 100])
ylim([0 0.15])
xlabel('\itf \rm (Hz)','LineWidth',2,'FontSize',19);
ylabel('\rm FFT(\it v_y\rm) \rm(m)','LineWidth',2,'FontSize',19);

saveas(gcf,['vy_spectrum_',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
set(gca,'yscale','log')
semilogy(f(1:nt/2), E(1:nt/2), 'b-');
grid on
grid minor
xlim([0 100])
ylim([1e-8 1e-1])
xlabel('\itf \rm (Hz)','LineWidth',2,'FontSize',19);
ylabel('\rm FFT(\it v_y\rm) \rm(m)','LineWidth',2,'FontSize',19);

saveas(gcf,['vy_log_',num2str(i)],'tif')

save('data_end')
clear vx vy vorticity strain
end

close all

% Centre of left channels
for i=1:8
    i
    vx=eval(['vx_1' num2str(i)]);
    vy=eval(['vy_1' num2str(i)]);
    strain=eval(['strain_1' num2str(i)]);
    vorticity=eval(['vorticity_1' num2str(i)]);

    t1=108;
    t2=109;
    [A,B]=min(abs(t-t1));
    [AA,BB]=min(abs(t-t2));

    [C,CC]=max(vy(B:BB));
    CC=CC+B;

    t11=117;
    t21=118;
    [A1,B1]=min(abs(t-t11));
    [AA1,BB1]=min(abs(t-t21));

```

```

[Cl,CC1]=max(vy(B1:BB1));
CC1=CC1+B1;

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(CC:CC1),vx(CC:CC1),'b')
grid on
grid minor
xlabel('\it t \rm (s)'
      , 'LineWidth',2, 'FontWeight','normal','FontSize',19);
ylabel('\itv_x \rm(m/s)'
      , 'LineWidth',2, 'FontWeight','normal','FontSize',19);
xlim(axes1,[t(CC) t(CC1)]);
ylim(axes1,[-0.15 0.15]);
box(axes1,'on');

saveas(gcf,['vx_1',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(CC:CC1),vy(CC:CC1),'b')
grid on
grid minor
xlabel('\it t \rm (s)'
      , 'LineWidth',2, 'FontWeight','normal','FontSize',19);
ylabel('\itv_y \rm(m/s)'
      , 'LineWidth',2, 'FontWeight','normal','FontSize',19);
xlim(axes1,[t(CC) t(CC1)]);
ylim(axes1,[-0.1 0.15]);
box(axes1,'on');

saveas(gcf,['vy_1',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all')
plot(t(CC:CC1),vorticity(CC:CC1),'b')
grid on
grid minor
xlabel('Flow time (s)', 'LineWidth',2, 'FontSize',19);
ylabel('\itvorticity \rm(s^-1)', 'LineWidth',2, 'FontSize',19);
xlim(axes1,[t(CC) t(CC1)]);
box(axes1,'on');

saveas(gcf,['vorticity__1',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);

```

```

box(axes1,'on');
hold(axes1,'all')
plot(t(CC:CC1),strain(CC:CC1),'b')
grid on
grid minor
xlabel('Flow time (s)','LineWidth',2,'FontSize',19);
ylabel('\itstrain rate \rm(s^{-1})','LineWidth',2,'FontSize',19);
xlim(axes1,[t(CC) t(CC1)]);
box(axes1,'on');

saveas(gcf,['strain_1',num2str(i)],'tif')

%Attractor -1 to 1

% normalize between [a, b]
% x=(b-a)*(x-min(x))/(max(x)-min(x))+a

vvx1=2*(vx(CC:CC1)-min(vx(CC:CC1)))/(max(vx(CC:CC1))-
    min(vx(CC:CC1)))-1;
vvy1=2*(vy(CC:CC1)-min(vy(CC:CC1)))/(max(vy(CC:CC1))-
    min(vy(CC:CC1)))-1;

vorticity1=2*(vorticity(CC:CC1)-min(vorticity(CC:CC1)))/
    (max(vorticity(CC:CC1))-min(vorticity(CC:CC1)))-1;

strain1=2*(strain(CC:CC1)-min(strain(CC:CC1)))/
    (max(strain(CC:CC1))-min(strain(CC:CC1)))-1;

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(vorticity1,strain1,'b');
box(axes1,'on');
hold(axes1,'all')
pbaspect([1 1 1])
grid on
grid minor
xlabel('\it \zeta^*',
    'LineWidth',2,'FontWeight','normal','FontSize',24);
ylabel('\it \epsilon^*',
    'LineWidth',2,'FontWeight','normal','FontSize',24);

saveas(gcf,['attractor_1',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(vvy1,vvx1,'b')
grid on
grid minor
xlabel('\it vy','LineWidth',2,'FontSize',16);
ylabel('\it vx','LineWidth',2,'FontSize',16);

```

```

saveas(gcf,['attractor_SEM_HPB_1',num2str(i)],'tif')

%Spectral Analysis vx
nt = length(t(CC:CC1));
tau_max = max(t(CC:CC1))-min(t(CC:CC1));

% subtracts the average component to the data
xmed=mean(vx(CC:CC1));
x=vx(CC:CC1)-xmed;

%time to frequency
f_min = 1/tau_max; % minimum detectable frequency [s^-1]
dt = tau_max/(nt-1); % time step [s]
tau_min =2*dt; % minimum detectable period [s]
f_max = 1/tau_min; % maximim detectable frequency [s^-1]
f = [0:nt-1]*f_min;

%abs(Fourrier transform)
y = fft(x)*dt;
E = abs(y);
figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(f(1:nt/2), E(1:nt/2), 'b-');
grid on
grid minor
xlim([0 100])
ylim([0 0.3])
xlabel('\itf \rm (Hz)','LineWidth',2,'FontSize',19);
ylabel('\rm FFT(\it v_x\rm) \rm(m)','LineWidth',2,'FontSize',19);

saveas(gcf,['vx_1',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
set(gca,'yscale','log')
semilogy(f(1:nt/2), E(1:nt/2), 'b-');
grid on
grid minor
xlim([0 100])
ylim([1e-8 1])
xlabel('\itf \rm (Hz)','LineWidth',2,'FontSize',19);
ylabel('\rm FFT(\it v_x\rm) \rm(m)','LineWidth',2,'FontSize',19);

saveas(gcf,['vx_log_1',num2str(i)],'tif')

%Spectral Analysis vy
nt = length(t(CC:CC1));
tau_max = max(t(CC:CC1))-min(t(CC:CC1));
% subtracts the average component to the data
ymed=mean(vy(CC:CC1));

```

```

x=vy(CC:CC1)-ymed;

%time to frequency
f_min = 1/tau_max; % minimum detectable frequency [s^-1]
dt = tau_max/(nt-1); % time step [s]
tau_min = 2*dt; % minimum detectable period [s]
f_max = 1/tau_min; % maximum detectable frequency [s^-1]
f = [0:nt-1]*f_min;

%abs(Fourrier transform)
y = fft(x)*dt;
E = abs(y);

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(f(1:nt/2), E(1:nt/2), 'b-');
grid on
grid minor
xlim([0 100])
ylim([0 0.15])
xlabel('\itf \rm (Hz)','LineWidth',2,'FontSize',19);
ylabel('\rm FFT(\it v_y\rm) \rm(m)','LineWidth',2,'FontSize',19);

saveas(gcf,['vy_spectrum_1',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
set(gca,'yscale','log')
semilogy(f(1:nt/2), E(1:nt/2), 'b-');
grid on
grid minor
xlim([0 100])
ylim([1e-8 1e-1])
xlabel('\itf \rm (Hz)','LineWidth',2,'FontSize',19);
ylabel('\rm FFT(\it v_y\rm) \rm(m)','LineWidth',2,'FontSize',19);

saveas(gcf,['vy_log_1',num2str(i)],'tif')

clear vx vy vorticity strain
end

%Plot in the centre on of the right channels
for i=1:8
    i
    vx=eval(['vx_r' num2str(i)]);
    vy=eval(['vy_r' num2str(i)]);
    strain=eval(['strain_r' num2str(i)]);
    vorticity=eval(['vorticity_r' num2str(i)]);

    t1=108;

```

```

t2=109 ;
[A,B]=min(abs(t-t1));
[AA,BB]=min(abs(t-t2));

[C,CC]=max(vy(B:BB));
CC=CC+B;

t11=117;
t21=118;
[A1,B1]=min(abs(t-t11));
[AA1,BB1]=min(abs(t-t21));

[C1,CC1]=max(vy(B1:BB1));
CC1=CC1+B1;

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(CC:CC1),vx(CC:CC1),'b')
grid on
grid minor
xlabel('\it t \rm (s)'
      , 'LineWidth',2, 'FontWeight','normal', 'FontSize',19);
ylabel('\itv_x \rm(m/s)'
      , 'LineWidth',2, 'FontWeight','normal', 'FontSize',19);
xlim(axes1,[t(CC) t(CC1)]);
ylim(axes1,[-0.15 0.15]);
box(axes1,'on');

saveas(gcf,['vx_r',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(t(CC:CC1),vy(CC:CC1),'b')
grid on
grid minor
xlabel('\it t \rm (s)'
      , 'LineWidth',2, 'FontWeight','normal', 'FontSize',19);
ylabel('\itv_y \rm(m/s)'
      , 'LineWidth',2, 'FontWeight','normal', 'FontSize',19);
xlim(axes1,[t(CC) t(CC1)]);
ylim(axes1,[-0.1 0.15]);
box(axes1,'on');

saveas(gcf,['vy_r',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all')
plot(t(CC:CC1),vorticity(CC:CC1),'b')

```



```

grid on
grid minor
xlabel('Flow time (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\itvorticity \rm(s^{-1})', 'LineWidth', 2, 'FontSize', 19);
xlim(axes1, [t(CC) t(CC1)]);
box(axes1, 'on');

saveas(gcf, ['vorticity_r', num2str(i)], 'tif')

figure1=figure
axes1 = axes('Parent', figure1, 'FontSize', 17);
box(axes1, 'on');
hold(axes1, 'all')
plot(t(CC:CC1), strain(CC:CC1), 'b')
grid on
grid minor
xlabel('Flow time (s)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\itstrain rate \rm(s^{-1})', 'LineWidth', 2, 'FontSize', 19);
xlim(axes1, [t(CC) t(CC1)]);
box(axes1, 'on');

saveas(gcf, ['strain_r', num2str(i)], 'tif')

%Attractor -1 to 1

% normalize between [a, b]
% x=(b-a)*(x-min(x))/(max(x)-min(x))+a

vvx1=2*(vx(CC:CC1)-min(vx(CC:CC1)))/(max(vx(CC:CC1))-min(vx(CC:CC1)))-1;
vvy1=2*(vy(CC:CC1)-min(vy(CC:CC1)))/(max(vy(CC:CC1))-min(vy(CC:CC1)))-1;
vorticity1=2*(vorticity(CC:CC1)-min(vorticity(CC:CC1)))/(max(vorticity(CC:CC1))-min(vorticity(CC:CC1)))-1;
strain1=2*(strain(CC:CC1)-min(strain(CC:CC1)))/(max(strain(CC:CC1))-min(strain(CC:CC1)))-1;

figure1=figure
axes1 = axes('Parent', figure1, 'FontSize', 17);
box(axes1, 'on');
hold(axes1, 'all');
plot(vorticity1, strain1, 'b');
box(axes1, 'on');
hold(axes1, 'all')
pbaspect([1 1 1])
grid on
grid minor
xlabel('\it \zeta^*', 'LineWidth', 2, 'FontWeight', 'normal', 'FontSize', 24);
ylabel('\it \epsilon^*', 'LineWidth', 2, 'FontWeight', 'normal', 'FontSize', 24);

saveas(gcf, ['attractor_r', num2str(i)], 'tif')

```

```

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(vvy1,vvx1,'b')
grid on
grid minor
xlabel('\it vy','LineWidth',2,'FontSize',16);
ylabel('\it vx','LineWidth',2,'FontSize',16);

saveas(gcf,['attractor_r',num2str(i)],'tif')

%Spectral Analysis vx
nt = length(t(CC:CC1));
tau_max = max(t(CC:CC1))-min(t(CC:CC1));

% subtracts the average component to the data
xmed=mean(vx(CC:CC1));
x=vx(CC:CC1)-xmed;

%time to frequency
f_min = 1/tau_max; % minimum detectable frequency [s^-1]
dt = tau_max/(nt-1); % time step [s]
tau_min =2*dt; % minimum detectable period [s]
f_max = 1/tau_min; % maximim detectable frequency [s^-1]
f = [0:nt-1]*f_min;

%abs(Fourrier transform)
y = fft(x)*dt ;
E = abs(y);

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(f(1:nt/2), E(1:nt/2), 'b-');
grid on
grid minor
xlim([0 100])
ylim([0 0.3])
xlabel('\itf \rm (Hz)','LineWidth',2,'FontSize',19);
ylabel('\rm FFT(\it v_x\rm) \rm(m)','LineWidth',2,'FontSize',19);

saveas(gcf,['vx_spectrum_r',num2str(i)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
set(gca,'yscale','log')
semilogy(f(1:nt/2), E(1:nt/2), 'b-');
grid on
grid minor
xlim([0 100])

```

```

ylim([1e-8 1])
xlabel('\itf \rm (Hz)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\rm FFT(\it v_x\rm) \rm(m)', 'LineWidth', 2, 'FontSize', 19);

saveas(gcf, ['vx_log_r', num2str(i)], 'tif')

%Spectral Analysis vy
nt = length(t(CC:CC1));
tau_max = max(t(CC:CC1))-min(t(CC:CC1));

% subtracts the average component to the data
ymed=mean(vy(CC:CC1));
x=vy(CC:CC1)-ymed;

%time to frequency
f_min = 1/tau_max; % minimum detectable frequency [s^-1]
dt = tau_max/(nt-1); % time step [s]
tau_min = 2*dt; % minimum detectable period [s]
f_max = 1/tau_min; % maximim detectable frequency [s^-1]
f = [0:nt-1]*f_min;

%abs(Fourrier transform)
y = fft(x)*dt ;
E = abs(y);
figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
plot(f(1:nt/2), E(1:nt/2), 'b-');
grid on
grid minor
xlim([0 100])
ylim([0 0.15])
xlabel('\itf \rm (Hz)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\rm FFT(\it v_y\rm) \rm(m)', 'LineWidth', 2, 'FontSize', 19);

saveas(gcf, ['vy_spectrum_r', num2str(i)], 'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',17);
box(axes1,'on');
hold(axes1,'all');
set(gca, 'yscale', 'log')
semilogy(f(1:nt/2), E(1:nt/2), 'b-');
grid on
grid minor
xlim([0 100])
ylim([1e-8 1e-1])
xlabel('\itf \rm (Hz)', 'LineWidth', 2, 'FontSize', 19);
ylabel('\rm FFT(\it v_y\rm) \rm(m)', 'LineWidth', 2, 'FontSize', 19);

saveas(gcf, ['vy_log_r', num2str(i)], 'tif')

clear vx vy vorticity strain
end

```

```
save('data_end_2')
close all
```

D.9 Poincaré Maps

D.9.1 2D Map

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% 2D SECTION %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%draw section: 85 intersections, 6.85; m=-1; b=-0.8;
%draw section: 79 intersections, 6.70
%draw section: 80 intersections, 6.65
%draw section: 75 intersections, 6.53; m=-1; b=-0.5;
%draw section: 42 intersections, 6.55
%draw section: 94 intersections, 6.57
%draw section: 66 intersections, 6.60
%draw section: 79 intersections, 6.70
%draw section: 84 intersections, 6.75
%draw section: 85 intersections, 6.45; m=-1; b=-0.1
%draw section: 87 intersections, 6.35; m=1; b=-0.2

% ni=[85, 79, 80, 75, 42, 94, 66, 79, 84, 85, 87];
% Dd=[6.85, 6.70, 6.65, 6.53, 6.55, 6.57, 6.60, 6.70, 6.75, 6.45,
      6.35];
% figure
% plot(Dd, ni, 'b')

name='C:\Users\Admin\Documents\6_55_ICM_mais_tempo'

cd(name)
load('data8')
close all

clearvars -except vorticity1 strain1 vvx1 vvy1

% Create folders
mkdir 2D_section
mkdir 2D_video

cd('2D_video')

mkdir p
mkdir pp
mkdir ppp
mkdir pppp
mkdir ppppp
mkdir data

cd ..

% Start
m=-1;
b=-0.5;
```

```

k=0;
for i=1:length(strain1)
    y(i)=m*(vorticity1(i))+b;

    if abs(strain1(i)-y(i))<=1e-2
        k=[k,i];
    end
end
k(k==0)=[];

%plot section
x=[-1:0.01:1];
y=m*x+b;

figure
plot(vorticity1,strain1,'marker','.', 'linestyle','-', 'color','b')
hold on
plot(x,y,'k')
grid on
grid minor
xlabel('\it vorticity')
ylabel('\it strain')
xlim([-1 1])
ylim([-1 1])

cd 2D_section

saveas(gcf, 'Poincare_SECTION', 'tif')

%%
%cut points

%6.85, 6.70, 6.65: -0.9
%6.53, 6.55, 6.57, 6.60, 6.70, 6.75: -0.8
%6.35: >0.85

% vf2=vorticity1(vorticity1>0.85);
% vf12=strain1(vorticity1>0.85);
%
% vff2=find(vorticity1>0.85);

%6.45: -0.7 e -0.4

% vf2=0;
% vf12=0;
% vff2=0;
% for i=1:length(vorticity1)
%     if vorticity1(i)>0.85 %&& vorticity1(i)<0.70
%         vf2=[vf2, vorticity1(i)];
%         vf12=[vf12, strain1(i)];
%         vff2=[vff2,i];
%     end
%
% end
%
% vf2(vf2==0)=[];

```

```

% vf12(vf12==0)=[];
% vff2(vff2==0)=[];

vf2=vorticity1(vorticity1<-0.8);
vf12=strain1(vorticity1<-0.8);

vff2=find(vorticity1<-0.8);

%Separate into series
aa=0;
for i=1:length(vf12)-1
    i
    if vff2(i+1)== vff2(i)+1
        aa=[aa,0];
    else
        aa=[aa,i];
    end
end

aa(aa==0)=[];
bbit{1}=vff2(1:aa(1))';
bbv{1}=vf2(1:aa(1))';
bbs{1}=vf12(1:aa(1))';
for i=2:length(aa)-1
    bbit{i}=vff2(aa(i-1)+1:aa(i))';
    bbv{i}=vf2(aa(i-1)+1:aa(i))';
    bbs{i}=vf12(aa(i-1)+1:aa(i))';
end
bbit{length(aa)}=vff2(length(aa):end)';
bbv{length(aa)}=vf2(length(aa):end)';
bbs{length(aa)}=vf12(length(aa):end)';

%Intercept with attractor
vpx=0;
vpy=0;
vpi=0;
for i=1:length(bbit)
    ccit=cell2mat(bbit(i));
    ccv=cell2mat(bbv(i));
    ccs=cell2mat(bbs(i));

    %select serie
    for ii=1:length(ccit)-1
        ii
        m2=(ccs(ii)-ccs(ii+1))/(ccv(ii)-ccv(ii+1));
        b2=ccs(ii+1)-m2*ccv(ii+1);

        xa=(b-b2)/(m2-m);
        ya=m*xa+b;

        if ya>ccs(ii) && ya<ccs(ii+1)
            %if xa>ccv(ii) && xa<ccv(ii+1)
            vpx=[vpx, xa];
            vpy=[vpy, ya];
            vpi=[vpi, ccit(ii)];
        end
    end
end

```

```

        %end
    end
end
clear ccit ccv ccs
end

vpx=vpx(2:end);
vpy=vpy(2:end);
vpi=vpi(2:end);

%plot
figure1=figure
axes1 = axes('Parent',figure1,'FontSize',14);
box(axes1,'on');
hold(axes1,'all');
plot(vorticity1,strain1,'-b')
hold on
plot(vpx,vpy,'.r')
grid on
grid minor
xlim([-1 1])
ylim([-1 1])
xlabel('\it vorticity')
ylabel('\it strain')

saveas(gcf,'Poincare_SECTION_1','tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',14);
box(axes1,'on');
hold(axes1,'all');
plot(vpx,vpy,'.b')
%xlim([min(vpx)-1e-10 max(vpx)+1e-10])
%ylim([min(vpy)-1e-10 max(vpy)+1e-10])
%set(gca,'xticklabel',[])
%set(gca,'xtick',[])
%set(gca,'yticklabel',[])
%set(gca,'ytick',[])
grid on
grid minor
xlabel('\it vorticity')
ylabel('\it strain')
%ylim([-1 1])

saveas(gcf,'Poincare_SECTION_2','tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',14);
box(axes1,'on');
hold(axes1,'all');
plot(vpx(1:end-1),vpx(2:end),'.b')
%xlim([min(vpx)-1e-10 max(vpx)+1e-10])
%ylim([min(vpx)-1e-10 max(vpx)+1e-10])
%set(gca,'xticklabel',[])
%set(gca,'xtick',[])
%set(gca,'yticklabel',[])

```



```

%set(gca,'ytick',[])
%ylim([-1 1])
xlim([min(vpx)-1e-10 max(vpx)+1e-10])
ylim([min(vpx)-1e-10 max(vpx)+1e-10])
grid on
grid minor
xlabel('\it vorticity(k)')
ylabel('\it vorticity(k+1)')

saveas(gcf,'Poincare_SECTION_3','tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',14);
box(axes1,'on');
hold(axes1,'all');
plot(vpx,vpi,'.b')
%xlim([min(vpx)-1e-10 max(vpx)+1e-10])
%ylim([min(vpi)-1e-10 max(vpi)+1e-10])
%set(gca,'xticklabel',[])
%set(gca,'xtick',[])
%set(gca,'yticklabel',[])
%set(gca,'ytick',[])
%ylim([-1 1])
xlim([min(vpx)-1e-10 max(vpx)+1e-10])
ylim([min(vpi)-1e-10 max(vpi)+1e-10])
grid on
grid minor
xlabel('\it vorticity')
ylabel('\it iteration')

saveas(gcf,'Poincare_SECTION_4','tif')

figure
plot(vorticity1,strain1,'marker','.', 'linestyle','-','color','b')
hold on
plot(x,y,'k')
hold on
plot(vpx,vpy,'.r')
grid on
grid minor
xlabel('\it vorticity')
ylabel('\it strain')
xlim([-1 1])
ylim([-1 1])

saveas(gcf,'Poincare_SECTION_5','tif')

save('data')

close all
clear vpxx vpyy vpx vpy vpxxx vf12 vf2 vff2 vpi vpx vpy aa bbit
      bbs bbv ccit ccv ccs

%%
%3D MAP
figure1=figure
axes1 = axes('Parent',figure1,'FontSize',14);

```

```

view(axes1, [-37.5 30])
box(axes1, 'on');
plot3(vpx(1:end-1), vpx(2:end), vpi(1:end-1), '.b')
set(gca, 'xticklabel', [])
set(gca, 'xtick', [])
set(gca, 'yticklabel', [])
set(gca, 'ytick', [])
set(gca, 'zticklabel', [])
set(gca, 'ztick', [])
grid on
grid minor
xlabel('\it vorticity(k)')
ylabel('\it vorticity(k+1)')
zlabel('\it Iteration')

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% 2D VIDEO %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
close all
clear all

name='C:\Users\Admin\Documents\6_85_ICM_mais_tempo\NEW'

cd(name)
load('data8')
close all
clearvars -except vorticity1 strain1 vx1 vy1

cd 2D_video

%%
%Parameters
is=5226; %485;

fator1=0.03;
fator2=0.03;
x1=vorticity1(is-1);
y1=strain1(is-1);
x2=vorticity1(is+1);
y2=strain1(is+1);

m1=(y1-y2)/(x1-x2);
m=-1/m1;
b=y1-m*x1;

x=[min(x1,x2)-fator1:0.01:max(x1,x2)+fator2];
y=m*x+b;

figure
plot(vorticity1, strain1, '-b')
hold on
plot(x, y, '-r')
xlim([-1 1])
ylim([-1 1])

for k= 5226:5255 %is:is+100 %5226:5255
    k

```

```

x1=vorticity1(k-1);
y1=strain1(k-1);
x2=vorticity1(k+1);
y2=strain1(k+1);

m1=(y1-y2)/(x1-x2);
m=-1/m1;
b=y1-m*x1;

x=[min(x1,x2)-fator1:0.01:max(x1,x2)+fator2];
y=m*x+b;

figure
plot(vorticity1,strain1,'-b')
hold on
plot(x,y,'-r','LineWidth',2)
xlim([-1 1])
ylim([-1 1])

saveas(gcf,['P_',num2str(k)],'tif')
close all

cd('C:\Users\Joana Matos\Documents\6_65\section')
end

%cut points

s3=strain1(vorticity1>min(x1,x2)-fator1);
it1=find(vorticity1);
it3=it1(vorticity1>min(x1,x2)-fator1);
v3=vorticity1(vorticity1>min(x1,x2)-fator1);

vf12=s3(v3<max(x1,x2)+fator2);
vff2=it3(v3<max(x1,x2)+fator2);
vf2=v3(v3<max(x1,x2)+fator2);

%Separate into series
aa=0;
for i=1:length(vf12)-1
    i
    if vff2(i+1)== vff2(i)+1
        aa=[aa,0];
    else
        aa=[aa,i];
    end
end
end

aa(aa==0)=[];

bbit{1}=vff2(1:aa(1))';
bbv{1}=vf2(1:aa(1))';
bbs{1}=vf12(1:aa(1))';
for i=2:length(aa)-1
    bbit{i}=vff2(aa(i-1)+1:aa(i))';
    bbv{i}=vf2(aa(i-1)+1:aa(i))';
    bbs{i}=vf12(aa(i-1)+1:aa(i))';
end

```

```

end
bbit{length(aa)}=vff2(length(aa):end)';
bbv{length(aa)}=vf2(length(aa):end)';
bbs{length(aa)}=vf12(length(aa):end)';

%Intercept with attractor
vpx=0;
vpy=0;
vpi=0;
for i=1:length(bbit)
    ccit=cell2mat(bbit(i));
    ccv=cell2mat(bbv(i));
    ccs=cell2mat(bbs(i));
    %select serie
    for ii=1:length(ccit)-1
        ii
        m2=(ccs(ii)-ccs(ii+1))/(ccv(ii)-ccv(ii+1));
        b2=ccs(ii+1)-m2*ccv(ii+1);

        xa=(b-b2)/(m2-m);
        ya=m*xa+b;

        if ya>ccs(ii) && ya<ccs(ii+1)
            %if xa>ccv(ii) && xa<ccv(ii+1)
                vpx=[vpx, xa];
                vpy=[vpy, ya];
                vpi=[vpi, ccit(ii)];
            %end
        end
    end
    clear ccit ccv ccs
end

vpx=vpx(2:end);
vpy=vpy(2:end);
vpi=vpi(2:end);

%plot
cd ..
cd pp
figure
plot(vorticity1, strain1, '-b')
hold on
plot(vpx, vpy, '.r')
xlim([-1 1])
ylim([-1 1])
xlabel('\it vorticity')
ylabel('\it strain')

saveas(gcf, ['PP_', num2str(k)], 'tif')

cd ..
cd ppp

figure
plot(vpx, vpy, '.b')

```

```

xlim([min(vpx)-1e-10 max(vpx)+1e-10])
ylim([min(vpy)-1e-10 max(vpy)+1e-10])
set(gca,'xticklabel',[])
set(gca,'xtick',[])
set(gca,'yticklabel',[])
set(gca,'ytick',[])
xlabel('\it vorticity')
ylabel('\it strain')
%ylim([-1 1])

saveas(gcf,['PPP_',num2str(k)],'tif')

cd ..
cd pppp

figure
plot(vpx(1:end-1),vpx(2:end),'.b')
xlim([min(vpx)-1e-10 max(vpx)+1e-10])
ylim([min(vpx)-1e-10 max(vpx)+1e-10])
set(gca,'xticklabel',[])
set(gca,'xtick',[])
set(gca,'yticklabel',[])
set(gca,'ytick',[])
%ylim([-1 1])xlabel('\it vorticity(k)')
ylabel('\it vorticity(k+1)')

saveas(gcf,['PPPP_',num2str(k)],'tif')

cd ..
cd ppppp
figure
plot(vpx,vpi,'.b')
xlim([min(vpx)-1e-10 max(vpx)+1e-10])
ylim([min(vpi)-1e-10 max(vpi)+1e-10])
set(gca,'xticklabel',[])
set(gca,'xtick',[])
set(gca,'yticklabel',[])
set(gca,'ytick',[])
%ylim([-1 1])
xlabel('\it vorticity')
ylabel('\it iteration')

saveas(gcf,['PPPPP_',num2str(k)],'tif')

cd ..
cd data

save(['data_',num2str(k)])

close all
clear vpxx vpyy vpx vpy vpxxx vf12 vf2 vff2 vpi vpx vpy aa bbit bbs
      bbv ccit ccv ccs

cd ..
%%
%3D_MAP
for ij=1:50
    ij

```

```

cd('C:\Users\Joana Matos\Documents\attractor\6_85\2D\data')
load(['data_', num2str(ij+484)]);

figure1=figure;
axes1 = axes('Parent',figure1);
hold(axes1,'on');
view(axes1,[-159.5 63.60000000000001]); %6.85
box(axes1,'on');
grid(axes1,'on');
plot3(vpx(1:end-1),vpx(2:end),vpi(1:end-1),'.b');
grid on
grid minor
set(gca,'xticklabel',[])
set(gca,'xtick',[])
set(gca,'yticklabel',[])
set(gca,'ytick',[])
set(gca,'zticklabel',[])
set(gca,'ztick',[])
%ylim([-1 1])
grid on
grid minor
%xlabel('\it vorticity(k)')
%ylabel('\it vorticity(k+1)')
%zlabel('\it Iteration')
minn=min(vpx(end))
maxx=max(vpx(end))

cd ('C:\Users\Joana Matos\Documents\attractor\6_85\2D\PPP_3D')

saveas(gcf,['NEW_PPP__3D',num2str(ij)],'tif')

close all
clear all
end

```

D.9.2 3D Map

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% 3D SECTION %%%%%%%%%
name='C:\Users\Admin\Documents\6_35_ICM_mais_tempo'

cd(name)
load('data8')

close all
clearvars -except vx1 vy1 vorticity1 strain1 t tt CC CC1

mkdir 3D_section
mkdir 3D_video

cd('3D_video')

mkdir p
mkdir pp
mkdir ppp
mkdir pppp
mkdir ppppp

```

```

mkdir data

cd ..

%%
%Set Axis View
[xx yy] = meshgrid(-1:0.1:1);
zp=0;
zz = zp*ones(size(xx, 1));

figure1 = figure;
axes1 = axes('Parent',figure1);
hold(axes1,'on');
plot3(vvx1, vorticity1, strain1,'Color',[0 0 1]);
hold on
surf(xx,yy,zz,'Parent',axes1,'FaceAlpha',0.5,...
      'FaceColor',[0.862745106220245 0.862745106220245
      0.862745106220245],...
      'EdgeColor',[0.831372559070587 0.815686285495758
      0.7843137383461]);
xlabel('\it strain');
ylabel('\it vorticity');
xlabel('\it vx');
set(axes1,'FontSize',14,'XMinorGrid','on','YMinorGrid','on',
      'ZMinorGrid','on');
view(axes1,[107.3 12.4]);
grid(axes1,'on');
set(axes1,'FontSize',14,'XMinorGrid','on','YMinorGrid','on',
      'ZMinorGrid','on');

%%
%6.65, 6.85
%aview=[107.3 12.4];
%6.75
%aview=[98.49999999999999 16.40000000000001];

%Set intersections parameters
%6.35
aview=[140.9 21.99999999999999];

%6.85
% ni=8;
% vmin=[-0.6 -1 -0.3 0.5 0.9 0.5 0.1 -0.7];
% vmax=[-0.4 -0.9 -0.1 0.7 1 0.8 0.3 -0.5];
% vxmin=[0.8 0.5 0.3 0 -0.9 -1 -0.5 -0.3];
% vxmax=[1 0.7 0.4 0.2 -0.5 -0.9 -0.4 -0.1];

%6.75
% ni=4;
% vmin=[-0.3 0.4 -0.7 -1];
% vmax=[0.8 1 0.4 -0.5];
% vxmin=[0.1 -1 -0.5 0.6];
% vxmax=[0.5 -0.5 -0.1 1];
%6.35
ni=3;
vmin=[-0.4 0.4 -0.8];
vmax=[0.2 0.6 -0.5];

```



```

vxmin=[0.7 -0.5 -0.2];
vxmax=[1 0.3 0.2];

%Attractor only
figure1 = figure;
axes1 = axes('Parent',figure1);
hold(axes1,'on');
plot3(vvx1, vorticity1, strain1,'Color',[0 0 1]);
zlabel('\it strain');
ylabel('\it vorticity');
xlabel('\it vx');
set(axes1,'FontSize',14,'XMinorGrid','on','YMinorGrid','on',
      'ZMinorGrid','on');
view(axes1,aview);
grid(axes1,'on');
set(axes1,'FontSize',14,'XMinorGrid','on','YMinorGrid','on',
      'ZMinorGrid','on');

saveas(gcf,'Poincare_SECTION_3D_sem_plano','tif')

%%
%Intersection with plane: Strain=0

[xx yy] = meshgrid(-1:0.1:1);
zp=0;
zz = zp*ones(size(xx, 1));

figure1 = figure;
axes1 = axes('Parent',figure1);
hold(axes1,'on');
plot3(vvx1, vorticity1, strain1,'Color',[0 0 1]);
hold on
surf(xx,yy,zz,'Parent',axes1,'FaceAlpha',0.5,...
      'FaceColor',[0.862745106220245 0.862745106220245
      0.862745106220245],...
      'EdgeColor',[0.831372559070587 0.815686285495758
      0.7843137383461]);
zlabel('\it strain');
ylabel('\it vorticity');
xlabel('\it vx');
view(axes1,aview);
grid(axes1,'on');
set(axes1,'FontSize',14,'XMinorGrid','on','YMinorGrid','on',
      'ZMinorGrid','on');

saveas(gcf,'Poincare_SECTION_3D','tif')

sss2=0;
vvv2=0;
vvvx2=0;
vf2=0;
for jj=1:ni
    % Select set of points
    vorticity2=vorticity1(vvx1<vxmax(jj));
    strain2=strain1(vvx1<vxmax(jj));
    vv2=vvx1(vvx1<vxmax(jj));
    it1=find(vvx1);

```

```

it2=it1(vvx1<vxmax(jj));

vorticity52=vorticity2(vvx2>vxmin(jj));
strain52=strain2(vvx2>vxmin(jj));
vvx52=vvx2(vvx2>vxmin(jj));
it52=it2(vvx2>vxmin(jj));

strain4=strain52(vorticity52<vmax(jj));
vvx4=vvx52(vorticity52<vmax(jj));
it4=it52(vorticity52<vmax(jj));
vorticity4=vorticity52(vorticity52<vmax(jj));

strain22=strain4(vorticity4>vmin(jj));
vvx22=vvx4(vorticity4>vmin(jj));
it22=it4(vorticity4>vmin(jj));
vorticity22=vorticity4(vorticity4>vmin(jj));

%cut points
vvx32=vvx22(strain22>zp-0.1); %0.04);
it32=it22(strain22>zp-0.1); %0.04);
vorticity32=vorticity22(strain22>zp-0.1); %0.04);
strain32=strain22(strain22>zp-0.1); %0.04);

vvx11=vvx32(strain32<zp+0.1); %0.04);
it11=it32(strain32<zp+0.1); %0.04);
vorticity11=vorticity32(strain32<zp+0.1); %0.04);
strain11=strain32(strain32<zp+0.1); %0.04);

xm11=0;
for i=1:length(it11)-1
    i
    if it11(i+1)==it11(i)+1
        syms x y z xm
        x11=vvx11(i)+xm*(vvx11(i+1)-vvx11(i));
        y11=vorticity11(i)+xm*(vorticity11(i+1)-vorticity11(i));
        z11=strain11(i)+xm*(strain11(i+1)-strain11(i));

        eqn=0*(x - 0) + 0*(y - 0) + 1*(z - 0) == zp;
        eqn=subs(eqn,{x,y,z},{x11,y11,z11});
        [xm]=vpa(solve(eqn,xm));

        xm11=double(xm);

        x11=vvx11(i)+xm11*(vvx11(i+1)-vvx11(i));
        y11=vorticity11(i)+xm11*(vorticity11(i+1)-vorticity11(i));
        z11=strain11(i)+xm11*(strain11(i+1)-strain11(i));

        xm11=[xm11,xm11];

        if z11>min(strain11(i),strain11(i+1)) &&
            z11<max(strain11(i),strain11(i+1))
            sss2=[sss2,z11];
            vvv2=[vvv2,y11];
            vvvx2=[vvvx2,x11];
            vf2=[vf2,i];
        end
    end
end

```

```

        end
    end
    clear vvx32 strain32 vorticity32 vorticity2 x11 y11 z11 xm11
        vorticity11 strain11 vvx11 strain2 vvx2 it2 it1 vorticity52
        strain52 vvx52 it52 strain4 vvx4 it4 vorticity4 strain22 vvx22
        it22 vorticity22
end

sss2=sss2(2:end);
vvv2=vvv2(2:end);
vvvx2=vvvx2(2:end);
vf2=vf2(2:end);

figure1 = figure;
axes1 = axes('Parent',figure1);
hold(axes1,'on');
plot3(vvx1, vorticity1, strain1,'Color',[0 0 1]);
hold on
plot3(vvvx2, vvv2, sss2,'Marker','.', 'LineStyle','none','Color',[1 0
0]);
hold on
surf(xx,yy,zz,'Parent',axes1,'FaceAlpha',0.5,...
    'FaceColor',[0.862745106220245 0.862745106220245
    0.862745106220245],...

    'EdgeColor',[0.831372559070587 0.815686285495758
    0.7843137383461]);
xlabel('\it strain');
ylabel('\it vorticity');
xlabel('\it vx');
view(axes1,aview);
grid(axes1,'on');
set(axes1,'FontSize',14,'XMinorGrid','on','YMinorGrid','on',
    'ZMinorGrid','on');

saveas(gcf,'Poincare_SECTION_3D_1','tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',14);
box(axes1,'on');
hold(axes1,'all');
%plot(vorticity11,vvx11,'.b')
%hold on
plot(vvvx2,vvv2 ,'.r')
grid on
grid minor
%xlim([min(vvv2)-1e-10 max(vvv2)+1e-10])
%ylim([min(vvx2)-1e-10 max(vvx2)+1e-10])
%set(gca,'xticklabel',[])
%set(gca,'xtick',[])
%set(gca,'yticklabel',[])
%set(gca,'ytick',[])
xlabel('\it vx','LineWidth',2,'FontSize',16);
ylabel('\it vorticity','LineWidth',2,'FontSize',16);

saveas(gcf,'Poincare_SECTION_3D_2','tif')

```

```

save('data_3D')

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% 3D VIDEO %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

name='C:\Users\Admin\Documents\6_35_ICM_mais_tempo'

cd(name)
load('data8')

close all
clearvars -except vx1 vy1 vorticity1 strain1 t tt CC CC1 aview

cd 3D_video

%%
%Set plane start and view

[xx yy] = meshgrid(-1:0.1:1)
zp=-0.6;
zz = zp*ones(size(xx, 1));

figure1 = figure;
axes1 = axes('Parent',figure1);
hold(axes1,'on');
plot3(vx1, vorticity1, strain1,'Color',[0 0 1]);
%hold on
%plot3(vx3,vorticity3,strain3,'.r')
%plot3(vx2(ss2), vorticity2(ss2),
strain2(ss2),'Marker','.', 'LineStyle','none','Color',[1 0 0]);
%hold on
%plot3(vf122, vf2, vf12,'Marker','.', 'LineStyle','none','Color',[1 0
0]);
%hold on
surf(xx,yy,zz,'Parent',axes1,'FaceAlpha',0.5,...
'FaceColor',[0.862745106220245 0.862745106220245
0.862745106220245],...
'EdgeColor',[0.831372559070587 0.815686285495758
0.7843137383461]);
xlabel('\it strain');
ylabel('\it vorticity');
xlabel('\it vx');
view(axes1,[-95.09999999999999 5.20000000000001]);
grid(axes1,'on');
set(axes1,'FontSize',14,'XMinorGrid','on','YMinorGrid','on',
'ZMinorGrid','on');

%%
aview=[-95.09999999999999 5.20000000000001];
zp=-0.6;
vmin=0.1;
vmax=0.6;
vxmin=-0.5;
vxmax=-0.2;

%%
for j=1:100

```

```

j
zz = zp*ones(size(xx, 1));

figure1 = figure;
axes1 = axes('Parent',figure1);
hold(axes1,'on');
plot3(vvx1, vorticity1, strain1,'Color',[0 0 1]);
hold on
surf(xx,yy,zz,'Parent',axes1,'FaceAlpha',0.5,...
      'FaceColor',[0.862745106220245 0.862745106220245
                  0.862745106220245],...
      'EdgeColor',[0.831372559070587 0.815686285495758
                  0.7843137383461]);
zlabel('\it strain');
ylabel('\it vorticity');
xlabel('\it vx');
view(axes1,aview);
grid(axes1,'on');
set(axes1,'FontSize',14,'XMinorGrid','on','YMinorGrid','on',
     'ZMinorGrid','on');

cd p
saveas(gcf,['P_',num2str(j)],'tif')

%Select points
vorticity2=vorticity1(vvx1<vxmax);
strain2=strain1(vvx1<vxmax);
vvx2=vvx1(vvx1<vxmax);
it1=find(vvx1);
it2=it1(vvx1<vxmax);

vorticity52=vorticity2(vvx2>vxmin);
strain52=strain2(vvx2>vxmin);
vvx52=vvx2(vvx2>vxmin);
it52=it2(vvx2>vxmin);

strain4=strain52(vorticity52<vmax);
vvx4=vvx52(vorticity52<vmax);
it4=it52(vorticity52<vmax);
vorticity4=vorticity52(vorticity52<vmax);

strain22=strain4(vorticity4>vmin);
vvx22=vvx4(vorticity4>vmin);
it22=it4(vorticity4>vmin);
vorticity22=vorticity4(vorticity4>vmin);

%cut points
vvx32=vvx22(strain22>zp-0.1); %0.04);
it32=it22(strain22>zp-0.1); %0.04);
vorticity32=vorticity22(strain22>zp-0.1); %0.04);
strain32=strain22(strain22>zp-0.1); %0.04);

vvx11=vvx32(strain32<zp+0.1); %0.04);
it11=it32(strain32<zp+0.1); %0.04);
vorticity11=vorticity32(strain32<zp+0.1); %0.04);
strain11=strain32(strain32<zp+0.1); %0.04);

```

```

%Intersection with plane
%(vvx11, vorticity11, strain11)
sss2=0;
vvv2=0;
vvvx2=0;
vf2=0;
xm11=0;
%zp=0;
for i=1:length(it11)-1
    i
    if it11(i+1)==it11(i)+1
        syms x y z xm
        x11=vvx11(i)+xm*(vvx11(i+1)-vvx11(i));
        y11=vorticity11(i)+xm*(vorticity11(i+1)-vorticity11(i));
        z11=strain11(i)+xm*(strain11(i+1)-strain11(i));

        eqn=0*(x - 0) + 0*(y - 0) + 1*(z - 0) == zp;
        eqn=subs(eqn,{x,y,z},{x11,y11,z11});
        [xm]=vpa(solve(eqn,xm));

        xm11=double(xm);

        x11=vvx11(i)+xm11*(vvx11(i+1)-vvx11(i));
        y11=vorticity11(i)+xm11*(vorticity11(i+1)-vorticity11(i));
        z11=strain11(i)+xm11*(strain11(i+1)-strain11(i));

        xm11=[xm11,xm11];

        if z11>min(strain11(i),strain11(i+1)) &&
            z11<max(strain11(i),strain11(i+1))
            sss2=[sss2,z11];
            vvv2=[vvv2,y11];
            vvvx2=[vvvx2,x11];
            vf2=[vf2,i];
        end
    end
end

sss2=sss2(2:end);
vvv2=vvv2(2:end);
vvvx2=vvvx2(2:end);
vf2=vf2(2:end);
xm11=xm11(2:end);

figure1 = figure;
axes1 = axes('Parent',figure1);
hold(axes1,'on');
plot3(vvx1, vorticity1, strain1,'Color',[0 0 1]);
hold on
plot3(vvvx2, vvv2, sss2,'Marker','.','LineStyle','none','Color'
    ,[1 0 0]);
hold on
%plot3(vf122, vf2, vf12,'Marker','.','LineStyle','none','Color'
    ,[1 0 0]);
%hold on
surf(xx,yy,zz,'Parent',axes1,'FaceAlpha',0.5,...

```

```

        'FaceColor',[0.862745106220245 0.862745106220245
        0.862745106220245],...
        'EdgeColor',[0.831372559070587 0.815686285495758
        0.7843137383461]);
xlabel('\it strain');
ylabel('\it vorticity');
xlabel('\it vx');
view(axes1,aview);
grid(axes1,'on');
set(axes1,'FontSize',14,'XMinorGrid','on','YMinorGrid','on',
    'ZMinorGrid','on');

cd ..
cd pp
saveas(gcf,['PP_',num2str(j)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',14);
box(axes1,'on');
hold(axes1,'all');
%plot(vorticity11,vvx11,'.b')
%hold on
plot(vvv2,vvvx2 ,'.b')
grid on
grid minor
xlim([min(vvv2)-1e-10 max(vvv2)+1e-10])
ylim([min(vvvx2)-1e-10 max(vvvx2)+1e-10])
set(gca,'xticklabel',[])
set(gca,'xtick',[])
set(gca,'yticklabel',[])
set(gca,'ytick',[])
xlabel('\it vorticity','LineWidth',2,'FontSize',16);
ylabel('\it vx','LineWidth',2,'FontSize',16);

cd ..
cd ppp
saveas(gcf,['PPP_',num2str(j)],'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',14);
box(axes1,'on');
hold(axes1,'all');
plot(vvv2, vf2, '.b')
grid on
grid minor
xlim([min(vvv2)-1e-10 max(vvv2)+1e-10])
ylim([min(vf2)-1e-10 max(vf2)+1e-10])
set(gca,'xticklabel',[])
set(gca,'xtick',[])
set(gca,'yticklabel',[])
set(gca,'ytick',[])
xlabel('\it vorticity','LineWidth',2,'FontSize',16);
ylabel('\it iteration','LineWidth',2,'FontSize',16);

cd ..

```



```

cd pppp
saveas(gcf,['PPPP_',num2str(j)], 'tif')

figure1=figure
axes1 = axes('Parent',figure1,'FontSize',14);
box(axes1,'on');
hold(axes1,'all');
%plot(vorticity11,vvx11,'.b')
%hold on
plot(vvv2(1:end-1),vvv2(2:end) ,'.b')
grid on
grid minor
xlim([min(vvv2)-1e-10 max(vvv2)+1e-10])
ylim([min(vvv2)-1e-10 max(vvv2)+1e-10])
set(gca,'xticklabel',[])
set(gca,'xtick',[])
set(gca,'yticklabel',[])
set(gca,'ytick',[])
xlabel('\it vorticity(k)', 'LineWidth',2, 'FontSize',16);
ylabel('\it vorticity(k+1)', 'LineWidth',2, 'FontSize',16);

cd ..
cd ppppp
saveas(gcf,['PPPPP_',num2str(j)], 'tif')

cd ..
cd data
save(['data_',num2str(j)])

close all

clearvars -except vx11 vy11 vorticity1 strain1 t tt CC CC1 xx yy
          zz zp aview vxmax vxmin vmax vmin

zp=zp+0.02;

cd ..
end

%3D_MAP
for ij=1:14
    ij
    cd('C:\Users\Joana Matos\Documents\attractor\7_15\3D\data')
    load(['data_',num2str(ij)]);
    close all

    figure1=figure;
    axes1 = axes('Parent',figure1);
    hold(axes1,'on');
    %axes1 = axes('Parent',figure1,'FontSize',14);

    %view(axes1,[-37.5 30]);
    %view(axes1,[-43.5 54.8]);
    %view(axes1,[-19.1 50]); %6.45
    %view(axes1,[-67.499999999999 66.8]); %6.45

```

```

%view(axes1,[-59.89999999999999 68.4]);% 6.55
%view(axes1,[-77.09999999999999 67.6]); %6.75
%view(axes1,[-79.49999999999999 52.4]); %6.75
%view(axes1,[63.7 47.6]); %6.85
%view(axes1,[-18.3 56.4]); %6.95
%view(axes1,[102.5 43.59999999999999]); %7.05

view(axes1,[-11.5 55.59999999999998]); %7.15

box(axes1,'on');
grid(axes1,'on');
%box(axes1,'on');
%hold(axes1,'all');
plot3(vvv2(1:end-1),vvv2(2:end),vf2(1:end-1),'.b');
%xlim([min(vpx)-1e-10 max(vpx)+1e-10])
%ylim([min(vpx)-1e-10 max(vpx)+1e-10])
grid on
grid minor
set(gca,'xticklabel',[])
set(gca,'xtick',[])
set(gca,'yticklabel',[])
set(gca,'ytick',[])
set(gca,'zticklabel',[])
set(gca,'ztick',[])
%ylim([-1 1])
grid on
grid minor
xlabel('\it vorticity(k)')
ylabel('\it vorticity(k+1)')
zlabel('\it Iteration')

cd ('C:\Users\Joana Matos\Documents\attractor\7_15\3D\PPP_3D')

saveas(gcf,['PPP_3D',num2str(ij)],'tif')

close all
clear all
end

```

D.10 Thickened Flame Model UDF

```

/*****
      UDF that specifies laminar flame speed
*****/

#include "udf.h"

DEFINE_PROPERTY(lam_flame,c,t)
{
    real ut, yi_h2;

    int h2_index=0; /* index of hydrogen species in mixture material */

    yi_h2 = C_YI(c, t, h2_index); /* hydrogen mass fraction */

```

```

ut = 93921460*pow(yi_h2,6)-38372450*pow(yi_h2,5)+6080096*pow(yi_h2,4) -
    457737*pow(yi_h2,3)+15269*pow(yi_h2,2)-116.6239*yi_h2+0.2387034;

return ut;
}

```

D.11 Lamellar Micromixing Model for Combustion

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%Required Functions %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%pdepe_solve - Main Code
%pdepe_system - System of Equations
%pdepe_striation_thickness - Striation Thickness Equation
%pdepe_striation_function - Striation Function Equation
%pdepe_bc - Boundary Conditions
%pdepe_ic - Initial Conditions
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Main Code %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

clc
close all
clear all

cd('C:\Users\Joana Matos\Documents\lamellar_model_H2')

folderName=('L1');

global P R s0 Dm tD tau Re n D d niu deltaH deltaS A b Ea cH2O1 cH2l
cO2l cH2Or cH2r cO2r T0 cN2r cN2l mH2 mO2 mH2O mN2

tt=0.0224; %flow time s
ttt=0.022; %plot time s
tx=1; %1D domain length
deltax=1e-3;
deltat=7.8e-6; %s

%Initial Concentration and Temperature
cH2l=0.0124; %kmol/m3
cO2l=0.0310; %kmol/m3
cH2Or=0; %kgmol/m3
cN2l=0.0185; %kmol/m3

cH2r=0.0124; %kmol/m3
cO2r=0.0310; %kmol/m3
cH2Or=0; %kgmol/m3
cN2r=0.0185; %kgmol/m3

T0=585+273.15; %K
%Molar Mass
mH2=2; %kg/kmol
mO2=32; %kg/kmol
mH2O=18; %kg/kmol
mN2=28; %kg/kmol

%kinetics

```

```

A=9.87e8; %rate in kgmol/m3s
b=0;
Ea=3.1e7; %J/kgmol

%Parameters
d=1e-3; %m Injector diameter
D=6.65e-3; %m Chamber diameter
Dm=2.88e-5; % m2/s Molecular diffusion coefficient of H2-air
P=1e5; %Pa
R=8.314*1000; %J/kgmol/K
Re=300; %Reynolds Number
%Mesh points
np=1000;
Z = linspace(-1,1,np);

%Display solution in time
time=[0:deltat:tt];

%Solver
m = 0; %Cartesian coordinates

sol = pdepe(m,@pdepe_system,@pdepe_ic,@pdepe_bc,Z,time);

options=odeset('RelTol',1e-15,'AbsTol',1e-15, 'InitialStep',1e-3,
'MaxStep', 1e-2 );

ccH2=sol(:, :, 1);
ccO2=sol(:, :, 2);
ccN2=sol(:, :, 3);
ccH2O=sol(:, :, 4);
T=sol(:, :, 5)-273.15;

xxH2=ccH2./(ccH2+ccO2+ccH2O+ccN2);
xxO2=ccO2./(ccH2+ccO2+ccH2O+ccN2);
xxN2=ccN2./(ccH2+ccO2+ccH2O+ccN2);
xxH2O=ccH2O./(ccH2+ccO2+ccH2O+ccN2);

cd('C:\Users\Joana Matos\Documents\lamellar_model_H2')
ss=pdepe_striation_thickness(time);

%% Plot

cd('C:\Users\Joana Matos\Documents\lamellar_model_H2')

mkdir (folderName)
cd (folderName)

save('data_end')
figure1=figure;
axes1 = axes('Parent',figure1);
box on;
hold(axes1,'on');
pcolor(time(1:length(ccH2(:,1))),Z,xxH2.')
shading interp
title('\it x_{H_2}')
ylabel('\it Z')

```

```

xlabel('\it t \rm (s)')
xlim([0 ttt])
colormap([1 1 1;0.98412698507309...1;0 0 1])
set(axes1,'FontSize',13,'Layer','top','TickLength',[0 0],'YTick',[-1
1],...
    'YTickLabel',{'0','1'},'ZTick',[0 1]);
set(gca,'Layer','top');
set(gca,'ticklength',[0 0]);
colorbar('peer',axes1);
h = colorbar;
caxis([0 1])
saveas(gcf,'xH2','tif')

```

```

figure2=figure;
axes1 = axes('Parent',figure2);
box on;
hold(axes1,'on');
h=pcolor(time(1:length(ccH2(:,1))),Z,xxO2.')
set(h,'edgecolor','k')
shading interp
title('\it x_{O_2}')
ylabel('\it Z')
xlabel('\it t \rm (s)')
xlim([0 ttt])
colormap([1 1 1;0.98412698507309...1;0 0 1])
set(axes1,'FontSize',13,'Layer','top','TickLength',[0 0],'YTick',[-1
1],...
    'YTickLabel',{'0','1'},'ZTick',[0 1]);
set(gca,'Layer','top');
set(gca,'ticklength',[0 0]);
colorbar('peer',axes1);
h = colorbar;
caxis([0 1])
saveas(gcf,'xO2','tif')

```

```

figure3=figure;
axes1 = axes('Parent',figure3);
box on;
hold(axes1,'on');
pcolor(time(1:length(ccH2(:,1))),Z,xxH2O.')
shading interp
title('\it x_{H_2O}')
ylabel('\it Z')
xlabel('\it t \rm (s)')
xlim([0 ttt])
colormap([1 1 1;0.98412698507309...1;0 0 1])
set(axes1,'FontSize',13,'Layer','top','TickLength',[0 0],'YTick',[-1
1],...
    'YTickLabel',{'0','1'},'ZTick',[0 1]);
set(gca,'Layer','top');
set(gca,'ticklength',[0 0]);
colorbar('peer',axes1);
h = colorbar;
caxis([0 1])

```

```

saveas(gcf,'xH2O','tif')

figure4=figure;
axes1 = axes('Parent',figure4);
box on;
hold(axes1,'on');
pcolor(time(1:length(ccN2(:,1))),Z,xxN2.);
shading interp
title('\it x_{N_2}');
ylabel('\it Z')
xlabel('\it t \rm (s)')
xlim([0 ttt])
colormap([1 1 1;0.98412698507309...1;0 0 1])
set(axes1,'FontSize',13,'Layer','top','TickLength',[0 0],'YTick',[-1
1],...
'YTickLabel',{'0','1'},'ZTick',[0 1]);
set(gca,'Layer','top');
set(gca,'ticklength',[0 0]);
colorbar('peer',axes1);
h = colorbar;
caxis([0 1])
saveas(gcf,'xN2','tif')

figure5=figure;
axes1 = axes('Parent',figure5);
box on;
hold(axes1,'on');
pcolor(time(1:length(ccH2(:,1))),Z,T.')
shading interp
title('\it T \rm (°C)')
ylabel('\it Z')
xlabel('\it t \rm (s)')
xlim([0 ttt])
colormap jet
set(axes1,'FontSize',13,'Layer','top','TickLength',[0 0],'YTick',[-1
1],...
'YTickLabel',{'0','1'},'ZTick',[0 1]);
set(gca,'Layer','top');
set(gca,'ticklength',[0 0]);
colorbar('peer',axes1);
h = colorbar;
caxis([585 T(23,1000)])
saveas(gcf,'T','tif')

figure6=figure;
axes1 = axes('Parent',figure6);
hold(axes1,'on');
plot(time,ss,'b')
ylabel('\it S \rm (m)')
xlabel('\it t \rm (s)')
xlim([0 ttt])
box(axes1,'on');
set(axes1,'FontSize',13);
grid on
grid minor
saveas(gcf,'Striation','tif')

```

```

figure7=figure;
axes1 = axes('Parent',figure7);
hold(axes1,'on');
plot(time(1:length(ccN2(:,1))),mean(xxN2,2),'-k', time
(1:length(ccH2(:,1))),mean(xxH2,2),'-b', time
(1:length(ccH2(:,1))),mean(xxO2,2),'-r', time
(1:length(ccH2(:,1))),mean(xxH2O,2),'-c')
ylabel('\it x')
xlabel('\it t \rm (s)')
xlim([0 ttt])
box(axes1,'on');
set(axes1,'FontSize',13);
grid on
grid minor
ylim([0 1])
legend('\it x_{N_2}','\it x_{H_2}','\it x_{O_2}','\it x_{H_2O}')
saveas(gcf,'c_all','tif')

```

```

figure8=figure;
axes1 = axes('Parent',figure8);
hold(axes1,'on');
plot(time(1:length(ccH2(:,1))),mean(T,2),'-r')
ylabel('\it T \rm (°C)')
xlabel('\it t \rm (s)')
xlim([0 ttt])
box(axes1,'on');
set(axes1,'FontSize',13);
grid on
grid minor
saveas(gcf,'T_perfil','tif')

```

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%pdepe_system%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

```

```

function [c,f,s] = pdepe_system(Z,time,u,dudZ)

```

```

global P R s0 Dm deltaH deltaS A b Ea tD cH2O1 cH2l cO2l cH2Or cH2r
cO2r T0 mH2 mO2 mH2O mN2

```

```

kf1=A*u(5)^b*exp(-Ea./(R*u(5))); % rate in kgmol/m3/s

```

```

rate1=u(1)*u(2)*kf1; %kgmol/m3/s

```

```

%rates

```

```

rateH2=-rate1;

```

```

rateO2=-0.5*rate1;

```

```

rateH2O=rate1;

```

```

%concentration

```

```

c1=u(1);

```

```

c2=u(2);

```

```

c3=u(3);

```

```

c4=u(4);

```

```

c5=u(5);

```

```

xxH2=c1/(c1+c2+c3+c4);

```

```

xxO2=c2/(c1+c2+c3+c4);

```

```

xxN2=c3/(c1+c2+c3+c4);

```



```

xxH2O=c4/(c1+c2+c3+c4);

%Specific Heat
cpH2=2.16248e-12*c5^5-1.36920e-8*c5^4+3.10250e-5*c5^3-2.95925e-
2*c5^2+1.34949e1*c5+2.68004e4; %J/kgmolK
cpO2=1.24933e-6*c5^3-7.43738e-3*c5^2+1.61512e1*c5+2.48539e4;
cpH2O=-2.07811e-6*c5^3+6.11412e-3*c5^2+6.25835*c5+3.09275e4;
cpN2=2.01264e-9*c5^4-1.09204e-5*c5^3+1.88337e-2*c5^2-
7.01037*c5+2.97104e4;

cpM= xxH2*cpH2+xxO2*cpO2+xxH2O*cpH2O+xxN2*cpN2;

%density
rroM=-1.46899e-17*c5^5+1.02660e-13*c5^4-2.81649e-10*c5^3+3.84231e-
7*c5^2-2.71647e-4*c5+9.32346e-2; %kgmol/m3

%enthalpy
eH2=1.73086*c5^2+2.70864e4*c5-8.16265e6; %J/kgmol
eO2=2.19450*c5^2+2.98707e4*c5-9.31966e6;
eH2O=5.54381*c5^2+3.00355e4*c5-9.48765e6;

%System of Equations
c = [1; 1; 1; 1; 1];
f = [1; 1; 1; 1; 1] .*
(pdepd_sstriation_function(time)*Z+Dm/(pdepe_striation_thickness(time)
)^2*dudZ);
s=[rateH2; rateO2; 0; rateH2O; -
(1/rroM)*(rateH2*eH2/cpH2+rateO2*eO2/cpO2+rateH2O*eH2O/cpH2O)];

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%pdepe_striation_thickness%%%%%%%%
function s=pdepe_striation_thickness(t)

s=exp(-log(66*exp(295*t)))*2e-3; % m

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%pdepe_striation_function%%%%%%%%
function ss=pdepe_striation_function(t)

ss=-295; 1/s

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%pdepe_ic%%%%%%%%
function u0 = pdepe_ic(Z)

global cH2O1 cH21 cO21 cH2Or cH2r cO2r cN21 cN2r T0 N2i O2i H2i

u0 = [(heaviside(Z)*cH21+heaviside(-Z)*cH2r);
(heaviside(Z)*cO21+heaviside(-Z)*cO2r); ...
(heaviside(Z)*cN21+heaviside(-Z)*cN2r);
(heaviside(Z)*cH2O1+heaviside(-Z)*cH2Or); ...
(heaviside(Z)+heaviside(-Z))*T0];

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%pdepe_bc%%%%%%%%
function [pl,ql,pr,qr] = pdepe_bc(xl,ul,xr,ur,t)
pl = [0; 0; 0; 0; 0];

```

```

ql = [1; 1; 1; 1; 1];
pr = [0; 0; 0; 0; 0];
qr = [1; 1; 1; 1; 1];

```

D.12 NETcombustor Model

```

//////// Required scrips: Model startModel, Model UnitCell //////////

```

```

Model start

```

```

outlet1    as output MaterialPort;
outlet2    as output MaterialPort;
outlet3    as output MaterialPort;
outlet4    as output MaterialPort;
outlet5    as output MaterialPort;
outlet6    as output MaterialPort;
outlet7    as output MaterialPort;
outlet8    as output MaterialPort;
outlet9    as output MaterialPort;
outlet10   as output MaterialPort;
outlet11   as output MaterialPort;
outlet12   as output MaterialPort;
outlet13   as output MaterialPort;
outlet14   as output MaterialPort;

```

```

Ainj as realvariable;
CH2([1:14]) as realvariable;
CO2([1:14]) as realvariable;
CAR([1:14]) as realvariable;
Dh as realvariable;
dd as realparameter (1.6148e-3);
Fout([1:14]) as flow_mol;
hout([1:14]) as enth_mol;
n as integerparameter (14);
p as pressure (fixed,1); //bar
phiG as realvariable;
Re as realparameter (300);
rhoin([1:14]) as dens_mass;
rhomolout([1:14]) as dens_mol;
T as temperature (fixed,25); //c
vetor ([1:14]) as realparameter;
vetori ([1:14]) as realparameter;
viscin ([1:14]) as viscosity;
vin ([1:14]) as realvariable;
w as realparameter (1e-3);

```

```

//geometry
dh=2*w*dd/(w+dd);
Ainj=dd*w; //m2

```

```

//inlet fraction
vetor(1):0; // yH2
vetor(2):0.9;
vetor(3):0;
vetor(4):0.9;
vetor(5):0;

```

```

vetor(6):0.9;
vetor(7):0;
vetor(8):0.9;
vetor(9):0;
vetor(10):0.9;
vetor(11):0;
vetor(12):0.9;
vetor(13):0;
vetor(14):0;

vetori(1):1; //yN2
vetori(2):0.1;
vetori(3):0.8;
vetori(4):0.1;
vetori(5):0.8;
vetori(6):0.1;
vetori(7):0.8;
vetori(8):0.1;
vetori(9):0.8;
vetori(10):0.1;
vetori(11):0.8;
vetori(12):0.1;
vetori(13):0.8;
vetori(14):1;

//outlet1
////////////////////////////////////

outlet1.z("H2")=vetor(1);
outlet1.z("N2")=vetori(1);
outlet1.z("O2")=1-vetor(1)-vetori(1);
outlet1.z("H2O")=0;

//properties
outlet1.P=P;
outlet1.T=T;
outlet1.av=1;
call (rhomolout(1)) = pDens_Mol_Vap (outlet1.T, outlet1.p,
    outlet1.z); // in kmol/m3
outlet1.V=1/rhomolout(1); // in m3/kmol
call (hout(1)) = pEnth_Mol (outlet1.T, outlet1.p, outlet1.z); //
    in GJ/kmol
outlet1.h=hout(1); // in GJ/kmol

//molar flow rate F
call (rhoin(1)) = pDens_Mass_Vap (outlet1.T, outlet1.p,
    outlet1.z); // in kg/m3
call (viscin(1)) = pVisc_Vap (outlet1.T, outlet1.p, outlet1.z); //
    in cP

vin(1)=Re*viscin(1)*1e-3/rhoin(1)/dh; //m/s
Fout(1)=vin(1)*Ainj;

outlet1.F=Fout(1)*rhomolout(1)*3600; // in kmol/hr

//concentration

```

```

cO2(1) = outlet1.z("O2")*rhomolout(1); // in kmol/m3
cH2(1) = outlet1.z("H2")*rhomolout(1); // in kmol/m3
cAR(1) = outlet1.z("N2")*rhomolout(1); // in kmol/m3

//outlet2////////////////////////////////////
outlet2.z("H2")=vetor(2);
outlet2.z("N2")=vetori(2);
outlet2.z("O2")=1-vetor(2)-vetori(2);
outlet2.z("H2O")=0;

//properties
outlet2.P=P;
outlet2.T=T;
outlet2.av=1;
call (rhomolout(2)) = pDens_Mol_Vap (outlet2.T, outlet2.p,
    outlet2.z); // in kmol/m3
outlet2.V=1/rhomolout(2); // in m3/kmol
call (hout(2)) = pEnth_Mol (outlet2.T, outlet2.p, outlet2.z); //
    in GJ/kmol
outlet2.h=hout(2); // in GJ/kmol

//molar flow rate F
call (rhoIn(2)) = pDens_Mass_Vap (outlet2.T, outlet2.p,
    outlet2.z); // in kg/m3
call (viscin(2)) = pVisc_Vap (outlet2.T, outlet2.p, outlet2.z); //
    in cP
vin(2)=Re*viscin(2)*1e-3/rhoIn(2)/dh; //m/s
Fout(2)=vin(2)*Ainj;

outlet2.F=Fout(2)*rhomolout(2)*3600; // in kmol/hr

//concentration
cO2(2) = outlet2.z("O2")*rhomolout(2); // in kmol/m3
cH2(2) = outlet2.z("H2")*rhomolout(2); // in kmol/m3
cAR(2) = outlet2.z("N2")*rhomolout(2); // in kmol/m3

//outlet3
////////////////////////////////////
/
outlet3.z("H2")=vetor(3);
outlet3.z("N2")=vetori(3);
outlet3.z("O2")=1-vetor(3)-vetori(3);
outlet3.z("H2O")=0;

//properties
outlet3.P=P;
outlet3.T=T;
outlet3.av=1;
call (rhomolout(3)) = pDens_Mol_Vap (outlet3.T, outlet3.p,
    outlet3.z); // in kmol/m3
outlet3.V=1/rhomolout(3); // in m3/kmol
call (hout(3)) = pEnth_Mol (outlet3.T, outlet3.p, outlet3.z); //
    in GJ/kmol
outlet3.h=hout(3); // in GJ/kmol

```

```

//molar flow rate F
call (rhoIn(3)) = pDens_Mass_Vap (outlet3.T, outlet3.p,
    outlet3.z); // in kg/m3
call (viscIn(3)) = pVisc_Vap (outlet3.T, outlet3.p, outlet3.z); //
    in cP
vin(3)=Re*viscIn(3)*1e-3/rhoIn(3)/dh; //m/s
Fout(3)=vin(3)*Ainj;

outlet3.F=Fout(3)*rhoMolout(3)*3600; // in kmol/hr

//concentration
cO2(3) = outlet3.z("O2")*rhoMolout(3); // in kmol/m3
cH2(3) = outlet3.z("H2")*rhoMolout(3); // in kmol/m3
cAR(3) = outlet3.z("N2")*rhoMolout(3); // in kmol/m3

//outlet4////////////////////////////////////
outlet4.z("H2")=vetor(4);
outlet4.z("N2")=vetori(4);
outlet4.z("O2")=1-vetor(4)-vetori(4);
outlet4.z("H2O")=0;

//properties
outlet4.P=P;
outlet4.T=T;
outlet4.av=1;
call (rhoMolout(4)) = pDens_Mol_Vap (outlet4.T, outlet4.p,
    outlet4.z); // in kmol/m3
outlet4.V=1/rhoMolout(4); // in m3/kmol
call (hout(4)) = pEnth_Mol (outlet4.T, outlet4.p, outlet4.z); //
    in GJ/kmol
outlet4.h=hout(4); // in GJ/kmol

//molar flow rate F
call (rhoIn(4)) = pDens_Mass_Vap (outlet4.T, outlet4.p,
    outlet4.z); // in kg/m3
call (viscIn(4)) = pVisc_Vap (outlet4.T, outlet4.p, outlet4.z); //in cP
vin(4)=Re*viscIn(4)*1e-3/rhoIn(4)/dh; //m/s
Fout(4)=vin(4)*Ainj;

outlet4.F=Fout(4)*rhoMolout(4)*3600; // in kmol/hr

//concentration
cO2(4) = outlet4.z("O2")*rhoMolout(4); // in kmol/m3
cH2(4) = outlet4.z("H2")*rhoMolout(4); // in kmol/m3
cAR(4) = outlet4.z("N2")*rhoMolout(4); // in kmol/m3

//outlet5
////////////////////////////////////
outlet5.z("H2")=vetor(5);
outlet5.z("N2")=vetori(5);
outlet5.z("O2")=1-vetor(5)-vetori(5);
outlet5.z("H2O")=0;

//properties
outlet5.P=P;
outlet5.T=T;

```

```

outlet5.av=1;
call (rhomolout(5)) = pDens_Mol_Vap (outlet5.T, outlet5.p,
    outlet5.z); // in kmol/m3
outlet5.V=1/rhomolout(5); // in m3/kmol
call (hout(5)) = pEnth_Mol (outlet5.T, outlet5.p, outlet5.z); //
    in GJ/kmol
outlet5.h=hout(5); // in GJ/kmol

//molar flow rate F
call (rhoIn(5)) = pDens_Mass_Vap (outlet5.T, outlet5.p,
    outlet5.z); // in kg/m3
call (viscin(5)) = pVisc_Vap (outlet5.T, outlet5.p, outlet5.z); //
    in cP

vin(5)=Re*viscin(5)*1e-3/rhoIn(5)/dh; //m/s
Fout(5)=vin(5)*Ainj;

outlet5.F=Fout(5)*rhomolout(5)*3600; // in kmol/hr

//concentration
cO2(5) = outlet5.z("O2")*rhomolout(5); // in kmol/m3
cH2(5) = outlet5.z("H2")*rhomolout(5); // in kmol/m3
cAR(5) = outlet5.z("N2")*rhomolout(5); // in kmol/m3

//outlet6
////////////////////////////////////
outlet6.z("H2")=vetor(6);
outlet6.z("N2")=vetori(6);
outlet6.z("O2")=1-vetor(6)-vetori(6);
outlet6.z("H2O")=0;

//properties
outlet6.P=P;
outlet6.T=T;
outlet6.av=1;
call (rhomolout(6)) = pDens_Mol_Vap (outlet6.T, outlet6.p,
    outlet6.z); // in kmol/m3
outlet6.V=1/rhomolout(6); // in m3/kmol
call (hout(6)) = pEnth_Mol (outlet6.T, outlet6.p, outlet6.z); //
    in GJ/kmol
outlet6.h=hout(6); // in GJ/kmol

//molar flow rate F
call (rhoIn(6)) = pDens_Mass_Vap (outlet6.T, outlet6.p,
    outlet6.z); // in kg/m3
call (viscin(6)) = pVisc_Vap (outlet6.T, outlet6.p, outlet6.z); //in cP
vin(6)=Re*viscin(6)*1e-3/rhoIn(6)/dh; //m/s
Fout(6)=vin(6)*Ainj;

outlet6.F=Fout(6)*rhomolout(6)*3600; // in kmol/hr

//concentration
cO2(6) = outlet6.z("O2")*rhomolout(6); // in kmol/m3
cH2(6) = outlet6.z("H2")*rhomolout(6); // in kmol/m3
cAR(6) = outlet6.z("N2")*rhomolout(6); // in kmol/m3

```

```

//outlet7
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
/
outlet7.z("H2")=vetor(7);
outlet7.z("N2")=vetori(7);
outlet7.z("O2")=1-vetor(7)-vetori(7);
outlet7.z("H2O")=0;

//properties
outlet7.P=P;
outlet7.T=T;
outlet7.av=1;
call (rhomolout(7)) = pDens_Mol_Vap (outlet7.T, outlet7.p,
    outlet7.z); // in kmol/m3
outlet7.V=1/rhomolout(7); // in m3/kmol
call (hout(7)) = pEnth_Mol (outlet7.T, outlet7.p, outlet7.z); //
    in GJ/kmol
outlet7.h=hout(7); // in GJ/kmol

//molar flow rate F
call (rhoIn(7)) = pDens_Mass_Vap (outlet7.T, outlet7.p,
    outlet7.z); // in kg/m3
call (viscin(7)) = pVisc_Vap (outlet7.T, outlet7.p, outlet7.z); //
    in cP

vin(7)=Re*viscin(7)*1e-3/rhoIn(7)/dh; //m/s
Fout(7)=vin(7)*Ainj;

outlet7.F=Fout(7)*rhomolout(7)*3600; // in kmol/hr

//concentration
cO2(7) = outlet7.z("O2")*rhomolout(7); // in kmol/m3
cH2(7) = outlet7.z("H2")*rhomolout(7); // in kmol/m3
cAR(7) = outlet7.z("N2")*rhomolout(7); // in kmol/m3

//outlet8
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
outlet8.z("H2")=vetor(8);
outlet8.z("N2")=vetori(8);
outlet8.z("O2")=1-vetor(8)-vetori(8);
outlet8.z("H2O")=0;

//properties
outlet8.P=P;
outlet8.T=T;
outlet8.av=1;
call (rhomolout(8)) = pDens_Mol_Vap (outlet8.T, outlet8.p,
    outlet8.z); // in kmol/m3
outlet8.V=1/rhomolout(8); // in m3/kmol
call (hout(8)) = pEnth_Mol (outlet8.T, outlet8.p, outlet8.z); //
    in GJ/kmol
outlet8.h=hout(8); // in GJ/kmol

//molar flow rate F
call (rhoIn(8)) = pDens_Mass_Vap (outlet8.T, outlet8.p,
    outlet8.z); // in kg/m3

```



```

call (viscin(8)) = pVisc_Vap (outlet8.T, outlet8.p, outlet8.z);//
    in cP

vin(8)=Re*viscin(8)*1e-3/rhoin(8)/dh; //m/s
Fout(8)=vin(8)*Ainj;

outlet8.F=Fout(8)*rhomolout(8)*3600; // in kmol/hr

//concentration
cO2(8) = outlet8.z("O2")*rhomolout(8); // in kmol/m3
cH2(8) = outlet8.z("H2")*rhomolout(8); // in kmol/m3
cAR(8) = outlet8.z("N2")*rhomolout(8); // in kmol/m3

//outlet9
////////////////////////////////////
outlet9.z("H2")=vetor(9);
outlet9.z("N2")=vetori(9);
outlet9.z("O2")=1-vetor(9)-vetori(9);
outlet9.z("H2O")=0;

//properties
outlet9.P=P;
outlet9.T=T;
outlet9.av=1;
call (rhomolout(9)) = pDens_Mol_Vap (outlet9.T, outlet9.p,
    outlet9.z); // in kmol/m3
outlet9.V=1/rhomolout(9); // in m3/kmol
call (hout(9)) = pEnth_Mol (outlet9.T, outlet9.p, outlet9.z); //
    in GJ/kmol
outlet9.h=hout(9); // in GJ/kmol

//molar flow rate F
call (rhoin(9)) = pDens_Mass_Vap (outlet9.T, outlet9.p,
    outlet9.z); // in kg/m3
call (viscin(9)) = pVisc_Vap (outlet9.T, outlet9.p, outlet9.z);//
    in cP

vin(9)=Re*viscin(9)*1e-3/rhoin(9)/dh; //m/s
Fout(9)=vin(9)*Ainj;

outlet9.F=Fout(9)*rhomolout(9)*3600; // in kmol/hr

//concentration
cO2(9) = outlet9.z("O2")*rhomolout(9); // in kmol/m3
cH2(9) = outlet9.z("H2")*rhomolout(9); // in kmol/m3
cAR(9) = outlet9.z("N2")*rhomolout(9); // in kmol/m3

//outlet10
////////////////////////////////////
outlet10.z("H2")=vetor(10);
outlet10.z("N2")=vetori(10);
outlet10.z("O2")=1-vetor(10)-vetori(10);
outlet10.z("H2O")=0;

//properties

```

```

outlet10.P=P;
outlet10.T=T;
outlet10.av=1;
call (rhomolout(10)) = pDens_Mol_Vap (outlet10.T, outlet10.p,
    outlet10.z); // in kmol/m3
outlet10.V=1/rhomolout(10); // in m3/kmol
call (hout(10)) = pEnth_Mol (outlet10.T, outlet10.p, outlet10.z);
    // in GJ/kmol
outlet10.h=hout(10); // in GJ/kmol

//molar flow rate F
call (rhoin(10)) = pDens_Mass_Vap (outlet10.T, outlet10.p,
    outlet10.z); // in kg/m3
call (viscin(10)) = pVisc_Vap (outlet10.T, outlet10.p,
    outlet10.z); // in cP

vin(10)=Re*viscin(10)*1e-3/rhoin(10)/dh; //m/s
Fout(10)=vin(10)*Ainj;

outlet10.F=Fout(10)*rhomolout(10)*3600; // in kmol/hr

//concentration
cO2(10) = outlet10.z("O2")*rhomolout(10); // in kmol/m3
cH2(10) = outlet10.z("H2")*rhomolout(10); // in kmol/m3
cAR(10) = outlet10.z("N2")*rhomolout(10); // in kmol/m3

//outlet11
////////////////////////////////////
outlet11.z("H2")=vetor(11);
outlet11.z("N2")=vetori(11);
outlet11.z("O2")=1-vetor(11)-vetori(11);
outlet11.z("H2O")=0;

//properties
outlet11.P=P;
outlet11.T=T;
outlet11.av=1;
call (rhomolout(11)) = pDens_Mol_Vap (outlet11.T, outlet11.p,
    outlet11.z); // in kmol/m3
outlet11.V=1/rhomolout(11); // in m3/kmol
call (hout(11)) = pEnth_Mol (outlet11.T, outlet11.p, outlet11.z);
    // in GJ/kmol
outlet11.h=hout(11); // in GJ/kmol

//molar flow rate F
call (rhoin(11)) = pDens_Mass_Vap (outlet11.T, outlet11.p,
    outlet11.z); // in kg/m3
call (viscin(11)) = pVisc_Vap (outlet11.T, outlet11.p,
    outlet11.z); // in cP

vin(11)=Re*viscin(11)*1e-3/rhoin(11)/dh; //m/s
Fout(11)=vin(11)*Ainj;

outlet11.F=Fout(11)*rhomolout(11)*3600; // in kmol/hr

//concentration

```

```

cO2(11) = outlet11.z("O2")*rhomolout(11); // in kmol/m3
cH2(11) = outlet11.z("H2")*rhomolout(11); // in kmol/m3
cAR(11) = outlet11.z("N2")*rhomolout(11); // in kmol/m3

//outlet12
////////////////////////////////////
outlet12.z("H2")=vetor(12);
outlet12.z("N2")=vetori(12);
outlet12.z("O2")=1-vetor(12)-vetori(12);
outlet12.z("H2O")=0;

//properties
outlet12.P=P;
outlet12.T=T;
outlet12.av=1;
call (rhomolout(12)) = pDens_Mol_Vap (outlet12.T, outlet12.p,
    outlet12.z); // in kmol/m3
outlet12.V=1/rhomolout(12); // in m3/kmol
call (hout(12)) = pEnth_Mol (outlet12.T, outlet12.p, outlet12.z);
    // in GJ/kmol
outlet12.h=hout(12); // in GJ/kmol

//molar flow rate F
call (rhoIn(12)) = pDens_Mass_Vap (outlet12.T, outlet12.p,
    outlet12.z); // in kg/m3
call (viscin(12)) = pVisc_Vap (outlet12.T, outlet12.p,
    outlet12.z); // in cP

vin(12)=Re*viscin(12)*1e-3/rhoIn(12)/dh; //m/s
Fout(12)=vin(12)*Ainj;

outlet12.F=Fout(12)*rhomolout(12)*3600; // in kmol/hr

//concentration
cO2(12) = outlet12.z("O2")*rhomolout(12); // in kmol/m3
cH2(12) = outlet12.z("H2")*rhomolout(12); // in kmol/m3
cAR(12) = outlet12.z("N2")*rhomolout(12); // in kmol/m3

//outlet13
////////////////////////////////////
outlet13.z("H2")=vetor(13);
outlet13.z("N2")=vetori(13);
outlet13.z("O2")=1-vetor(13)-vetori(13);
outlet13.z("H2O")=0;

//properties
outlet13.P=P;
outlet13.T=T;
outlet13.av=1;
call (rhomolout(13)) = pDens_Mol_Vap (outlet13.T, outlet13.p,
    outlet13.z); // in kmol/m3
outlet13.V=1/rhomolout(13); // in m3/kmol
call (hout(13)) = pEnth_Mol (outlet13.T, outlet13.p, outlet13.z);
    // in GJ/kmol
outlet13.h=hout(13); // in GJ/kmol

```

```

//molar flow rate F
call (rhoIn(13)) = pDens_Mass_Vap (outlet13.T, outlet13.p,
    outlet13.z); // in kg/m3
call (viscin(13)) = pVisc_Vap (outlet13.T, outlet13.p,
    outlet13.z); // in cP
vin(13)=Re*viscin(13)*1e-3/rhoIn(13)/dh; //m/s
Fout(13)=vin(13)*Ainj;

outlet13.F=Fout(13)*rhomolout(13)*3600; // in kmol/hr

//concentration
cO2(13) = outlet13.z("O2")*rhomolout(13); // in kmol/m3
cH2(13) = outlet13.z("H2")*rhomolout(13); // in kmol/m3
cAR(13) = outlet13.z("N2")*rhomolout(13); // in kmol/m3

//outlet14
////////////////////////////////////
outlet14.z("H2")=vetor(14);
outlet14.z("N2")=vetori(14);
outlet14.z("O2")=1-vetor(14)-vetori(14);
outlet14.z("H2O")=0;

//properties
outlet14.P=P;
outlet14.T=T;
outlet14.av=1;
call (rhomolout(14)) = pDens_Mol_Vap (outlet14.T, outlet14.p,
    outlet14.z); // in kmol/m3
outlet14.V=1/rhomolout(14); // in m3/kmol
call (hout(14)) = pEnth_Mol (outlet14.T, outlet14.p, outlet14.z);
    // in GJ/kmol
outlet14.h=hout(14); // in GJ/kmol

//molar flow rate F
call (rhoIn(14)) = pDens_Mass_Vap (outlet14.T, outlet14.p,
    outlet14.z); // in kg/m3
call (viscin(14)) = pVisc_Vap (outlet14.T, outlet14.p,
    outlet14.z); // in cP

vin(14)=Re*viscin(14)*1e-3/rhoIn(14)/dh; //m/s
Fout(14)=vin(14)*Ainj;

outlet14.F=Fout(14)*rhomolout(14)*3600; // in kmol/hr

//concentration
cO2(14) = outlet14.z("O2")*rhomolout(14); // in kmol/m3
cH2(14) = outlet14.z("H2")*rhomolout(14); // in kmol/m3
cAR(14) = outlet14.z("N2")*rhomolout(14); // in kmol/m3

//phi global
phiG =
    (outlet1.F*outlet1.z("H2")+outlet2.F*outlet2.z("H2")+outlet3.F*o

```

```

utlet3.z("H2")+outlet4.F*outlet4.z("H2")+outlet5.F*outlet5.z("H2")+out
let6.F*outlet6.z("H2")+outlet7.F*outlet7.z("H2")+outlet8.F*outlet8.z("
H2")+outlet9.F*outlet9.z("H2")+outlet10.F*outlet10.z("H2")+outlet11.F*
outlet11.z("H2")+outlet12.F*outlet12.z("H2")+outlet13.F*outlet13.z("H2
")+outlet14.F*outlet14.z("H2"))/(2*(outlet1.F*outlet1.z("O2")+outlet2.
F*outlet2.z("O2")+outlet3.F*outlet3.z("O2")+outlet4.F*outlet4.z("O2")+
outlet5.F*outlet5.z("O2")+outlet6.F*outlet6.z("O2")+outlet7.F*outlet7.
z("O2")+outlet8.F*outlet8.z("O2")+outlet9.F*outlet9.z("O2")+outlet10.F
*outlet10.z("O2")+outlet11.F*outlet11.z("O2")+outlet12.F*outlet12.z("O
2")+outlet13.F*outlet13.z("O2")+outlet14.F*outlet14.z("O2")));

```

End

Model UnitCell

```

// Units  T: °C // P: bar // Visc: cP // cp: kJ/kmol/K // rho:
kg/m3 // Q: m3/hr //

// Ports declaration as default Material Streams
inlet1    as input MaterialPort;
inlet2    as input MaterialPort;
outlet1   as output MaterialPort;
outlet2   as output MaterialPort;

// Declaration of Variables
A as realparameter; //kg/m3 s
AA as realparameter; //kg/m3 s
Ainj as area(description:"NETmix Channels Area"; free); // m2
b as realparameter;
bb as realparameter;
c(componentlist) as conc_mole(description: "Outlet
Concentration"); //kmol/m3
Dh as length(description:"Channel Hydraulic Diameter",free); //m
EE as realvariable;
E as holdup_heat(description:"Chamber Hold-Up Heat", free); //GJ
ea as realparameter;
eaa as realparameter;
Fout as flow_mol(description:"Outlet Molar Flow rate");//kmol/hr
hout as enth_mol(description:"Outlet Enthalpy", free); //GJ/kmol
Kf as realvariable(description:"Reaction Rate",free);
kb as realvariable(description:"Reaction Rate",free);
M(componentlist) as molweight(description:"components molar
mass"); //kg/kmol
p as pressure(description:"Reactor Pressure",fixed,1.01325); //bar
Phi as Realvariable(description:"Equivalence Ratio",
fixed,0.6);
phiin1 as realvariable(description:"Equivalence Ratio of Inlet
1",free);
phiin2 as realvariable(description:"Equivalence Ratio of Inlet
2",free);
phiout as realvariable(description:"Equivalence Ratio of
Outlet",free);
qext as enthflow(description:"External Heat Flow", fixed,0);
//GJ/hr
Rate as realvariable(description:"Reaction Rate",free);
//mol/m3/s

```

```

rateH2 as realvariable (description:"Reaction Rate",free);
rateO2 as realvariable (description:"Reaction Rate",free);
rateH2O as realvariable (description:"Reaction Rate",free);
Rein1 as realvariable(description:"Inlet 1 Reynolds
    Number",free);
Rein2 as realvariable(description:"Inlet 2 Reynolds
    Number",free);
Reout1 as realvariable(description:"Outlet 1 Reynolds
    Number",free);
Reout2 as realvariable(description:"Outlet 2 Reynolds
    Number",free);
rhoIn1 as dens_mass(description:"Inlet 1 Mixture Density",
    free); //kg/m3
rhoIn2 as dens_mass(description:"Inlet 2 Mixture Density",
    free); //kg/m3
rhoOut as dens_mass(description:"Outlet 1 Mixture Density",
    free); //kg/m3
Rhomolout as dens_mol(description:"Molar Volume at
    Outlet",free); //kmol/m3
T as temperature(description:"Reactor Temperature", free,
    25); //°C
VV as volume(description:"NETmix Chamber Volume"; free); //m3
vin1 as velocity(description:"Channel Velocity of Inlet 1",
    free); //m/s
vin2 as velocity(description:"Channel Velocity of Inlet 2",
    free); //m/s
viscin1 as viscosity(description:"Inlet 1 Mixture Viscosity",
    free); //cP
viscin2 as viscosity(description:"Inlet 2 Mixture Viscosity",
    free); //cP
viscout as viscosity(description:"Outlet 1 Mixture Viscosity",
    free); //cP
vout as velocity(description:"Channel Velocity of Outlet 1",
    free); //m/s
y(componentlist) as molefraction(description: "Outlet Molar
    Fraction");
yin(componentlist) as molefraction(description: "Inlet Molar
    Fraction");

// Parameters declaration
D as Realparameter(description:"NETmix Chamber Diameter",10.9e-
    3); //m
dd as Realparameter(description:"NETmix Channels
    Width",1.6148e-3); //m
Kkin as realparameter(description:"Combustion Reaction Kinetic
    Constant",1e7);
R as Realparameter(description:"Universal Gas Constant",
    8.314*1000); //J/mol/K
W as Realparameter(description:"NETmix Network Depth",1e-3);
// m

// Set default values
c("H2"): 0.005;
c("O2"): 0.005;
c("H2O"): 0.005;
c("N2"): 0.005;

```

```

y("H2"): c("H2")/(c("H2")+c("O2")+c("H2O")+c("N2"));
y("O2"): c("O2")/(c("H2")+c("O2")+c("H2O")+c("N2"));
y("H2O"): c("H2O")/(c("H2")+c("O2")+c("H2O")+c("N2"));
y("N2"): c("N2")/(c("H2")+c("O2")+c("H2O")+c("N2"));

// Geometric equations
VV = atan(1)*4*(D/2)^2*w; // in m3
Ainj = dd*w; // in m2
dh = 2*w*dd/(w+dd); // in m

//////////NO Backward//////////

// Kinetic rate
A: 9.87e8; //kg/m3 s // 1 reaction only forward
ea:3.1e7; //J/kgmol
b: 0;

1e-15*kf=1e-15*(A*(T+273.15)^b*exp(-ea/R/(T+273.15)));

rate1=kf*c("H2")*c("O2"); // in mol/m3/s
rateH2=rate1;
rateH2O=-rate1;
rateO2=0.5*rate1;

*/
////////// With Backward //////////

A: 9.87e8; //kg/m3 s
ea:3.1e7; //J/kgmol
b: 0;
f11:0.5;
deltaH:-241800000;
deltaS:-44300;

1e-15*kf=1e-15*(A*(T+273.15)^b*exp(-ea/R/(T+273.15)));
1e-15*kb=1e-15*((A*(T+273.15)^b*exp(-ea/R/(T+273.15)))/
((1.01325e5/R/(T+273.15))^f11)
/(exp(deltaS/R-deltaH/R/(T+273.15))));

rate1=kf*c("H2")*c("O2")-kb*c("H2O"); // in mol/m3/s
rateH2=rate1;
rateH2O=-rate1;
rateO2=0.5*rate1;

*/

*/
//////////with Backward - large kb //////////
// Kinetic rate
A: 9.87e8; //kg/m3 s // 1 reaction only forward
ea:3.1e7; //J/kgmol
b: 0;

```



```

AA: 1e15; //kg/m3 s // 1 reaction backward
eaa:1e8; //J/kgmol
bb: 0;

1e-15*kf=1e-15*(A*(T+273.15)^b*exp(-ea/R/(T+273.15)));
1e-15*kb=1e-15*(AA*(T+273.15)^bb*exp(-eaa/R/(T+273.15)));

rate1=kf*c("H2")*c("O2")-kb*c("H2O"); // in kmol/m3/s
rateH2=rate1;
rateH2O=-rate1;
rateO2=0.5*rate1;
*/

// Molar compositions
c("H2") = y("H2")*rhomolout; // in kmol/m3
c("O2") = y("O2")*rhomolout; // in kmol/m3
c("H2O") = y("H2O")*rhomolout; // in kmol/m3
c("N2") = y("N2")*rhomolout; // in kmol/m3

if inlet2.IsConnected then
  if inlet1.IsConnected then
    // Mass Balances
    inlet1.F*inlet1.z("H2")+inlet2.F*inlet2.z("H2") =
    Fout*y("H2")+VV*rateH2*3600+VV*$c("H2")*3600; // H2 in
    kmol/hr
    inlet1.F*inlet1.z("O2")+inlet2.F*inlet2.z("O2") =
    Fout*y("O2")+VV*rateO2*3600+VV*$c("O2")*3600; //O2 in
    kmol/hr
    inlet1.F*inlet1.z("H2O")+inlet2.F*inlet2.z("H2O") =
    Fout*y("H2O")+VV*rateH2O*3600+VV*$c("H2O")*3600; // H2O
    in kmol/hr
    inlet1.F*inlet1.z("N2")+inlet2.F*inlet2.z("N2") =
    Fout*y("N2")+VV*$c("N2")*3600; //N2 in kmol/hr

    y("H2")+y("O2")+y("H2O")+y("N2")=1;

    //Energy Blance
    inlet1.F*inlet1.h+inlet2.F*inlet2.h+qext=
    Fout*hout+$E*3600; //in GJ/hr

    E=VV*rhomolout*hout-P*VV*10^5/10^9; //in GJ

    qext=0;

    With Heat removal
    // qext=5*10^7*(3600/10^9)*VV*((T+273.15)-(50+273.15));
    //H2 Energy
    EE=(inlet2.F*inlet2.z("H2")+inlet1.F*inlet1.z("H2")-
    Fout*y("H2"))*M("H2")*141.65*2; // MJ/hr

    // Properties
    call (hout) = pEnth_Mol(T, p, y); // in GJ/kmol
    call(rhoin1) = pDens_Mass_Vap inlet1.T,inlet1.P,inlet1.z);
    // in kg/m3
    Call(rhoin2) =pDens_Mass_Vap(inlet2.T,inlet2.P,inlet2.z);
    // in kg/m3

```

```

call (rhoout) = pDens_Mass_Vap (T, p, y); // in kg/m3
call (viscin1) = pVisc_Vap (inlet1.T,inlet1.P,inlet1.z);
//in cP
call (viscin2) = pVisc_Vap (inlet2.T,inlet2.P,inlet2.z);
// in cP
call (viscout) = pVisc_Vap (T, p, y); // in cP
call (rhomolout) = pDens_Mol_Vap (T, p, y); // in kmol/m3
call (M) = pMolWeights();

else

// Material balances
inlet2.F*inlet2.z("H2")=
Fout*y("H2")+VV*rateH2*3600+VV*$c("H2")*3600; //H2 in
kmol/hr
inlet2.F*inlet2.z("O2")=
Fout*y("O2")+VV*rateO2*3600+VV*$c("O2")*3600; //O2 in
kmol/hr
inlet2.F*inlet2.z("H2O")=
Fout*y("H2O")+VV*rateH2O*3600+VV*$c("H2O")*3600; //H2O in
kmol/hr
inlet2.F*inlet2.z("N2")=Fout*y("N2")+VV*$c("N2")*3600;
//N2 in kmol/hr

y("H2")+y("O2")+y("H2O")+y("N2")=1;

//Energy Balance
inlet2.F*inlet2.h+qext=Fout*hout+$E*3600; // in GJ/hr
E=VV*rhomolout*hout-P*VV*10^5/10^9; // in GJ

// qext=5*10^7*VV*(T+273.15)-(50+273.15)); For heat removal
qext=0;

// H2 Energy
EE=(inlet2.F*inlet2.z("H2")-Fout*y("H2"))*M("H2")*141.65;
//KW

// Properties
call (hout) = pEnth_Mol (T, p, y); // in GJ/kmol
call (rhoin2) =pDens_Mass_Vap (inlet2.T,inlet2.P,inlet2.z);
// in kg/m3
call (rhoout) = pDens_Mass_Vap (T, p, y); // in kg/m3
call (viscin2) = pVisc_Vap (inlet2.T,inlet2.P,inlet2.z);
// in cP
call (viscout) = pVisc_Vap (T, p, y); // in cP
call (rhomolout) = pDens_Mol_Vap (T, p, y); // in kmol/m3
call (M) = pMolWeights();

endif

else

// Material balances
inlet1.F*inlet1.z("H2")=
Fout*y("H2")+VV*rateH2*3600+VV*$c("H2")*3600;
//H2 in kmol/hr
inlet1.F*inlet1.z("O2")=

```

```

Fout*y("O2")+VV*rateO2*3600+VV*$c("O2")*3600;
//O2 kmol/hr
inlet1.F*inlet1.z("H2O")=
Fout*y("H2O")+VV*rateH2O*3600+VV*$c("H2O")*3600;
//H2O in kmol/hr
inlet1.F*inlet1.z("N2")Fout*y("N2")+VV*$c("N2")*3600;
//N2 in kmol/hr

y("H2")+y("O2")+y("H2O")+y("N2")=1;

// Energy Balance
inlet1.F*inlet1.h+qext=Fout*hout+$E*3600; // in GJ/hr
E=VV*rhomolout*hout-P*VV*10^5/10^9; // in GJ

// qext=5*10^7*VV*((T+273.15)-(50+273.15)); For heat removal
qext=0;

// H2 Energy
EE=(inlet1.F*inlet1.z("H2")-Fout*y("H2"))*M("H2")*141.65;

// Properties
call (hout) = pEnth_Mol (T, p, y); // in GJ/kmol
call (rhoIn1) =pDens_Mass_Vap (inlet1.T,inlet1.P,inlet1.z);
// in kg/m3
call (rhoout) = pDens_Mass_Vap (T, p, y); // in kg/m3
call (viscin1) = pVisc_Vap (inlet1.T,inlet1.P,inlet1.z);
// in cP
call (viscout) = pVisc_Vap (T, p, y); // in cP
call (rhomolout) = pDens_Mol_Vap (T, p, y); // in kmol/m3
call (M) = pMolWeights();

endif
//outlet1
if outlet2.IsConnected then
  if outlet1.IsConnected then
    vout=Fout/2*(1/rhomolout)/3600/Ainj; // in m/s
    Reout2 = rhoout*vout*dh/(viscout*1e-3);
    Reout1 = rhoout*vout*dh/(viscout*1e-3);
  else
    vout=Fout*(1/rhomolout)/3600/Ainj; // in m/s
    Reout1 = 0;
    Reout2 = rhoout*vout*dh/(viscout*1e-3);
  endif
else
  vout=Fout*(1/rhomolout)/3600/Ainj; // in m/s
  Reout1 = rhoout*vout*dh/(viscout*1e-3);
  Reout2 = 0;
endif

// Write values in outlet streams
if outlet1.IsConnected then
  if outlet2.IsConnected then
    outlet1.h=hout; // in GJ/kmol
    outlet2.h=hout; // in GJ/kmol
    outlet1.F=Fout/2; // in kmol/hr
    outlet2.F=Fout/2; // in kmol/hr
    outlet1.z=y;
  
```

```

        outlet2.z=y;
        outlet1.P=p; // in bar
        outlet2.P=p; // in bar
        outlet1.T=T; // in C
        outlet2.T=T; // in C
        outlet1.V=1/rhomolout; // in m3/kmol
        outlet2.V=1/rhomolout; // in m3/kmol
        outlet1.av=1;
        outlet2.av=1;
    else
        outlet1.h=hout; // in GJ/kmol
        outlet1.F=Fout; // in kmol/hr
        outlet1.z=y;
        outlet1.P=p; // in bar
        outlet1.T=T; // in C
        outlet1.V=1/rhomolout; // in m3/kmol
        outlet1.av=1;
    endif
else
    outlet2.h=hout; // in GJ/kmol
    outlet2.F=Fout; // in kmol/hr
    outlet2.z=y;
    outlet2.P=p; // in bar
    outlet2.T=T; // in C
    outlet2.V=1/rhomolout; // in m3/kmol
    outlet2.av=1;
endif
END

```

D.13 NETcombustor Maps

D.13.1 Temperature Map

Option Explicit

```

'.....
'.....'Required routines: Sub matrix, Sub NETmix '.....
'.....

Sub matrix()

Folha1.Select

    Dim i As Integer
    Dim j As Integer
    Dim k As Integer
    Dim nl As Integer
    Dim nc As Integer
    Dim n As Integer

    nl = 17
    nc = 8
    n = nl * nc - nc

```

```

k = 2
For i = 1 To nl
    If (i Mod 2) = 0 Then
        nc = 7
    Else
        nc = 8
    End If

    For j = 1 To nc
        Cells(i + 1, j + 1) = Cells(k, 11)
        k = k + 1
    Next
Next
End Sub

```

.....

```

Sub NETmix()

Folhal.Select

'index
Dim ii As Integer
Dim i As Integer
Dim j As Integer
Dim k As Integer

'circle
Dim radius As Double
Dim x As Double
Dim y As Double
Dim dx As Double
Dim dy As Double
radius = 10
x = 50
y = 50
dx = 25
dy = 25

'Data
Dim T() As Double

'NETmix network
Dim nl As Integer
Dim nc As Integer
nl = 17
nc = 8
ReDim T(nl, nc) As Double

'RGB color scheme
Dim Max As Double
Dim Min As Double
Dim delta As Double
Dim cc As Integer
Max = 460 'Cells(20, 4)
Min = 0 'Cells(20, 6)
cc = 765

```

```

delta = (Max - Min) / cc

Dim R() As Integer
Dim G() As Integer
Dim B() As Integer

ReDim R(1 To cc) As Integer
ReDim G(1 To cc) As Integer
ReDim B(1 To cc) As Integer
Dim RR As Integer
Dim GG As Integer
Dim BB As Integer

R(1) = 0
G(1) = 0
B(1) = 255

For i = 2 To cc
    If i <= 255 Then
        R(i) = 0
        G(i) = G(i - 1) + 1
        B(i) = 255
    ElseIf i > 255 And i <= 255 + 255 Then
        R(i) = R(i - 1) + 1
        G(i) = 255
        B(i) = B(i - 1) - 1
    ElseIf i > 255 + 255 And i <= 255 + 255 + 127 Then
        R(i) = 255
        G(i) = G(i - 1) - 1
        B(i) = 0
    Else
        R(i) = 255
        G(i) = G(i - 1) - 1
        B(i) = 0
    End If
Next

'Read data
For i = 1 To nl
    If (i Mod 2) = 0 Then
        nc = 7
    Else
        nc = 8
    End If
    For j = 1 To nc
        T(i, j) = Cells(i + 1, j + 1)
    Next
Next

'color scheme
Folha2.Select

'build network

For i = 1 To nl
    If (i Mod 2) = 0 Then
        nc = 7

```

```

        x = 50 + dx / 2
Else
    nc = 8
    x = 50
End If

For j = 1 To nc
    If T(i, j) >= Min And T(i, j) < Min + delta * 1 Then
        RR = R(1)
        GG = G(1)
        BB = B(1)

        With ActiveSheet.Shapes.AddShape(msoShapeOval, x, y,
            radius * 2, radius * 2)
            .Name = "CIRCLE1"
            .Fill.ForeColor.RGB = RGB(RR, GG, BB)
            .Line.Transparency = 1
            .Placement = 1
        End With
    End If

For k = 2 To cc - 1
    If T(i, j) >= Min + delta * (k - 1) And T(i, j) < Min
        + delta * k Then
        RR = R(k)
        GG = G(k)
        BB = B(k)

        With ActiveSheet.Shapes.AddShape(msoShapeOval, x,
            y, radius * 2, radius * 2)
            .Name = "CIRCLE1"
            .Fill.ForeColor.RGB = RGB(RR, GG, BB)
            .Line.Transparency = 1
            .Placement = 1
        End With
    End If
Next

If T(i, j) >= Min + delta * cc Then
    RR = R(cc)
    GG = G(cc)
    BB = B(cc)
    With ActiveSheet.Shapes.AddShape(msoShapeOval, x, y,
        radius * 2, radius * 2)
        .Name = "CIRCLE1"
        .Fill.ForeColor.RGB = RGB(RR, GG, BB)
        .Line.Transparency = 1
        .Placement = 1
    End With
End If

    x = x + dx
Next

y = y + dy
x = 50
Next

```



```
'save
ActiveSheet.ExportAsFixedFormat Type:=xlTypePDF, _
Filename:="C:\Users\Joana
Matos\Documents\Joana\pp_word_exel\combustao\H2\ALL_cases_H2_NEW_N2\non
premixed_S10\T.pdf"

End Sub
```

D.13.2 Molar Fraction Map

```
Option Explicit
```

```
.....
'Required routines: Sub matrix, Sub NETmix
'.....
```

```
Sub matrix()
```

```
Folha3.Select
```

```
Dim i As Integer
Dim j As Integer
Dim k As Integer
Dim nl As Integer
Dim nc As Integer
Dim n As Integer
```

```
nl = 17
nc = 8
n = nl * nc - nc
```

```
k = 2
For i = 1 To nl
    If (i Mod 2) = 0 Then
        nc = 7
    Else
        nc = 8
    End If
```

```
    For j = 1 To nc
        Cells(i + 1, j + 1) = Cells(k, 12)
        k = k + 1
    Next
Next
```

```
End Sub
```

```
.....
```

```
Sub NETmix()
```

```
Folha3.Select
```

```
'index
Dim i As Integer
```

```

Dim j As Integer
Dim k As Integer

'circle
Dim radius As Double
Dim x As Double
Dim y As Double
Dim dx As Double
Dim dy As Double
radius = 10
x = 50
y = 50
dx = 25
dy = 25

'Data
Dim T() As Double

'NETmix network
Dim nl As Integer
Dim nc As Integer
nl = 17
nc = 8
ReDim T(nl, nc) As Double

'RGB color scheme
Dim Max As Double
Dim Min As Double
Dim delta As Double
Dim cc As Integer
Max = 0.0014
Min = 0
cc = 255
delta = (Max - Min) / cc

Dim R() As Integer
Dim G() As Integer
Dim B() As Integer

ReDim R(1 To cc) As Integer
ReDim G(1 To cc) As Integer
ReDim B(1 To cc) As Integer
Dim RR As Integer
Dim GG As Integer
Dim BB As Integer

R(1) = 255
G(1) = 255
B(1) = 255

For i = 2 To cc
    R(i) = R(i - 1) - 1
    G(i) = G(i - 1) - 1
    B(i) = 255
Next

'Read data

```

```

For i = 1 To nl
    If (i Mod 2) = 0 Then
        nc = 7
    Else
        nc = 8
    End If
    For j = 1 To nc
        T(i, j) = Cells(i + 1, j + 1)
    Next
Next

'build network
Folha4.Select

For i = 1 To nl
    If (i Mod 2) = 0 Then
        nc = 7
        x = 50 + dx / 2
    Else
        nc = 8
        x = 50
    End If

    For j = 1 To nc
        If T(i, j) >= Min And T(i, j) < Min + delta * 1 Then
            RR = R(1)
            GG = G(1)
            BB = B(1)

            With ActiveSheet.Shapes.AddShape(msoShapeOval, x, y,
                radius * 2, radius * 2)
                .Name = "CIRCLE1"
                .Fill.ForeColor.RGB = RGB(RR, GG, BB)
                .Line.Transparency = 0
                .Placement = 1
            End With
        End If

        For k = 2 To cc - 1
            If T(i, j) >= Min + delta * (k - 1) And T(i, j) < Min
                + delta * k Then
                RR = R(k)
                GG = G(k)
                BB = B(k)

                With ActiveSheet.Shapes.AddShape(msoShapeOval, x,
                    y, radius * 2, radius * 2)
                    .Name = "CIRCLE1"
                    .Fill.ForeColor.RGB = RGB(RR, GG, BB)
                    .Line.Transparency = 0
                    .Placement = 1
                End With
            End If
        Next

        If T(i, j) >= Min + delta * cc Then
            RR = R(cc)

```

```

        GG = G(cc)
        BB = B(cc)
        With ActiveSheet.Shapes.AddShape(msoShapeOval, x, y,
            radius * 2, radius * 2)
            .Name = "CIRCLE1"
            .Fill.ForeColor.RGB = RGB(RR, GG, BB)
            .Line.Transparency = 0
            .Placement = 1
        End With
    End If

    x = x + dx
Next

    y = y + dy
    x = 50
Next

'save
ActiveSheet.ExportAsFixedFormat Type:=xlTypePDF, _
    Filename:="C:\Users\Joana
    Matos\Documents\Joana\pp_word_exel\combustao\combustion\ALL_cases\0.1h
    2_alternado\y_H2.pdf"

End Sub

```