



M 2024

CFD APPLICATION IN PARAMETRIC STUDIES OF NON-ISOTHERMAL REACTORS

ANA CATARINA ROCHA MOREIRA MONTEIRO
MASTER THESIS IN CHEMICAL ENGINEERING
PRESENTED TO THE FACULTY OF ENGINEERING
OF THE UNIVERSITY OF PORTO

Master in Chemical Engineering

CFD application in parametric studies of non-isothermal reactors

Master Thesis

of

Ana Catarina Rocha Moreira Monteiro

Developed within the course of dissertation

held in

Associate Laboratory in Chemical Engineering



Supervisor at FEUP: Prof. José Araújo

Joint supervisor(s) at FEUP: Prof. Miguel Madeira



July 2024

Acknowledgment

First and foremost, I would like to extend my heartfelt gratitude to my parents for providing me with the opportunity to undertake this course and allowing me to focus exclusively on it. Additionally, I wish to express my appreciation for the emotional support they have given me, as well as the support from my friends and family.

Secondly, I would like to express my deepest gratitude to Professor José Daniel Araújo, my academic supervisor, for his guidance and insightful contributions.

To Professor Luís Miguel Madeira, I extend my gratitude for all the knowledge and contributions given.

To doctoral student Joana Almeida, for all the availability, help and knowledge passed to me regarding 3D printing.

To Doctor Luís Carlos Matos, my heartfelt thanks for his promptness in facilitating the laboratory work and for his unwavering kindness and humour throughout the process.

Abstract

CFD simulations open doors to numerous benefits, such as reduction of time and materials consumption by allowing to perform detailed parametric studies without developing various laboratory experiments. From the many existent possibilities, Ansys package was the computation fluid dynamics tool used in this work, due to its user-friendly and intuitive interface and extensively optimized and thoroughly tested physical models.

The main goal of this work was to highlight the usefulness of CFD parametric studies to study and improve the performance in non-isothermal reactors. By using a CFD tool, there was no need to use catalysers or consumption of reagents to produce relevant data. However, experimental activities are still crucial for validation purposes. The second objective was to apply 3D printing to manufacture a vessel design and perform tracer tests to validate the CFD models and solvers applied. Since metal printing was not an option for this work, the validation procedure did not include heat transfer and reaction experiments.

The major advance of this work was to incorporate surface wall reactions on obstacles inside a domain that represented a small reactor design. It was intended to predict the effects of exothermic reactions, and so, illustrative systems with two different two levels of heat of reaction were considered: 1) $\Delta H = -30 \text{ kJ}\cdot\text{mol}^{-1}$ - typical of a liquid phase homogeneous reaction such as the neutralization of a weak acid; 2) $\Delta H = -300 \text{ kJ}\cdot\text{mol}^{-1}$ - possible in a gas phase oxidation occurring in the surface wall of a catalyst. The focus of the work was placed on performing a detailed study about the effect of different parameters, such as the inlet conditions, external convective coefficient, h , and the temperature exponent in the Arrhenius law, a , (only for the surface wall reaction).

The method of validation used was adequate and that is possible to manipulate the energy released and the formation of product C of a reaction by changing certain parameters. In the manipulation of the convection coefficient, it was possible to maintain the average Y_C in the outlet while still decreasing the temperatures inside the reactor. Relatively to the effect of the inlet compositions, it was noticeable that the lower the mass fraction of reagents, the latter the reaction achieve significant values. While changing the values of the inlet temperatures, the impact on the average Y_C in the outlet and on the temperatures was practically not detectable, in opposition, the increase of the velocity meant the decrease of the output variables. For the temperature exponential values of 0 and 1, the results obtained were very similar for most simulations. However, the value of $a = -1$ caused a major decrease in the output variables.

Finally, and regarding the most exothermic reaction, simulations using more diluted inlet streams were performed, i.e., less intense in terms of generated heat, and interesting values were obtained for $Y_A = 0.15$, $Y_B = 0.05$, $v = 0.1 \text{ m}\cdot\text{s}^{-1}$, $k_0 = 100 \text{ m}^3\cdot\text{kgmol}^{-1}\cdot\text{s}^{-1}$, $E_a = 50 \text{ J}\cdot\text{kgmol}^{-1}$, $T_{in1} = T_{in2} = 50 \text{ }^\circ\text{C}$, $a = 0$ and $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

Keywords (theme):

CFD, 3D printing, heat transfer, tracer experiments and exothermic reaction.

Resumo

As simulações CFD (Computational Fluid Dynamics) proporcionam numerosos benefícios, como a redução do tempo e do consumo de materiais, e permitindo realizar estudos paramétricos sem a necessidade de desenvolver experiências laboratoriais. Das muitas possibilidades existentes, o pacote Ansys foi a ferramenta de CFD utilizada neste trabalho, devido à sua interface intuitiva, e aos modelos físicos extensivamente otimizados e rigorosamente testados.

O principal objetivo deste trabalho foi destacar a utilidade dos estudos paramétricos em CFD para estudar e melhorar o desempenho em reatores não isotérmicos, não sendo necessário utilizar catalisadores ou consumir reagentes para a realização de experiências. No entanto, as atividades experimentais ainda são cruciais para fins de validação. O segundo objetivo foi aplicar a impressão 3D para fabricar um *design* de reator e realizar testes de *tracer* de forma a validar os modelos CFD e as equações aplicadas. Como a impressão em metal não foi uma opção para este trabalho, o procedimento de validação não incluiu experiências de transferência de calor ou de reação.

A principal inovação deste trabalho foi incorporar reações na superfície das paredes de obstáculos num domínio que representava um pequeno *design* de reator. Para prever os efeitos de reações exotérmicas, sistemas ilustrativos com dois níveis diferentes de calor de reação foram considerados: 1) $\Delta H = -30 \text{ kJ}\cdot\text{mol}^{-1}$ - típico de uma reação homogênea em fase líquida, como a neutralização de um ácido fraco; 2) $\Delta H = -300 \text{ kJ}\cdot\text{mol}^{-1}$ - possível numa oxidação em fase gasosa que ocorre na superfície da parede de um catalisador. O foco do trabalho foi realizar um estudo detalhado sobre o efeito de diferentes parâmetros, como as condições de entrada, o coeficiente convectivo externo, e o expoente de temperatura na lei de Arrhenius, a , (apenas para a reação na superfície da parede).

O método de validação utilizado foi adequado, sendo possível manipular a energia libertada e a formação de um produto de uma reação alterando certos parâmetros. Na manipulação do coeficiente de convecção, foi possível manter o valor de Y_C médio à saída, enquanto diminuía as temperaturas dentro do reator. Relativamente ao efeito das composições de entrada, foi notório que quanto menor a fração mássica dos reagentes, mais tarde a reação atinge valores significativos. Ao alterar os valores das temperaturas de entrada, o impacto no valor médio de Y_C à saída e nas temperaturas foi praticamente indetetável; em contrapartida, o aumento da velocidade significou a diminuição das variáveis de saída. Para os valores exponenciais de temperatura de 0 e 1, os resultados obtidos foram muito semelhantes para a maioria das simulações. No entanto, o valor de $a = -1$ causou uma grande diminuição nas variáveis de saída.

Finalmente, e relativamente à reação mais exotérmica, foram realizadas simulações usando correntes de entrada mais diluídas, ou seja, menos intensas em termos de calor gerado, e valores interessantes foram obtidos para $Y_A = 0.15$, $Y_B = 0.05$, $v = 0.1 \text{ m}\cdot\text{s}^{-1}$, $k_0 = 100 \text{ m}^3\cdot\text{kgmol}^{-1}\cdot\text{s}^{-1}$, $E_a = 50 \text{ J}\cdot\text{kgmol}^{-1}$, $T_{in1} = T_{in2} = 50 \text{ }^\circ\text{C}$, $a = 0$ and $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot\text{ }^\circ\text{C}^{-1}$.

Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions is indicated and due reference is given to the author and source

Ana Catarina Rocha Moreira Monteiro

Porto, 1st of July of 2024

Index

1. Introduction.....	1
1.1. Framing and presentation of the work	1
1.2. Presentation of the laboratory	2
1.3. Contribution of the author to the work	3
1.4. Organization of the dissertation	3
2. Context and State of the art.....	5
2.1. Computational Fluid Dynamics	5
2.1.1. Governing equations in CFD	5
2.1.2. Tools within the Ansys tools.....	6
2.1.3. Importance CFD in Chemical Engineering	7
2.2. 3D-printing	9
2.2.1. Symbiosis between additive manufacturing and Chemical Engineering.....	11
2.3. Combination of CFD with 3D printing to design reactors.....	12
2.3.1. Printing of reactor with static mixing elements.....	12
2.3.2. Printing of reactor to be used in absorption of CO ₂	13
2.3.3. Printing of a stainless-steel reactor for an exothermic reaction at cryogenic temperature and high-pressure.....	14
2.4. Tracer experiments	15
3. Materials and Methods	17
3.1. Learning phase	17
3.2. 3D printing and laboratory experiments (validation of the method)	19
3.3. Simulation of tracer tests	21
3.4. Reaction	23
4. Results and discussion	25
4.1. CFD learning phase	25
4.2. Experimental and simulation tracer tests	31
4.3. Parametric study with a low exothermic reaction	33
4.4. Parametric study with a highly exothermic reaction	35
5. Conclusions	45
6. Assessment of the work done	47
6.1. Objectives Achieved.....	47
6.2. Contribution to the Sustainable Development Goals.....	47
6.3. Final Assessment	47
7. References	49

Annex A - Sustainable Development Goals.....	51
Appendix A- Dimensions of the 3 sketches used in this thesis.....	53
Appendix B - General Workbench used for all the simulations	57
Appendix C - Main page of Fluent case	59
Appendix D - Example of the creation of material N_2	61
Appendix E - How to define the boundaries conditions	63
Appendix F - How to define a reaction	65
Appendix G - How to define the depth of the sketch in Fluent	67
Appendix H - Properties of the materials used of the two exothermic reactions.....	69
Appendix I - Calculations necessary to perform the simulations described in this document	71
Appendix J - Photos taken of the setup used during the 3D printing process and of	
Preform Program.....	73
Appendix K - Results related to the mesh independency test	77
Appendix L - Contours of static temperature from the CFD learning phase	79
Appendix M - Results obtained from the study of the effects of the combination of the	
production of heat flux in the obstacles and convection in the exterior walls.....	81
Appendix N - Tracer experiments for the learning phase	83
Appendix O - Contours resultant from the parametric study of the less exothermic	
reaction.....	87
Appendix P - Contours resultant from the parametric study of the more exothermic	
reaction.....	89
Appendix Q - Calculations associated with the values of h considered throughout this	
thesis.....	91

List of Figures

Figure 2-1: Number of CFD publications made in all Chemical Engineering Journals (on the left) and made on Chemical Engineering Research and Design (on the right). ^[1]	8
Figure 2-2: Distribution of the publications on computational fluid dynamics between the subjects and objects of study. ^[15]	9
Figure 2-3: Demonstrations of some of the 3D printing techniques. ^[16]	9
Figure 2-4: Advantages resulting from the symbioses of CFD, Modelling and 3D printing. ^[17]	12
Figure 2-5: 3D sketch of the design incorporating SMEs. ^[17]	12
Figure 2-6: Contour of velocity of the design: without SMEs (on the left) and with SMEs (on the right). ^[17]	13
Figure 2-7: a) 3D sketch of the printed reactor including the supports. b) Gas volume fraction contour. ^[18]	14
Figure 2-8: 3D sketch (left) and printed reactor(right). ^[19]	14
Figure 3-1: Sketch of Design A.	17
Figure 3-2: 3D image of the printed design: a) in Space Claim and b) in PreForm with the supports added.	19
Figure 3-3: Images of the setup used for 3D printing: a) Formlabs Form 3+and included tools ^[23] ; b) Formlabs Form Cure with the printed piece inside.	20
Figure 3-4: Image of the setup used to execute the experimental tracer experiments.	20
Figure 3-5: Sketch of a) Design B.	21
Figure 4-1: Graph of the T_{out} in function of y direction for an iso-surface created in a zone between the beginning of the outlet and the end of all obstacles.	26
Figure 4-2: Graph of the v_{out} in function of y direction for an iso-surface created in a zone between the beginning of the outlet and the end of all obstacles.	26
Figure 4-3: Contours of velocity magnitude: a) $Re = 100$; b) $Re = 400$; c) $Re = 700$; d) $Re = 900$	27
Figure 4-4: Zoom of the velocity contours for $Re = 900$	28
Figure 4-5: Contours of mass fraction of CH_4 : a) $Re = 100$; b) $Re = 400$; c) $Re = 700$; d) $Re = 900$	28
Figure 4-6: Static temperature contours with $Re = 100$ and $H_F = 50 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	29
Figure 4-7: Static temperature contours with $Re = 100$ and $H_F = 200 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	29

Figure 4-8: Static temperature contours with $Re = 100$ and $H_F = 400 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	29
Figure 4-9: Static temperature contours with $Re = 400$ and $H_F = 400 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	30
Figure 4-10: Static temperature contours with $Re = 700$ and $H_F = 400 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	30
Figure 4-11: Static temperature contours with $Re = 900$ and $H_F = 400 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	30
Figure 4-12: Comparing the results of experimental and simulation data for $Re = 27$	32
Figure 4-13: Comparing the results of experimental and simulation data for $Re = 58$	32
Figure 4-14: Comparing the results of experimental and simulation data for $Re = 133$	32
Figure 4-15: Contours of mass fraction of C for: a) $v = 0.01 \text{ m}\cdot\text{s}^{-1}$, b) $v = 0.1 \text{ m}\cdot\text{s}^{-1}$ and c) $v = 0.5 \text{ m}\cdot\text{s}^{-1}$	34
Figure 4-16: Average $Y_{C/out}$ results obtained from the conjugation of various inlet compositions where $Y_A = Y_B$	36
Figure 4-17: Average T_{out} results obtained from the conjugation of various inlet compositions where $Y_A = Y_B$	36
Figure 4-18: Average T_{max} results obtained from the conjugation of various inlet compositions where $Y_A = Y_B$	36
Figure 4-19: Static temperature contours for: a) $h = 0 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$, b) $h = 7 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$, c) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$ and d) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$, when $Y_A = Y_B = 0.1$	37
Figure 4-20: Average $Y_{C/out}$ results obtained from the conjugation of various inlet compositions where Y_A and Y_B are not equal.	38
Figure 4-21: Average T_{out} results obtained from the conjugation of various inlet compositions where Y_A and Y_B are not equal.....	38
Figure 4-22: T_{max} results obtained from the conjugation of various inlet compositions where Y_A and Y_B are not equal.	38
Figure 4-23: Contours of mass fraction of C for a) $Y_A = Y_B = 0.3$, b) $Y_A = 0.5$ and $Y_B = 0.7$, c) $Y_A = 0.3$ and $Y_B = 0.1$	39
Figure 4-24: Comparison of average $Y_{C/out}$ results obtained for different values of a	40
Figure 4-25: Comparison of T_{max} results obtained for different values of a	41
Figure 4-26: Comparison of average T_{out} results obtained for different values of a	42
Figure 4-27: Results obtained for the variation of v , Y_A and Y_B	43

Figure 4-28: Contours resulting from the combination of $Y_A = Y_B = 0.05$ with $v = 0.01 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.....	43
Figure 4-29: Contours resulting from the combination of $Y_A = 0.15$ and $Y_B = 0.05$ with $v = 0.1 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.	44
Figure 4-30: Contours resulting from the combination of $Y_A = 0.05$ and $Y_B = 0.15$ with $v = 1.5 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.	44
Figure Annex A. 1: Symbols of the SDGs associated to this thesis. ^[26]	51
Figure Appendix A. 1: Zoom of the sketch of Design A.....	53
Figure Appendix A. 2: Zoom of the sketch of Design B.....	54
Figure Appendix A. 3: Zoom of the sketch of Design B with the inlets modifications.....	55
Figure Appendix B. 1: Workbench used for all the simulations.	57
Figure Appendix C. 1: Fluent front page.	59
Figure Appendix D. 1; Tutorial about how to create a material in Fluent.	61
Figure Appendix E. 1: Tutorial about how to define the inlet conditions in Fluent.	63
Figure Appendix E. 2: Tutorial about how to define the obstacles walls conditions in Fluent.	63
Figure Appendix E. 3: Tutorial about how to define the exterior walls conditions in Fluent.....	64
Figure Appendix F. 1: Tutorial about how to create a mixture in Fluent.	65
Figure Appendix F. 2: Tutorial about how to define a reaction in Fluent.	65
Figure Appendix F. 3: Tutorial about how to define a mechanism of reaction in Fluent.	66
Figure Appendix G. 1: Tutorial about how to define the depth of the reactor.	67
Figure Appendix J. 1: Image of the printed design and the definitions made for the 3D-printing in PreForm.	73
Figure Appendix J. 2: Image of Formlabs Form Cure (on the left) and Form 3 (on the right) used in the experiment.....	73
Figure Appendix J. 3: Image of the end of the printing where the piece is still attached to the removable part of the printer.	74
Figure Appendix J. 4: Image of the manual extraction utensils and the 2 solutions of IPA used to refine the printed piece.	74
Figure Appendix J. 5: Image of the printed piece while the cure device is pre-heating.....	75
Figure Appendix J. 6: Image of the printed piece after tracer experiments with the auxiliar tubes, to prevent the leakage of fluid, in the inlet and in the outlet.	75
Figure Appendix K. 1: Image of the four meshes generated.	77

Figure Appendix L. 1: Static temperature contours with $Re = 400$ and $H_F = 50 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	79
Figure Appendix L. 2: Static temperature contours with $Re = 400$ and $H_F = 200 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	79
Figure Appendix L. 3: Static temperature contours with $Re = 700$ and $H_F = 50 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	79
Figure Appendix L. 4: Static temperature contours with $Re = 700$ and $H_F = 200 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	80
Figure Appendix L. 5: Static temperature contours with $Re = 900$ and $H_F = 50 \text{ W}\cdot\text{m}^{-2}$ for: a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	80
Figure Appendix L. 6: Static temperature contours with $Re = 900$ and $H_F = 200 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	80
Figure Appendix N. 1: Graphics of the Dankwerts F curve for a) total time = τ and b) total time = $5\cdot\tau$ for $Re = 100$	83
Figure Appendix N. 2: Graphics of the Dankwerts F curve for a) total time = τ and b) total time = $5\cdot\tau$ for $Re = 400$	83
Figure Appendix N. 3: Graphics of the Dankwerts F curve for a) total time = τ and b) total time = $5\cdot\tau$ for $Re = 700$	83
Figure Appendix N. 4: Graphics of the Dankwerts F curve for a) total time = τ and b) total time = $5\cdot\tau$ for $Re = 900$	84
Figure Appendix N. 5: Graphics of the time residence distribution for a) $Re = 100$; b) $Re = 400$; c) $Re = 700$; d) $Re = 900$	84
Figure Appendix O. 1: Contours Static temperature for: a) $h = 0 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$, b) $h = 7 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$, c) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$, d) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	87
Figure Appendix O. 2: Contours of mass fraction of C for: a) $Y_A = Y_B = 0.05$, b) $Y_A = 0.5$ and $Y_B = 0.1$, c) $Y_A = 0.25$ and $Y_B = 0.1$, d) $Y_A = Y_B = 0.25$	87
Figure Appendix P. 1: Contours resulting from the combination of $a = 0$ with $v = 0.05 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.	89
Figure Appendix P. 2: Contours resulting from the combination of $a = 0$ with $v = 0.1 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.	89
Figure Appendix P. 3: Contours resulting from the combination of $a = 0$ with $v = 0.5 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.	89
Figure Appendix P. 4: Contours resulting from the combination of $a = 1$ with $v = 0.05 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.	90

Figure Appendix P. 5: Contours resulting from the combination of $a = 1$ with $v = 0.1 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C..... 90

Figure Appendix P. 6: Contours resulting from the combination of $a = 1$ with $v = 0.5 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C..... 90

List of Tables

Table 3-1: Definitions of the Fluent case for the learning phase.	18
Table 3-2: Values of velocity in the inlets according to Design A.	19
Table 3-3: Values of coefficient of convection and heat flux used in the simulations.	19
Table 3-4: Values of ω and Q for the experimental tracer experiments.	20
Table 3-5: Definitions of the Fluent case for the tracer experiments.	22
Table 3-6: Values of velocity in the inlets and the simulation time according to each of the designs.	22
Table 3-7: Definitions of the Fluent case for the reactions.	23
Table 3-8: Specifications of the Mixture Properties of the reaction.	24
Table 4-1: Definition of the properties of mesh 1 and 2 and respective results.	25
Table 4-2: Definition of the properties of mesh 3 and 4 and respective results.	26
Table 4-3: Results from the simulation of assay 9 of T_{max} and the average T_{out} for each mesh.	27
Table 4-4: Mesh properties resulting from the application of Mesh 2 definitions in Design B.	31
Table 4-5: Comparison between the experimental and the simulation data.	32
Table 4-6: Definitions made for the study of the velocity effect and respective results.	33
Table 4-7: Definitions made for the study of the effect of h and respective results.	34
Table 4-8: Definitions made for the study of the effect of the inlet compositions and respective results.	35
Table 4-9: Definitions made for the study of the effect of the inlet temperatures and respective results.	35
Table 6-1: Contributions of the work for the Sustainable Development Goals and respective indicators.	47
Table Appendix A. 1: Dimensions corresponding to Figure Appendix A. 1.	53
Table Appendix A. 2: Dimensions corresponding to Figure Appendix A. 2.	54
Table Appendix A. 3: Value of porosity for each section of Design B.	55
Table Appendix A. 4: Dimensions corresponding to Figure Appendix A. 3.	55
Table Appendix H. 1: Properties of the materials used to simulate the first exothermic reaction.	69
Table Appendix H. 2: Properties of the materials used to simulate the second exothermic reaction.	69
Table Appendix I. 1: Physical properties of N_2 and O_2 obtained from Fluent Database.	71
Table Appendix I. 2: Physical properties of liquid water obtained from Fluent Database.	71

<i>Table Appendix I. 3: Values of the volume of the reactor and the flow rate in the inlets for each design.</i>	<i>72</i>
<i>Table Appendix I. 4: Values needed to calculate the porosity of each section of Design B.</i>	<i>72</i>
<i>Table Appendix M. 1: Values of temperatures minimum, maximum and average in the outlet for each assay simulated.</i>	<i>81</i>
<i>Table Appendix N. 1: Comparison between the average t_r and τ.</i>	<i>84</i>
<i>Table Appendix Q. 1: Physical properties of air.</i>	<i>92</i>
<i>Table Appendix Q. 2: Values of h calculated for natural convection.</i>	<i>92</i>
<i>Table Appendix Q. 3: Physical properties of water.</i>	<i>93</i>
<i>Table Appendix Q. 4: Values of h calculated for forced convection.</i>	<i>93</i>

Notation and Glossary

A	Area	m^2
C	Concentration of tracer	$mol \cdot m^{-3}$
C_p	Heat capacity	$J \cdot kg^{-1} \cdot K^{-1}$
e	Size of inlet of the reactor	m
E_a	Activation Energy	$J \cdot mol^{-1}$
$\vec{g}$	Gravitational acceleration	$m^2 \cdot s^{-1}$
Gr	Grashof number	
h	Convection coefficient	$W \cdot m^{-2} \cdot K^{-1}$
h_e	Sensible Enthalpy	J
H_F	Heat flux	$W \cdot m^{-2}$
J	Diffusion flux	$kg \cdot m^{-2} \cdot s^{-1}$
k	Velocity of reaction	$mol \cdot m^{-3} \cdot s^{-1}$
k_0	Pre-exponential factor	
l	Depth of the reactor	m
L	Characteristic dimension of the fluid flow	m
M	Molecular mass	$g \cdot mol^{-1}$
N	Number of obstacles in each section of the reactor	
Nu	Nusselt number	
Pr	Prandtl number	
q	Heat transferred per unit area	$J \cdot m^{-2}$
Q	Flow rate	$m^3 \cdot s^{-1}$
r	Radius	m
R	Reaction rate production of a species	$mol \cdot m^{-3} \cdot s^{-1}$
Re	Reynolds number	
R_g	Ideal gas constant	$8.314 J \cdot mol^{-1} \cdot K^{-1}$
$S(C)$	Source term	
T	Temperature	$^{\circ}C$
t	Time	s
$\bar{t}_r$	Mean residence time	s
V	Volume	m^3
$\vec{v}$	Velocity	$m \cdot s^{-1}$
Y	Mass fraction of a species	
ΔH	Enthalpy variation	J
ΔS	Entropy variation	$J \cdot K^{-1}$
ΔT	Temperature variation	$^{\circ}C$

Greek Letters

a	Temperature exponent in velocity of reaction equation	
β	Thermal expansion coefficient	K^{-1}
ε	Porosity	
λ	Thermal conductivity	$W \cdot m^{-1} \cdot K^{-1}$
μ	Dynamic viscosity	$Pa \cdot s$
π	PI number	
ρ	Mass density	$kg \cdot m^{-3}$
τ	Residence time	s
$\bar{\tau}$	Viscous stress tensor	Pa
ω	Rotational speed of the peristaltic pump	rpm

Indexes

eff	Effective
inb	Inlet number b
j	Species
max	Maximum
min	Minimum
out	Outlet
t	Turbulent
T	Total
x	Horizontal coordinate
y	Vertical coordinate

Functions

$E(t)$	Residence time distribution function
$F(t)$	Dankwerts F curve

List of Acronyms

2D	Two dimensional
3D	Three dimensional
3DP	3D printing
ALICE	Associate Laboratory for Innovation in Chemical Engineering
CEFT	Transport Phenomena Research Centre
CFD	Computational Fluid Dynamics
FEUP	Faculty of Engineering of the University of Porto
IPA	Isopropanol
LEPABE	Laboratory for Process Engineering
PDMS	Poly(dimethylsiloxane)
PISO	Pressure-Implicit with Splitting of Operators
PTERF	Pseudo Time Explicit Relaxation Factor
RTD	Residence time distribution
SDG	Sustainable Development Goals
SLA	Stereolithography
SLM	Selective Laser Melting
SME	Static Mixing Elements

1. Introduction

1.1. Framing and presentation of the work

When the COVID pandemic stroke, employees were forced to work from home, and that was when a lot of companies realised just how important simulation could be, as experimental testing had been drastically restricted.^[1] This simply was the more recent wake up call for companies to explore simulation in a lot of different ways, because nowadays, more and more people aspire to achieve a mix between teleworking days and office days. Beyond this, simulation can bring various benefits relatively to the implementation of changes. This tool has gained a huge importance over the years, as it allows the possibility of imagining new design systems and to quantify and observe complex phenomena behaviour. Through simulation, the study of alternative designs or to diagnose problems in existing systems is an increasingly frequent reality. With these techniques, it is easy and less expensive to predict how existing systems might perform if modified, or how a new system is likely to function prior to the prototyping being finished, cutting time and lead times.^[2]

In order to experience and try to take advantage of these benefits, it was planned to create a small customized reactor with an illustrative design to study numerically with Computation Fluid Dynamic (CFD) tools. The commercial CFD package Ansys V24 was chosen to perform this work. This kind of programs represent a powerful technique to model various processes involving heat and mass transfer and chemical reactions and analyse the flow behaviour by a clear and detailed visualisation of results. The development of CFD technologies as Ansys, permits the modification of geometric parameters without the need to materialise them by modifying the equipment used. In sum, the application of CFD means time and resources savings, while performing deeper and more detailed studies on the behaviour of systems involving fluid flow.^[1, 3]

Another relevant technology experienced during this thesis was 3D printing. This additive manufacturing technology had a crucial role on the validation step of the numerical results. Relatively to additive manufacturing, it enables the possibility to design complex structures that are difficult to create by other manufacturing techniques and the capacity to do it in small scale. However, there are still some limitations for the common user, such as the reduced range of printable materials, the fact that is not possible to produce structures with high volumes and the low mechanical properties of the printed structures.^[4, 5] In this work, it was used the reverse stereolithography technique, where the piece is printed in invert position and solidifies with the help of a laser, making it ecologically friendly cause there is no material wasted.^[6, 7]

Concluding, modelling and simulation are emerging as key technologies to support manufacturing in the 21st century. However, one of the main questions relies on how to validate these methods. In the case of this thesis, the validation method was tracer experiments.

The present work had three main goals: 1) in terms of personal training, to experience and gain skills in highly relevant technologies like CFD and 3D printing; 2) explore the benefits of combining the synergies between these two technologies; 3) illustrate the role of CFD modelling in the study of non-isothermal systems. Regarding the latter point, it is important to highlight that a highly exothermic system with reaction at surface walls (to mimic the presence of a catalyst) was addressed with CFD tools for the first time in the host research groups.

1.2. Presentation of the laboratory

The presented thesis represents the end of a cycle called Master's Degree in Chemical Engineering at Faculty of Engineering of University of Porto (FEUP), and was developed in the ambit of the dissertation course. The research was conducted within an academic setting and jointly supervised by members of two research units: CEFT and LEPABE, both affiliated with the Associate Laboratory for Innovation in Chemical Engineering (ALICE).^[8, 9]

CEFT, the “Centro de Estudos de Fenómenos de Transporte”, is an integral research unit within the Chemical and Mechanical Engineering Departments based at FEUP and at Polytechnic Institutes of Coimbra, Viseu and Bragança. Established in 1996 by four faculty members, CEFT specializes in transport phenomena, bridging key areas of Chemical and Mechanical Engineering. CEFT's research is structured into two main areas: Energy and Fluids.^[9]

The Energy team's focus is on cleaner fuels, such as natural gas and biomass, as well as issues related to carbon emissions and hydrogen economy. Efforts in this area include the optimization and development of fuel cell technologies and systems for hydrogen production and storage.^[9]

The Fluids team's focus is on encompassing several interconnected sub-topics such as complex fluids, multiphase flows, intelligent fluids and biofluids. This research leverages the extensive expertise of the group's researchers in both experimental techniques and advanced computational methods.^[9]

LEPABE, founded in 1998, functions primarily within the Chemical Engineering Department FEUP. It operates as an interdisciplinary group with research centred on three pillars: Sustainability and Energy, Processes and Products, and Environment and Health. LEPABE's mission is to develop innovative processes and products that address societal challenges effectively, utilizing chemical and biological engineering principles to enhance the quality of life in a sustainable and safe way.^[8]

1.3. Contribution of the author to the work

All the results presented in this thesis were obtained by simulations made exclusively by the author, as well as the tracer experiments made in the laboratory. The author was also responsible for the calculation of all the velocities and simulation times, for creating the sketches used in Fluent and the 2D version of the imprinted design, for refining all the meshes needed and for finding the convergence parameters necessary for each simulation. The implementation of a surface reaction also resulted from the author, with some help of the supervisor in finding some of the reaction parameters. The post-processing of the data resulting from Fluent and from the lab work, was carried out by the author. Finally, the interpretation of the experimental data was made by the author and the main conclusions were discussed with the supervisors.

1.4. Organization of the dissertation

In context and state of the art, first there is an introduction to the concepts involved in CFD as well as demonstrations of the increase of its application in solving world problems and specifically in Chemical Engineering. Then, it is explained the connection between CFD and tracer experiments and are presented the main equations applied in the calculations carried out in the course of this thesis. The second part of this chapter, initiates with the definition of the key terms of 3D printing, plus the mentioning of the areas of application and some of the 3DP techniques. After that, is featured the advantages of the combination of 3D printing with Chemical Engineering. Finally, in a way to combine all the aforementioned information, the benefits associated with the symbiose of CFD and 3D printing were addressed, with the presentation of specific examples that predict a little what is pretended to achieve with the development of this theme.

In Materials and Methods, the designed sketches and the respective dimensions are shown, and the detail of all the selections needed to replicate the Fluent cases are introduced. The procedures endured during the 3D printing process, post-processing treatment and the methodologies used to perform the tracer experiment in the laboratory were also described.

In Results and Discussion, the first results presented are related to the preliminary study of the effect of heat production inside the vessel, and the presence of external convection. The behaviour of the flow inside the vessel, including a mesh independence test, and the distribution of reagents mass fraction, velocity and temperature in the domain were analysed and discussed. Then, it was presented the comparison between the experimental results and the simulation data resulting from step input tracer tests. At last, is made an extensive study on the effect of variation of inlet conditions and the presence or absence of convection in the

exterior walls, with focus on the average $Y_{C/out}$, on the average T_{out} and on T_{max} , of two non-isothermal systems with different levels of ΔH .

In Conclusions, are presented the major conclusions of this work, including suggestions for future work.

In Assessment of the work done, it was made an evaluation between the defined goals and what was possible to achieve. The SDGs with potential to be impacted by this project were also presented. In the end, is described the individual experience of this thesis.

In Annex, is presented the symbols of the SDGs applied to this thesis.

In Appendixes, firstly are introduced the tables with the dimensions of the three sketches designed, then are presented photos of the experimental setup of the 3D printing including a photo of the resulted printed structure. The next appendixes feature visual explanations on how to define certain settings in Fluent. Then, there is an appendix which includes the explanation of the calculations of velocity and simulation time. At last, exists a few appendixes that feature complementary results to the main ones shown in Results and Discussion.

2. Context and State of the art

2.1. Computational Fluid Dynamics

Computational Fluid Dynamics (CFD) is the field of fluid mechanics that explores computer science and mathematics to numerically predict the behaviour of systems involving fluid flow. The fundamental equations of fluid flow (Navier-Stokes) can be solved together with conservation equations for energy, species, multiple phases, radiation flux, electric and magnetic potential to simulate a multitude of real-world problems. Depending on the field of application, the complexity of the required models is highly variable and may determine the input of many sub-models to solve the equations.^[1, 3]

2.1.1. Governing equations in CFD

As aforementioned, a CFD simulation involves the numerical resolution of models that may include several equations and features. The main ones that can be highlighted are: continuity, momentum, energy and species transport.

The conservation equations presented below are defined for laminar flow in an inertial reference frame.^[10]

The **Mass Conservation Law (or Continuity Equation)** is based on the principle that the mass of the fluid flow is constant, which means it can't be generated or consumed. In Eq. (2.1), the time rate of change at a fixed point is represented by $\partial \rho / \partial t$, $\nabla (\rho \cdot \vec{v})$ symbolises the time rate of change due to the motion of the fluid element from one place to another in the flow field and $S(C)$ stands for the source term that represents the mass added to the continuous phase from the dispersed second phase and any user-defined sources:^[10, 11]

$$\frac{\partial \rho}{\partial t} + \nabla (\rho \cdot \vec{v}) = S(C) \quad (2.1)^{[10]}$$

where ρ represent the mass per unit of volume of the fluid, t symbolises time and $\vec{v}$ stands for velocity.

The **Momentum Conservation Equation** is the law of conservation of momentum for a moving fluid, which means that the total momentum rate of any unit in the flow field is equal to the resultant force of all external forces applied to the same unit. Eq. (2.2) is composed by six parts: the first one is related to the local variation with time, the second one is associated with the momentum convection, the third one is referent to the surface forces, the next one represents the diffusion term, the following one symbolises the gravitational body force and $S(C)$ stands for the source term of external body forces and other model-dependent source terms such as porous-media and user-defined sources:^[10, 11]

$$\frac{\partial(\rho \cdot \vec{v})}{\partial t} + \nabla \cdot (\rho \cdot \vec{v} \cdot \vec{v}) = -\nabla p + \nabla(\bar{\tau}) + \rho \cdot \vec{g} + S(C) \quad (2.2)^{[10]}$$

where p represents the static pressure, $\bar{\tau}$ symbolizes the stress tensor and $\vec{g}$ stands for the gravitational acceleration.

The **Energy Conservation Equation** results from the first law of thermodynamics applied to an infinitesimal volume of fluid, E is equivalent to $h_e + \frac{p}{\rho} + \frac{v^2}{2}$, λ_{eff} is equal to $\lambda + \lambda_t$ (where λ_t is the turbulent thermal conductivity) and where $S(C)$ is a source term that includes the heat of chemical reaction, and any other volumetric heat sources:^[10, 11]

$$\frac{\partial(\rho \cdot E)}{\partial t} + \nabla \cdot (\vec{v} \cdot (\rho \cdot E + p)) = \nabla \cdot \left(\lambda_{eff} \cdot \nabla T - \sum_j h_{e_j} \cdot \vec{J}_j + (\bar{\tau}_{eff} \cdot \vec{v}) \right) + S(C) \quad (2.3)^{[10]}$$

where λ_{eff} represents the effective conductivity, T symbolizes the temperature, h_{e_j} stands for sensible enthalpy of species j , $\vec{J}_j$ represents the diffusion flux of species j and $\bar{\tau}_{eff}$ symbolizes the effective stress tensor.

The **Species Transport** predicts the local mass fraction of each species j , Y_j , and is described by Eq. (2.4), where R_j represents the net rate of production of species j and $S(C)$ is the rate of creation by addition from the dispersed phase plus any user-defined sources:^[10, 12]

$$\frac{\partial(\rho \cdot Y_j)}{\partial t} + \nabla \cdot (\rho \cdot \vec{v} \cdot Y_j) = -\nabla \cdot \vec{J}_j + R_j + S(C) \quad (2.4)^{[10]}$$

Another equation that is very important for the work of this thesis is the reaction velocity (k) equation for a second order reaction involving two reagents, A and B, that is described by Eq.(2.5)^[10]:

$$k = k_0 \cdot [A] \cdot [B] \cdot T^\alpha \cdot \exp^{-\frac{E_a}{R_g \cdot T}} \quad (2.5)^{[10]}$$

where k_0 symbolises the pre-exponential factor, $[A]$ and $[B]$ represent the concentration of reagents A and B, α is the temperature exponent, E_a stands for activation energy and R_g symbolises the ideal gas constant.

2.1.2. Tools within the Ansys tools

To perform a simulation, there are several steps before obtaining a result or a post-processed graph, and those stages will be addressed in this section. The first stage is to create a Workbench which is project management tool where all the programs involved in the simulation will be linked to each other. Workbench also makes it easy to perform parametric analysis (without the user having to manually launch each application in turn).^[10, 13]

The next step is to create the necessary geometry that represents the systems, and for that there are three programs available Discovery, SpaceClaim and Design Modeler, and all these softwares enable the possibility of creating 2D and 3D domains.^[10, 13]

Having the domain defined, the next phase is to generate the mesh. The purpose of meshing is to allow the solving of the equations involved in the simulations because it is required to discretize them in space and time. The better the quality of the mesh, the better the accuracy of the solution. Ways to increase the quality of the mesh are associated with the refinement (define smaller cells) in certain zones that are more complex and need more detail and define a less dense mesh in regions where the fluid is more stabilized. Some methods and parameters that help defining the quality of the mesh are: Inflation (a refinement tool) in specific zones or Edge Sizing that sets a reference size for the cells in the domain. These are just some options that were used in the course of this thesis.^[10, 13]

Finally in FLUENT®: in this tool, the major simulation definitions are set and there are a lot of decisions to make. The overall model can be taken as for steady state or transient state. Relatively to the remaining CFD model features, it is possible to include several simultaneous features and some of the options are: Energy, Radiation, Heat Exchanger, Viscous, Multiphase, Species and Discrete Phase. Focusing on the Materials involved in the system, there is a database included in FLUENT® with numerous substances, with properties defined, where is possible to choose the fluids, solids and mixtures to use in the simulation. The next step in a CFD simulation is to define the Boundary Conditions such as, for example, the velocity and the temperature of the inlets or the heat flux produced on walls, or the convection between the walls and the exterior. After all the physics features are defined, it is important to go to the mathematical options and choose the Solution Methods, where we can define the adequate discretization methodologies to apply in the model resolution. Finally, in Solution Controls, the Under-Relaxation Factors can be defined for each equation, and they may help stabilize the iterative process.^[10, 13]

2.1.3. Importance CFD in Chemical Engineering

Computer-based simulation has made a major contribution to process understanding by enabling the simulation of complex physics and chemistry and by developing validated models to be used in the scale-up and scale-down, in the optimisation and in the control of processes. CFD is a powerful technique for modelling a variety of processes involving heat and mass transfer and chemical reactions. The development of CFD technology allowed to significantly reduce the time and cost for designing efficient chemical engineering equipment with its versatility to modify design geometric parameters without the necessity of materializing them in research equipment changes. It is also important to emphasize the relevancy of simulation in ensuring process safety, as the consequences of unplanned operating conditions can be

studied and mitigation strategies developed, which is not always possible by experimental means. Besides the economy of resources and time and the endurance of safety, another advantage of numerical investigation compared to experimental is that CFD can provide a clear and detailed visualisation of results. More specifically, and as a highly relevant example in chemical engineering, the application of CFD allows us to predict, visualize and optimise the entire velocity, concentration and temperature distribution in catalytic fixed beds, fluidized or moving bed reactors (particularly multiphase stirred (slurry) reactors), as well as mixers, adsorbers, and bubble columns with moving media.^[1, 3]

The importance of this thematic in Chemical Engineering will continue to grow due to the fact that decarbonisation, the development of green processes, hydrogen production, storage and consumption are all subjects that require high quality simulation to support process design. However, in an era of such fast technological change, it's difficult to predict how a field of research will develop, although according to a NASA report, about 85 % of the total computing power of the world's supercomputers is already used to solve CFD problems. Furthermore, the same organisation presented the report "CFD Vision 2030: A Path to Revolutionary Computational Aerosciences"^[3, 14], which outlined the perspectives for the implementation of numerical modelling of several physical and chemical phenomena. For example, this previously referred report estimates that the computing capacity for solving CFD problems will increase in about 10-12 % per year over the next two decades. Additionally, the growing computing capacity will further leverage the continuous increase on the number of CFD publications observed in the last decades. More specifically, and for the last 30 years, Figure 2-1 clearly depicts this continuous increase in all Chemical Engineering journals (left graph) and in one particular journal (right graph).^[1]

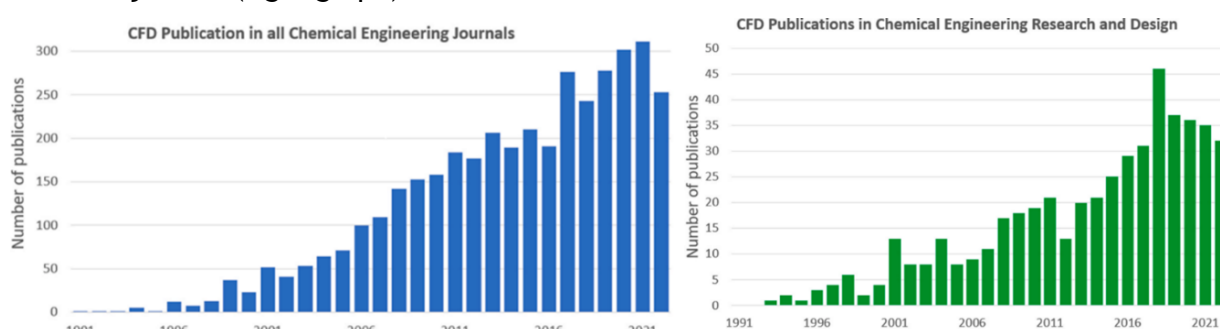


Figure 2-1: Number of CFD publications made in all Chemical Engineering Journals (on the left) and made on Chemical Engineering Research and Design (on the right).^[1]

To provide a more detailed picture, the CFD publications linked to Chemical Engineering can be subdivided by subjects of study (Figure 2-2).

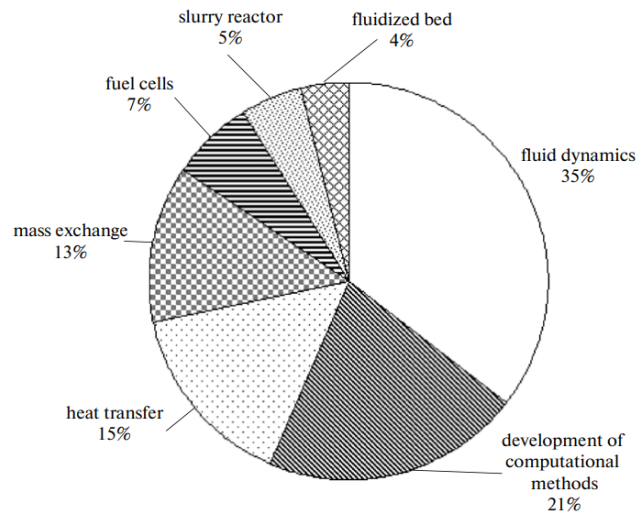


Figure 2-2: Distribution of the publications on computational fluid dynamics between the subjects and objects of study.^[15]

Figure 2-2 simply shows how the deployment of CFD into solving real engineering problems will increase overall and specifically in Chemical Engineering considering all the advantages enclosed on this technology. It is also worth highlighting that during COVID-19 pandemic period, with employees being forced to work from home, simulation gained even more importance for companies as experimental testing had been drastically restricted. Companies with well-established simulation teams have reaped the benefits, while those without have suffered delays and are currently scrambling to catch up.^[1]

2.2. 3D-printing

Additive manufacturing, commonly referred as 3D printing (3DP), has emerged as one of the most innovative and capable tools available as a technology for precision manufacturing from lab scale to mass production.^[4, 5]

There are several 3D printing techniques some of those are presented in Figure 2-3:

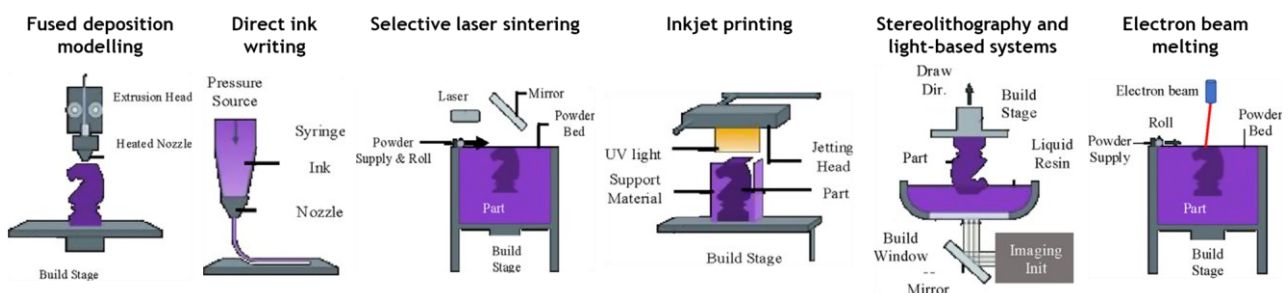


Figure 2-3: Demonstrations of some of the 3D printing techniques.^[16]

The technique used in the work developed in this thesis, is reverse stereolithography and by looking at Figure 2-3 it is easy to understand the reverse part because we can see that the object is printed in an opposite direction compared to the other techniques. Relatively to stereolithography, the process starts with the mechanical arm slightly immersed in liquid resin and as the arm rises, the light irradiation that the resin suffers, allows the solidification of

layers in the platform of the mechanical arm. The resin is a photosensitive material that suffers fast photopolymerization under light irradiation, otherwise the resin is liquid which makes it easier to remove when some fluid is stuck inside the printed structure. The mechanical and physical properties of the printed objects are dependent on factors such as the thickness defined for each layer, the degree of polymerization and the cure process. This technique integrates the group of photocuring 3D printing, that allows high printing speed, high precision and the objects produced have polished surface. However, there are some disadvantages associated with photocuring because the object printed commonly is brittle, easy to deform and has low resistance. Stereolithography is known to be ecological and economically positive/viable because it is an additive printing which means there is much less material waste.^[6, 7]

In many aspects, 3DP provides a wide range of fascinating possibilities, however there are two fundamental characteristics that stand out: the ability to create complex structures that are difficult (or unaffordable) to obtain by other manufacturing techniques, and the capacity to do so on a small scale, unlike other manufacturing methods that demand the production of high volumes of the same products to be economically viable. In addition, 3DP manufacturing usually doesn't involve over-expensive equipment or advanced user training to achieve reasonable results, which makes it an accessible technology that can be implemented in an industry or laboratory. A further major benefit is the ability to create prototypes or end products, as well as the equipment itself, which can mean an enormous interest for process optimisation and even process scaling. All these aforementioned characteristics result in advantages such as weight savings, waste minimisation and energy economy. Nevertheless, there are also some challenges associated, such as widening the range of printable materials, optimising the process to attain higher volumes of production and upgrading the performance of the printed parts (accuracy, mechanical properties) so that they can be used as final product.^[4, 5]

Some of the fields implementing 3D printing are prototyping, instrumentation, dentistry, microfluidics, production of biomedical devices, tissue engineering, drug delivery, construction of houses and buildings and Chemical Engineering.^[4, 5]

Simply defined, Chemical Engineering is the science of turning one thing into another, if 'one thing' is a digital design and 'another' is a tangible object, we have the basic principle of 3DP. This is why it is so important to discuss the symbiotic relationship between Chemical Engineering and additive manufacturing. Chemical Engineering knowledge will continue to develop better materials and devices for 3DP, while additive manufacturing can help in the training of chemical engineers to design and develop more tailored solutions.^[4, 5]

2.2.1. Symbiosis between additive manufacturing and Chemical Engineering

To 3DP, Chemical Engineering contributes by formulating printable polymers with the using of different additives to control the polymerisation and the flow behaviour and enhance the properties of 3D printed parts. With the application of this engineering, it is now possible to print using a wide variety of polymers, resins and plasticizers. Other material that benefits from Chemical Engineering to achieve high quality when printed is metal, because it is necessary to control the flow properties of powders or molten metals, as also the heat transfer features involved.^[4, 5]

The potential of additive manufacturing (AM) in Chemical Engineering is vast: AM is predicted to revolutionise reaction and separation technology and could have a dramatic impact on the chemical industry. On one hand, the focus is on heat exchangers as they contain the promise of saving energy. Fluidic devices are also currently attracting attention, and chemical reactors in particular are being looked at as their geometries, and therefore their efficiencies, could benefit greatly from the possibility of 3D printing. In particular, the impact of bespoke designs and manufacturing techniques will change the way reactors and separation units are built.^[4, 5]

Still, additive manufacturing combined with CFD makes it possible to print customised reactors, which expands the possibilities for reaction protocols and reactor optimisation. In addition, because catalyst can be immobilised in the reactor by direct printing, 3DP can help simplifying chemical reactions such as those involved in heterogeneous catalysis. Beyond that, 3D printing can be used to manufacture catalysts with optimised geometries to maximise efficiency while minimising pressure drop, which affects positively the mass transfer and the heat transfer. It is important to highlight that, besides the educational relevance of contacting with both CFD and 3DP, illustrating these features is also one the main focus of this thesis.^[4, 5]

The purpose of the creation of complex or intricate shapes is to increase surface area, so additive manufacturing enables the creation of reactors, mixers and packed columns with geometries that boost the performance in continuous flow and batch processes. Filters, adsorbent structures and membranes can also be 3D printed, which can be extremely beneficial in environmental applications.^[4, 5]

Another example of the utility of 3D printing in Chemical Engineering, some companies use it to print lab equipment and to maintain process equipment. For instance, if an asset fails due to some breakage, it is possible to replace it immediately by printing a part on site. Producing replacement parts in situ can reduce significantly inventory costs and increase overall asset uptime. On-site printing has other advantages related to the lack of need for transportation, which helps reduce waste and carbon impact.^[4, 5]

2.3. Combination of CFD with 3D printing to design reactors

As seen before, the combination of a modelling program (CAD or Design Modeler, for example) with CFD bears the potential to simplify reactor design optimization because it can bypass the manufacturing cost and it allows the customisation of reactors to specific needs which leads to complete freedom over the reactor design. To increase even more the time and cost-effectiveness of the process of designing a customised reactor, we can add 3D-printing to the equation making the project feasible and improvable as demonstrated in the graph of Figure 2-4^[17]:

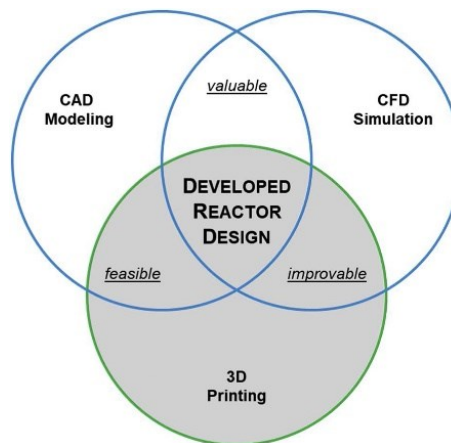


Figure 2-4: Advantages resulting from the symbioses of CFD, Modelling and 3D printing.^[17]

There are already several examples of the symbiose 3D-printing with CFD simulation and below will be shown some experiments made by University of Hamburg (Germany), by Chalmers University of Technology (Sweden) and by Graz University (Austria).

2.3.1. Printing of reactor with static mixing elements

The Institute for Technical and Macromolecular Chemistry of the University of Hamburg studied options on how to maximize the mixing in a tubular reactor by implementing static mixing elements (SMEs) in various positions. However, the SMEs caused a slight pressure drop that was examined via experimental tests on the 3D-printed reactor and compared with the simulated data of the pressure drop. It was concluded that there was a good agreement between the two values and therefore demonstrated that the CFD simulation produces data that represents the reality with high accuracy. The result of the reactor they produced is presented in Figure 2-5^[17]:



Figure 2-5: 3D sketch of the design incorporating SMEs.^[17]

With the implementation of the SMEs, the Institute wanted to study the effect of this barriers on the velocity of the flow, for that they obtained the velocity contours of the geometry without the SMEs, Figure 2-6 on left, and the with the SMEs, Figure 2-6 on right. With these images they were able to conclude that the implementation of obstacles in the geometry (SMEs), promoted an increase of the velocity in all most all zones.^[17]

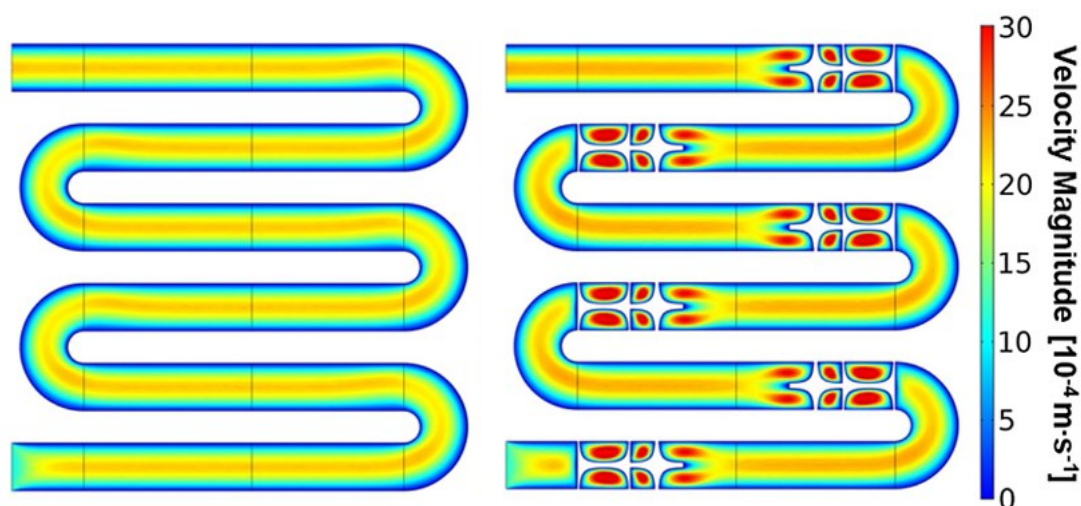


Figure 2-6: Contour of velocity of the design: without SMEs (on the left) and with SMEs (on the right).^[17]

This example shows some of the advantages of coupling 3D-printing with CFD and also proves the concordance between the data produced by each method. It also demonstrates some impacts of the inclusion of static mixing elements, which is a subject related to this thesis since it is addressed the effect of obstacles to the flow.

2.3.2. Printing of reactor to be used in absorption of CO₂

Another example of the successful combination of CFD and 3D-printing was demonstrated by the Chalmers University of Technology, where a geometry was designed to avoid forced-mixing while maximizing the CO₂ absorption in a NaOH solution. The results obtained through the CFD simulations confirmed that the design used promoted better mixing and the analysis made in relation to the absorption of CO₂ in the NaOH solution inside the printed reactor, allowed the conclusion that this method was efficient while reducing the electrical energy consumed by the process and avoiding the use of extra equipment (mixer). In Figure 2-7, a sketch of the printed reactor is presented on the left and, on the right, is shown a contour of the gas volume fraction in the NaOH solution^[18]:

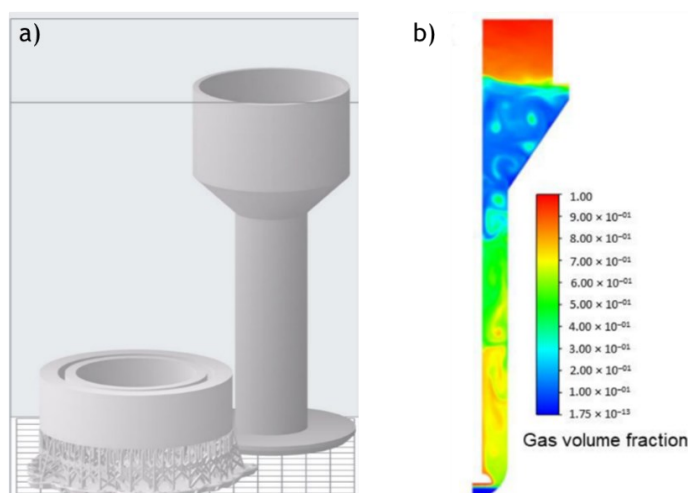


Figure 2-7: a) 3D sketch of the printed reactor including the supports. b) Gas volume fraction contour.^[18]

The authors used CFD to design a multiphasic system which is not under the scope of this thesis, but definitely represents a subject that will be interesting to look into in the future.

2.3.3. Printing of a stainless-steel reactor for an exothermic reaction at cryogenic temperature and high-pressure

3D printing normally uses a material called PDMS, characterized by low stability towards a variety of reagents and common organic solvents and by having low thermal conductivity. A study conducted at Graz University, intended to design a customised reactor to produce difluoromethylation, that involves organic solvents and is very exothermic. To overcome the issues associated with printing using PDMS, they printed a stainless-steel reactor by selective laser melting (SLM). The publication goes even further to explain that with the development of high-powered lasers for additive manufacturing, it is now possible to print using a wide range of metals with SLM. In this case, the application of stainless steel promoted faster heat transfer and elevated pressure resistance, allowing difluoromethylation reaction (an exothermic reaction) to be carried out at cryogenic temperatures and high-pressures. In Figure 2-8 is demonstrated the sketch of the reactor (on the left), and on the right are presented some images of the printed reactor^[19].

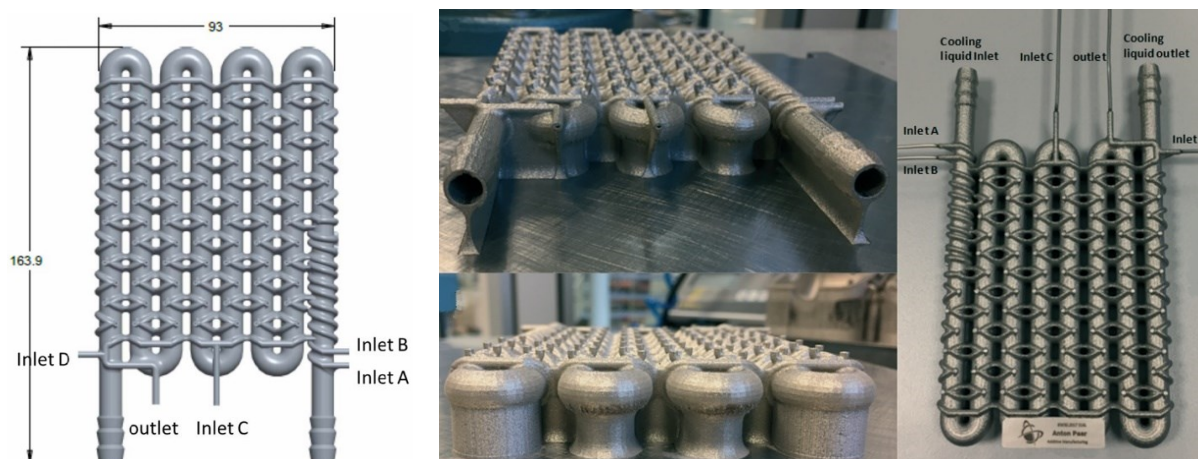


Figure 2-8: 3D sketch (left) and printed reactor(right).^[19]

As previously mentioned, PDMS is a common material used in 3D-printing. However, it has low thermal conductivity, which limits the range of applications to reactions at room temperature and that do not generate large amounts of heat. An alternative to this issue is selective laser melting to print with metals that will provide thermal conductivity as well as chemical, mechanical and thermal stability.^[19] In the present work, a preliminary CFD study was performed in a simple geometry to illustrate exothermic reaction effects. The information provided from Graz University let us to conclude that printing with metals will be a strong possibility to consider in future work.

2.4. Tracer experiments

A procedure that can be used to prove that simulation provides accurate results when compared to experimental testing is to 3D print a structure and run tracer experiments to compare.

Tracer experiments can be resume to the making of a perturbation in a vessel, impulse or step, by injecting tracer in the inlet and register the concentration of tracer in the outlet. A tracer should be an inert substance and, for example, can be a mixture of water with a die. Tracer experiments are indispensable for the determination of theoretical functions such as residence time distribution, which are vital for hydrodynamics characterization, reactor modelling, prediction of conversion and for diagnosis of equipment operation. Experimental RTD tracking is relatively simple and reliable, and it is capable of providing a number of important hydrodynamic parameters but can't provide detailed visualisation of the flow pattern inside the vessel/equipment. Experimental tracer RTD results are, a good source of experimental data for verification and validation of CFD models. This complementarity is very important because the experimental RTD detects and characterises key flow features (mixing and recirculation) whereas CFD enables them to be located and detailed. Having that in mind, in the study developed in this thesis, tracer experiments will be used to validate a method: will be made simulations of tracer experiments and compared with the same tests developed in the laboratory.^[12, 20, 21]

RTD analysis provides important information about process units, such as preferential flow paths, stagnant regions, back mixing and bypassing. The response curve from the outlet detector is known as the RTD function when a pulse or a step (inputs) of tracer is injected into the inlet of a process unit or vessel. This function provides a vast amount of information about the dynamics of the process stream.^[20, 21]

Using a non-reactive tracer and the stimulus-response technique, is the simplest and most direct way to determine the RTD, and also the approach that will be made in this thesis. However, through the raw data obtained from CFD, it is not possible to define the RTD directly. First, it is necessary to obtain the Dankwerts' F curve ($F(t)$), which is a normalized response to

a step input, calculated by Eq. (2.6). Then with that curve it is possible to calculate the RTD curve ($E(t)$) using Eq. (2.7), both presented below:^[22]

$$F(t) = \frac{C_{out}(t)}{C_{in}} \quad (2.6)$$

where C_{out} represents the concentration of tracer in the outlet, t stands for time and C_{in} corresponds to the concentration in the inlet:

$$E(t) = \frac{dF(t)}{dt} \quad (2.7)$$

Knowing the RTD curve, it is feasible to calculate the mean residence time ($\bar{t}_r$) with Eq. (2.8), described below:^[12]

$$\bar{t}_r = \int_0^{\infty} t \cdot E(t) \quad (2.8)$$

Another parameter that is important to characterize a device and particularly a chemical reactor is the space time, which can be calculated by the division of the volume of the vessel (V) and the flow rate (Q), presented in Eq. (2.9):

$$\tau = \frac{V}{Q} \quad (2.9)$$

Another crucial factor to characterize the hydrodynamic of the flow is the dimensionless Reynolds number: it helps assessing if the flow is in laminar, transient or turbulent regime and can be defined by Eq. (2.10):

$$Re = \frac{\rho \cdot v \cdot e}{\mu} \quad (2.10)$$

where ρ represents the mass density of the fluid, v symbolises the velocity of the fluid, e stands for the size of the inlet and μ represents the viscosity of the fluid.

3. Materials and Methods

The study developed is divided into 4 parts: Learning phase, Tracer Experiments, 3D Printing and Laboratory work and Reaction.

3.1. Learning phase

The purpose of the first phase was to get familiar with the programs within the Ansys 2024 R1 package: Workbench, Design Modeler, Meshing and Fluent. The first step was to create the Workbench which is project management tool where all the programs involved in the simulation will be linked to each other (see Figure Appendix B. 1). Then, using Design Modeler, a first scratch of a vessel with obstacles inside was drawn, Design A featured in Figure 3-1 and its dimensions are presented in Table Appendix A. 1. Then, the Meshing program was used to generate the mesh and the evaluation was based on orthogonal quality (minimum value between 0.2 and 0.69 is considered a good mesh and between 0.7 and 0.95 is considered a very good one). The last step of this part was developed in FLUENT®, where was created a case with the choices presented in Table 3-1:

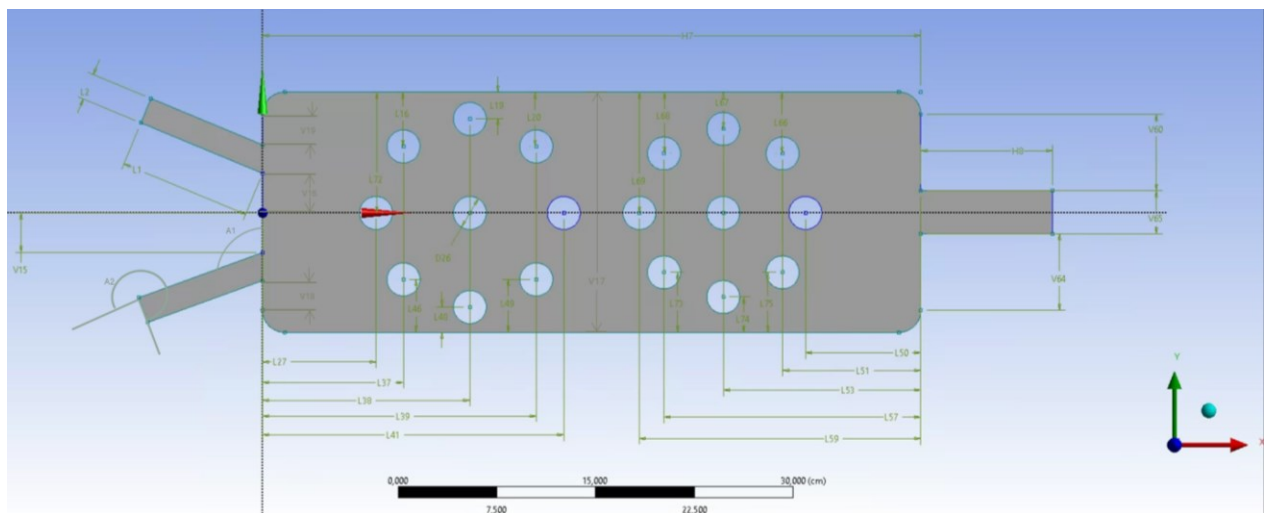


Figure 3-1: Sketch of Design A.

Table 3-1: Definitions of the Fluent case for the learning phase.

Setup	General	Type Velocity formula Time	Pressure-Based Absolute Steady		
		Energy Viscous Species Transport	On Laminar On Mixture Properties	Density Cp (Specific Heat) Thermal Conductivity Viscosity Mass Diffusivity / $\text{m}^2\cdot\text{s}^{-1}$	volume-weighted-mixing-law mixing-law mass-weighted-mixing-law mass-weighted-mixing-law 2.88×10^{-5}
	Materials	Fluid	N ₂ CH ₄ O ₂		
	Boundary Conditions	Inlet 1	Velocity magnitude / m s^{-1} Temperature / °C Species Mass Fractions / -	dependent from Reynolds number * 50 N ₂ CH ₄ O ₂	
				0 1 0	
		Inlet 2	Velocity magnitude Temperature / °C Species Mass Fractions	dependent from Reynolds number * 50 N ₂ CH ₄ O ₂	
				0 0 1	
		Reaction Walls	Thermal	Heat Flux / $\text{W}\cdot\text{m}^{-2}$	dependent from the essay**
		Exterior Walls	Thermal	Heat Transfer Coefficient / $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ Free Stream Temperature / °C	dependent from the essay** 20
Solution	Methods	Pressure - Velocity Coupling	Scheme	Coupled	
	Controls	PTERF	Momentum	0.05	
	Monitors	Residuals	Equations	continuity x-velocity y-velocity energy N ₂ CH ₄ O ₂	1×10^{-6} 1×10^{-6} 1×10^{-6} 1×10^{-6} 1×10^{-6} 1×10^{-6} 1×10^{-6}
	Initialization	Methods	Standard Initialization		
		Initial Values	Gauge Pressure / Pa X velocity / $\text{m}\cdot\text{s}^{-1}$ Y velocity / $\text{m}\cdot\text{s}^{-1}$ N ₂ CH ₄ O ₂ Temperature / °C	0 0 0 1 0 0 20	
	Run Calculation	Fluid Time Scale	Time Step Method	Automatic	
		Parameters	Number of Iterations	5500	

These gases were chosen as initially was supposed to perform the simulation of the combustion of methane. Relatively to the physical properties of the gases chosen, were used the pre-defined values present in the Fluent Database, more information about the creation of materials is presented in Figure Appendix D. 1. In Appendix D is shown in more detail how to define all the Boundary Conditions presented in Table 3-1. At the Solution Controls level, the values of the others Pseudo Time Explicit relaxation factors (PTERF) weren't changed as well.

In Run Calculation tab, the rest of the parameters were also maintained as default by the program.

The inlet velocities addressed in this preliminary state are presented in Table 3-2 together with the corresponding Reynolds number:

Table 3-2: Values of velocity in the inlets according to Design A.

Re	100	400	700	900
$v_{in1} / \text{m} \cdot \text{s}^{-1}$	8.14×10^{-2}	3.25×10^{-1}	5.70×10^{-1}	7.32×10^{-1}
$v_{in2} / \text{m} \cdot \text{s}^{-1}$	7.38×10^{-2}	2.95×10^{-1}	5.17×10^{-1}	6.64×10^{-1}

The demonstration of the calculation of these velocities is featured in Appendix I. For each Reynolds number were made 9 assays, where the value of the heat flux produced in the obstacles and the value of the external convection coefficient were varied. The data used is featured in Table 3-3:

Table 3-3: Values of coefficient of convection and heat flux used in the simulations.

Assay	1	2	3	4	5	6	7	8	9
$H_F / \text{W m}^{-2}$	50	200	400	50	200	400	50	200	400
$h / \text{W m}^{-2} \text{C}^{-1}$	7			200			1500		

3.2. 3D printing and laboratory experiments (validation of the method)

In order to verify if the CFD simulations represent accurately the flow in real life, Design B (Figure 3-5) was prepared for printing using PreForm software from Formlabs (Somerville, USA), where the configuration of the supports and the chosen places to insert them were based to avoid the risk of collapse of some of the zones of the structure (Figure 3-2). In this software, was also defined Adaptative Printing so that the program would choose what would be the best thickness (0.025 mm or 0.1 mm) for each layer depending on the resolution needed. More images of the program are presented in Appendix H.

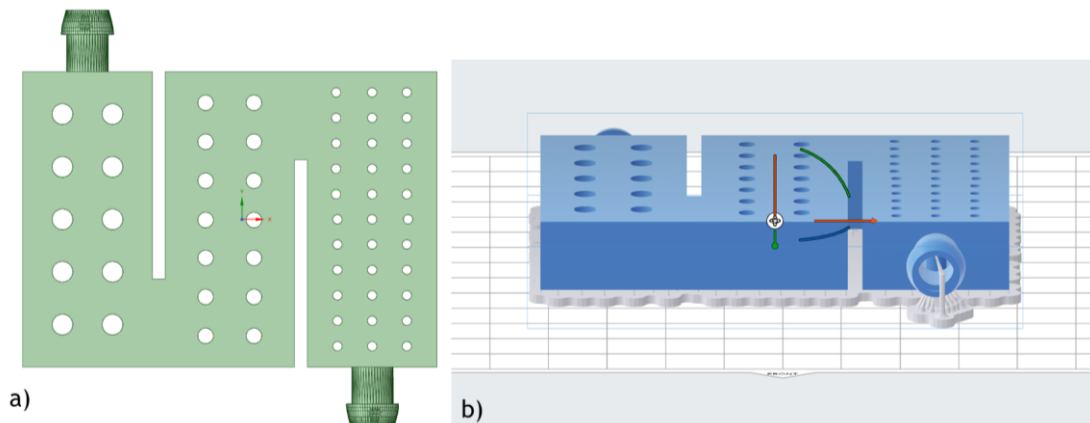


Figure 3-2: 3D image of the printed design: a) in Space Claim and b) in PreForm with the supports added.

Afterwards the model was 3D printed using Formlabs Form 3+^[23] (Figure 3-3 b)) printer during 2 hours and 55 minutes using Clear Resin V4^[24]. When the printing was finished, it was necessary

to forcefully extract it from the removable part of the printer with some of the tools presented in Figure 3-3 a). Then, aqueous Solution 1 (90 % of IPA) was inserted inside the printed piece to remove liquid resin and the piece was also immersed in the same solution. The follow up step was to do the exact procedure with aqueous Solution 2 (70 % of IPA). To endure the mechanical properties of the piece, it went under two processes of cure, using Formlabs Form Cure^[25] (Figure 3-3 b)), the first one lasted 8 minutes at a temperature of 60 °C (in the position shown in Figure 3-3) and the second one lasted 7 minutes at a temperature of 60 °C (in the opposite position to before). Finally, the piece remained at rest for 3 days at ambient conditions.

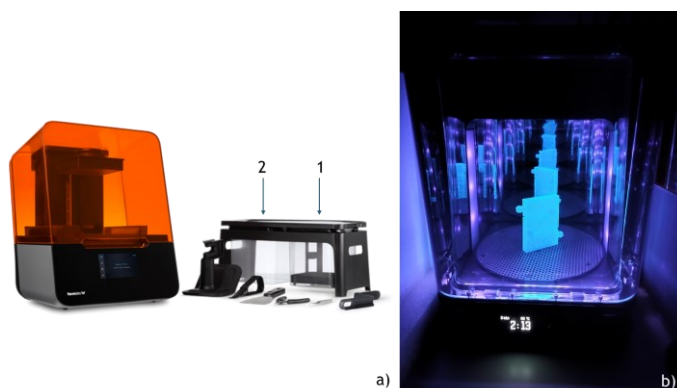


Figure 3-3: Images of the setup used for 3D printing: a) Formlabs Form 3+ and included tools^[23]; b) Formlabs Form Cure with the printed piece inside.

Relatively to the experimental protocol used to perform the tracer experiments, the reactor was first filled with water, and then an aqueous solution of 0.0025 % in Indigo Carmin (tracer) was fed to the reactor with the help of a peristaltic pump (model 323 Watson Marlow). Then, the liquid exiting the reactor entered the spectrophotometer UV/Vis (model Jenway 6305) where it measured the absorbance of the outlet solution and registered the value in the computer through LabView. In Figure 3-4 is represented the setup described above:



Figure 3-4: Image of the setup used to execute the experimental tracer experiments.

There were made 3 assays and the number of rotations per minute of the pump used, and the volumetric flow rate at the outlet are presented in Table 3-4:

Table 3-4: Values of ω and Q for the experimental tracer experiments.

Assay	1	2	3
ω / rpm	12	25	55
Q / $\text{m}^3 \cdot \text{s}^{-1}$	2.07×10^{-7}	4.39×10^{-7}	1.00×10^{-6}

3.3. Simulation of tracer tests

To execute the numerical replication of the tracer experiments, the first steps were the same as the ones made in the 3.1, at the level of the Design Modeler and Meshing. However, for the training stage, Design A was used while for the study of the reproducibility of the simulations at the laboratory level, it was decided to increase a little the design complexity (Design B was used). In Figure 3-5 Design B is presented, and the dimensions of this geometry are featured in Table Appendix A. 2. The major differences from 3.1 were the definitions made in Fluent, which are presented in Table 3-5.

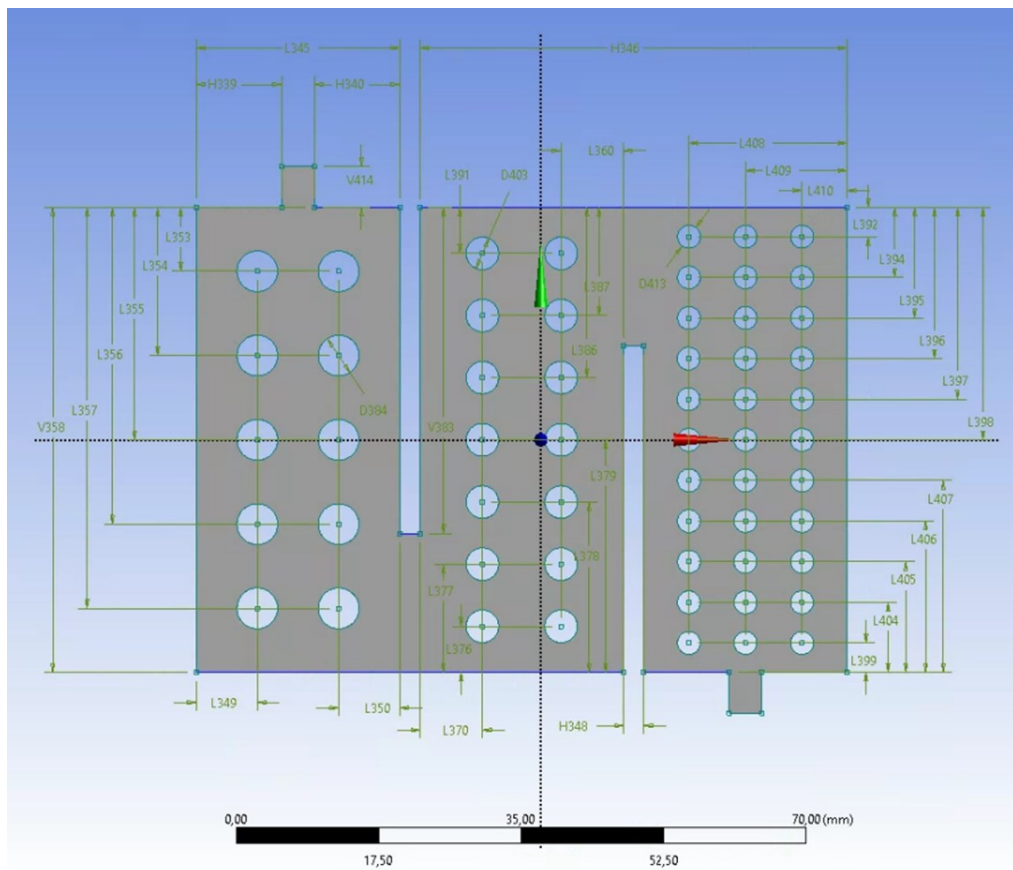


Figure 3-5: Sketch of a) Design B.

Table 3-5: Definitions of the Fluent case for the tracer experiments.

Setup	General	Type	Pressure-Based			
		Time	Transient			
	Model	Viscous	Laminar	Density	volume-weighted-mixing-law	
		Species Transport	On	Cp (Specific Heat)	mixing-law	
			Mixture Properties	Thermal Conductivity	mass-weighted-mixing-law	
				Viscosity	mass-weighted-mixing-law	
	Materials			Mass Diffusivity / m ² ·s ⁻¹	1.00 x 10 ⁻⁹	
		Fluid	liquid H ₂ O			
	Boundary Conditions		Tracer			
		Inlet 1	Velocity magnitude / m·s ⁻¹	dependent from Reynolds number *		
		Temperature / °C	20			
		Species Mass Fractions / -	H ₂ O liquid	0		
			Tracer	1		
Solution		Inlet 2	Same definitions as Inlet 1			
	Methods	Pressure - Velocity Coupling	Scheme	Coupled		
	Monitors	Residuals	Equations	continuity	1 x 10 ⁻⁶	
				x-velocity	1 x 10 ⁻⁶	
				y-velocity	1 x 10 ⁻⁶	
				energy	1 x 10 ⁻⁶	
				H ₂ O liquid	1 x 10 ⁻⁶	
				Tracer	1 x 10 ⁻⁶	
	Iniatialization	Methods	Standard Initialization			
Initial Values		Gauge Pressure / Pa	0			
		X velocity / m·s ⁻¹	0			
		Y velocity / m·s ⁻¹	0			
		H ₂ O liquid	1			
		Tracer	0			
Run Calculation		Temperature / °C	20			
	Time Advancement	Type	Adaptive			
		Duration Specification Method	Total Time			
		Parameters	Total Time	depends on the Reynolds number **		
			Max iteration / Time Step	100		

3.4. Reaction

The final step was to study the effect of some inlet parameters on some output parameters related to two hypothetical exothermic reactions, one with $\Delta H = -30 \text{ kJ}\cdot\text{mol}^{-1}$ and the other with $\Delta H = -300 \text{ kJ}\cdot\text{mol}^{-1}$. The first one is described by $A + B \rightarrow C + D$, and the second one by $2 A + B \rightarrow 2 C$, both second order (first order to each reagent) at the kinetics level. To perform these simulations, was added another inlet to Design B (Figure Appendix A. 3) and Meshing was used to generate the mesh. In Table 3-7 are presented the definitions to build the Fluent file for the more exothermic reaction. To build the case for the first reaction was necessary to consider that it is a liquid phase reaction, so the mass diffusivity value was defined as $1.00 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$, and that it is a volumetric reaction and does not have Wall Surface Reaction on, in Model and in Boundary Conditions.

Table 3-7: Definitions of the Fluent case for the reactions.

Setup	General				
		Type Time	Pressure-Based Steady		
	Model	Energy	On		
		Viscous	Laminar		
		Species Transport	On		
			Mixture Properties *	Reaction Mechanism	finite-rate reaction-mechs
				Density	volume-weighted-mixing-law
	Materials			Cp (Specific Heat)	mixing-law
				Thermal Conductivity	mass-weighted-mixing-law
				Viscosity	mass-weighted-mixing-law
				Mass Diffusivity / m ² ·s ⁻¹	2.88 x 10 ⁻⁵
			Reactions	Volumetric	
	Boundary Conditions		Wall Surface Reaction Options	Wall Surface	
				Heat of Surface Reactions	On
		Fluid	A		
			B		
			C		
Solution	Methods	Inlet 1	Velocity magnitude / m·s ⁻¹	*	
			Temperature / °C	*	
			Species Mass Fractions / -	A	*
				D	*
		Inlet 2	Velocity magnitude / m·s ⁻¹	*	
			Temperature / °C	*	
			Species Mass Fractions / -	B	*
				D	*
		Reactionwalls	Species	Reaction	On
		Exterior Walls	Thermal	Heat Transfer Coefficient / W·m ⁻² ·°C ⁻¹	*
				Free Stream Temperature / °C	20
Solution	Monitors	Pressure - Velocity Coupling	Scheme	Coupled	
		Residuals	Equations	continuity	1 x 10 ⁻⁶
	Initialization	Initial Values		x-velocity	1 x 10 ⁻⁶
				y-velocity	1 x 10 ⁻⁶
				energy	1 x 10 ⁻⁶
				A	1 x 10 ⁻⁶
				B	1 x 10 ⁻⁶
				C	1 x 10 ⁻⁶
				D	1 x 10 ⁻⁶
				Temperature / °C	*
	Run Calculation	Fluid Time Scale	Time Step Method	Automatic	
		Parameters	Number of Iterations	500000	

Relatively to the physical properties of the materials considered for each of the reactions, they were taken from Fluent Database and are presented in Table Appendix H. 1 and Table Appendix

H. 2. More details about the creation of materials are presented in Figure Appendix D. 1. Figure Appendix E. 1 and Figure Appendix E. 2 can be helpful to create the case. At the Solution Controls level, the remaining definitions were sustained as pre-specified by FLUENT®.

The particularity of modelling a reaction lies in the Mixture Properties of the Species Transport Model, therefore more details about those definitions are presented in Table 3-8. Between the two reaction mentioned, the differences for building the case of the first reaction are that exists one more product (D) with a stoichiometric coefficient of 1, a rate exponent of 0, the stoichiometric coefficient of A is 1 and the Reaction Type is Volumetric.

Table 3-8: Specifications of the Mixture Properties of the reaction.

Mixture Properties *	Reaction	finite-rate	Mixture	Mixture-template
			Total Number of Reactions	1
			Reaction Type	Wall Surface
			Number of Reactants	2
			Stoich. Coefficient A	1
			Rate Exponent A	1
			Stoich. Coefficient B	1
			Rate Exponent B	1
			Number of Products	1
			Stoich. Coefficient C	2
			Rate Exponent C	0
			Arrhenius Rate	Pre-Exponential Factor *
				Activation Energy / J·kgmol ⁻¹ *
				Temperature Exponent *
	Mechanism	reaction-mechs	Reaction Type	Wall Surface

As the objective of this section is to study the effect of various properties on the concentration of product in the outlet, the values missing from Table 3-7 and Table 3-8 were varied and are presented in Results and Discussion.

In Appendix F, it is presented how to perform all the steps related to the reaction implementation, complementing the information of Table 3-8. To better understand the reasoning and organisation of Table 3-1, Table 3-5 and Table 3-7 consult the Appendix C. In all the Fluent cases, it is necessary to create a mixture of all the fluids/substances involved in the simulation. For more information on how to generate any mixture consult Figure Appendix F. 1.

4. Results and discussion

One of the main objectives of this work was to predict the behaviour of systems with exothermic reactions in a customized small-sized reactor using CFD tools. This parametric study involved the effect of different conditions in the reagent's conversion and temperature distribution. The validation of the suitability of these tools was achieved by performing experimental and simulation tracer tests and comparing the results of the concentration evolution at the outlet. The tracer experiments were made in a vessel design materialized by additive manufacturing techniques (3D printing).

4.1. CFD learning phase

As mentioned before, the results can be organized in four main parts. In the first part, it was used a simple design of a vessel with two entries, one outlet and 9 circular obstacles. These obstacles had the possibility of being a heat source, as in to mimic the thermal effect of an exothermic reaction happening in the surface of a solid catalyst. In the external walls of the vessel, it was included a heat convection condition to introduce the effect of cooling the vessel by a fluid flowing (or not) on the outside.

After the generation of the sketch/domain of the vessel, it was necessary to define a proper mesh for the simulations. For that purpose, a mesh independence test was performed with four different meshes, where the main element size and the refinement level/methods near the walls was changed. It is important to refer that the skewness and orthogonal quality range of the cells were also considered to choose the meshes. All of this information is compiled in Table 4-1 and Table 4-2, along with the values of Orthogonal Quality, number of elements and the number of convergence iteration resulting from simulating assay 9 for Re 900, since it was the assay where is expected a more significant gradient close to the walls. In Figure Appendix K. 1 is presented images of the four meshes generated. In Figure Appendix K. 1 is presented images of the four meshes generated.

Table 4-1: Definition of the properties of mesh 1 and 2 and respective results.

	Mesh 1		Mesh 2	
Element size / mm	1.3		1	
Number of divisions in obstacles	10		10	
Number of divisions in exterior walls	12		12	
Refinement	Option	Smooth transition	Option	Smooth transition
	Number of layers	0.272	Translational Ratio	0.272
	Growth Rate	7	Maximum layers	7
	Maximum Thickness	1.3	Growth Rate	1.3
Number of Elements	59668		96588	
Orthogonal Quality	Min	0.592	Min	0.656
	Max	1.000	Max	1.000
	Average	0.988	Average	0.990
	Standard Deviation	0.028	Standard Deviation	0.024
Convergence for essay evaluated	Value of PTERF for momentum	0.05	Value of PTERF for momentum	0.05
	Number of iteration	8145	Number of iteration	5294

Table 4-2: Definition of the properties of mesh 3 and 4 and respective results.

	Mesh 3		Mesh 4	
Element size / mm	1.3		1	
Number of divisions in obstacles	10		10	
Number of divisions in exterior walls	12		12	
Refinement	Option	Total Thickness	Option	Total Thickness
	Number of layers	5	Number of layers	5
	Growth Rate	1.4	Growth Rate	1.4
	Maximum Thickness	0.001	Maximum Thickness	0.001
Number of Elements	60045		99333	
Orthogonal Quality	Min	0.678	Min	0.671
	Max	1.000	Max	1.000
	Average	0.991	Average	0.992
	Standard Deviation	0.023	Standard Deviation	0.022
Convergence for essay evaluated	Value of PTERF for momentum	0.02	Value of PTERF for momentum	0.05
	Number of iteration	40000	Number of iteration	50000

So, simulation of assay 9 was performed in the four meshes, and the results for the temperature (Figure 4-1) and velocity (Figure 4-2) profiles in the outlet, and the values of the maximum temperature in the domain and the average temperature in the outlet (Table 4-3) were extracted for comparison.

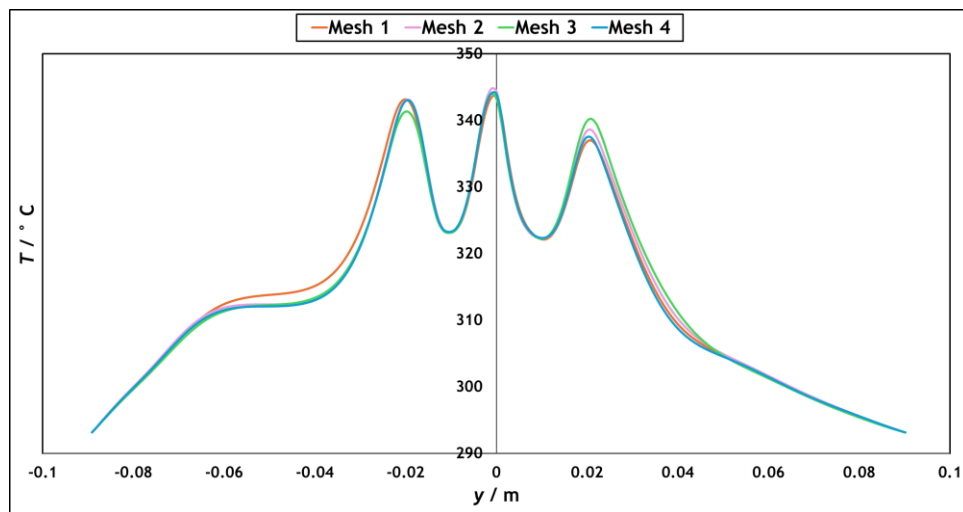


Figure 4-1: Graph of the T_{out} in function of y direction for an iso-surface created in a zone between the beginning of the outlet and the end of all obstacles.

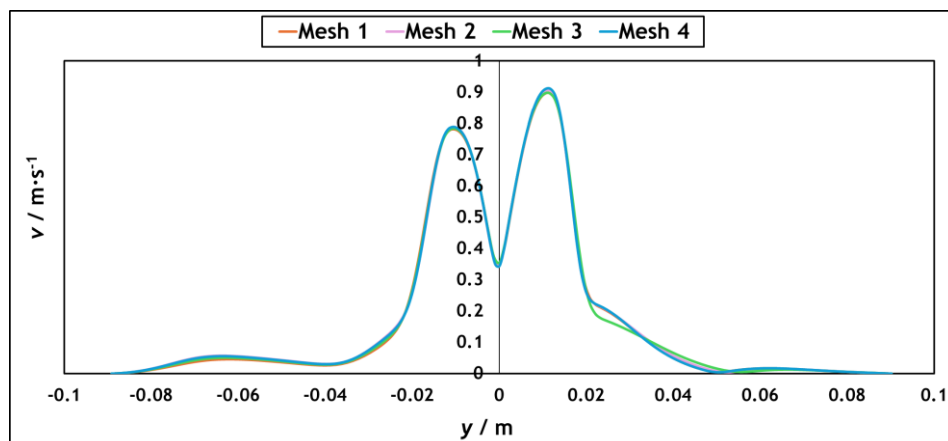


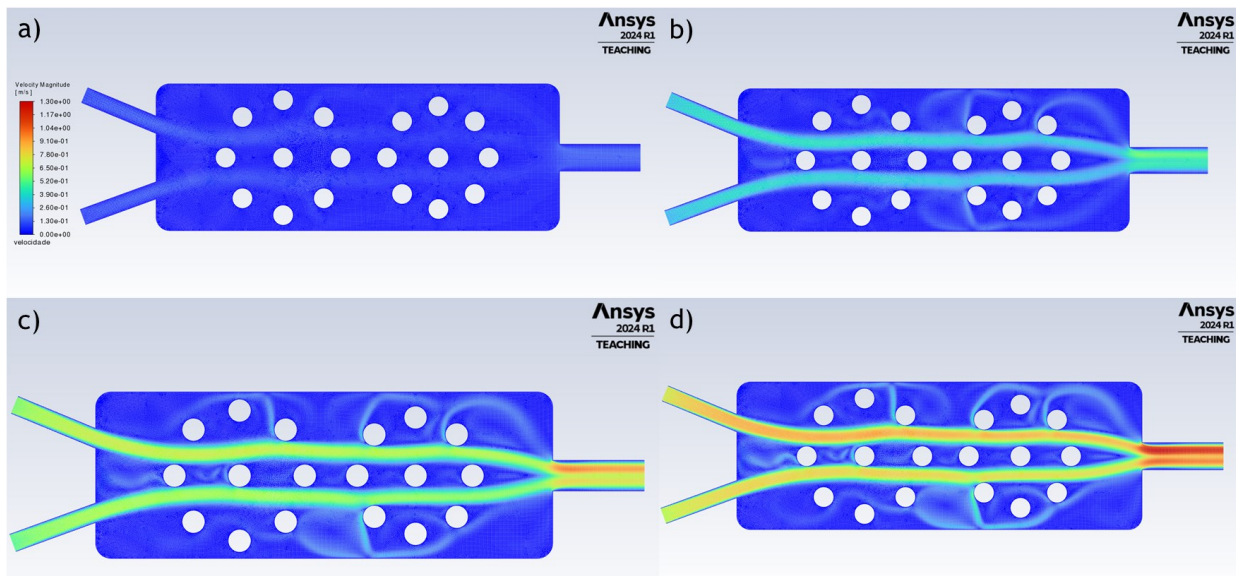
Figure 4-2: Graph of the v_{out} in function of y direction for an iso-surface created in a zone between the beginning of the outlet and the end of all obstacles.

Table 4-3: Results from the simulation of assay 9 of T_{max} and the average T_{out} for each mesh.

	Mesh 1	Mesh 2	Mesh 3	Mesh 4
$T_{max} / ^\circ\text{C}$	267.06	260.09	258.82	261.58
Average $T_{out} / ^\circ\text{C}$	53.83	54.06	53.87	53.96

Combining the information of these two graphs and from the table, it is visible that the less dense mesh (mesh 1) produces results with higher deviation. The results obtained with the remaining meshes do not vary significantly, but the deviations between mesh 2 and mesh 4 are less accentuated. So, it was chosen the less dense mesh from these two, and the element size and refinement data of Mesh 2 was used as a reference for all the simulations performed in this thesis.

After the mesh independence tests, the next phase was to perform the set of simulations corresponding to the instructions from Table 3-1, the velocities from Table 3-2 simulate for all the assays present in Table 3-3. A compilation of some of the results obtained are presented below. Firstly, are shown the contours of velocity and of mass fraction for each Reynolds number, as they are independent from heat flux or convection:

Figure 4-3: Contours of velocity magnitude: a) $Re = 100$; b) $Re = 400$; c) $Re = 700$; d) $Re = 900$.

From Figure 4-3 it is visible that this geometry creates very well-defined preferential paths for the fluid to flow around the middle circles. However, there is still some level of dispersion at velocities inferior to the maximum velocity, that is reached in the two central lines for each value of Reynolds. In the outlet is also noticeable that the top flow occupies more space and that is because the fluid that enters the top inlet is CH_4 which is denser than O_2 entering at the bottom inlet.

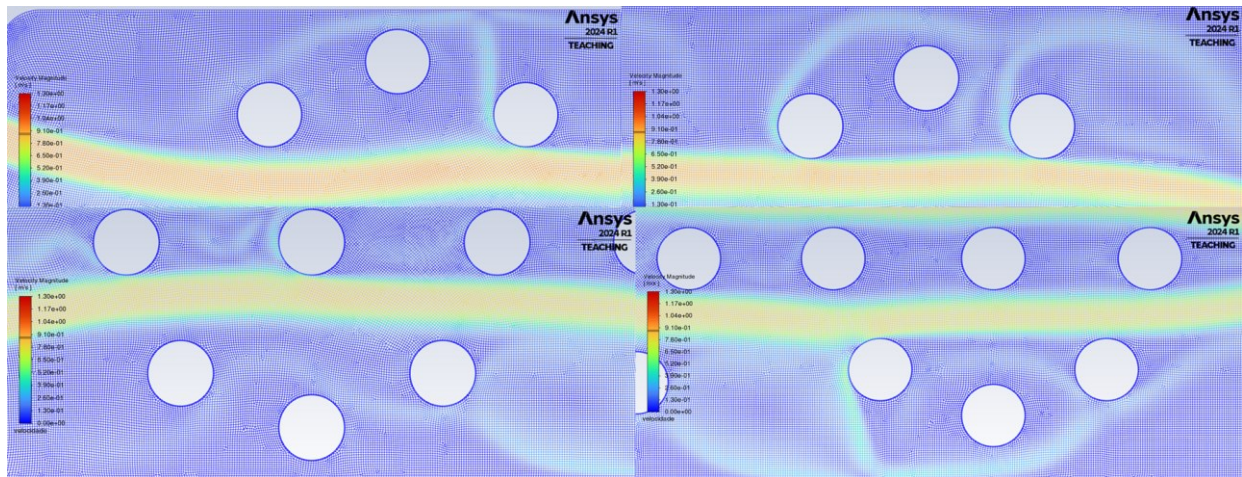


Figure 4-4: Zoom of the velocity contours for $Re = 900$.

From Figure 4-4, it is noticeable that the two fluid paths do not mix or even touch each other, making possible to conclude that this illustrative design is not adequate to promote mixing, and significant adjustments should be made to if it was intended to improve this aspect.

These observations are reinforced by mass fraction distribution of CH_4 in Figure 4-5.

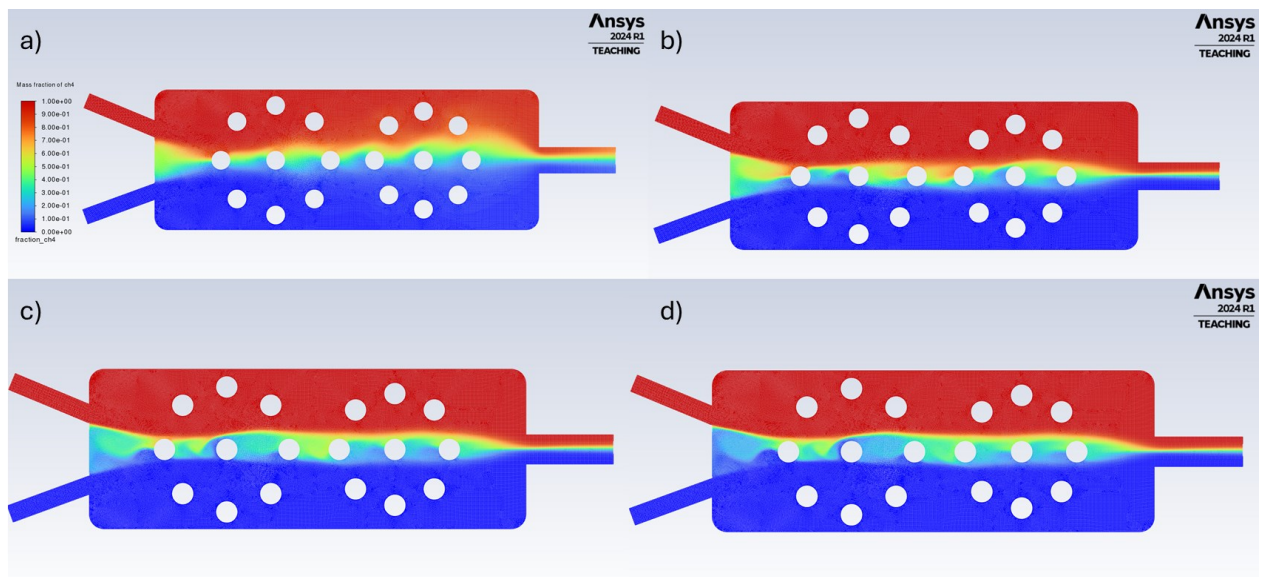


Figure 4-5: Contours of mass fraction of CH_4 : a) $Re = 100$; b) $Re = 400$; c) $Re = 700$; d) $Re = 900$.

With these images, it's possible to conclude that the increase of the velocity causes a decrease in the dispersion of CH_4 , the line above the central circles become more defined and there is only mixture between the 2 streams in between the middle circles.

The values of the convection coefficients were chosen to mimic three specific scenarios of external cooling by convection: 1) $7 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$ can represent the natural convection between horizontal flat plaque; 2) $200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$, symbolises forced convection occurring in a flat plate with parallel liquid water flow at low velocities; 3) $1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$, illustrates forced convection in a flat plate with parallel liquid water flow at higher velocities. Appendix Q can be checked for further details.

The illustrations bellow shows the temperature distribution influenced by the changes in the heat flux produced in the circles for different values of the convection coefficient in the exterior walls, for the four Reynolds number mentioned before.

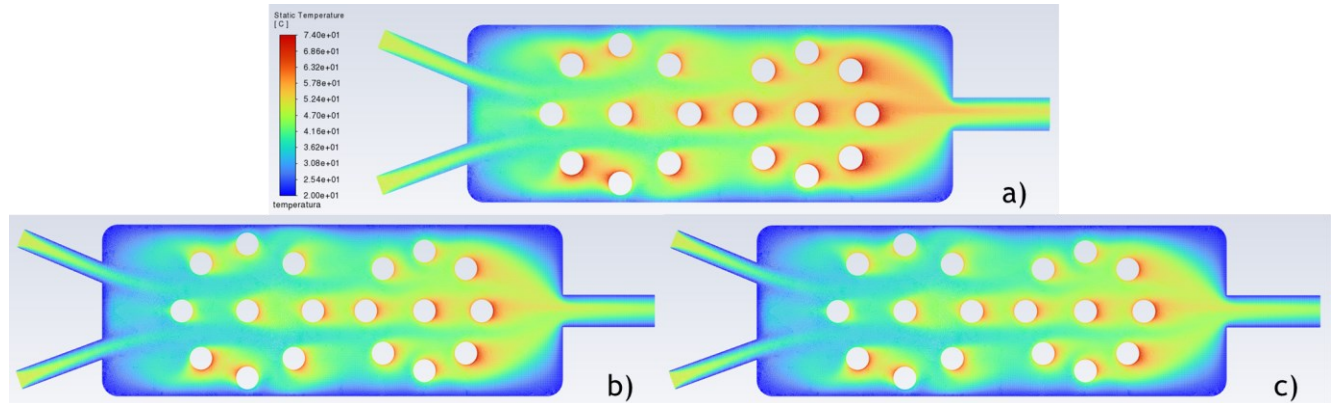


Figure 4-6: Static temperature contours with $Re = 100$ and $H_F = 50 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

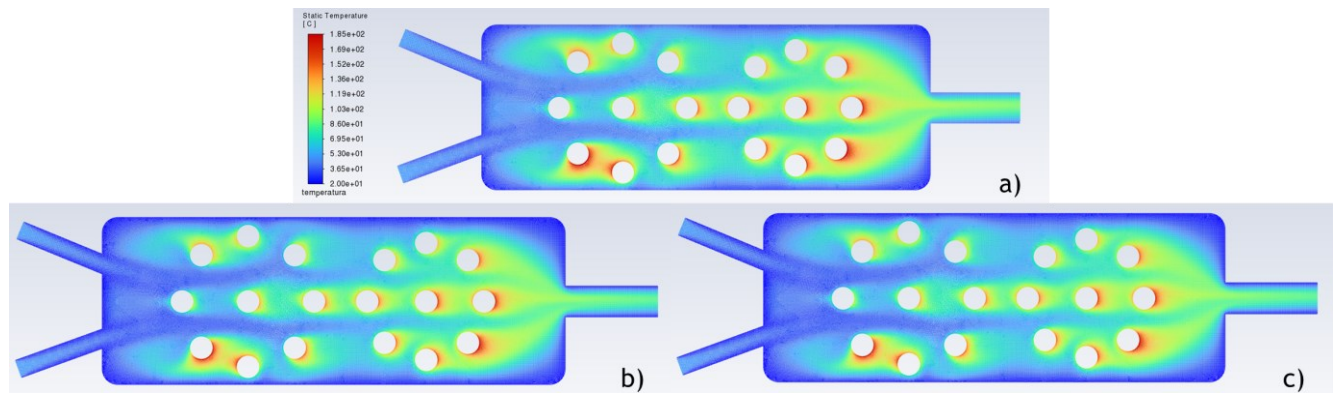


Figure 4-7: Static temperature contours with $Re = 100$ and $H_F = 200 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

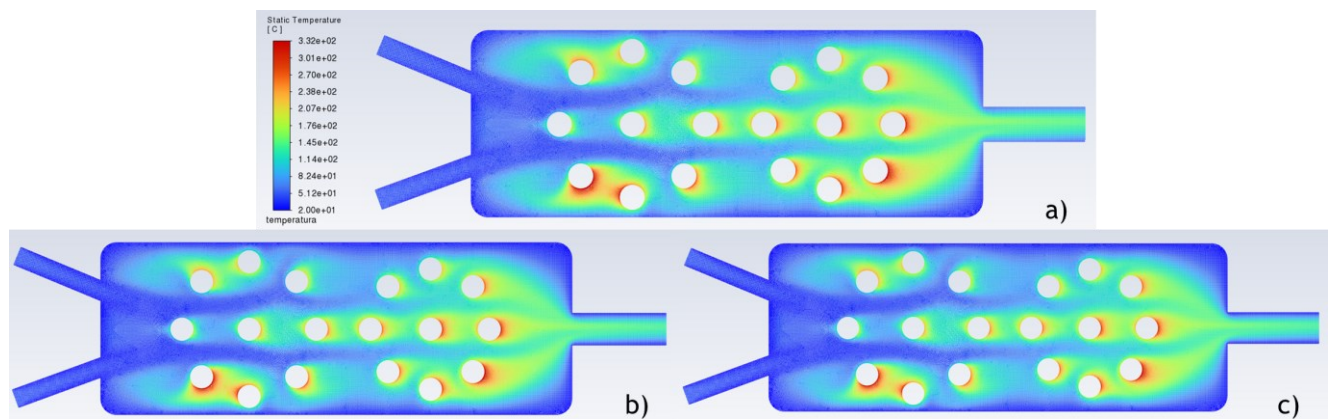


Figure 4-8: Static temperature contours with $Re = 100$ and $H_F = 400 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

In Figure 4-6, the heat production is lower than for the other values used, so the temperature levels inside the vessel are very similar to the inlet temperatures and that results in more coloured contours. Comparing the three images, as expected, the increase in the heat flux produced in the obstacles implies an increase in the maximum temperature of the system. Relatively to the convection coefficient, its effect is very noticeable because as the value of h rise, the area in blue close to the walls increases as well.

To compare the effect of the inlets velocity in the temperature contours, is shown below the contours of $H_F = 400 \text{ W}\cdot\text{m}^{-2}$ for Re 400, 700 and 900. The contours of the remaining assays are featured in Appendix L.

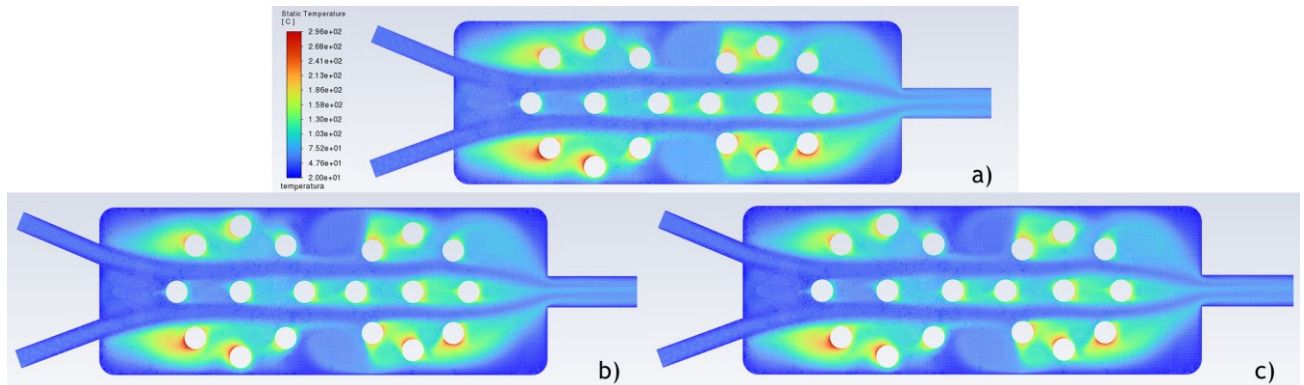


Figure 4-9: Static temperature contours with $Re = 400$ and $H_F = 400 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

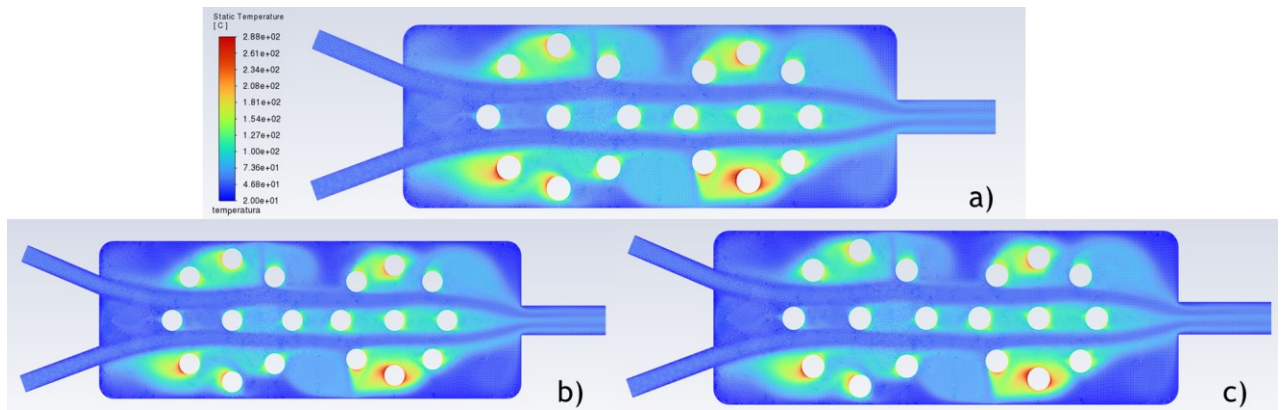


Figure 4-10: Static temperature contours with $Re = 700$ and $H_F = 400 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

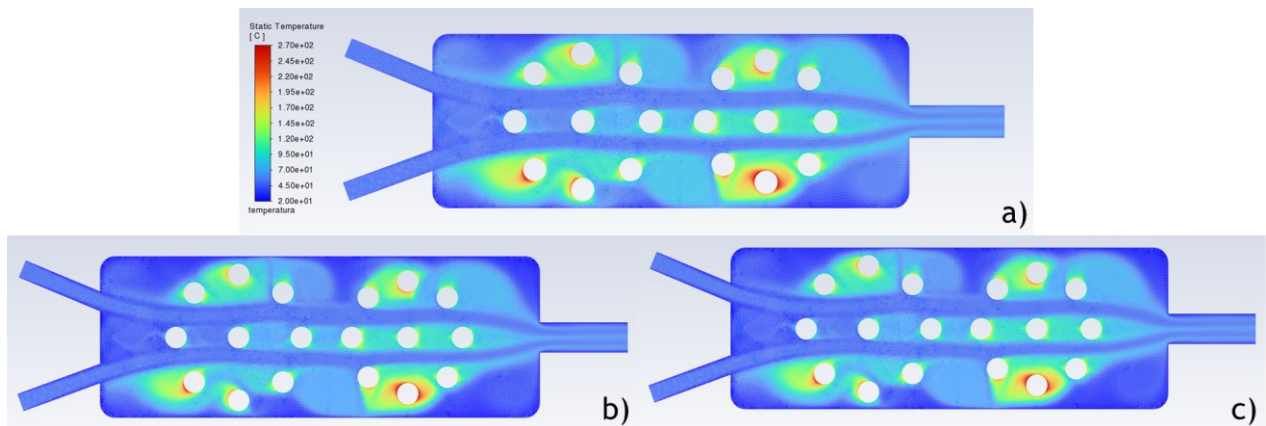


Figure 4-11: Static temperature contours with $Re = 900$ and $H_F = 400 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

Observing all these contours, it's perceptible that the increase of the velocity leads to decrease of the maximum temperature obtained on each assay, being the temperature distribution of Re 100 the one with the highest value. This phenomenon is explained by the fact that, if the fluid flows at lower velocity, the residence time inside of the vessel is higher, so the duration of the exposure to the heat generation increases and the amount of energy received is much higher.

Appendix M is related to the values of the maximum and minimum temperature in the reactor for each assay made, as well as the average T_{out} . From Table Appendix M. 1, is possible to concluded that for higher values of convection, the difference between the maximum temperatures is very low, from $200 \text{ W}\cdot\text{m}^{-2}\cdot^{\circ}\text{C}^{-1}$ to $1500 \text{ W}\cdot\text{m}^{-2}\cdot^{\circ}\text{C}^{-1}$ the maximum temperature only lowered 1°C or less in most assays.

As mentioned before, were also made tracer experiments using Design A and Mesh 2 to comprehend the details and the calculations involved in analysing the results of tracer experiments. Those results are presented in Appendix N.

4.2. Experimental and simulation tracer tests

The validation step of the CFD methodology applied was performed by replicating step input tracer tests with simulation and comparing the experimental and numerical $F(t)$ and $E(t)$ curves. The geometry used on these tests concerns Design C (Design B with modifications): this design was 3D printed with a depth of 1 cm to perform the experiments, and the simulations were made in the same design with a 2D planar approach. The data for the mesh creation is presented in Table 4-4 and the parameters/methods are related with Mesh 2 from the previous section.

Table 4-4: Mesh properties resulting from the application of Mesh 2 definitions in Design B.

Design B		
Element size / mm	1	
Number of divisions in obstacles	10	
Number of divisions in exterior walls	12	
Refinement	Option	Smooth transition
	Number of layers	0.272
	Growth Rate	7
	Maximum Thickness	1.3
Number of Elements	15171	
Orthogonal Quality	Min	0.602
	Max	1.000
	Average	0.975
	Standard Deviation	0.036

To obtain the experimental data of the tracer experiments, was applied the methodology described in 3.2 and the values of velocity present in Table 3-4. To perform the respective simulations of those experimental assay, were applied the definitions present in Table 3-5 combined with the values from Table 3-6. The results of concentration in the outlet were processed using Eq. (2.6) and Eq. (2.7), described in 2.3, and was possible to compare the Danckwerts F curve and the distribution of residence time, of the experimental and simulation data. Those results are shown in Figure 4-12, Figure 4-13 and Figure 4-14. To calculate the values of τ and $\bar{t}_r$, for the experimental and simulation results, was applied Eq. (2.8) and Eq. (2.9) and the results are presented in Table 4-5. More details about the calculation involved in the tracer experiments are featured in Appendix I.

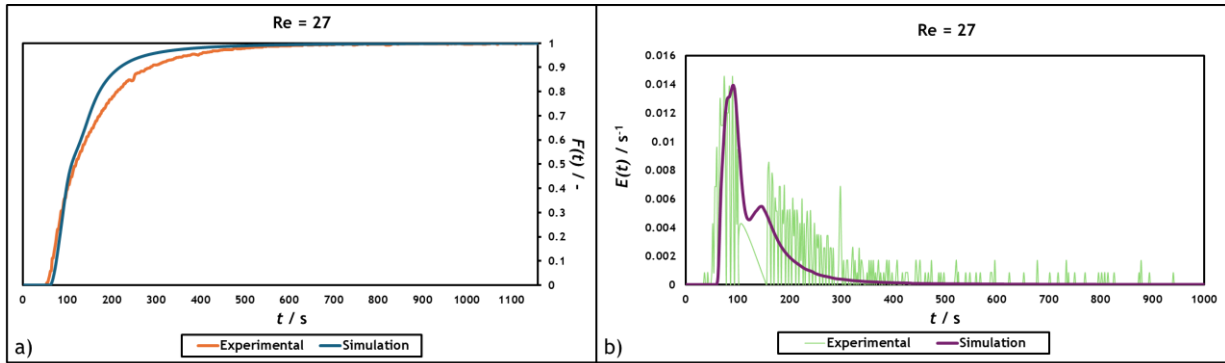
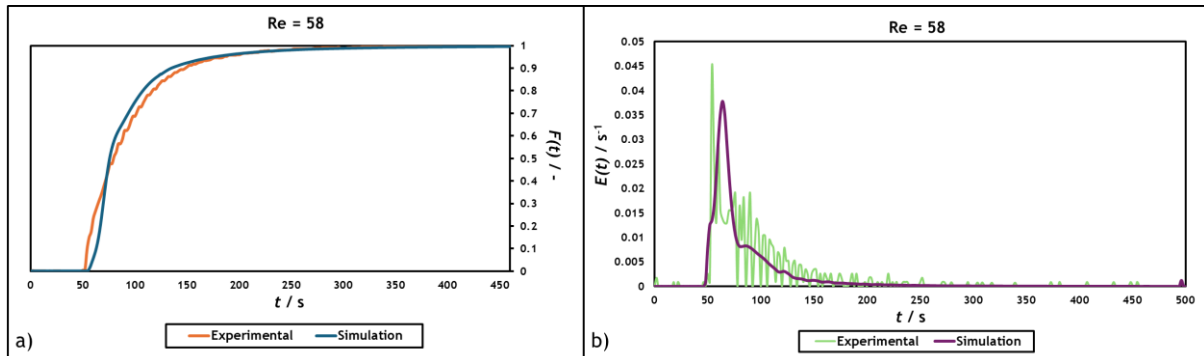
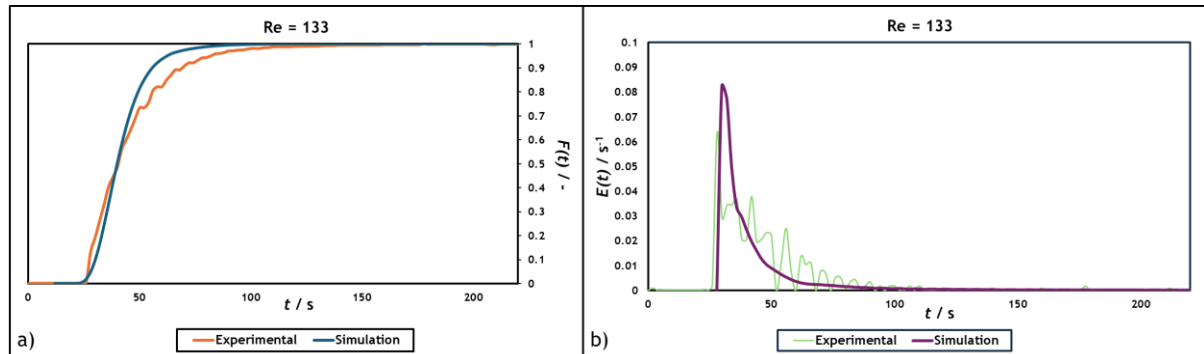
Figure 4-12: Comparing the results of experimental and simulation data for $Re = 27$.Figure 4-13: Comparing the results of experimental and simulation data for $Re = 58$.Figure 4-14: Comparing the results of experimental and simulation data for $Re = 133$.

Table 4-5: Comparison between the experimental and the simulation data.

Re	$\tau_{\text{experimental}} / s$	$\bar{t}_{r\text{experimental}} / s$	$\tau_{\text{simulation}} / s$	$\bar{t}_{r\text{simulation}} / s$
27	144.56	191.53	138.18	138.20
58	68.31	94.83	65.31	66.77
133	29.94	46.25	28.63	12.72

Combining all these results is possible to conclude that visually the results of the $F(t)$ with lower deviation are for $Re = 27$ and 58 . However by observing Table 4-5, the values of $\bar{t}_{r\text{experimental}}$ for $Re = 27$ were the ones with higher deviation from the simulation results and from the corresponding $\tau_{\text{experimental}}$. This can be explained by the $E(t)$, as this curve does not present the expected shape causing the larger deviation of this value. The difference between the experimental and the simulation curves and residence times, can be explained by factors such as the fact that peristaltic pumps are unable to produce a consistent steady state flow rate, or by measurement errors associated with the spectrophotometer, or because the experimental

setup was not adapted to the size of the 3D printed vessel (the connection tubes were too long). Despite these observations, the similarities between the experimental and the simulation data allows the conclusion that the method was validated and is possible to combine 3D-printing with CFD and optimize reactions with the study of different geometries.

4.3. Parametric study with a low exothermic reaction

To assess the impact of a low exothermic reaction, an illustrative homogenous liquid reaction was considered within the framework of Design C (Design B with modifications). The simulations of this small reactor were based on continuous operation mode (2 inlets and 1 outlet) and the procedures and conditions are referred in Table 3-7 and Table 3-8. In each of the inlets, only enters one of the reagents mixed with the solvent of, in inlet 1 enters A and D and in inlet 2 enters B and D. For simplicity of the study, this hypothetical reaction is described by $A + B \rightarrow C + D$ and occurs in all volume inside of the reactor. The kinetics was assumed to be second order (first order to each reagent) and the heat of reaction is $\Delta H = -30 \text{ kJ}\cdot\text{mol}^{-1}$. The simulations were performed to achieve the steady state solution for each assay, and it was made a study of the influence of parameters, such as inlets composition, velocity and temperature and the presence of convection. The outputs that received our focus were the average temperature and average mass fraction of the product C at the outlet, and in the maximum and minimum temperature inside the reactor. The kinetics parameters were the same for all the simulations and set at the following values: $k_0 = 100 \text{ m}^3\cdot\text{kgmol}^{-1}\cdot\text{s}^{-1}$, $E_a = 50 \text{ kJ}\cdot\text{mol}^{-1}$ $a = 0$.

In Table 4-6, are presented the conditions defined for the inlets and the values of h used in the study of the effect of the velocity in the output variables considered.

Table 4-6: Definitions made for the study of the velocity effect and respective results.

$v_1 / \text{m}\cdot\text{s}^{-1}$	$v_2 / \text{m}\cdot\text{s}^{-1}$	$Y_A / -$	$Y_B / -$	$T_{in1} / ^\circ\text{C}$	$T_{in2} / ^\circ\text{C}$	$h / \text{W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	average $Y_C / \text{out} / -$	average $T_{out} / ^\circ\text{C}$	$T_{max} / ^\circ\text{C}$	$T_{min} / ^\circ\text{C}$
0.01	0.01	0.1		50		200	0.03288	48.7	54.6	24.4
0.1	0.1						0.02574	51.9	56.2	31.6
0.5	0.5						0.02338	52.1	56.0	34.5

With these results, it is possible to conclude that the increase in v has the effect of decreasing all the output variables, specially T_{min} of the system. In addition to these results, is presented in Figure 4-15, the visual effect of the changing of the velocity in average Y_C in the outlet.

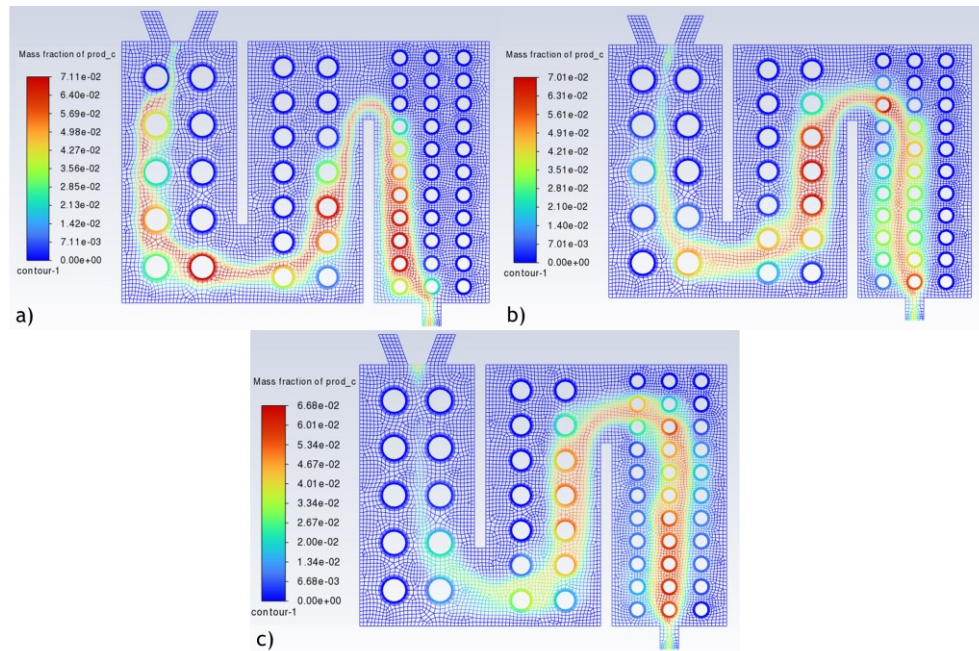


Figure 4-15: Contours of mass fraction of C for: a) $v = 0.01 \text{ m}\cdot\text{s}^{-1}$, b) $v = 0.1 \text{ m}\cdot\text{s}^{-1}$ and c) $v = 0.5 \text{ m}\cdot\text{s}^{-1}$.

With these mass fraction distributions, it is possible to observe that the increase of the velocity changes the preferential pathway of the reaction. Figure 4-15 a) suggests that the two inlets may not be geometrically identical and that is why there is a deviation to the left in the path of this contour.

Now in Table 4-7, are the conditions defined for the inlets used in the study of the effect of h in the output variables considered.

Table 4-7: Definitions made for the study of the effect of h and respective results.

$v_1 / \text{m}\cdot\text{s}^{-1}$	$v_2 / \text{m}\cdot\text{s}^{-1}$	$Y_A / -$	$Y_B / -$	$T_{in1} / ^\circ\text{C}$	$T_{in2} / ^\circ\text{C}$	$h / \text{W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	average $Y_{C / out} / -$	average $T_{out} / ^\circ\text{C}$	$T_{max} / ^\circ\text{C}$	$T_{min} / ^\circ\text{C}$
0.05	0.1	50				0	0.02655	52.6	56.1	50.0
						7	0.02996	52.5	56.1	48.5
						200	0.02997	51.4	56.0	29.6
						1500	0.03003	49.5	55.6	20.6

As this reaction is exothermic, it is favoured with the decrease of temperatures. The increase in h (with consequent decrease in the system temperature), caused an increase, even if it was slight, in the average $Y_{C/out}$. The effect of h is also noticeable in the output temperatures, with the increase of h the temperatures studied decrease. It is also perceptible that the effect of the increase of h is more noticeable in T_{min} and does not cause a significant impact on average T_{out} or T_{max} .

To compliment these affirmations, in Appendix O are shown the static temperature contours of these four assays, where is visible the increase of the blue area close to the exterior walls, due to the decrease of temperature close to them.

The next parameter addressed was the effect of changing the inlet composition, and for that were applied the definitions presented in Table 4-8. The results obtained are also described in the same table.

Table 4-8: Definitions made for the study of the effect of the inlet compositions and respective results.

$v_1 / \text{m}\cdot\text{s}^{-1}$	$v_2 / \text{m}\cdot\text{s}^{-1}$	$Y_A / -$	$Y_B / -$	$T_{in1} / ^\circ\text{C}$	$T_{in2} / ^\circ\text{C}$	$h / \text{W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	average $Y_{C / out} / -$	average $T_{out} / ^\circ\text{C}$	$T_{max} / ^\circ\text{C}$	$T_{min} / ^\circ\text{C}$
0.05		0.05		50		0	0.01584	51.2	52.9	50.0
		0.5	0.1				0.20707	56.2	62.3	50.0
		0.25	0.1				0.04420	54.4	59.6	50.0
		0.25					0.08083	58.4	66.2	50.0

Based on these results, and as expected, it is possible to conclude that higher values of mass fraction of reagents produce higher values of Y_C , and that the highest value of Y_C is associated with assays with higher mass fractions for each reagent.

To further understand the influence of the inlet composition, the mass fraction distributions of C are presented in Appendix O for all these assays. In those images, it is possible to observe how much the preferred path changes with the variations of the composition in the inlets.

Finally, the last parameter studied was the temperature in the inlets. The simulations were carried out using the definitions in Table 4-9, where are shown the respective results as well.

Table 4-9: Definitions made for the study of the effect of the inlet temperatures and respective results.

$v_1 / \text{m}\cdot\text{s}^{-1}$	$v_2 / \text{m}\cdot\text{s}^{-1}$	$Y_A / -$	$Y_B / -$	$T_{in1} / ^\circ\text{C}$	$T_{in2} / ^\circ\text{C}$	$h / \text{W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$	average $Y_{C/out} / -$	average $T_{out} / ^\circ\text{C}$	$T_{max} / ^\circ\text{C}$	$T_{min} / ^\circ\text{C}$
0.05		0.1		70		0	0.02739	73.0	76.5	70.0
				30			0.02300	32.1	35.5	30.0
				50			0.02655	52.6	56.1	50.0

The results suggest that this parameter does not cause a significant effect in none of the output variables, as the average Y_C does not vary much between assays, and as all the temperatures considered do not vary significantly from the inlet temperature. However, there is a slight increase in the average $Y_{C/out}$, as the inlet temperatures are raised.

4.4. Parametric study with a highly exothermic reaction

In order to inspect the impact of a highly exothermic reaction, an illustrative catalytic gas phase reaction was considered in the domain of Design C. The simulations of this small reactor were based on continuous operation mode (2 inlets and 1 outlet) and the options/procedures and conditions are referred in Table 3-7 and Table 3-8. In each of the inlets, only enters one of the reagents mixed with an inert, in inlet 1 enters A and D and in inlet 2 enters B and D. For simplicity of the study, this hypothetical reaction is described by $2A + B \rightarrow 2C$ and only occurs at the walls of the obstacles, the kinetics was assumed to be second order (first order to each reagent) and the heat of reaction is $\Delta H = -302 \text{ kJ}\cdot\text{mol}^{-1}$. The simulations were performed to achieve the steady state solution for each assay, and it was made a study of the influence of parameters, such as inlets composition, velocity and temperature and the presence of convection, in the average temperature and average mass fraction of the product C at the outlet and in the maximum temperature inside the reactor.

The first study was related to the variation of the inlet composition: 1) with equal mass fraction of reagents in the two inlets, $Y_A = Y_B = \{0.1, 0.3, 0.5, 0.7\}$; 2) reagents in excess, with Y_A and Y_B varied between $\{0.1, 0.3, 0.5, 0.7\}$. Another parameter addressed in this study was the external

convective coefficient, h , that oscillated between $\{0, 7, 200, 1500\} \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$. The remaining conditions were kept constant and with the following values: $v = 0.1 \text{ m}\cdot\text{s}^{-1}$, $T_{in1} = T_{in2} = 25^\circ\text{C}$, $k_0 = 1 \text{ m}^3\cdot\text{kgmol}^{-1}\cdot\text{s}^{-1}$, $Ea = 50 \text{ kJ}\cdot\text{mol}^{-1}$, $a = 0$.

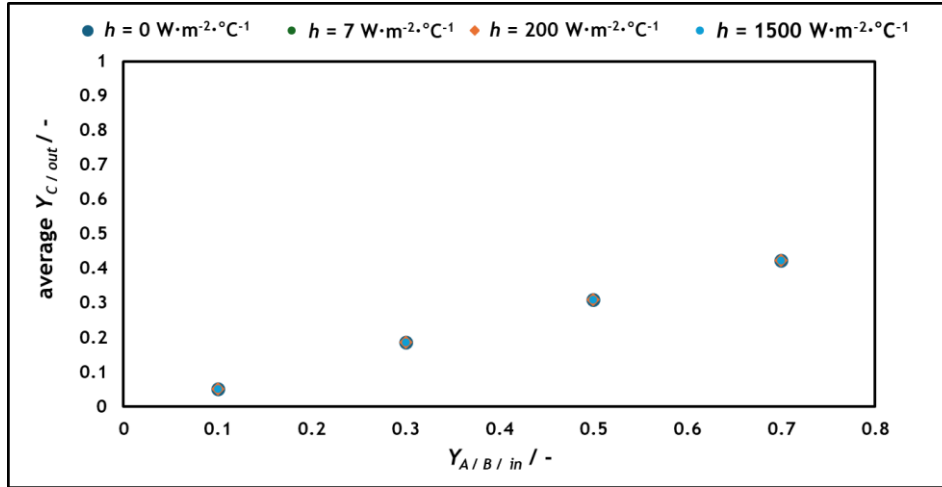


Figure 4-16: Average $Y_{C/out}$ results obtained from the conjugation of various inlet compositions where $Y_A = Y_B$.

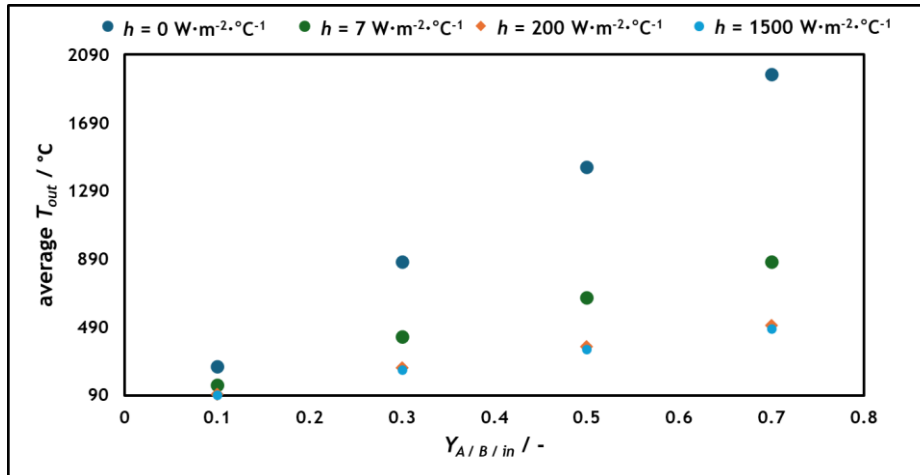


Figure 4-17: Average T_{out} results obtained from the conjugation of various inlet compositions where $Y_A = Y_B$.

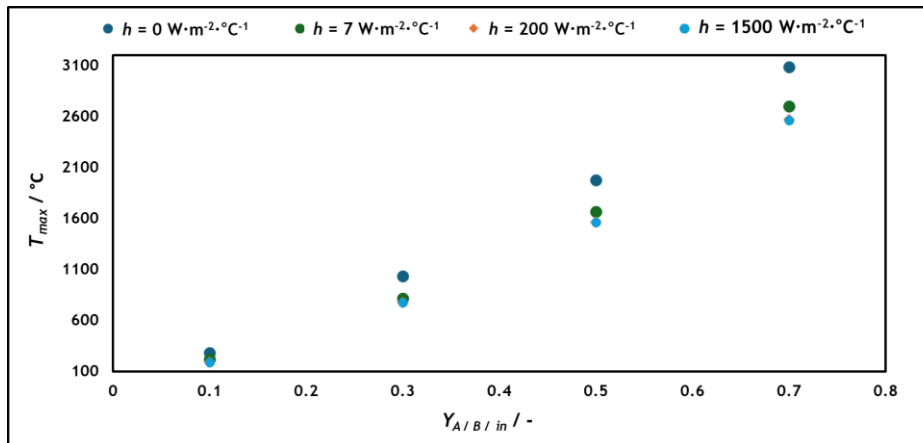


Figure 4-18: Average T_{max} results obtained from the conjugation of various inlet compositions where $Y_A = Y_B$.

In Figure 4-16, as expected, the bigger the mass fraction of each reagent the higher the average Y_C in the outlet. The presence of convection through the exterior walls did not had a significant impact on the average Y_C but it lowered considerably the values of T_{max} and average T_{out} . As

this reaction is exothermic, it is favoured with the decrease of temperatures, so it was expected that the increase in h (with consequent decrease in the system temperature), caused an increase in the average $Y_{C/out}$. The effect on the average T_{out} is more emphasised, which is associated with the fact that in the outlet is formed a gradient as the value of h rises, so the low temperatures close to the walls cause a greater decrease in the average value of the temperatures in the outlet.

Additionally, to these graphs, in Figure 4-19 are presented the contours of temperature of $Y_A = Y_B = 0.1$, for all values of convection.

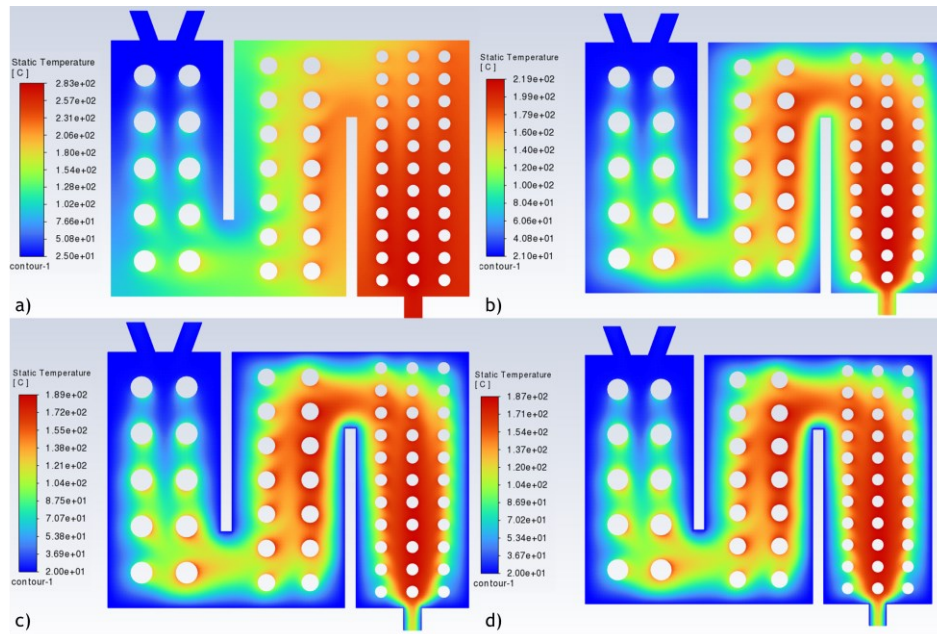


Figure 4-19: Static temperature contours for: a) $h = 0 \text{ W}\cdot\text{m}^{-2}\cdot^{\circ}\text{C}^{-1}$, b) $h = 7 \text{ W}\cdot\text{m}^{-2}\cdot^{\circ}\text{C}^{-1}$, c) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^{\circ}\text{C}^{-1}$ and d) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^{\circ}\text{C}^{-1}$, when $Y_A = Y_B = 0.1$.

This image is in agreement with the conclusions made before, as is possible to observe the growing of the blue area close to the walls as the h increases. In this image is also visible a conclusion made in 4.1, where was affirmed that for high values of h the effect on the temperature decreases, as is evident for $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^{\circ}\text{C}^{-1}$ and $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^{\circ}\text{C}^{-1}$, where the difference between T_{max} is 2°C .

The second study was also related to the variation of the inlet composition: with reagents in excess, with Y_A and Y_B varied between $\{0.1, 0.3, 0.5, 0.7\}$. The remaining conditions were kept constant and with the following values: $v = 0.1 \text{ m}\cdot\text{s}^{-1}$, $T_{in1} = T_{in2} = 25^{\circ}\text{C}$, $k_0 = 1 \text{ m}^3\cdot\text{kgmol}^{-1}\cdot\text{s}^{-1}$, $E_a = 50 \text{ kJ}\cdot\text{mol}^{-1}$ and $a = 0$.

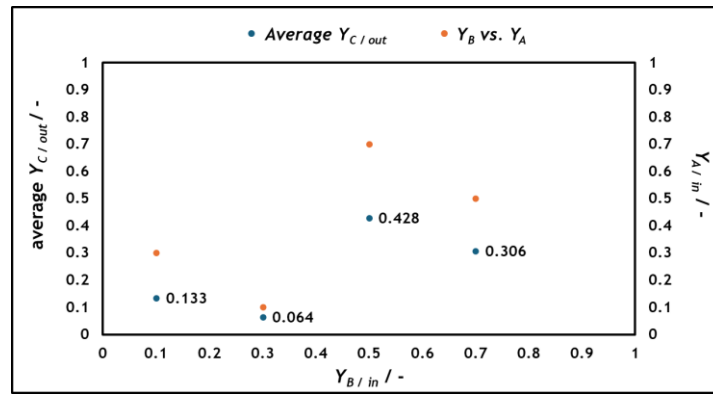


Figure 4-20: Average $Y_{C/out}$ results obtained from the conjugation of various inlet compositions where Y_A and Y_B are not equal.

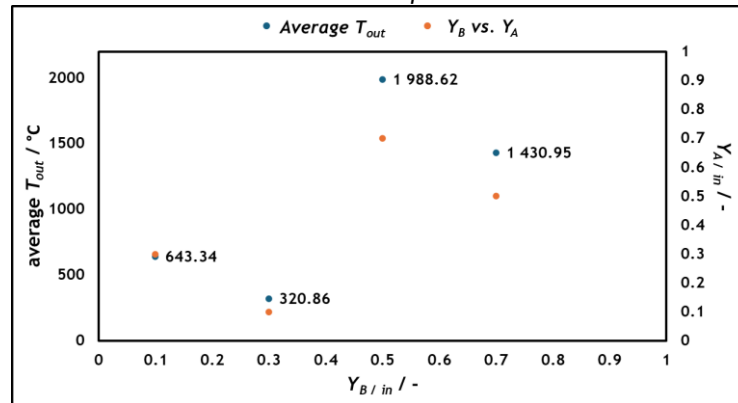


Figure 4-21: Average T_{out} results obtained from the conjugation of various inlet compositions where Y_A and Y_B are not equal.

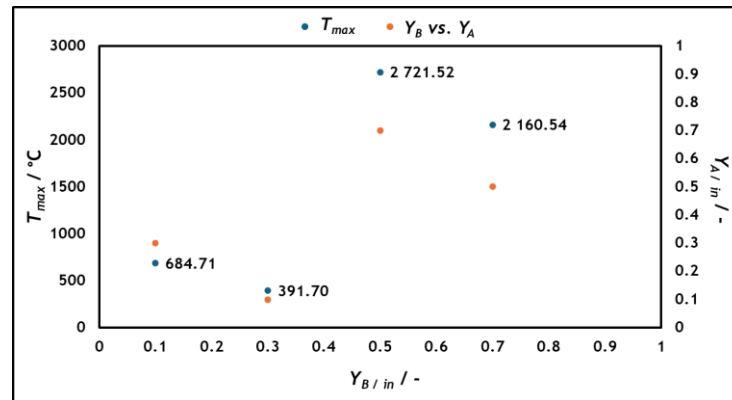


Figure 4-22: T_{max} results obtained from the conjugation of various inlet compositions where Y_A and Y_B are not equal.

In Figure 4-20, Figure 4-21 and Figure 4-22 is possible to verify that there is a higher formation of C when there is a higher composition of A in relation to the composition of B, and this is because its stoichiometric coefficient is 2 while B's is 1.

Additionally, to these graphs, is presented in Figure 4-23 the contours of mass fraction of C for $Y_A = Y_B = 0.3$, $Y_A = 0.5$ and $Y_B = 0.7$, $Y_A = 0.3$ and $Y_B = 0.1$, without convection.

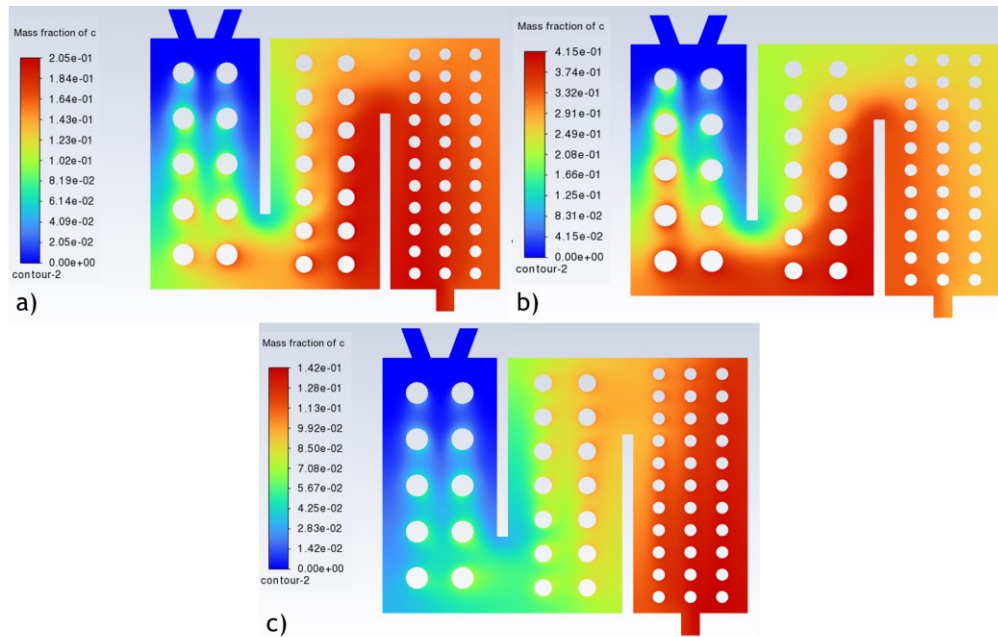


Figure 4-23: Contours of mass fraction of C for a) $Y_A = Y_B = 0.3$, b) $Y_A = 0.5$ and $Y_B = 0.7$, c) $Y_A = 0.3$ and $Y_B = 0.1$.

With these images it is very visible that the lower the mass fraction of reagents, the later the reaction occurs as its possible to observe the difference between Figure 4-23 b) and c), as is noticeable that in c) the reaction does not happen in the first obstacles.

After that, it was studied the effect of the inlet temperature, of a and of the velocity altogether. So, the variation of the temperature exponent, a , was within the range $\{-1, 0, 1\}$, of v was $\{0.05, 0.1, 0.5\} \text{ m}\cdot\text{s}^{-1}$ and of $T_{\text{in}1} = T_{\text{in}2} = \{5, 25, 50\} ^\circ\text{C}$. For each value of a , three graphs were plotted for each output variable measured, where the output variable is shown as a function of velocity and $T_{\text{in}1} = T_{\text{in}2}$. The remaining conditions were kept constant and with the following values: $k_0 = 1 \text{ m}^3\cdot\text{kgmol}^{-1}\cdot\text{s}^{-1}$ (for $a = 0$), $k_0 = 1 \text{ m}^3\cdot^\circ\text{C}\cdot\text{kgmol}^{-1}\cdot\text{s}^{-1}$ (for $a = -1$), $k_0 = 1 \text{ m}^3\cdot^\circ\text{C}^{-1}\cdot\text{kgmol}^{-1}\cdot\text{s}^{-1}$ (for $a = 1$), $Y_A = Y_B = 0.5$ and $E_a = 50 \text{ kJ}\cdot\text{mol}^{-1}$.

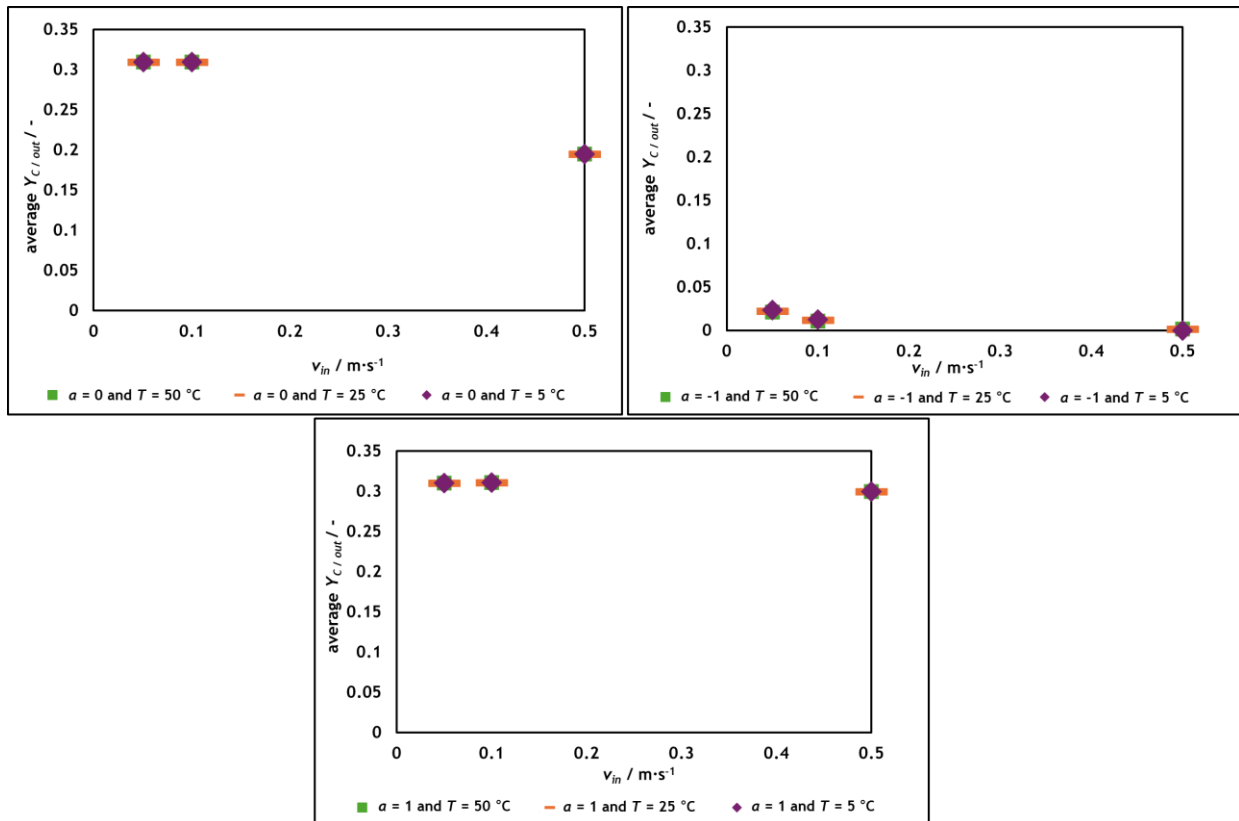


Figure 4-24: Comparison of average $Y_{C/out}$ results obtained for different values of a .

For all values of a , the effect of the inlet temperature on the average Y_C was not very perceptible as the points for each velocity are practically overlapped. For $a = 1$ and $v = 0.5 m \cdot s^{-1}$, the effect of a caused an increase in the average Y_C making it close to the value obtained for the other velocities. For $a = -1$, there was a major decrease in Y_C , in comparison with the other values of a , as it was expected by introducing a term that implies inverse proportionality of reaction rate with temperature. The increase in the velocity meant a decrease in the average Y_C for all the values of a , specially for $a = -1$. This is explained by the fact that for higher velocities the residence time is lesser, and that results in less formation of average Y_C .

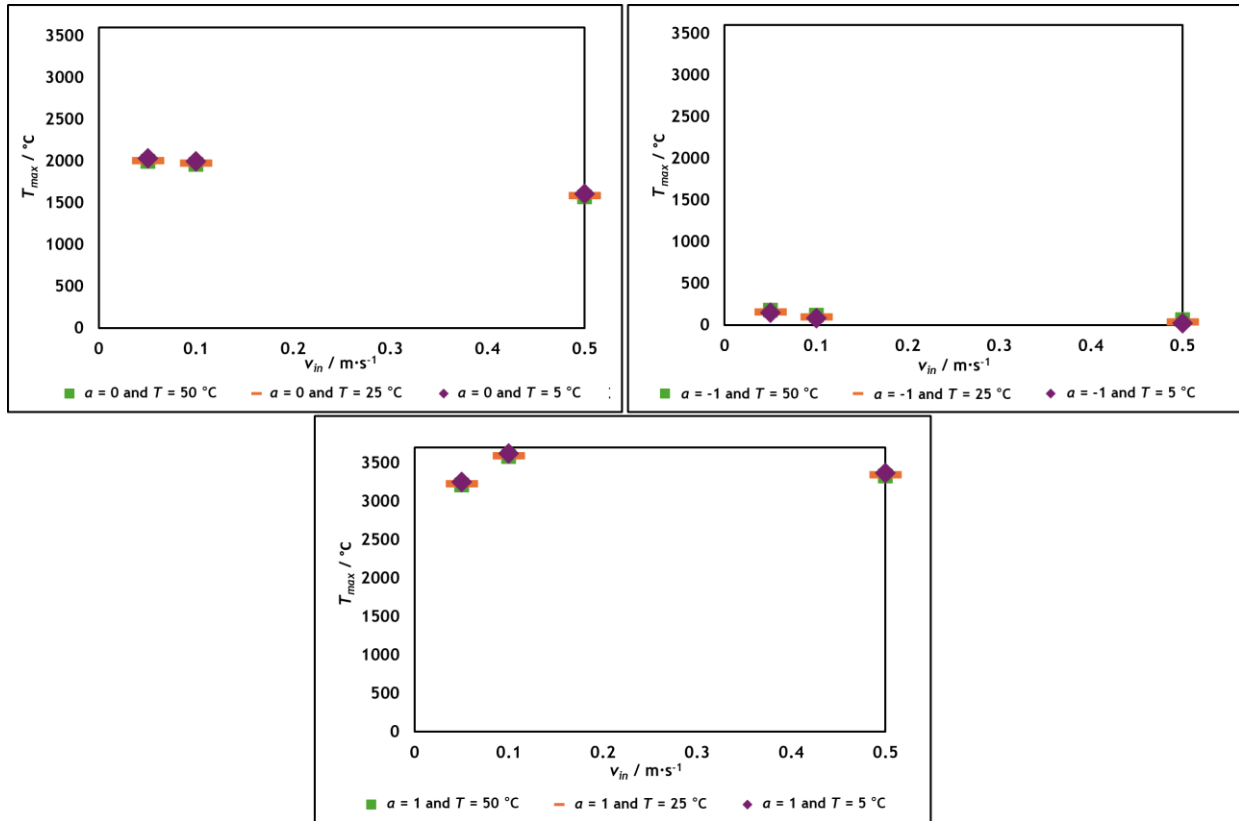


Figure 4-25: Comparison of T_{max} results obtained for different values of a .

Regarding the effect on T_{max} , for all values of a , the effect of the inlet temperature was similar to the previous analyse made above. For $a = 0$ and -1 , the increase of velocity implied a decrease in the value of the maximum temperature. However, for $a = 1$, the T_{max} was higher for $v = 0.1$ $m \cdot s^{-1}$ and not for the lower velocity as seen before. Once again, the behaviour of $a = 1$ combined with $v = 0.5$ $m \cdot s^{-1}$ meant an increase in the temperature.

Considering the results of average $Y_{C/out}$ and T_{max} for all values of a , is possible to affirm that it was expected that the results of average $Y_{C/out}$ for $a = 1$ would be higher than those for $a = 0$, as there is an extra term with direct proportionality with rate reaction, for $a = 1$, that would result in higher formation of C, however that was only verified for $v = 0.5$ $m \cdot s^{-1}$. The T_{max} is defined by the place inside the reactor where there is higher formation of D. Is visible that for $a = 1$ there are places in the reactor with much higher formation of C when compared to $a = 0$, and that is reflected in the results for the higher velocity because in that case the reaction takes place later and there is less fraction of C that is retained inside of the reactor and does not reach the outlet. For the two lower velocities occurs the opposite because, as is visible in the contours presented in Appendix P, for $a = 1$ the reaction occurs more intensively earlier when compared to the results of $a = 0$, and that is why the higher formation of C for $a = 1$ is not reflected in the outlet fraction. To complement these conclusions are presented the contours of temperature and mass fraction of C in Appendix P.

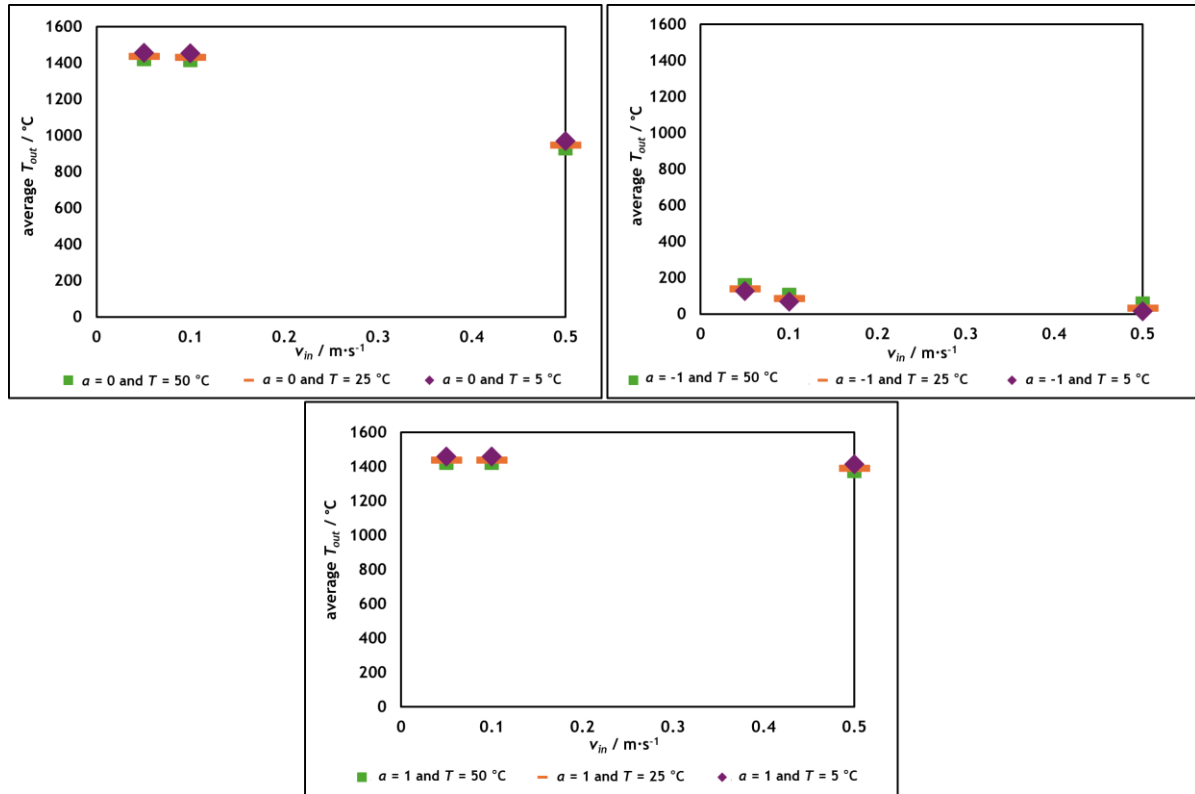


Figure 4-26: Comparison of average T_{out} results obtained for different values of a .

In the average T_{out} , the effect of the changing the inlet temperature maintained a low impact. For $a = 1$ and $v = 0.5$ $m \cdot s^{-1}$, it caused an increase in the temperature making it close to the value obtained for the other velocities. For $a = -1$, the effect of changing the inlet temperature variations was also not very significantly on the output mass fraction of C but, comparing to the results with $a = 1$, it implied a major decrease in Y_C . The increase in the velocity meant a decrease in average T_{out} specially for $a = -1$.

Finally, the study was focused on systems with more diluted inlet streams with convection in the exterior walls. For that, it was defined that Y_A and Y_B would vary between $\{0.05, 0.15\}$ and v between $\{0.01, 0.1, 1.5\}$ $m \cdot s^{-1}$. The remaining conditions were kept constant and with the following values: $k_0 = 100$ $m^3 \cdot kgmol^{-1} \cdot s^{-1}$, $E_a = 50$ $kJ \cdot mol^{-1}$, $T_{in1} = T_{in2} = 50$ °C, $a = 0$ and $h = 200$ $W \cdot m^{-2} \cdot s^{-1}$.

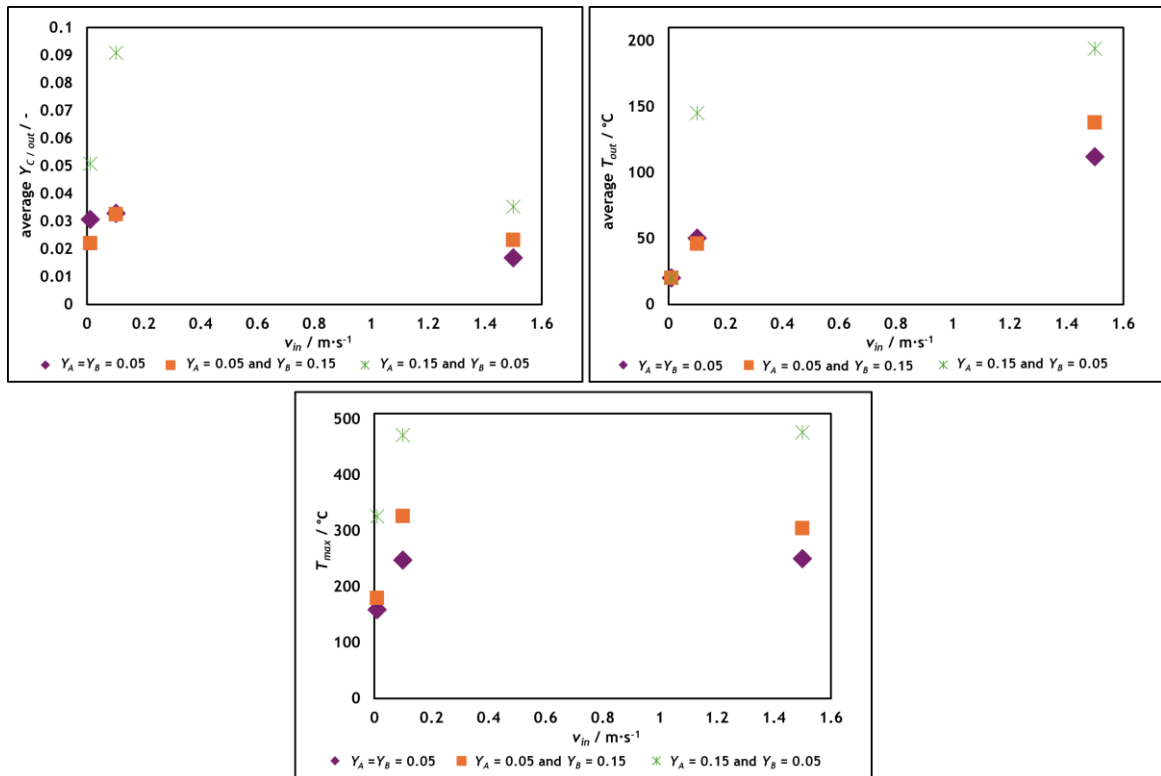


Figure 4-27: Results obtained for the variation of v , Y_A and Y_B .

With these results, it is possible to conclude that very low and very high velocities do not mean higher values of conversion. The feed of lower mass fractions implies the release of lower quantities of energy that, combined with external convection conditions, may allow a smoother control of the temperature levels, namely, the average T_{out} and T_{max} . Once again, assays with excess of the reagent with higher stoichiometric coefficient produced higher values of reaction product with similar temperature.

To complement this information, and to show a more detailed influence of the inlets concentration and the effect of inlet velocity in the output variables considered, the temperature and of mass fraction of C distributions are presented below for $Y_A = Y_B = 0.05$ with $v = 0.01 m \cdot s^{-1}$, $Y_A = 0.05$ and $Y_B = 0.15$ with $v = 1.5 m \cdot s^{-1}$, $Y_A = 0.15$ and $Y_B = 0.05$ with $v = 0.1 m \cdot s^{-1}$.

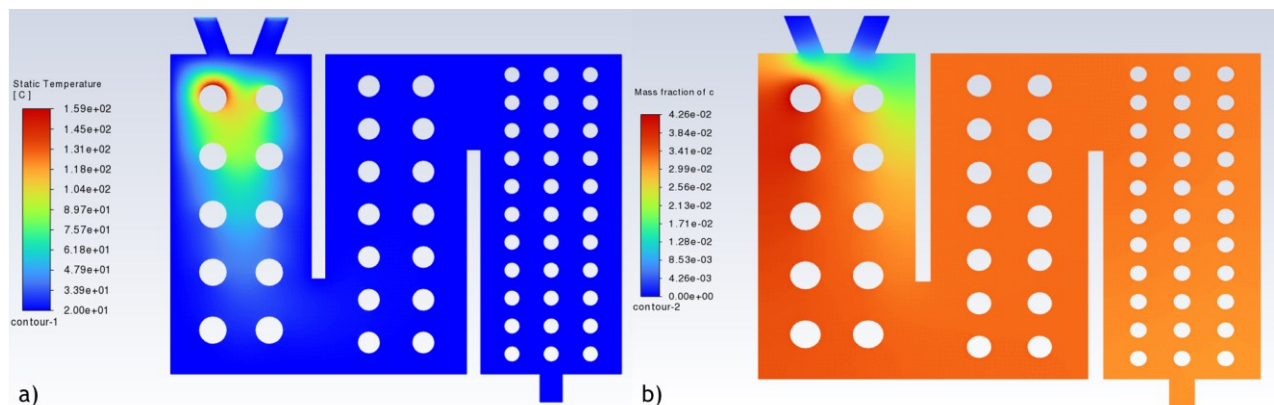


Figure 4-28: Contours resulting from the combination of $Y_A = Y_B = 0.05$ with $v = 0.01 m \cdot s^{-1}$: a) Static temperature and b) mass fraction of C.

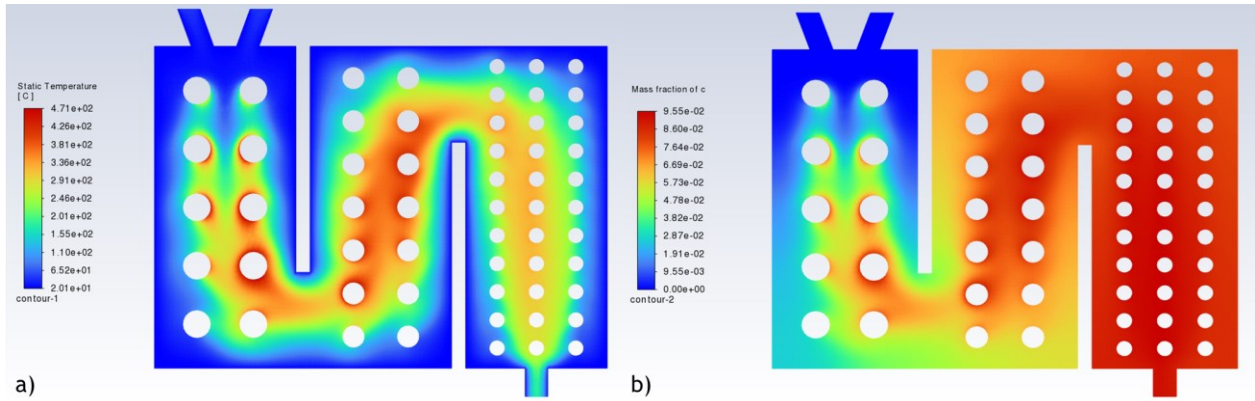


Figure 4-29: Contours resulting from the combination of $Y_A=0.15$ and $Y_B=0.05$ with $v=0.1 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.

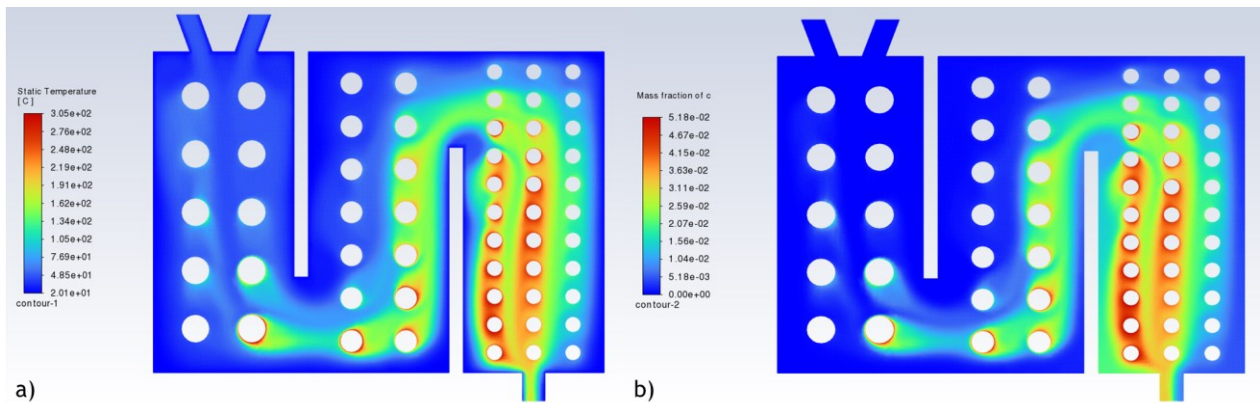


Figure 4-30: Contours resulting from the combination of $Y_A=0.05$ and $Y_B=0.15$ with $v=1.5 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.

With these images, it is perceptible the effect of velocity, with values too low the reaction only occurs in the first obstacles, while using a moderated value is possible to reach various obstacles. With a velocity too high the extension of the reactions is lower cause the residence time inside the reactor is lower, and so is the time for reaction to occur. In these images is also visible that the greater presence of A in relation to B, increases the extension of the reaction.

With Figure 4-27, and with the contours presented above, is possible to the average T_{out} increases in agreement with the increase of the inlets velocity, because the reaction takes place progressively later, so the heat produced by the reaction spends less time inside the reactor, gradually suffering fewer convective losses.

With all these figures mentioned before is also noticeable that there is a very significant decrease in the average $Y_{C/\text{out}}$ with the rise of the velocity from 0.1 to 1.5 , however the values of T_{max} for these two velocities are very similar. As explained previously, the T_{max} indicates the point with highest C formation, and for $v=0.1 \text{ m}\cdot\text{s}^{-1}$ and $1.5 \text{ m}\cdot\text{s}^{-1}$, that point is very similar, however for $v=0.1 \text{ m}\cdot\text{s}^{-1}$ that point of maximum C formation occurs more frequently, as seen in the contours, resulting in higher values of average $Y_{C/\text{out}}$. For $v=0.1 \text{ m}\cdot\text{s}^{-1}$, the point of maximum C formation occurs more often because the residence time is much higher than for $v=1.5 \text{ m}\cdot\text{s}^{-1}$.

5. Conclusions

The present thesis is framed on an ongoing collaboration between two research groups from the Associate Laboratory ALiCE regarding synergies of CFD tools with 3D printing applied to the study of catalytic reactors. The main step forward of this work was the simultaneous application of the energy equation and surface wall reaction (illustrating the presence of a catalyst) in the CFD model. This simulation approach allowed to achieve some insights about the effects of reaction exothermicity and the presence of an external cooling medium. This achievement is highly relevant since it opens the possibility for deeper studies in non-isothermal systems.

At the beginning of this thesis, a simple sketch of a small vessel with two inlets and some internal circular obstacles was designed. Afterwards, a mesh independence test was successfully performed, and the chosen mesh was composed by 96588 elements with refined regions near the walls where higher temperature and concentrations gradients were expected.

The familiarization with the software tools applied (Ansys V24 package) was made through a preliminary study of the effects of combining the production of heat flux in the internal surface walls and convection in the exterior medium of the vessel. The results obtained permitted to conclude that, within the laminar range, lower values of the inlet velocity led to higher temperature levels in the vessel, as the residence time of the fluid is higher which means longer exposure time the heat produced.

The following step was to validate the applicability of the CFD methodology with an experimental approach feasible with our available resources. So, a vessel was produced by SLA 3D printing techniques and step input tracer experiments were performed on it. For this purpose, a new design with a little more complexity was considered - it included more circular obstacles with different sizes that were divided by three defined zones with different porosities. This validation step was also completed with success as the experimental and numerical Danckwerts F curves for different inlet flow rates were very similar.

The final part of this work concerned a numerical study of a small non-isothermal reactor involving illustrative reactions with different levels of exothermicity, i.e., with heat of reaction around $-30 \text{ kJ}\cdot\text{mol}^{-1}$ and $-302 \text{ kJ}\cdot\text{mol}^{-1}$.

Relatively to the reaction with heat of reaction around $-30 \text{ kJ}\cdot\text{mol}^{-1}$, the effect of increasing the velocity caused a decrease in the output variables and significant changes in the preferential pathway of the flow. The increase of the convection coefficient, as expected promoted the decrease in average T_{out} , T_{max} and T_{min} , specially in T_{min} . The influence on the average Y_C was not detectable. Relatively to the impact of the variation of the inlets composition, the higher the values of the mass fraction of Y_A and Y_B , the higher the average Y_C in the outlet. At last, was studied the influence of the temperature in the inlet, the increase

in its value caused a slight increase in average Y_C in the outlet and did not significantly change the values of the average T_{out} , T_{max} and T_{min} as they present values similar to the inlet temperatures.

Relatively to the reaction with heat of reaction around $-300 \text{ kJ}\cdot\text{mol}^{-1}$, firstly, was studied the influence of the external convection coefficient was also addressed. It was showed that it is possible to maintain the conversion of the reaction while decreasing the temperatures inside the reactor. While testing the effects of convection with different inlet compositions, it was noticeable that the lower the mass fraction of reagents, the latter the reaction occurs.

The Arrhenius equation could include a temperature dependent term defined by T^a - frequently called as modified Arrhenius equation. During the analysis of the effect of this exponent a , it was possible to conclude that for values of 0 and 1, the behaviour of the system was very similar when operating at higher inlet velocities. Relatively to $a = -1$, it promoted a higher decrease in the average Y_C , in the average T_{out} and in T_{max} . With these same simulations was also studied the effect of the inlets temperatures and was noted that for values between 5 and 50 °C, the effect was unnoticeable. Other variable tested was the increase of the velocity, which caused the decrease of the output variables evaluated.

Finally, a set of simulations with more diluted inlet streams were performed, i.e., less aggressive in terms of generated heat, and was noticeable that the reaction does not develop well while using too low values of inlet compositions (0.05) combined with very low velocities ($0.01 \text{ m}\cdot\text{s}^{-1}$). It was also confirmed that too high values of velocity do not allow sufficient residence time for the reagents conversion to occur, and that higher feed of the reagent A favours the conversion. Acceptable results were obtained for $Y_A = 0.15$, $Y_B = 0.05$, $v = 0.1 \text{ m}\cdot\text{s}^{-1}$, $k_0 = 100 \text{ m}^3\cdot\text{kgmol}^{-1}\cdot\text{s}^{-1}$, $E_a = 50 \text{ kJ}\cdot\text{mol}^{-1}$, $T_{in1} = T_{in2} = 50 \text{ °C}$, $a = 0$ and $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot\text{°C}^{-1}$.

Regarding the prospects for future work, and based on the experience gathered during this thesis, some lines of action can be easily pointed out: 1) deepen the presented preliminary study by including the effect of design geometrical parameters and focusing on an optimization of the reactant conversion and temperatures distributions; 2) implement and explore the influence of catalyst properties (such as surface per unit volume); 3) apply the present approach to a real non-isothermal system with well-defined kinetic data and physical properties values; 4) use SLS 3D printing (or equivalent technique) to produce metal structures and extend the validation range to experiments with high temperature.

6. Assessment of the work done

6.1. Objectives Achieved

All the goals were achieved even though there had to be made some adaptations. The learning phase was done with a lot of success and the tracer simulations replicated the experimental results in a very acceptable way. Relatively to the reactions, it was not possible to simulate real reactions in the surface walls of obstacles, and make them converge without errors, however a fictitious exothermic reaction was created, and the parameters of reaction and of the inlet conditions were variated and it was possible to study the sensibilities of the program and the effects of each parameter in the average $Y_{C/out}$, in the average T_{out} and in T_{max} .

6.2. Contribution to the Sustainable Development Goals

Table 6-1: Contributions of the work for the Sustainable Development Goals and respective indicators.

SDG	Target	Contribution	Indicators of performance and metrics
8	2	Enabling a technological upgrade by combining CFD with 3D printing to design customised operation units.	Decrease in process cost by optimization of design and by only acquiring the optimized model.
9	5	Enhance in scientific research by proving that tracer experiments are an exemplar validation method for the relation between simulation and experimental data.	The deviation between the two results was not very perceptible.
12	2	The use of reverse stereolithography, consumes only the resin needed to incorporate the structure, avoid the creation of residues.	Reduce in residuals by using additive manufacturing.

6.3. Final Assessment

My first assessment of this work is a desire for additional time to further explore the functionalities of the surface reaction in time transient. Nonetheless, this experience has provided valuable insight into the frustrating and time consuming nature of simulation, particularly when encountering challenging bugs. Despite these difficulties, it was a rewarding experience, offering a comprehensive understanding of how Fluent operates, especially regarding the use of Relaxation Factors and of different methods to achieve simulation convergence. Relatively to Design Modeler, I acquired proficiency in utilizing many of the available tools during the sketching process of the 3D model intended for printing. Regarding

Meshing, I effectively applied methods, Inflation and Edge Sizing and gained an understanding of the effect of each parameter on the generated mesh. It was even possible to understand the value limits of each parameter for mesh readability in Fluent, as well as the constraints of conjugating different meshing tools. A significant achievement of this thesis was the opportunity to deepen my knowledge about 3D printing, including the experience of printing a design I created, thereby acquiring a valuable new skill.

7. References

- [1] D. F. Fletcher, "The future of computational fluid dynamics (CFD) simulation in the chemical process industries," *Chemical Engineering Research and Design*, vol. 187, pp. 299-305, 2022.
- [2] F. Hosseinpour and H. Hajhosseini, "Importance of simulation in manufacturing," *World Academy of Science, Engineering and Technology*, vol. 51, no. 3, pp. 292-295, 2009.
- [3] D. Pashchenko, "Effect of the geometric dimensionality of computational domain on the results of CFD-modeling of steam methane reforming," *International Journal of Hydrogen Energy*, vol. 43, no. 18, pp. 8662-8673, 2018.
- [4] I. D. Amores, J. González-Gutiérrez, I. M. García, J. M. Franco, and C. Gallegos, "3D printing-Present and future-A Chemical Engineering perspective," *Chemical Engineering Research and Design*, vol. 187, pp. 598-610, 2022.
- [5] J. Madabhushi, A. Kalamdani, A. Tyagi, and N. Mehta, "3D printing in chemical engineering: A review," *World Journal of Advanced Engineering Technology and Sciences*, vol. 7, no. 1, pp. 086-095, 2022.
- [6] H. Quan, T. Zhang, H. Xu, S. Luo, J. Nie, and X. Zhu, "Photo-curing 3D printing technique and its challenges," *Bioactive materials*, vol. 5, no. 1, pp. 110-115, 2020.
- [7] A. Della Bona, V. Cantelli, V. T. Britto, K. F. Collares, and J. W. Stansbury, "3D printing restorative materials using a stereolithographic technique: a systematic review," *Dental Materials*, vol. 37, no. 2, pp. 336-350, 2021.
- [8] LEPABE. "25 years of Science and Innovation." <https://www.lepabe.fe.up.pt/> (accessed 2024).
- [9] CEFT. "Energy. Fluids. Science." <https://ceft.fe.up.pt/> (accessed 2024).
- [10] U. Manual, "ANSYS FLUENT 12.0," *Theory Guide*, vol. 67, 2009.
- [11] M. H. Zawawi, A. Saleha, A. Salwa, N. Hassan, N. M. Zahari, M. Z. Ramli, and Z. C. Muda, "A review: Fundamentals of computational fluid dynamics (CFD)," in *AIP conference proceedings*, 2018, vol. 2030, no. 1: AIP Publishing.
- [12] M. A. A. a. A. E. R. Luís M. Madeira, Teaching Nonideal Reactors with CFD Tools, Chemical Engineering Education, Vol. 38, No. 2, 2004, p. 154-160. (accessed).
- [13] J. E. Matsson, *An Introduction to Ansys Fluent 2023*. Sdc Publications, 2023.
- [14] J. P. Slotnick, A. Khodadoust, J. Alonso, D. Darmofal, W. Gropp, E. Lurie, and D. J. Mavriplis, "CFD vision 2030 study: a path to revolutionary computational aerosciences," 2014.
- [15] O. Klenov and A. Noskov, "Computational fluid dynamics in the development of catalytic reactors," *Catalysis in Industry*, vol. 3, pp. 331-349, 2011.
- [16] I. Karakurt and L. Lin, "3D printing technologies: techniques, materials, and post-processing," *Current Opinion in Chemical Engineering*, vol. 28, pp. 134-143, 2020.
- [17] S. Bettermann, F. Kandelhard, H.-U. Moritz, and W. Pauer, "Digital and lean development method for 3D-printed reactors based on CAD modeling and CFD simulation," *Chemical Engineering Research and Design*, vol. 152, pp. 71-84, 2019.
- [18] E. Leventaki, F. M. Baena-Moreno, G. Sardina, H. Ström, E. Ghahramani, S. Naserifar, P. H. Ho, A. M. Kozłowski, and D. Bernin, "In-line monitoring of carbon dioxide capture with sodium hydroxide in a customized 3D-printed reactor without forced mixing," *Sustainability*, vol. 14, no. 17, p. 10795, 2022.
- [19] B. Gutmann, M. Köckinger, G. Glotz, T. Ciaglia, E. Slama, M. Zdravec, S. Pfanner, M. C. Maier, H. Gruber-Wölfler, and C. O. Kappe, "Design and 3D printing of a stainless steel reactor for continuous difluoromethylations using fluoroform," *Reaction Chemistry & Engineering*, vol. 2, no. 6, pp. 919-927, 2017.
- [20] *Integration of Tracing with Computational Fluid Dynamics for Industrial Process Investigation - Final Report of a Coordinated Research Project 2001-2003*. Vienna: INTERNATIONAL ATOMIC ENERGY AGENCY, 2004.
- [21] L. Y. C. P. Hojo, R. V. de Paula Rezende, S. R. Lautenschlager, and L. P. Sabogal-Paz, "Household slow sand filters operating in continuous and intermittent flows: computational fluid dynamics simulation and validation by tracer experiments," *Chemical Engineering Science*, vol. 247, p. 117058, 2022.

- [22] A. M. a. F. D. M. Luís M. Madeira, Teaching Laminar-Flow Reactors: From Experimentation to CFD Simulation, *The International Journal of Engineering Education*, Vol. 22, No. 1, 2006, p. 188-196. (accessed.
- [23] Formlabs. "Form 3+." <https://formlabs.com/3d-printers/form-3/> (accessed 2024.
- [24] Formlabs. "Materials Catalog. Advanced Resins and Powders for 3D Printing." <https://formlabs.com/materials/> (accessed 2024.
- [25] Formlabs. "Form Cure." <https://formlabs.com/store/post-processing/form-cure/> (accessed 2024).
- [26] U. Nations. "The 17 Goals." <https://sdgs.un.org/goals> (accessed.
- [27] J. H. Lienhard, *A heat transfer textbook*. Phlogistron, 2005.
- [28] F. P. Incropera, D. P. DeWitt, T. L. Bergman, and A. S. Lavine, *Fundamentals of heat and mass transfer*. Wiley New York, 1996.

Annex A - Sustainable Development Goals



Figure Annex A. 1: Symbols of the SDGs associated to this thesis.^[26]

Appendix A- Dimensions of the 3 sketches used in this thesis

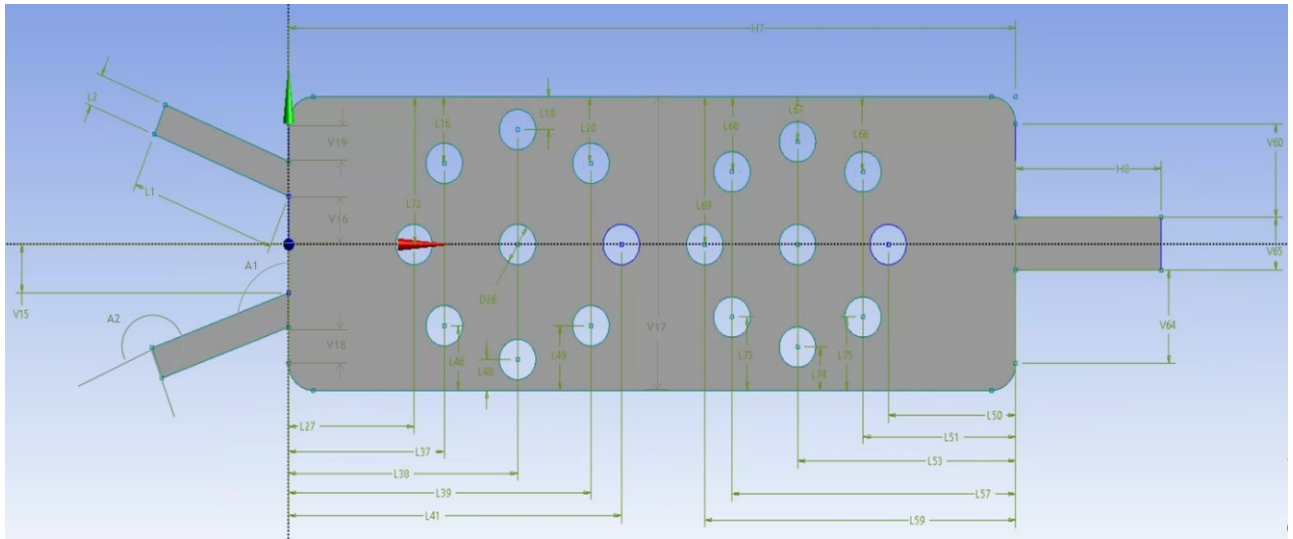


Figure Appendix A. 1: Zoom of the sketch of Design A.

Table Appendix A. 1: Dimensions corresponding to Figure Appendix A. 1.

A1	70 °	L38	15.75 cm
A2	270 °	L39	20.79 cm
V15	3 cm	L41	22.88 cm
V16	3 cm	L46	4.02 cm
V17	18.32 cm	L48	1.93 cm
V18	cm	L49	4.02 cm
V19	cm	L50	8.77 cm
V60	5.8 cm	L51	10.5 cm
V65	3.26 cm	L53	15 cm
V64	5.8 cm	L57	19.51 cm
D26	2.5 cm	L59	21.38 cm
H7	50 cm	L66	4.66 cm
H8	10 cm	L67	2.79 cm
L1	10 cm	L68	4.66 cm
L2	2 cm	L69	9.16 cm
L16	4.12 cm	L72	9.16 cm
L19	2.03 cm	L73	4.55 cm
L20	4.12 cm	L74	2.69 cm
L27	8.61 cm	L75	4.55 cm
L37	10.7 cm		

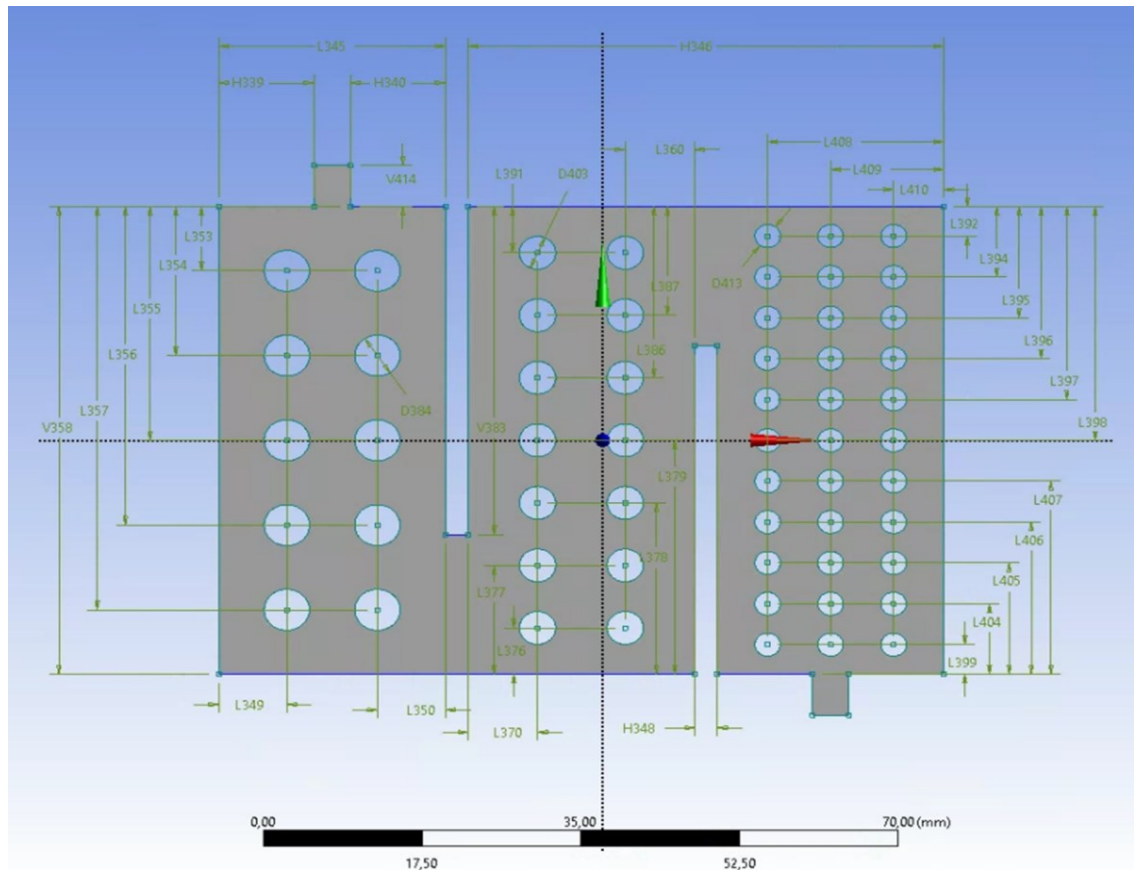


Figure Appendix A. 2: Zoom of the sketch of Design B.

Table Appendix A. 2: Dimensions corresponding to Figure Appendix A. 2.

V358	57 mm	L377	13.25 mm
V383	40 mm	L378	20.875 mm
V414	5 mm	L378	18.5 mm
D384	5 mm	L386	20.875 mm
D403	4 mm	L387	13.25 mm
D413	2.8 mm	L391	5,625 mm
H339	10.5 mm	L392	3.583 mm
H340	10.5 mm	L394	8.566 mm
H346	52.5 mm	L395	13.55 mm
H348	2.5 mm	L396	18.532 mm
L345	25 mm	L397	23.515 mm
L349	7.5 mm	L398	28.5 mm
L350	7.5 mm	L399	3.583 mm
L353	7.83 mm	L404	8.566 mm
L354	18.16 mm	L405	13.549 mm
L355	28.5 mm	L406	18.532 mm
L356	38.84 mm	L407	23.515 mm
L357	49.17 mm	L408	19.459 mm
L360	7.67 mm	L409	12.509 mm
L370	7.67 mm	L410	5.55 mm
L376	5.625 mm		

Table Appendix A. 3: Value of porosity for each section of Design B.

Section	1	2	3
r / mm	2.5	2	1.4
$\epsilon / -$	0.138	0.123	0.143

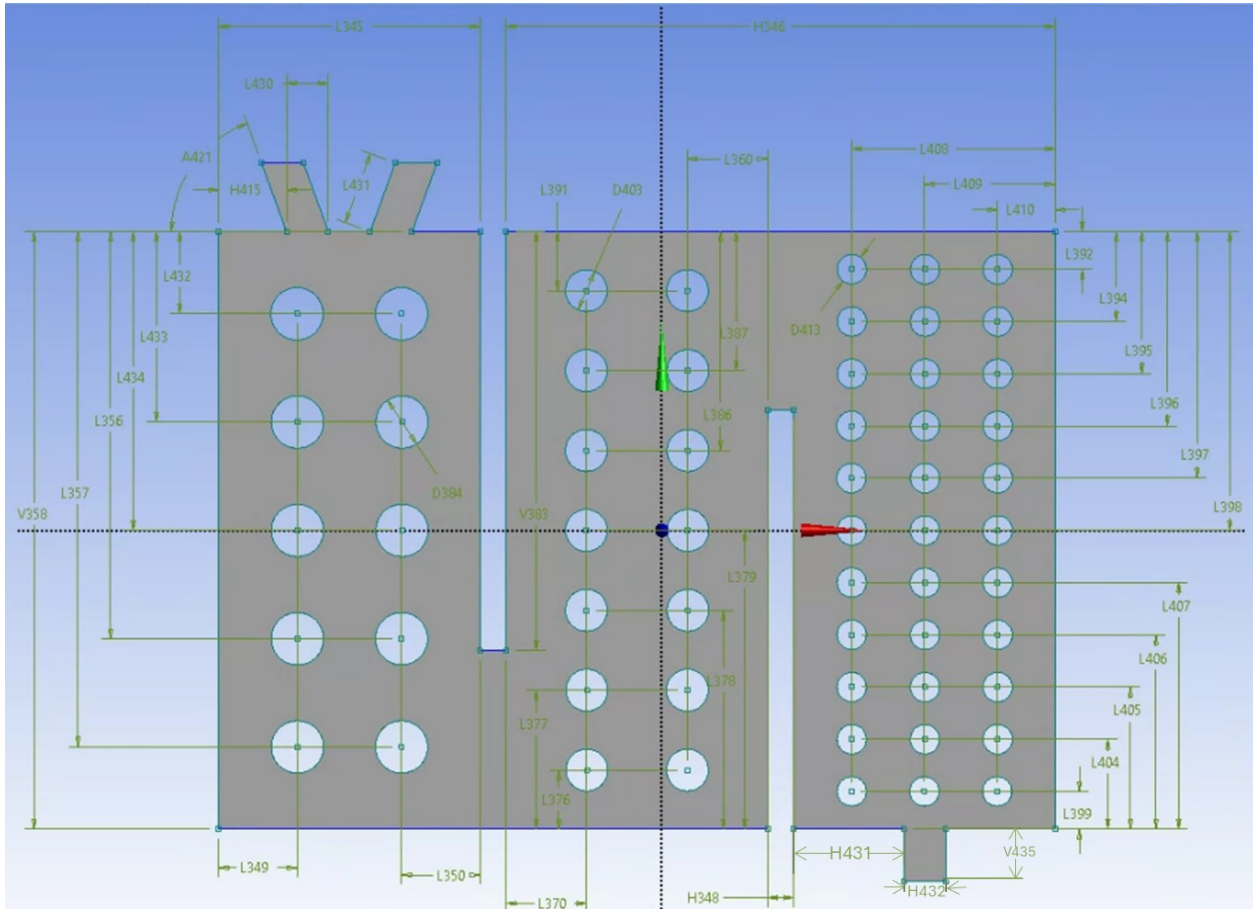


Figure Appendix A. 3: Zoom of the sketch of Design B with the inlets modifications.

Table Appendix A. 4: Dimensions corresponding to Figure Appendix A. 3

A421	70	L378	18.5 mm
V358	57 mm	L386	20.875 mm
V383	40 mm	L387	13.25 mm
V384	5 mm	L391	5.625 mm
D384	5 mm	L392	3.583 mm
D403	4 mm	L394	8.566 mm
D413	2.8 mm	L395	13.55 mm
H346	52.5 mm	L396	18.532 mm
H348	2.5 mm	L397	23.515 mm
H415	6.5 mm	L398	28.5 mm
H430	4 mm	L399	3.583 mm
H431	10.5 mm	L404	8.566 mm
H432	4 mm	L405	13.549 mm
L345	25 mm	L406	18.532 mm
L349	7.5 mm	L407	23.515 mm
L350	7.5 mm	L408	19.459 mm
L356	38.84 mm	L409	12.509 mm
L357	49.17 mm	L410	5.55 mm
L360	7.67 mm	L430	4 mm
L370	7.67 mm	L431	7 mm
L376	5.625 mm	L432	7.83 mm
L377	13.25 mm	L433	18.16 mm
L378	20.875 mm	L434	28.5 mm

Appendix B - General Workbench used for all the simulations

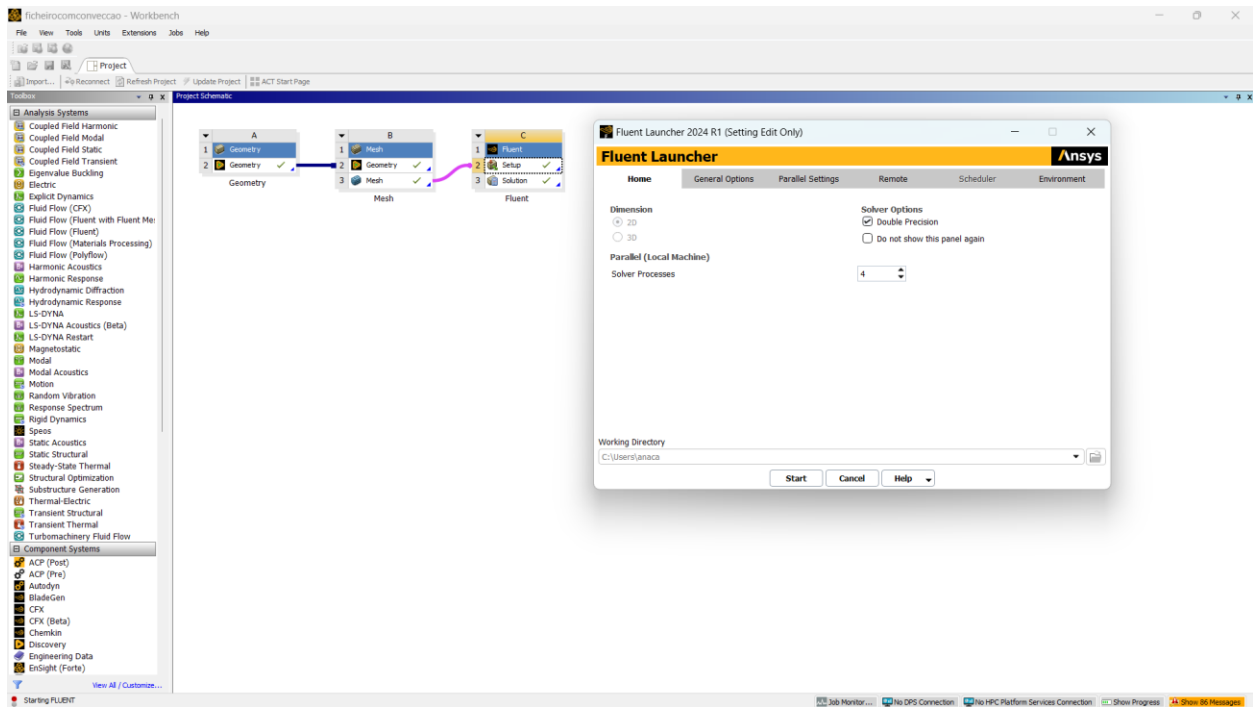


Figure Appendix B. 1: Workbench used for all the simulations.

Appendix C - Main page of Fluent case

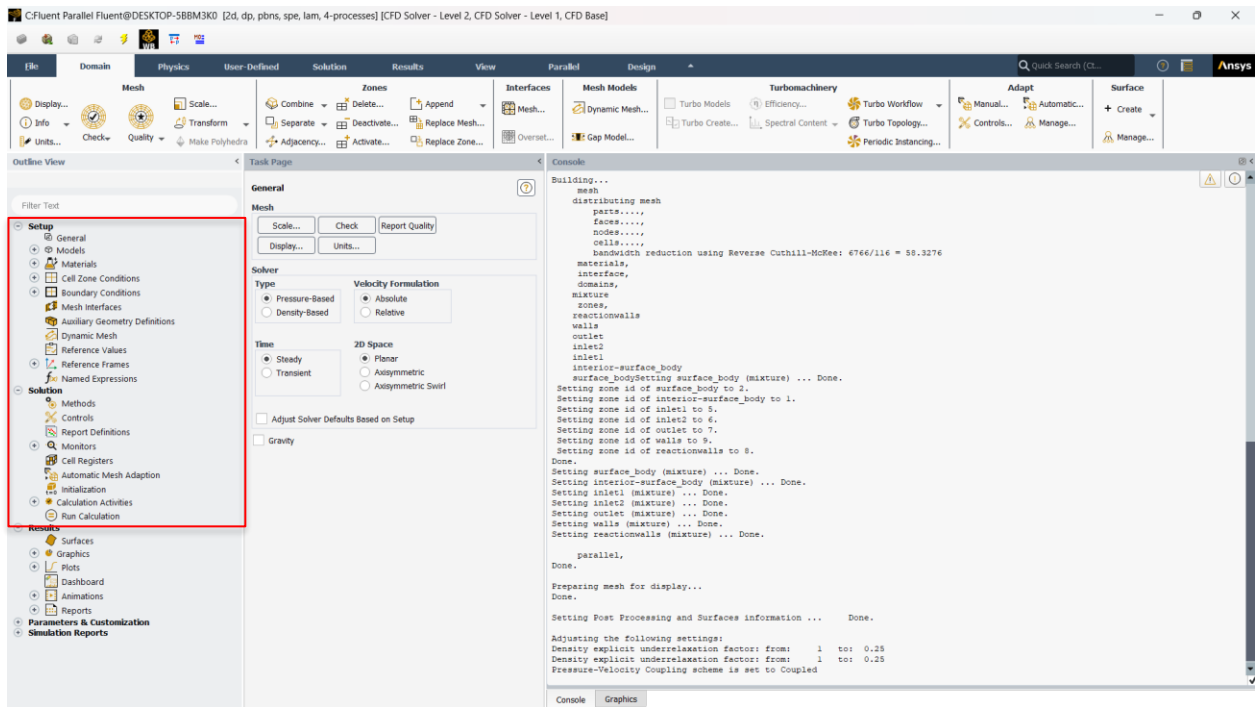


Figure Appendix C. 1: Fluent front page.

Appendix D - Example of the creation of material N₂

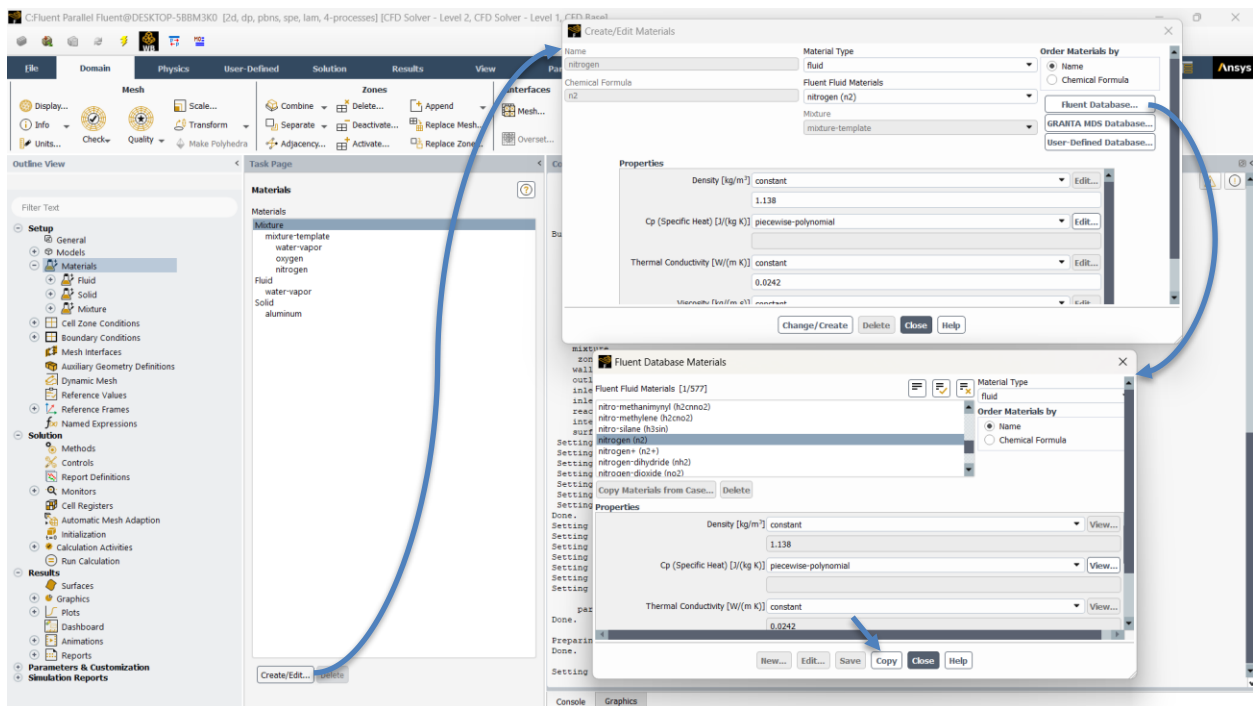


Figure Appendix D. 1; Tutorial about how to create a material in Fluent.

Appendix E - How to define the boundaries conditions

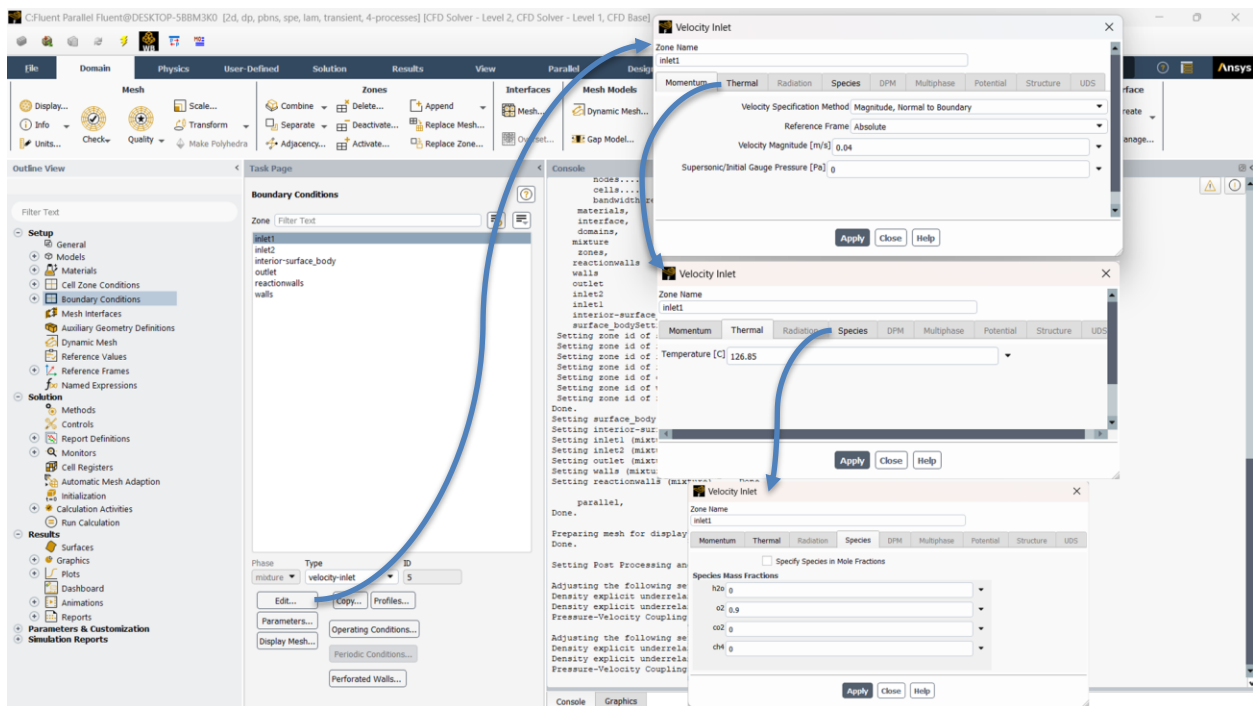


Figure Appendix E. 1: Tutorial about how to define the inlet conditions in Fluent.

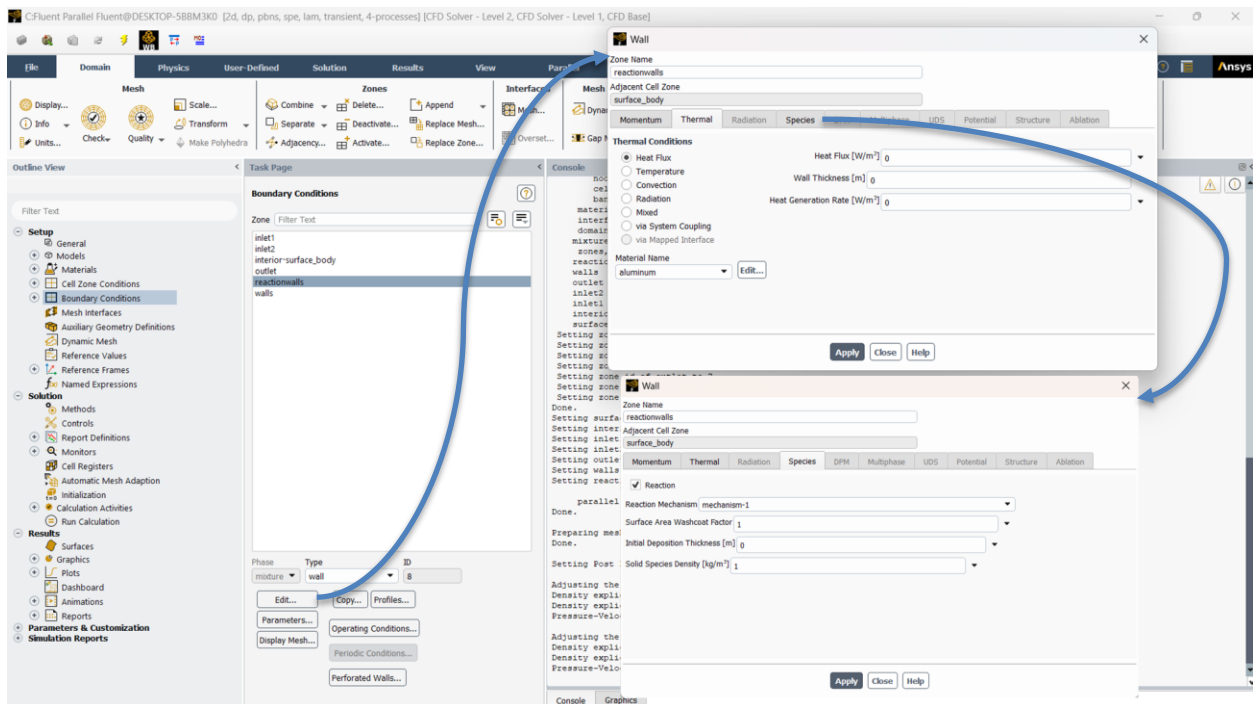


Figure Appendix E. 2: Tutorial about how to define the obstacles walls conditions in Fluent.

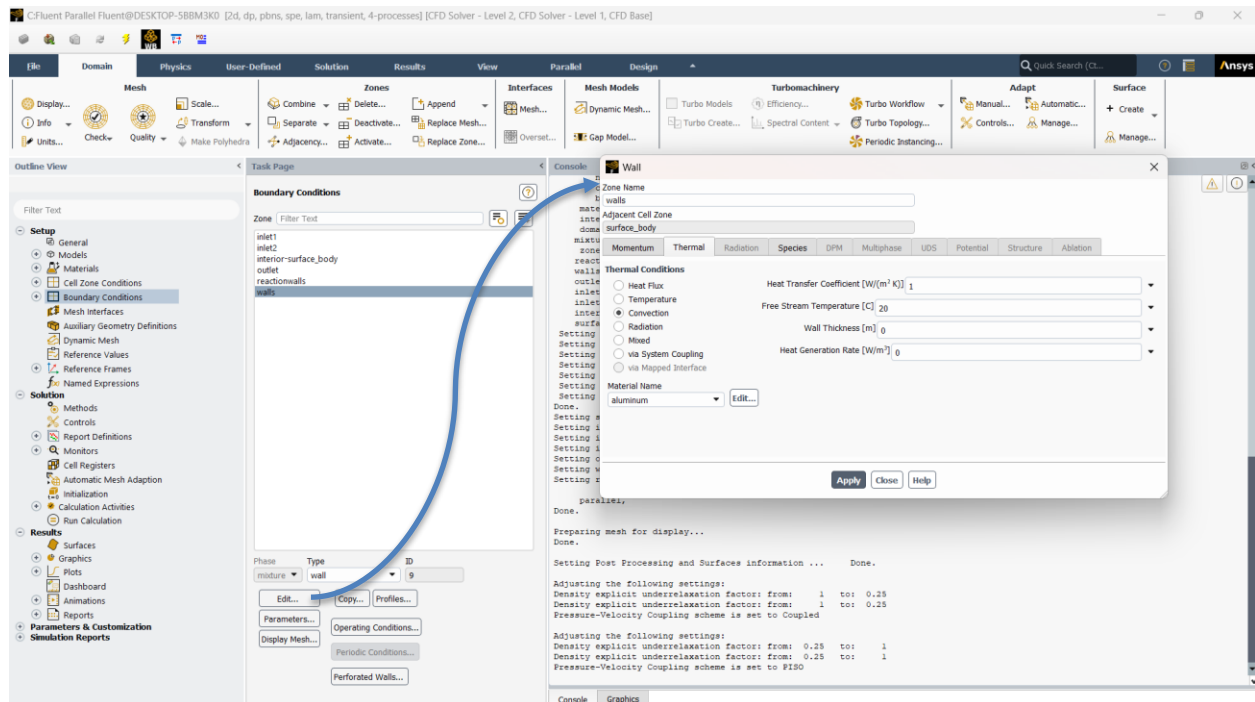


Figure Appendix E. 3: Tutorial about how to define the exterior walls conditions in Fluent.

Appendix F - How to define a reaction

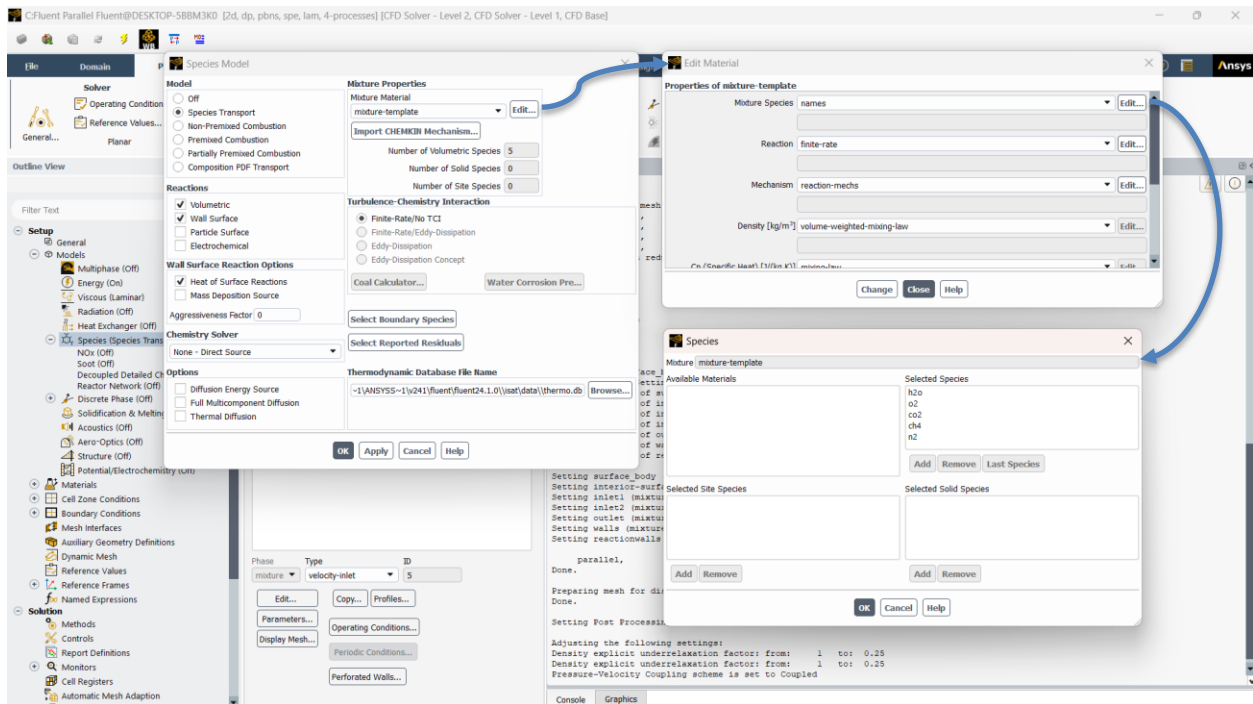


Figure Appendix F. 1: Tutorial about how to create a mixture in Fluent.

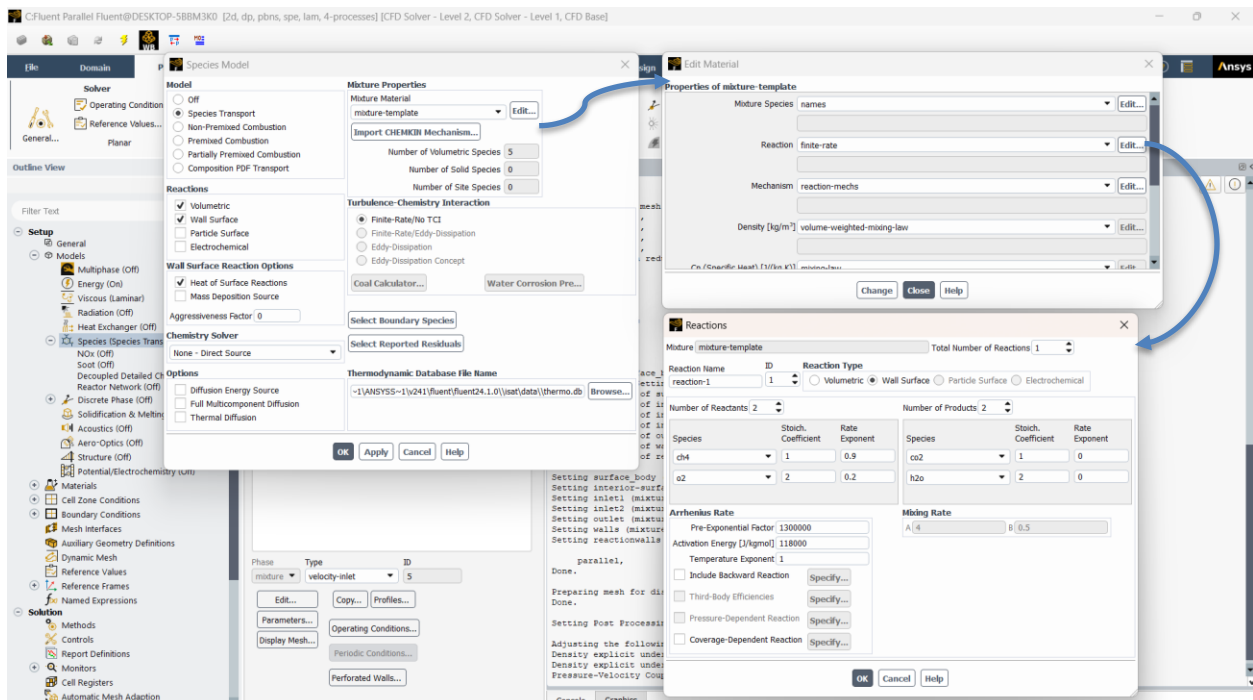


Figure Appendix F. 2: Tutorial about how to define a reaction in Fluent.

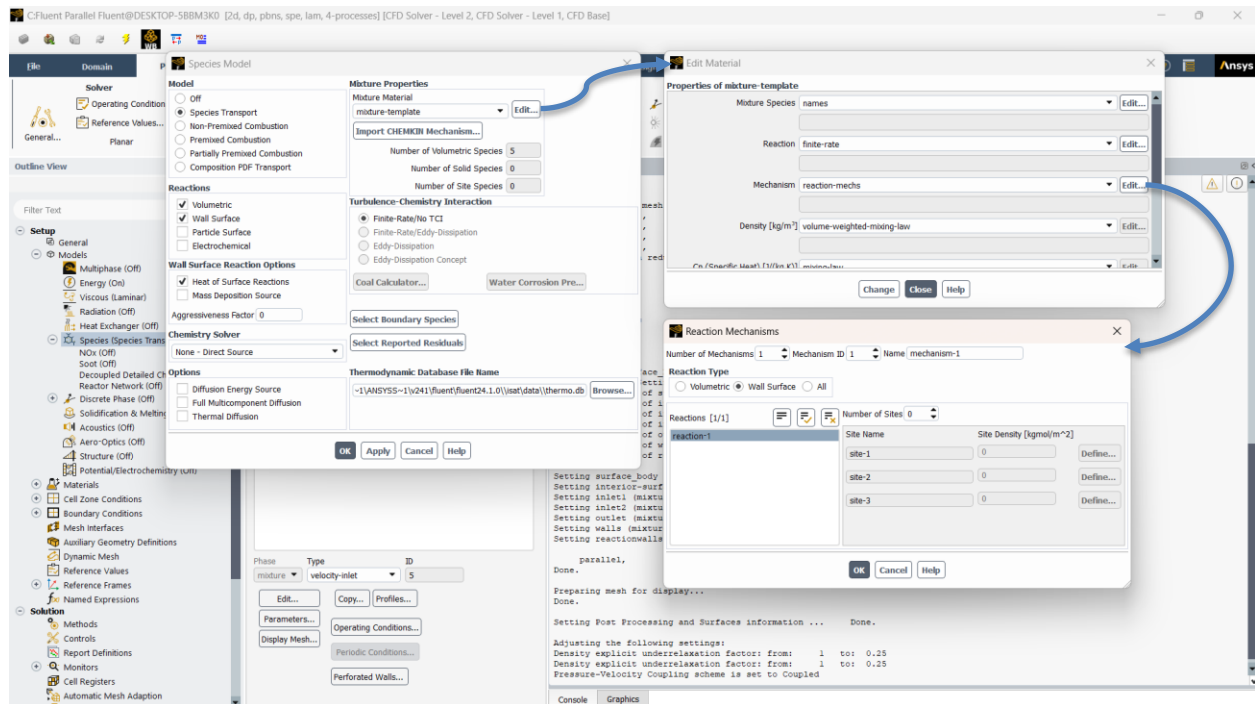


Figure Appendix F. 3: Tutorial about how to define a mechanism of reaction in Fluent

Appendix G - How to define the depth of the sketch in Fluent

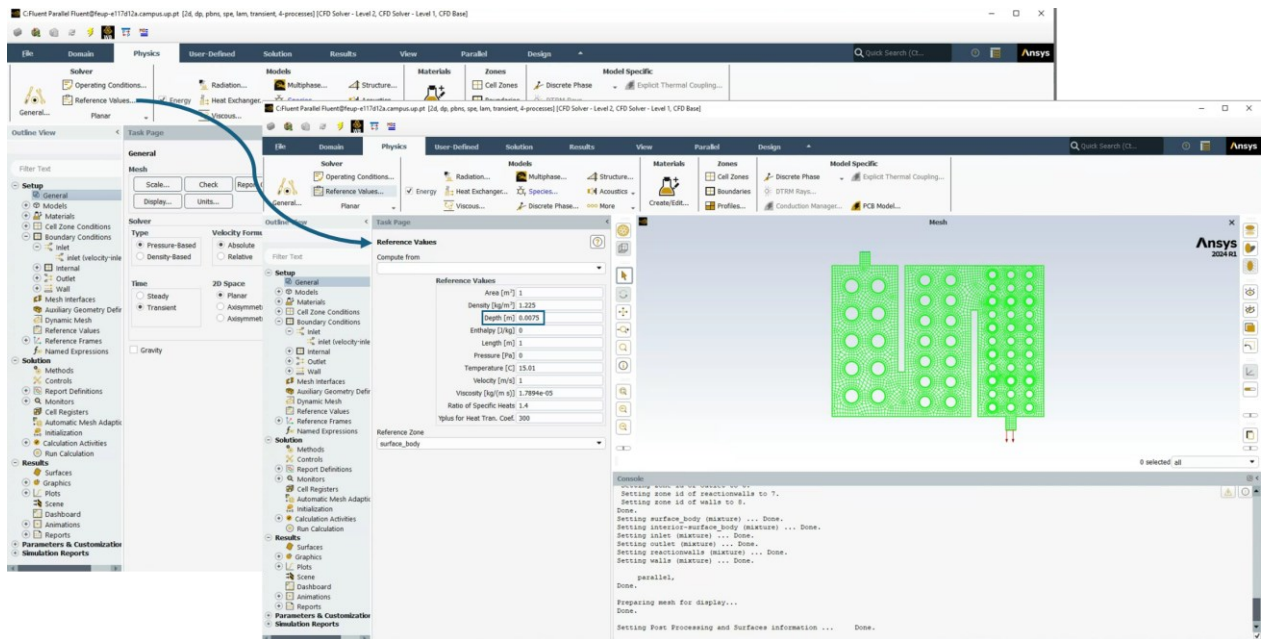


Figure Appendix G. 1: Tutorial about how to define the depth of the reactor.

Appendix H - Properties of the materials used of the two exothermic reactions

Table Appendix H. 1: Properties of the materials used to simulate the first exothermic reaction.

Material	Properties			
	$\rho / \text{kg}\cdot\text{m}^{-3}$	$\mu / \text{Pa}\cdot\text{s}$	$M / \text{kg}\cdot\text{mol}^{-1}$	$\Delta H / \text{J}\cdot\text{mol}^{-1}$
A	1050	1.20×10^{-3}	6.00×10^{-2}	-4.84×10^8
B	1400	7.80×10^{-2}	4.00×10^{-2}	-4.17×10^8
C	1160	5.00×10^{-3}	8.2×10^{-2}	-6.45×10^8
D	998.2	1.00×10^{-3}	1.80×10^{-2}	-2.86×10^8

Table Appendix H. 2: Properties of the materials used to simulate the second exothermic reaction.

Material	Properties			
	$\rho / \text{kg}\cdot\text{m}^{-3}$	$\mu / \text{Pa}\cdot\text{s}$	$M / \text{kg}\cdot\text{mol}^{-1}$	$\Delta H / \text{J}\cdot\text{mol}^{-1}$
A	1.00	1.72×10^{-5}	4.81×10^{-2}	5.00×10^3
B	1.30	1.92×10^{-5}	3.20×10^{-2}	0
C	2.77	1.20×10^{-5}	6.41×10^{-2}	-2.97×10^5
D	1.14	1.66×10^{-5}	2.80×10^{-2}	0

Appendix I - Calculations necessary to perform the simulations described in this document

For the learning phase the 2 gases used were CH₄ and O₂, on Table Appendix I. 1 is presented the physical properties of those materials collected from the Fluent Database:

Table Appendix I. 1: Physical properties of N₂ and O₂ obtained from Fluent Database.

	$\rho / \text{kg}\cdot\text{m}^{-3}$	$\mu / \text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$
CH ₄	1.14	1.66×10^{-5}
O ₂	1.30	1.92×10^{-5}

With these values was possible to obtain the velocity at each inlet using Eq. (2.10), also knowing that the size of the inlets is 0.02 m in Design A. An example of how the velocities presented in Table 3-2 were calculated is shown in Eq. (0.1):

$$v = \frac{\text{Re} \cdot \mu}{\rho \cdot e} = \frac{100 \times 1.66 \times 10^{-5}}{1.14 \times 0.02} = 7.31 \times 10^{-2} \text{ m s}^{-1} \quad (0.1)$$

For the tracer experiments, the physical properties of liquid water were obtained from the Fluent Database, and are represented in Table Appendix I. 2:

Table Appendix I. 2: Physical properties of liquid water obtained from Fluent Database.

	$\rho / \text{kg}\cdot\text{m}^{-3}$	$\mu / \text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$
H ₂ O liquid / tracer	998.20	1.00×10^{-3}

For the tracer experiments made with Design A, the procedure to obtain the velocity in the inlets (shown in Table 3-6) was the same as demonstrated in Eq. (0.1) considering Table Appendix I. 2.

For the calculation of the velocities for simulating the replications of the laboratorial assays (shown in Table 3-6), it was necessary to take into account that the printed design had a cylindrical inlet opposed to the simulation sketch that had a parallelepiped inlet (Design B). Knowing that the 3D printed structure had 3.09 mm of radius, it is feasible to calculate it is area. Having the inlet area calculated and considering the flow rates presented in Table 3-4, it is possible to calculate the velocity for Fluent using Eq. (0.2). Below is an example for $Q = 3.47 \times 10^{-3} \text{ m}^3\cdot\text{s}^{-1}$:

$$v = \frac{Q}{A} = \frac{3.47 \times 10^{-3}}{(3.09^2 \times \pi) \times 10^{-6}} = \frac{1.04 \times 10^{-7}}{3.00 \times 10^{-5}} = 3.47 \times 10^{-3} \text{ m} \cdot \text{s}^{-1} \quad (0.2)$$

Still about the replication simulations, even though the Designs are sketched in 2D, Fluent assumes a value of depth for each draw, so it was necessary to change it because for the flow fluxes to maintain the same value with the inlet geometry change, its necessary to calculate the correct depth. This calculation is presented in Eq. (0.3), using the values from example above:

$$l = \frac{Q}{v \cdot e} = \frac{1.04 \times 10^{-7}}{3.47 \times 10^{-3} \times 4 \times 10^{-3}} = 7.50 \times 10^{-3} \text{ m} \quad (0.3)$$

Then, to obtain the Reynolds number of the flow it was applied Eq. (2.10) considering the properties of Table Appendix I. 2. The demonstration of this calculation, for the values of the example above are featured in Eq. (0.4).

$$\text{Re} = \frac{\rho \cdot e \cdot v}{\mu} = \frac{998.20 \times 4 \times 10^{-3} \times 3.47 \times 10^{-3}}{1.00 \times 10^{-3}} = 13.813 \quad (0.4)$$

Even though the Designs were sketched in 2D, Fluent assumes a value of depth for each draw (1 m) which makes it possible to obtain values of the volume of the reactor and of the flow rate in the inlets. Those 2 values were necessary to calculate the Total Time of simulations, featured in Table 3-6, and are presented in Table Appendix I. 3:

Table Appendix I. 3: Values of the volume of the reactor and the flow rate in the inlets for each design.

	Design A				Design B and C			
Re	100	400	700	900	13.813	27.543	58.284	132.961
V / m ³	8.9 × 10 ⁻²				2.87 × 10 ⁻⁵			
Q / m ³ ·s ⁻¹	1.00 × 10 ⁻⁴	4.02 × 10 ⁻⁴	7.04 × 10 ⁻⁴	9.04 × 10 ⁻⁴	1.04 × 10 ⁻⁷	2.08 × 10 ⁻⁷	4.39 × 10 ⁻⁷	1.00 × 10 ⁻⁶

With these values and multiplying Eq. (2.9) by 5, is possible to obtain the values of Total Time featured in Table 3-6, an example of the calculation of one of the Total simulation Time is presented in Eq. (0.5):

$$5 \times \tau = 5 \times \frac{V}{Q} = 5 \times \frac{8.90 \times 10^{-2}}{1.00 \times 10^{-4}} = 4431 \text{ s} \quad (0.5)$$

In appendix A, in Table Appendix A. 3 is presented the porosity of the 3 sections of Design B, for the calculation of those porosities is necessary to consider all the data in Table Appendix I.

4. The A_T was obtained directly from Design Modeler.

Table Appendix I. 4: Values needed to calculate the porosity of each section of Design B.

Section	1	2	3
r / mm	2.5	2	1.4
N / -	10	14	33
A / mm ²	196.350	175.929	203.198
A_T / mm ²	1425		
ε / -	0.138	0.123	0.143

Having these values into consideration, is described in Eq. (0.6) how to calculate the porosities, having as example the values for section 1.

$$\varepsilon = \frac{N \cdot r^2 \cdot \pi}{A_T} = \frac{10 \times (2.5^2 \times \pi)}{1425} = \frac{196.350}{1425} = 0.138 \quad (0.6)$$

Appendix J - Photos taken of the setup used during the 3D printing process and of Preform Program

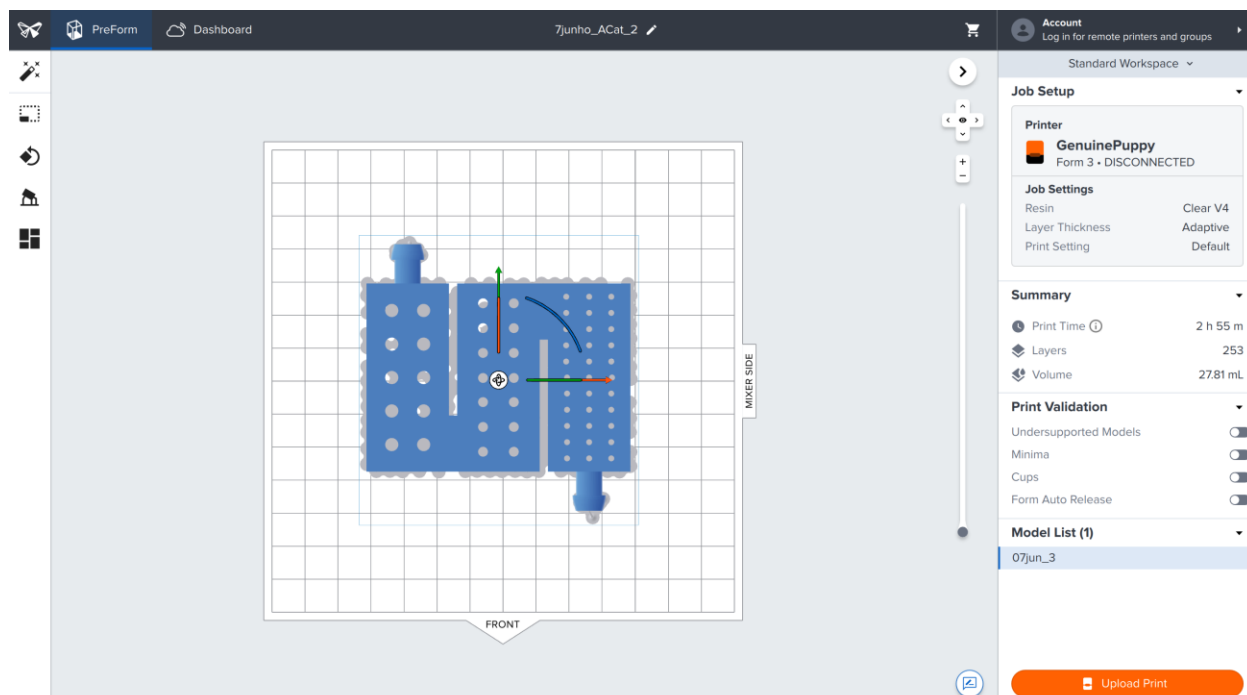


Figure Appendix J. 1: Image of the printed design and the definitions made for the 3D-printing in PreForm.

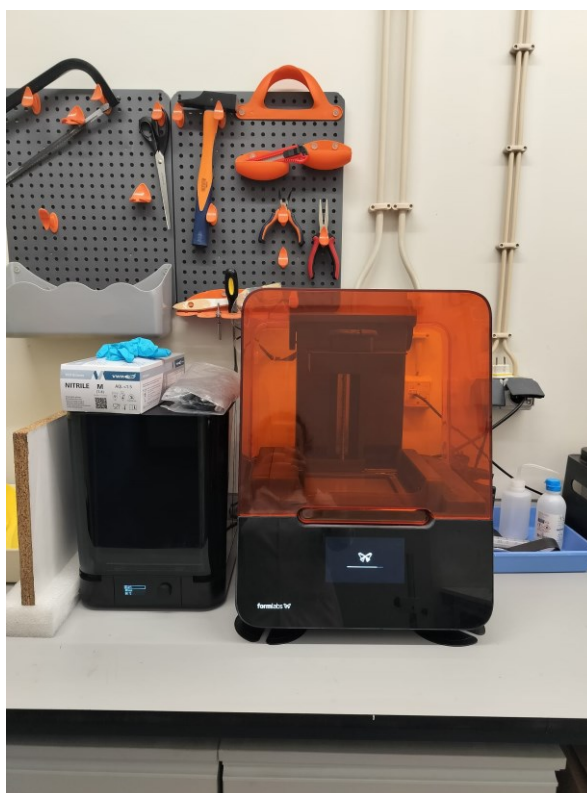


Figure Appendix J. 2: Image of Formlabs Form Cure (on the left) and Form 3 (on the right) used in the experiment.

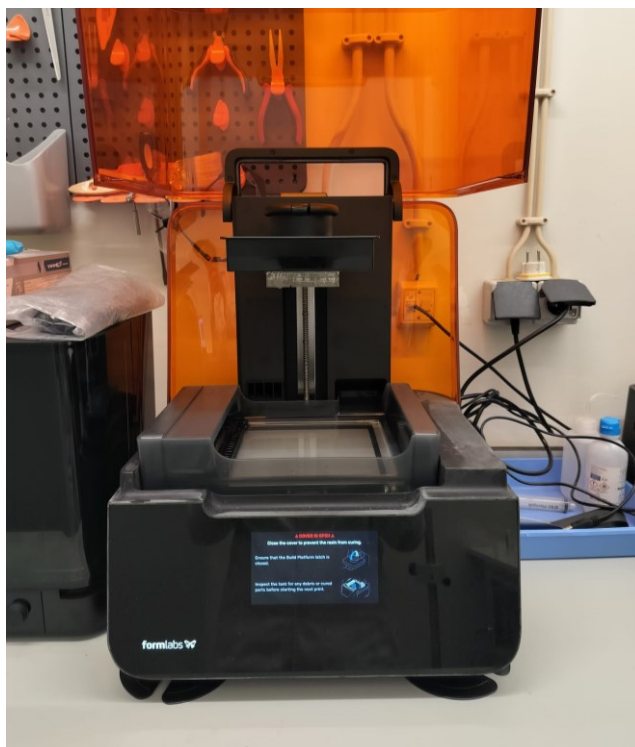


Figure Appendix J. 3: Image of the end of the printing where the piece is still attached to the removable part of the printer.

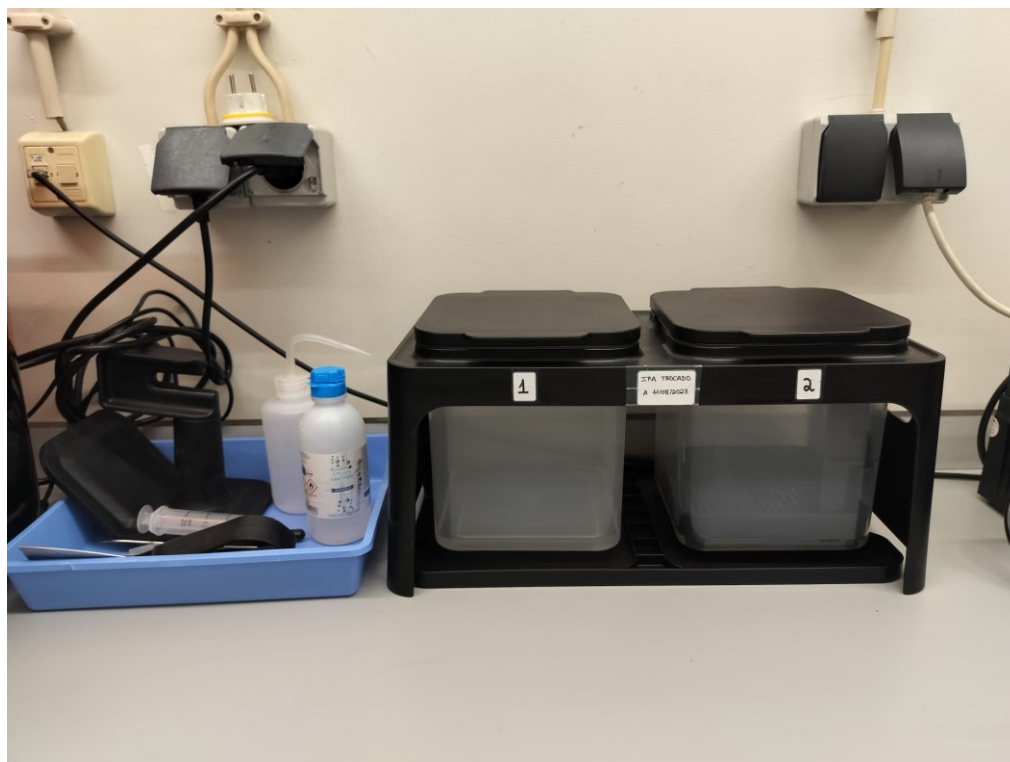


Figure Appendix J. 4: Image of the manual extraction utensils and the 2 solutions of IPA used to refine the printed piece.



Figure Appendix J. 5: Image of the printed piece while the cure device is pre-heating.

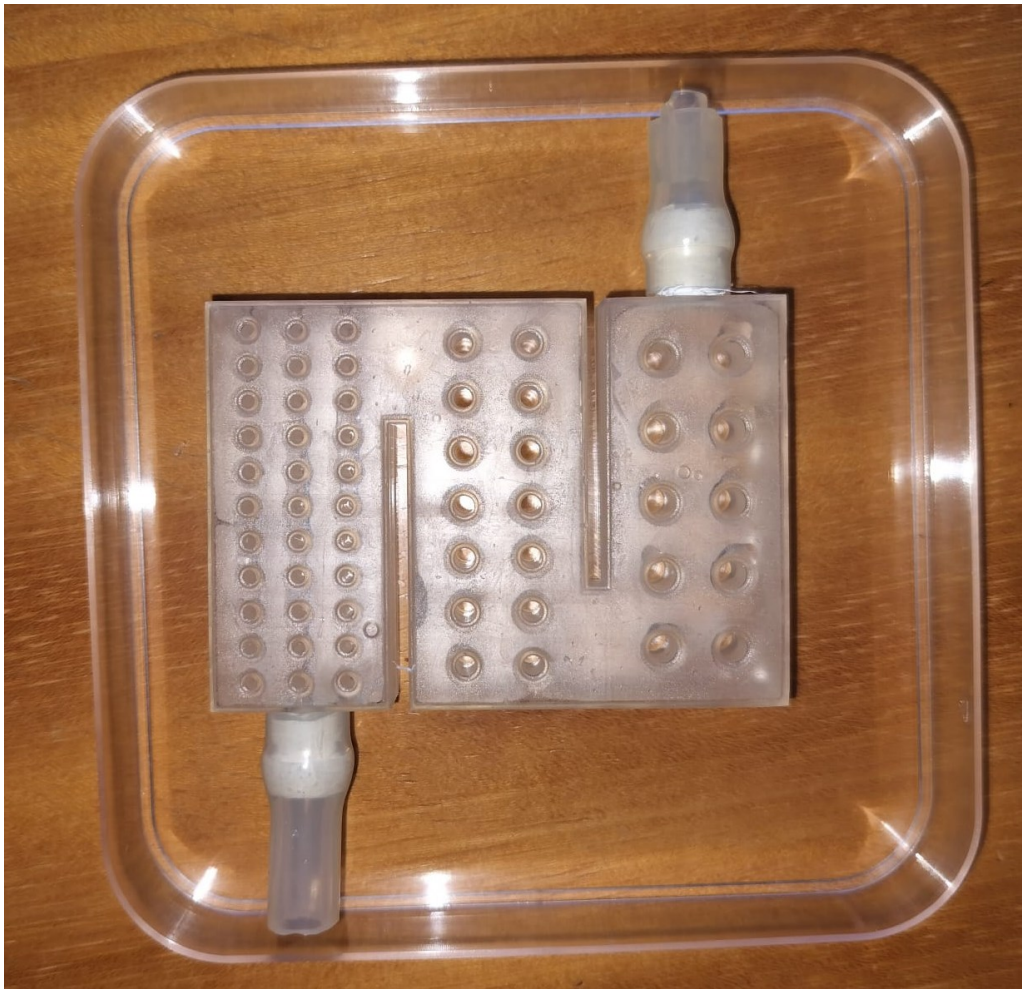


Figure Appendix J. 6: Image of the printed piece after tracer experiments with the auxiliar tubes, to prevent the leakage of fluid, in the inlet and in the outlet.

Appendix K - Results related to the mesh independency test

Observing Figure Appendix K. 1 is very perceptible the difference between Refinement type Smooth Transition and Total Thickness. However, from the data in the table is not possible to define which method is better, it is simply a matter of try and error to see which adapts better according to the element size defined, until you reach convergence in the case.

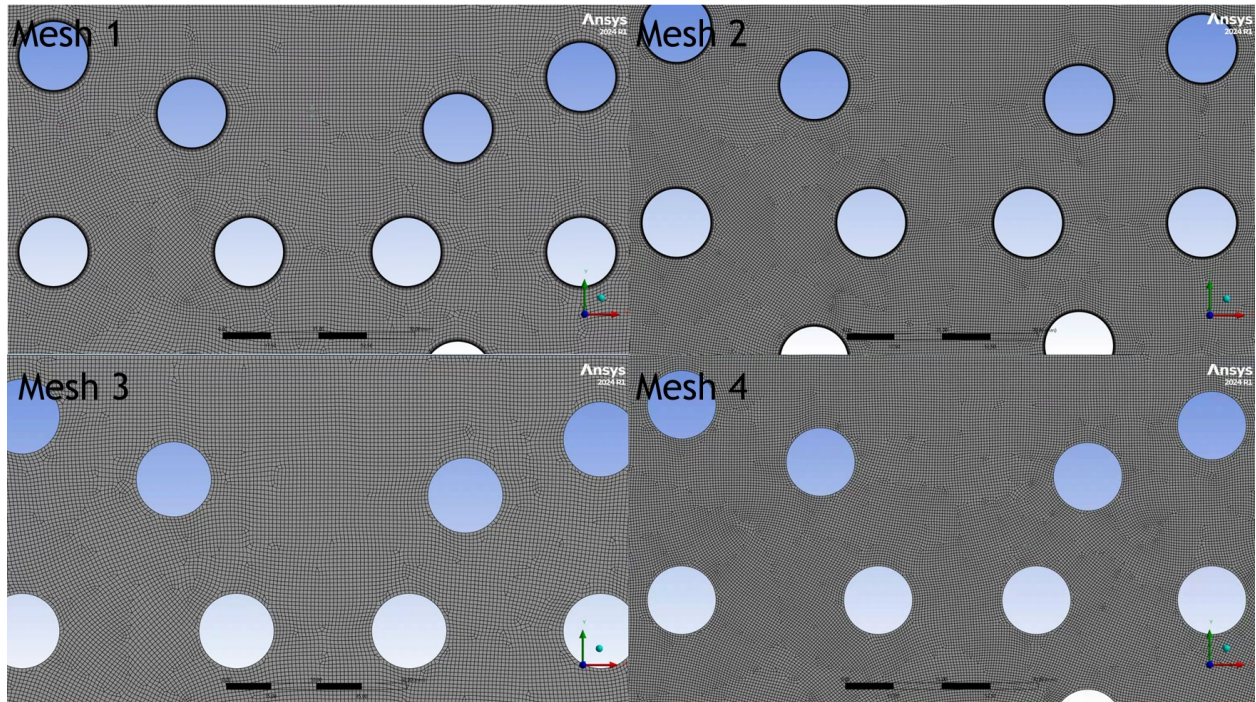


Figure Appendix K. 1: Image of the four meshes generated.

Appendix L - Contours of static temperature from the CFD learning phase

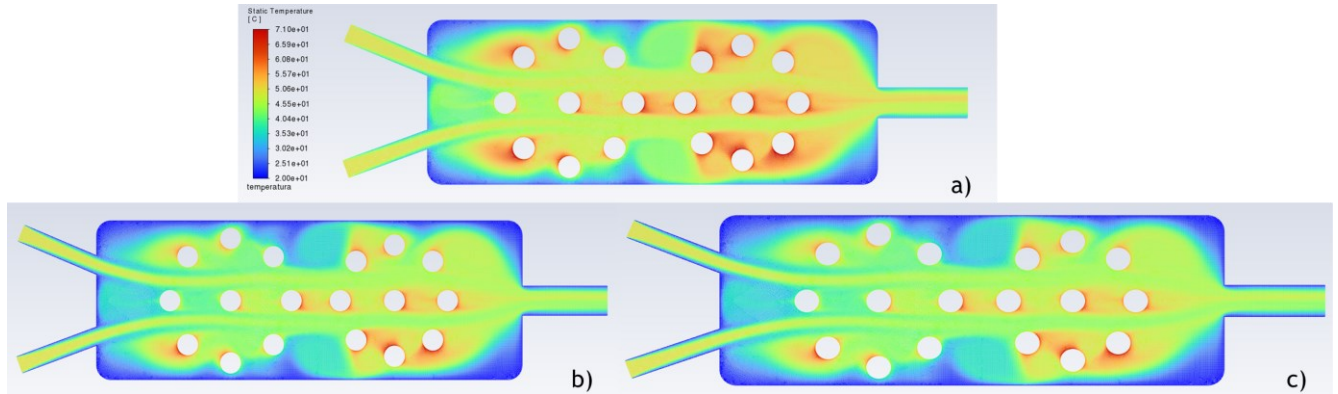


Figure Appendix L. 1: Static temperature contours with $Re = 400$ and $H_F = 50 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

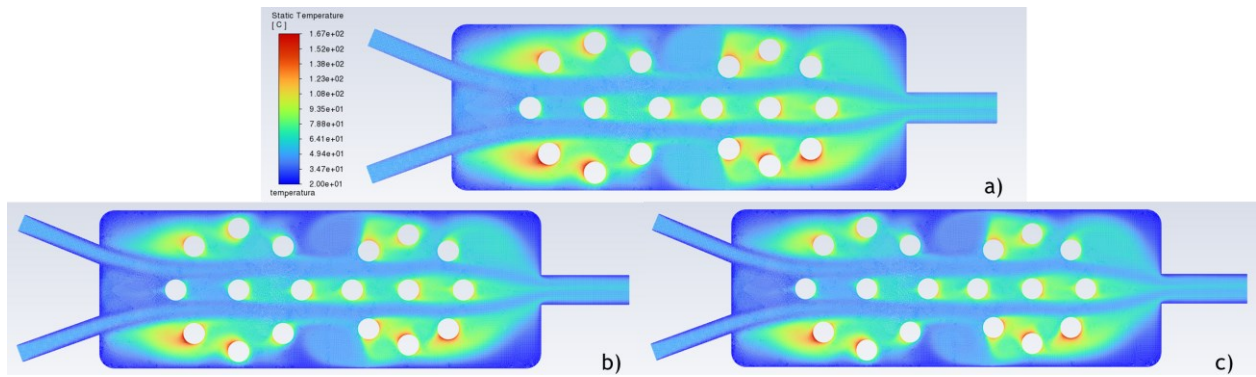


Figure Appendix L. 2: Static temperature contours with $Re = 400$ and $H_F = 200 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

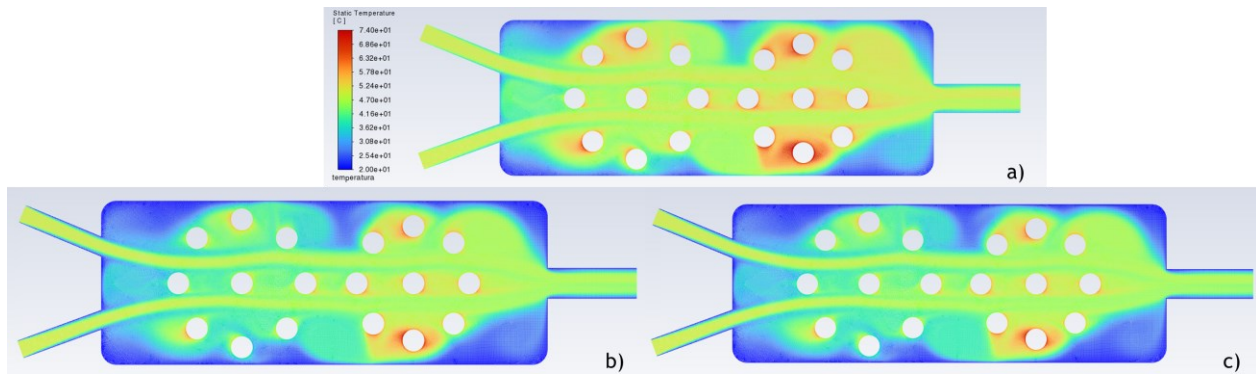


Figure Appendix L. 3: Static temperature contours with $Re = 700$ and $H_F = 50 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

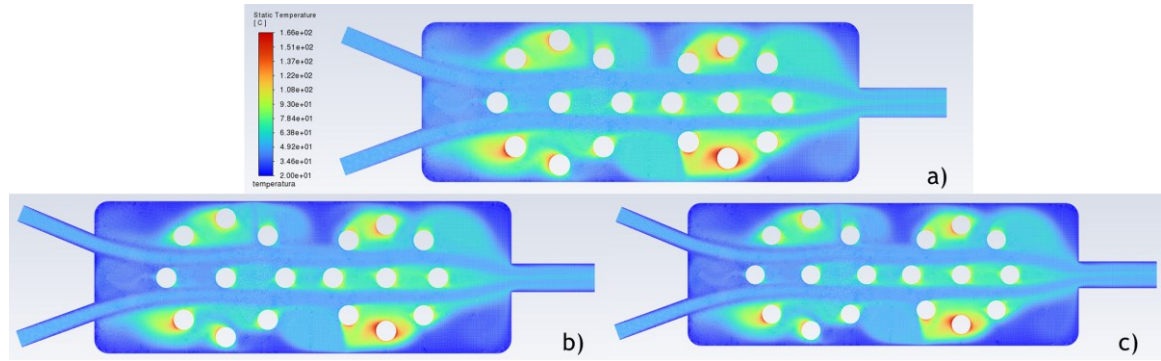


Figure Appendix L. 4: Static temperature contours with $Re = 700$ and $H_F = 200 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

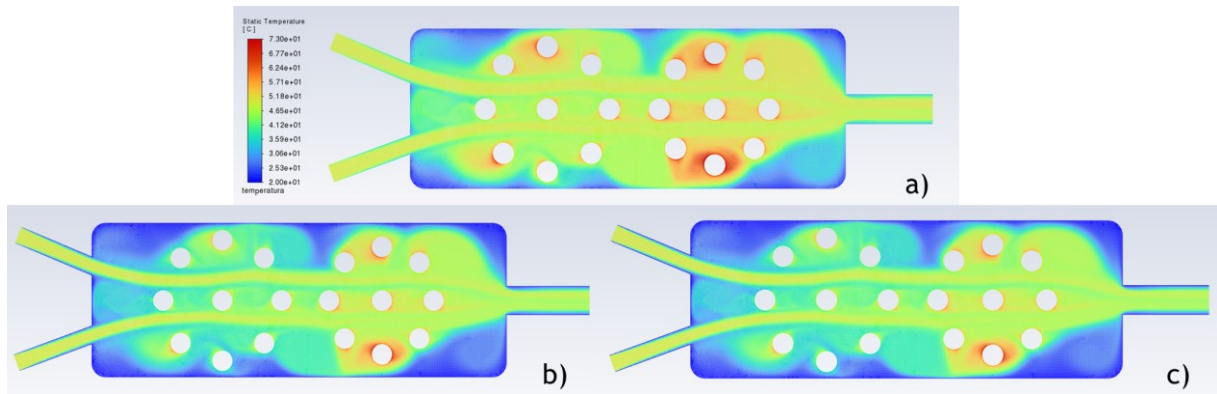


Figure Appendix L. 5: Static temperature contours with $Re = 900$ and $H_F = 50 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

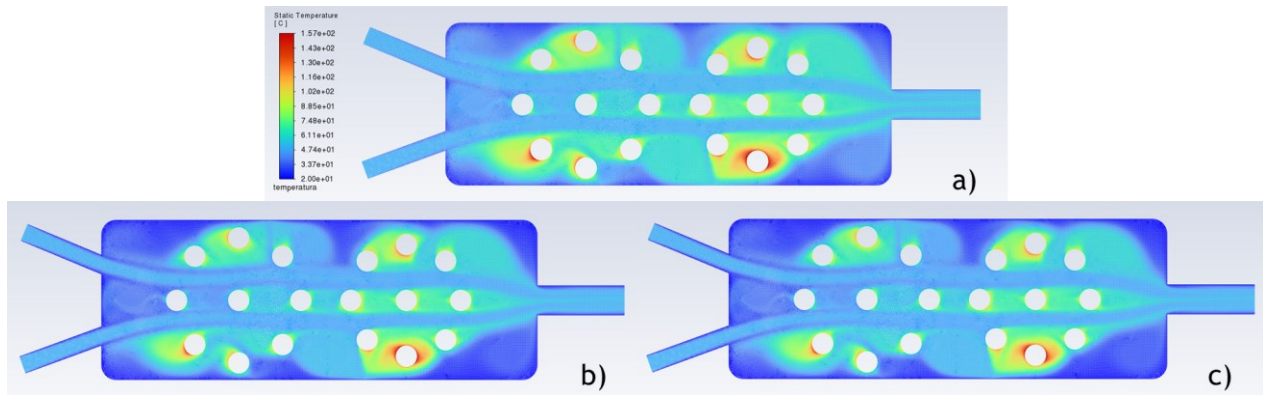


Figure Appendix L. 6: Static temperature contours with $Re = 900$ and $H_F = 200 \text{ W}\cdot\text{m}^{-2}$ for a) $h = 50 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; b) $h = 200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$; c) $h = 1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$.

Appendix M - Results obtained from the study of the effects of the combination of the production of heat flux in the obstacles and convection in the exterior walls

Table Appendix M. 1: Values of temperatures minimum, maximum and average in the outlet for each assay simulated.

Re	$h / \text{W}\cdot\text{m}^{-2}\cdot^{\circ}\text{C}^{-1}$	$H_F / \text{W}\cdot\text{m}^{-2}$	$T_{min} / ^{\circ}\text{C}$	$T_{max} / ^{\circ}\text{C}$	average $T_{out} / ^{\circ}\text{C}$
100	7	50	20.88	73.35	45.28
		200	22.25	184.74	78.62
		400	25.14	331.22	121.65
	200	50	20.02	68.70	39.40
		200	20.06	179.04	69.39
		400	20.10	324.19	108.24
	1500	50	20.00	68.49	39.13
		200	20.01	178.79	68.97
		400	20.01	323.90	107.63
400	7	50	20.78	70.62	46.55
		200	21.34	166.71	56.25
		400	22.08	295.34	69.08
	200	50	20.01	66.87	42.28
		200	20.03	159.00	50.96
		400	20.04	284.69	62.46
	1500	50	20.00	66.65	42.01
		200	20.00	158.63	50.65
		400	20.01	284.22	62.08
700	7	50	21.02	73.84	47.48
		200	22.13	165.76	53.39
		400	22.97	287.90	61.23
	200	50	20.02	68.38	43.93
		200	20.03	158.75	49.13
		400	20.05	278.80	56.04
	1500	50	20.00	67.98	43.68
		200	20.00	158.31	48.84
		400	20.01	278.24	55.69
900	7	50	21.04	72.12	47.83
		200	22.17	156.74	52.59
		400	22.98	269.20	58.88
	200	50	20.02	66.74	44.62
		200	20.03	150.03	48.78
		400	20.04	260.65	54.38
	1500	50	20.00	66.36	44.38
		200	20.00	149.58	48.53
		400	20.01	260.09	54.06

Appendix N - Tracer experiments for the learning phase

Having finalised the study of the behaviour of the fluid in steady state, the next step was to study the flow in transient for all four Reynolds numbers used before, to better understand the concepts related to tracer experiments. Using the instructions from Table 3-5, the information on Table 3-6 and Fluent was possible to obtain the mass fraction in the outlet in function of time and then using Eq. (2.6), was possible to calculate the $F(t)$ that characterizes the flow. The results of the Dankwerts F curve for τ and $5 \cdot \tau$, in function of the four Reynolds number used before, are presented in Figure Appendix N. 1, Figure Appendix N. 2, Figure Appendix N. 3, Figure Appendix N. 4:

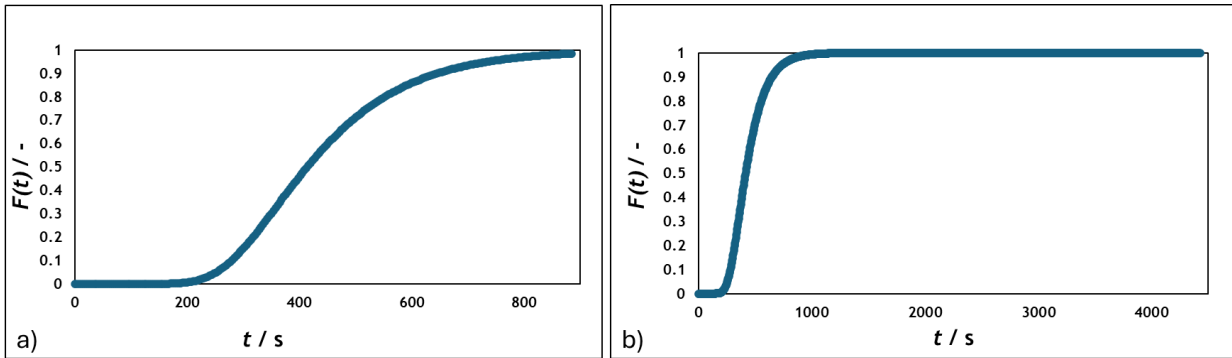


Figure Appendix N. 1: Graphics of the Dankwerts F curve for a) total time = τ and b) total time = $5 \cdot \tau$ for $Re = 100$.

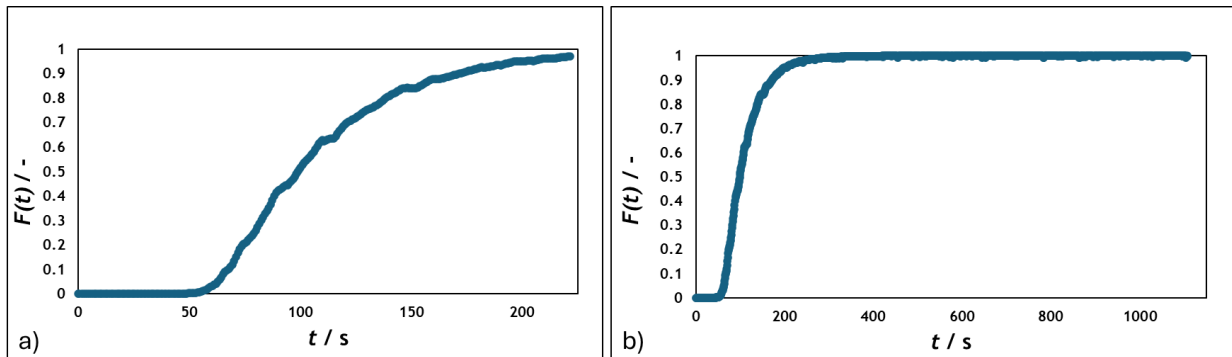


Figure Appendix N. 2: Graphics of the Dankwerts F curve for a) total time = τ and b) total time = $5 \cdot \tau$ for $Re = 400$.

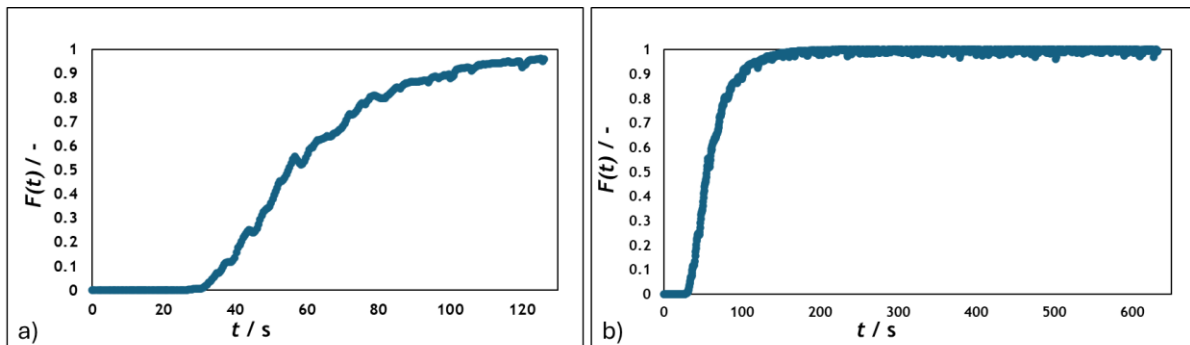


Figure Appendix N. 3: Graphics of the Dankwerts F curve for a) total time = τ and b) total time = $5 \cdot \tau$ for $Re = 700$.

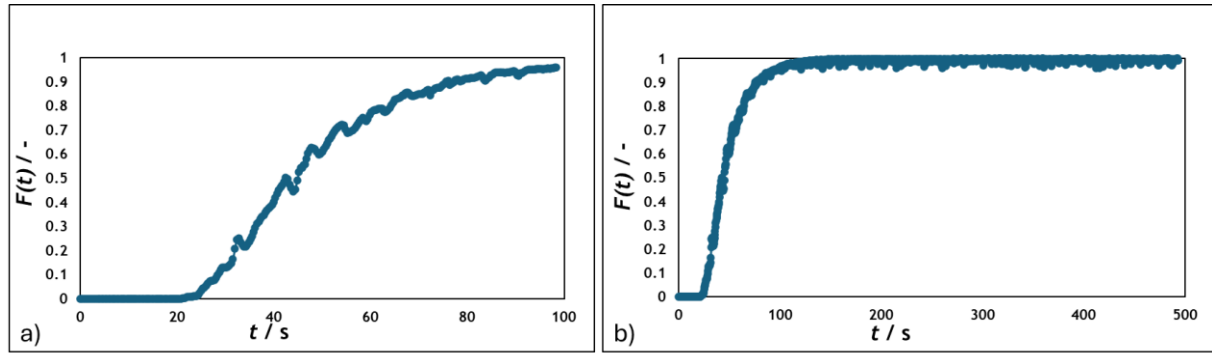


Figure Appendix N. 4: Graphics of the Dankwerts F curve for a) total time = τ and b) total time = $5 \cdot \tau$ for $Re = 900$.

With the values of the Dankwerts F curve, the residence time distribution is calculated using Eq. (2.7), the results obtained are presented in Figure Appendix N. 5:

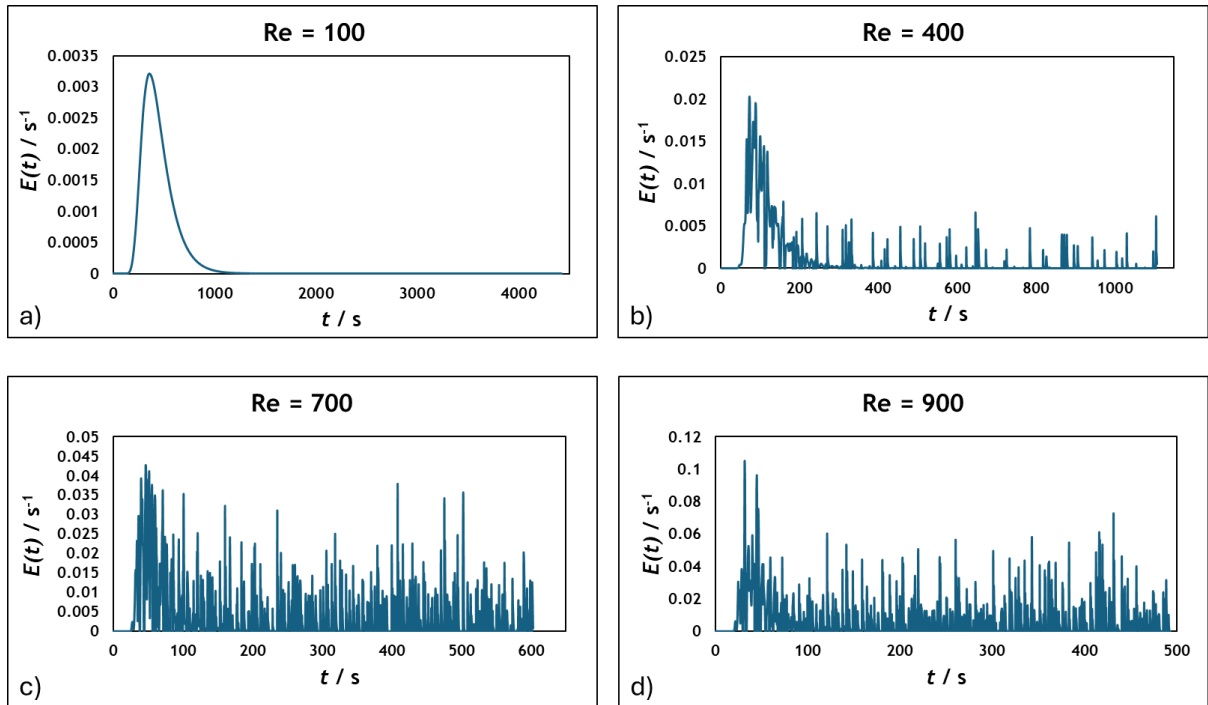


Figure Appendix N. 5: Graphics of the time residence distribution for a) $Re = 100$; b) $Re = 400$; c) $Re = 700$; d) $Re = 900$.

Note: After submitting this report, was noticed that that the mass diffusivity assumed for the mixture used in these simulations corresponded to a diffusivity value for gaseous mixtures and not for liquid mixture such as one of a tracer with water, so the results presented above show greater noise than expected.

Knowing the time residence distribution and combining with Eq. (2.7), the t_r is calculated, and τ is obtained with Eq. (2.9) with the values presented in Appendix I. The comparison of these two methods to determine the residence time is featured in Table Appendix N. 1.

Table Appendix N. 1: Comparison between the average t_r and τ .

	Re			
	100	400	700	900
$\bar{t}_r / s$	444.95	108.86	60.54	46.66
τ / s	884.77	221.19	126.40	98.31

With the results from the $F(t)$ curves, it is easy to understand that the theoretical residence time is not sufficient from the step injection to reach the outlet, which indicates the presence of dead volumes inside the reactor for all the number of Reynolds. This is also observed in the $E(t)$ curves due to the presence of those spikes instead of a simple line with one spike. Lastly, its possible to confirm this even more by detecting how much bigger the average t_r is in comparison to τ .

Appendix O - Contours resultant from the parametric study of the less exothermic reaction

In Figure Appendix O. 1 is visible the increase in the blue area close to the walls as the value of h increases.

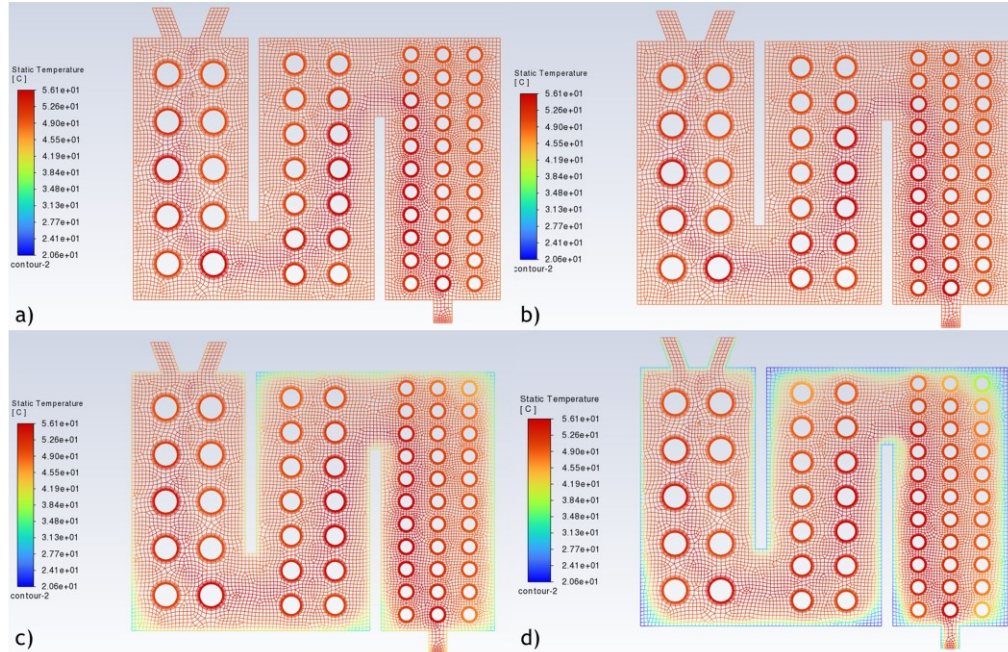


Figure Appendix O. 1: Contours Static temperature for: a) $h = 0 \text{ W} \cdot \text{m}^{-2} \cdot ^\circ\text{C}^{-1}$, b) $h = 7 \text{ W} \cdot \text{m}^{-2} \cdot ^\circ\text{C}^{-1}$, c) $h = 200 \text{ W} \cdot \text{m}^{-2} \cdot ^\circ\text{C}^{-1}$, d) $h = 1500 \text{ W} \cdot \text{m}^{-2} \cdot ^\circ\text{C}^{-1}$.

In Figure Appendix O. 2 is noticeable the change in the preferential pathways, as the inlet compositions vary.

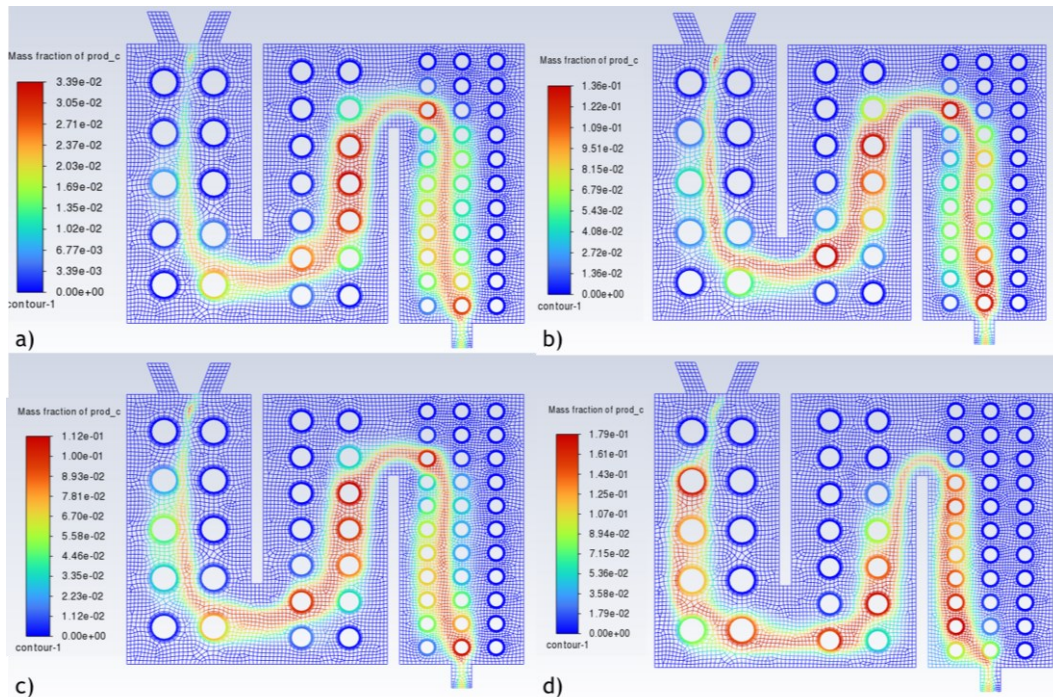


Figure Appendix O. 2: Contours of mass fraction of C for: a) $Y_A = Y_B = 0.05$, b) $Y_A = 0.5$ and $Y_B = 0.1$, c) $Y_A = 0.25$ and $Y_B = 0.1$, d) $Y_A = Y_B = 0.25$.

Appendix P - Contours resultant from the parametric study of the more exothermic reaction

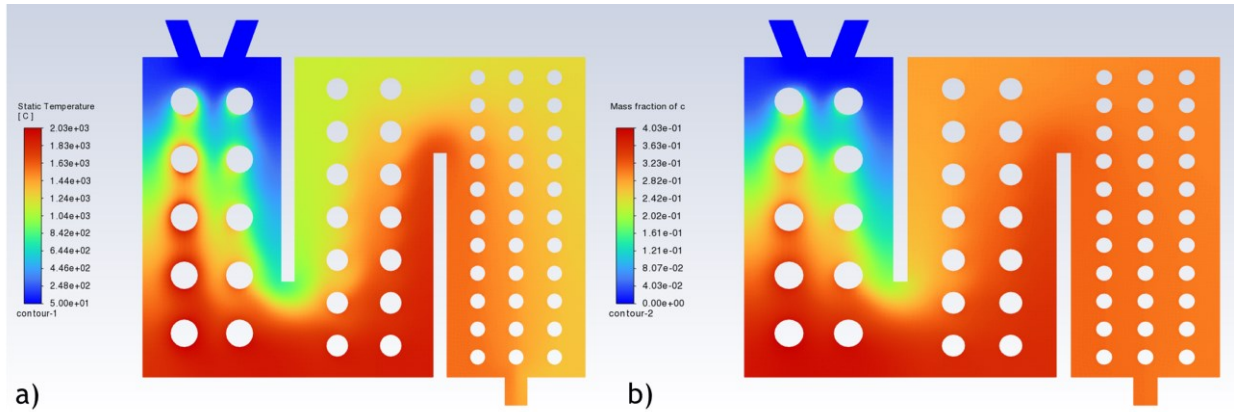


Figure Appendix P. 1: Contours resulting from the combination of $a = 0$ with $v = 0.05 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.

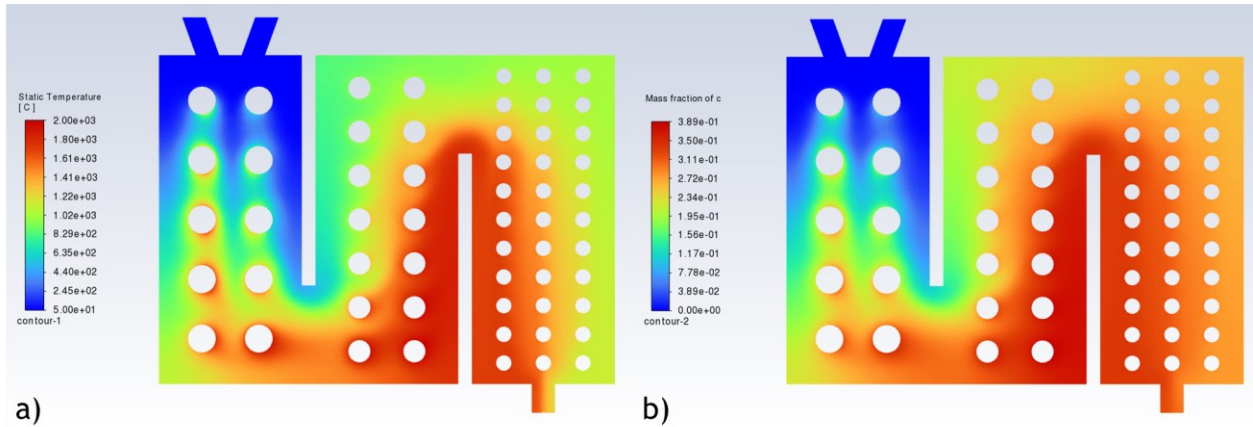


Figure Appendix P. 2: Contours resulting from the combination of $a = 0$ with $v = 0.1 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.

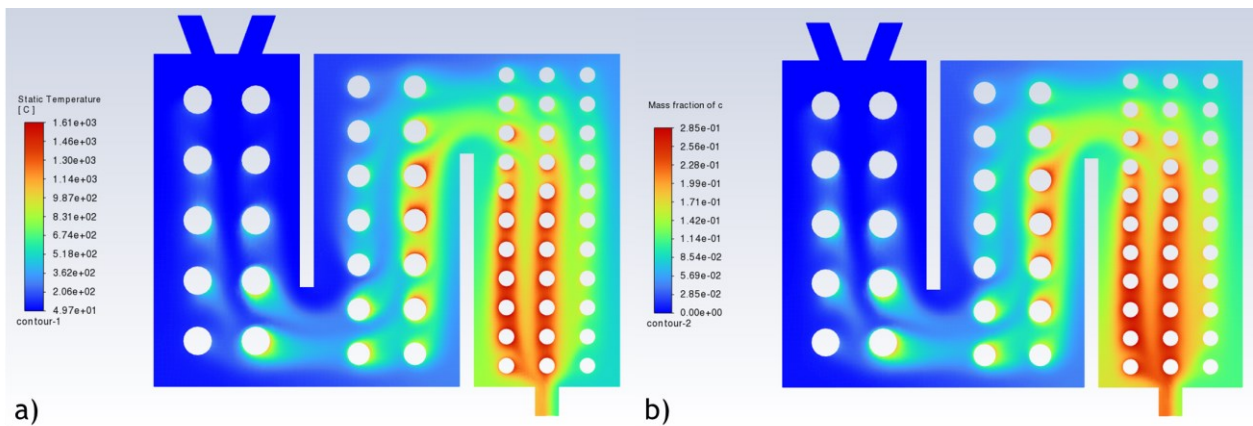


Figure Appendix P. 3: Contours resulting from the combination of $a = 0$ with $v = 0.5 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.

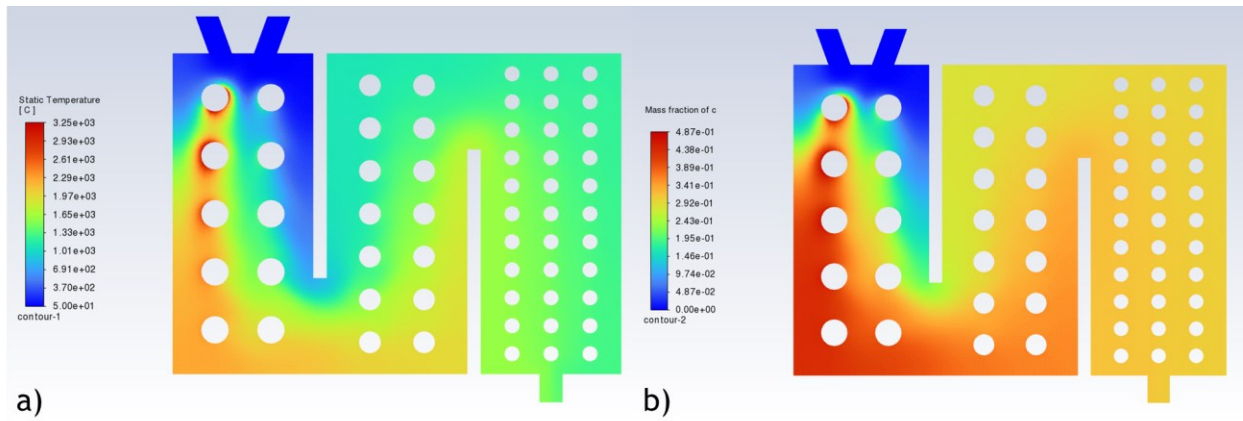


Figure Appendix P. 4: Contours resulting from the combination of $a = 1$ with $v = 0.05 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.

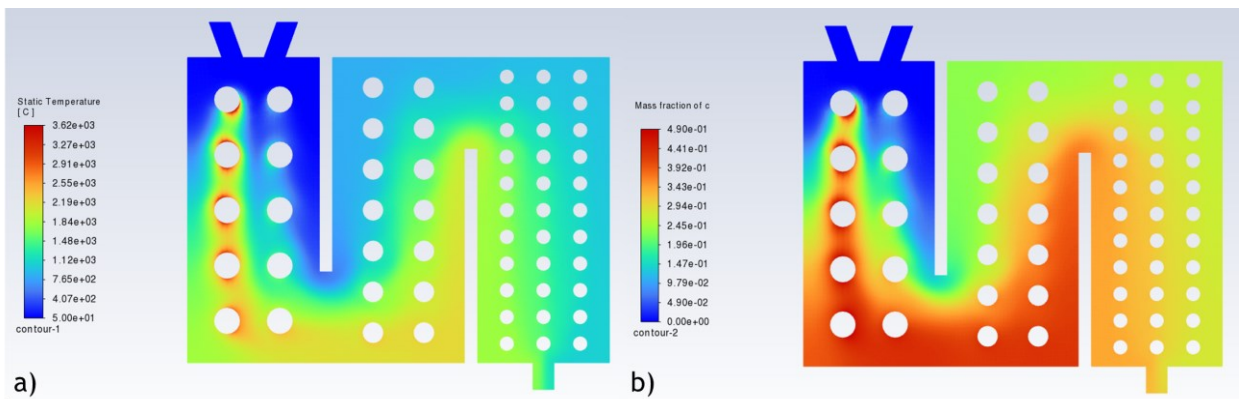


Figure Appendix P. 5: Contours resulting from the combination of $a = 1$ with $v = 0.1 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.

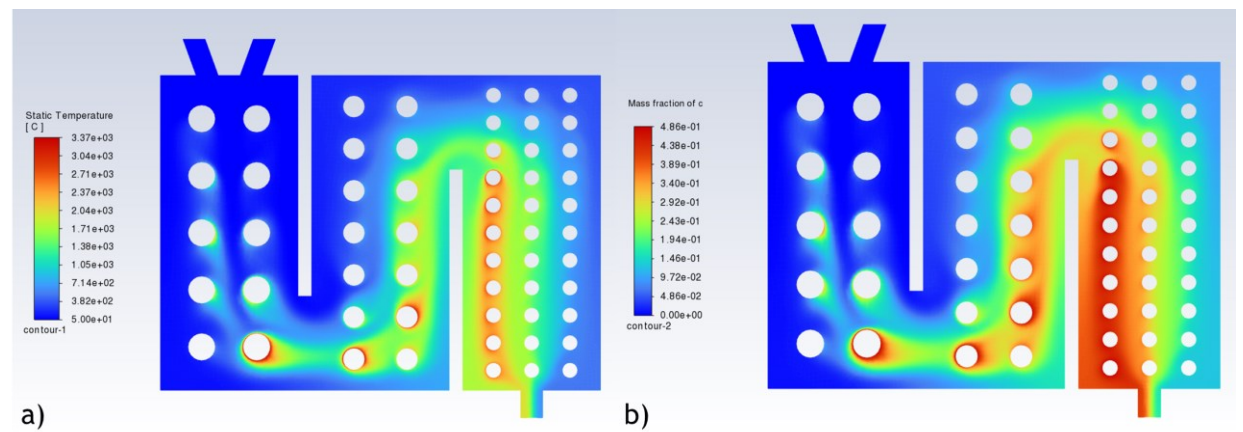


Figure Appendix P. 6: Contours resulting from the combination of $a = 1$ with $v = 0.5 \text{ m}\cdot\text{s}^{-1}$: a) Static temperature and b) mass fraction of C.

Appendix Q - Calculations associated with the values of h considered throughout this thesis

Heat transfer by convection is a phenomenon that is influenced by several parameters and this dependence can be expressed as:^[27, 28]

$$q = f(\rho, \mu, \lambda, C_p, v, L, \Delta T, \beta g) \quad (0.7)$$

where q is the amount of heat transferred per unit area; ρ is the volumetric mass of the fluid involved; μ is the dynamic viscosity of the fluid; λ is the thermal conductivity of the fluid involved, C_p is the heat capacity of the fluid; v is the characteristic velocity of the fluid flow; L is the characteristic dimension of the fluid flow; ΔT expresses the temperature difference between the surface and the bulk of the fluid; β is the thermal expansion coefficient of the fluid; and g is the gravitational acceleration.^[27, 28]

Performing a dimensional analysis to this dependence, i.e., applying the Buckingham's π theorem, the dependence can be defined in terms of dimensionless groups:^[27, 28]

$$Nu = f'(Re, Pr, Gr) \quad (0.8)$$

$$\text{Nusselt number: } Nu = \frac{h \cdot L}{\lambda}$$

$$\text{Prandtl number: } Pr = \frac{\mu \cdot C_p}{\lambda}$$

$$\text{Reynolds number: } Re = \frac{\rho \cdot v \cdot L}{\mu}$$

$$\text{Grashof number: } Gr = \frac{(\beta \cdot g) \cdot \rho^2 \cdot L^3 \cdot \Delta T}{\mu^2}$$

Natural convection

This is the predominant convection mechanism when there is an absence of external factors promoting fluid movement, and only parts of the fluid are moving (upwards or downwards) due density gradients caused by temperature differences. When we are dealing with natural convection, the influence of Re is negligible and Grashof number is relevant (predominance of gravitational forces).^[27, 28]

The correlations used to estimate the convection coefficient h in natural convection normally obeys the following functionality:

$$Nu = C \cdot (Pr \cdot Gr)^n \quad (0.9)$$

where C and n depends on the surface geometry/orientation and on the value of the product $Pr \cdot Gr$.^[27, 28]

In order to illustrate the systems addressed in this thesis, let us assume a common fluid like air and flat surfaces of a small vessel with horizontal orientation. The properties of the fluid should

be evaluated at the average temperature between the surface and the bulk. Just to have an idea of the magnitude of h values, we will assume 30 °C and 50 °C for this average temperature.

Table Appendix Q. 1: Physical properties of air.

$T_{av} / ^\circ\text{C}$	$\rho / \text{kg}\cdot\text{m}^{-3}$	$\mu / \text{Pa}\cdot\text{s}$	$\lambda / \text{W}\cdot\text{m}^{-1} \cdot ^\circ\text{C}^{-1}$	$C_p / \text{J}\cdot\text{kg}^{-1} \cdot ^\circ\text{C}^{-1}$	Pr
30	1.177	1.86×10^{-5}	0.026	1007	0.713
50	1.103	1.94×10^{-4}	0.028	1008	0.708

The temperature difference will also be considered at 50 °C, and the characteristic length L is defined as the ratio between the area and the perimeter of the surface. For a surface with a rectangular section with 12 cm x 8 cm, the value of L should be around 2.4 cm. Additionally, it should also be taking in consideration if the hot horizontal surface is facing upwards or downwards, since this clearly affects the natural movement in the fluid. We will consider both options, as we can assume to have both surfaces in our small vessel/reactor. The values obtained from the correlation are summarized below:

Table Appendix Q. 2: Values of h calculated for natural convection.

Hot surface	$T_{av} / ^\circ\text{C}$	$\Delta T / ^\circ\text{C}$	Gr·Pr	C	N	$h / \text{W}\cdot\text{m}^{-2} \cdot ^\circ\text{C}^{-1}$
Facing upwards	30	50	6.47×10^4	0.54	0.25	9.4
	50		4.87×10^4	0.54	0.25	9.2
Facing downwards	30	50	6.47×10^4	0.27	0.25	4.7
	50		4.87×10^4	0.27	0.25	4.6

From the data of h estimated above, it seems to be adequate to assume a value around $7 \text{ W}\cdot\text{m}^{-2} \cdot ^\circ\text{C}^{-1}$) to represent the presence of natural convection of air in the exterior of the vessel.

Forced convection

If a surface is exposed to fluid flow promoted by an external factor (such as a ventilator, mixer, pump or wind), it can experience heat transfer by forced convection. In this mechanism, the effect of the Grashof number is negligible and the preponderance of Re becomes crucial.

The range of possible scenarios with forced convection is much wider, so the list of available correlations is more extensive, and care should always be taken to select the one that better fits the conditions of each system. In the case of this thesis, we will assume flow of water parallel to flat surfaces as a possible way to represent the external cooling of our vessels. The correlation of Churchill and Ozoe can be applied:^[27, 28]

$$\text{Nu} = \frac{0.6774 \cdot \text{Re}^{1/2} \cdot \text{Pr}^{1/3}}{\left[1 + \left(\frac{0.0468}{\text{Pr}}\right)^{2/3}\right]^{1/4}} \quad (0.10)$$

Table Appendix Q. 3: Physical properties of water.

$T_{av} / ^\circ\text{C}^{-1}$	$\rho / \text{kg}\cdot\text{m}^{-3}$	$\mu / \text{Pa}\cdot\text{s}$	$\lambda / \text{W}\cdot\text{m}^{-1}\cdot^\circ\text{C}^{-1}$	$C_p / \text{J}\cdot\text{kg}^{-1}\cdot^\circ\text{C}^{-1}$	Pr
30	996.5	8.54×10^{-4}	0.610	4181	5.85
50	989.3	5.77×10^{-4}	0.640	4181	3.77

Based on the Churchill and Ozoe correlation, values of h were estimated for different magnitudes of water velocity:

Table Appendix Q. 4: Values of h calculated for forced convection.

$T_{av} / ^\circ\text{C}$	$v / \text{m}\cdot\text{s}^{-1}$	Re	$h / \text{W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$
30	0.005	700	162.7
50		1029	177.9
30	0.01	1401	230.0
50		2058	251.6
30	0.05	7003	514.4
50		10288	562.6
30	0.5	70028	1626.7
50		102881	1779.0

From the estimated data of h presented above, it was decided to use the values of $200 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$ and of $1500 \text{ W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$ to represent two different intensities of forced convection in the exterior of the vessel.