

**Titre:** Development of a Micro-GtL Technology Through Risk Assessment  
and Temperature Control of Fischer-Tropsch Process

**Auteur:** Mahdi Sharifian  
Author:

**Date:** 2023

**Type:** Mémoire ou thèse / Dissertation or Thesis

**Référence:** Sharifian, M. (2023). Development of a Micro-GtL Technology Through Risk  
Assessment and Temperature Control of Fischer-Tropsch Process [Thèse de  
doctorat, Polytechnique Montréal]. PolyPublie.  
Citation: <https://publications.polymtl.ca/57071/>

 **Document en libre accès dans PolyPublie**  
Open Access document in PolyPublie

**URL de PolyPublie:** <https://publications.polymtl.ca/57071/>  
PolyPublie URL:

**Directeurs de  
recherche:** Gregory Scott Patience, & Nicolas Hudon  
Advisors:

**Programme:** Génie chimique  
Program:

**POLYTECHNIQUE MONTRÉAL**

affiliée à l'Université de Montréal

**Development of a Micro-GtL Technology through Risk Assessment and  
Temperature Control of Fischer-Tropsch Process**

**MAHDI SHARIFIAN**

Département de génie chimique

Thèse présentée en vue de l'obtention du diplôme de *Philosophiæ Doctor*  
Génie chimique

Décembre 2023

**POLYTECHNIQUE MONTRÉAL**

affiliée à l'Université de Montréal

Cette thèse intitulée :

**Development of a Micro-GtL Technology through Risk Assessment and  
Temperature Control of Fischer-Tropsch Process**

présentée par **Mahdi SHARIFIAN**

en vue de l'obtention du diplôme de *Philosophiæ Doctor*  
a été dûment acceptée par le jury d'examen constitué de :

**Michel PERRIER**, président

**Gregory PATIENCE**, membre et directeur de recherche

**Nicolas HUDON**, membre et codirecteur de recherche

**Moncef CHIOUA**, membre

**Luis RICARDEZ-SANDOVAL**, membre externe

## DEDICATION

*This dissertation is dedicated to my beloved wife, Azadeh, who has been a constant source of support and encouragement during my PhD adventure and life. I am truly thankful for having her in my life. This work is also dedicated to my lovely children, Shayan and Shahrzad, for all the single moments that they were being with me...*

## ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor Prof. Gregory S. Patience for his technical and financial supports during this adventurous career. I am also profoundly grateful to my co-supervisor Prof. Nicolas Hudon from Queen's University for his detailed and constructive comments, and for his substantial support, encouragement, and advice throughout this work. I would also thank the great technicians of our group; Jean Ghantous and Alejandro Velez-Garcia for their technical assistance on the setup from installation to maintenance and troubleshooting of equipment and instruments. I would like to thank my colleagues, Nooshin Moradi Kazerooni and Jildimara Santana for their unique partnership and assistance on the experiments. This research is supported by funding from the Canada Research Chairs program and I gratefully acknowledge the financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Canada Foundation for Innovation (CFI).

## RÉSUMÉ

La technologie compacte Gas-to-Liquid, appelée Micro-GtL, est l'une des solutions substantielles pour minimiser la pollution de l'environnement et du climat, ainsi que pour monétiser le gaz brûlé à la torche / échoué dans les têtes de puits de pétrole éloignées. Le processus intègre deux unités complexes, l'oxydation partielle catalytique (CPOX) à 20 bar et 900 °C, suivie de la synthèse Fischer-Tropsch (FTS) à 300 °C et à la même pression. L'exécution de cette opération, qui concerne un mélange explosif et l'émission de gaz toxiques à des pressions modérées et à des températures élevées, est risquée et comporte des accidents catastrophiques qui doivent être reconnus avec précision et complètement évités. En outre, le FTS, en tant que partie critique de cette installation pilote, nécessite des attentions techniques spécifiques, car il n'est pas seulement un élément essentiel de l'installation. Il s'agit non seulement d'une réaction exothermique extrême, mais aussi d'une réaction dont les caractéristiques sont facilement affectées par des perturbations en amont. Un régulateur de température approprié est donc nécessaire, et la capacité de refroidissement du réacteur à lit fluidisé doit être assurée pour éviter l'emballement de la réaction pendant le démarrage et le fonctionnement normal. C'est pourquoi nous avons proposé une méthodologie de "décision de mode de défaillance et de risque" pour analyser tous les scénarios dangereux potentiels, quantifier les risques inhérents et attribuer des mesures de protection appropriées pour atténuer le risque en conséquence. Nous avons également conçu un régulateur PI de température à rétroaction basé sur la simulation et testé ses performances en fonction des incertitudes des paramètres cinétiques et du coefficient de transfert de chaleur, ainsi que des perturbations potentielles des conditions de fonctionnement en amont, notamment le rapport  $H_2/CO$ , la température d'alimentation et le débit, et nous l'avons finalement considéré comme un régulateur préliminaire fiable pour le fonctionnement réel, qui pourrait être réajusté au cours de l'opération. Enfin, nous avons conçu une expérience en mode sûr, en l'absence de réaction, pour mesurer la capacité de refroidissement de l'échangeur de chaleur à tubes internes et nous avons modélisé deux contrôleurs PI et PID pour nous assurer que le système peut éliminer rapidement l'énorme chaleur de réaction, au point de démarrage. Sur la base des résultats, un PID plus un filtre utilisant une approche de windup anti-réinitialisation fournit une performance rapide et régulière sur le mécanisme de refroidissement, ce qui est plus pratique que le PI avec un gain modifié. Toutes ces stratégies visent à assurer un fonctionnement sûr et régulier, que ce soit dans le cas du démarrage du processus ou pendant la période de refroidissement. que ce soit lors du démarrage du processus ou pendant le fonctionnement normal du pilote micro-GtL.

## ABSTRACT

Compact Gas-to-Liquid technology, called Micro-GtL, is one of the substantial solutions to minimize the environmental and climate pollution as well as monetizing the wasted flared / stranded gas in remote oil wellheads. The process integrates two complex units, catalytic partial oxidation (CPOX) at 20 bar and 900 °C followed by Fischer-Tropsch synthesis (FTS) at 300 °C and the same pressure. Running this operation that deals with explosive mixture and emission of toxic gases at moderate pressures and high temperatures, is risky and consists of catastrophic accidents that must be precisely recognized and completely prevented. Furthermore, the FTS as the critical part of this pilot plant, needs specific technical attentions since it is not only an extreme exothermic reaction but also its characterizations are readily affected by upstream disturbances. Hence, a suitable temperature controller is required and the cooling capacity of the fluidized bed reactor must be assured to avoid runaway reaction during startup and normal operation. Therefore, we proposed 'Failure mode risk decision' methodology to analyze all the potential hazardous scenarios, quantify the inherent risks and allocate appropriate safeguards to mitigate the risk accordingly. We also designed a simulation-based feedback temperature PI controller and tested its performance for uncertainties in the kinetic parameters and heat transfer coefficient as well as potential disturbances in the upstream operating conditions including  $H_2/CO$  ratio, feed temperature, and flow rate and eventually considered it as a reliable preliminary controller in the actual operation that could be re-tuned during the operation. Finally, we designed a safe-mode experiment, in absence of reaction, to measure the cooling capacity of the internal tube heat exchanger and modelled two PI and PID controllers to ensure that the system is able to remove the huge heat of reaction quickly, in particular at the startup point. Based on the results, a PID plus filter using anti-reset windup approach provides a fast and smooth performance on the cooling mechanism which is more convenient than the PI with modified gain. All these strategies are targeted to handle a safe and smooth operation either in the case of starting the process or during the normal operation within the micro-GtL pilot.

## TABLE OF CONTENTS

|                                                         |       |
|---------------------------------------------------------|-------|
| DEDICATION . . . . .                                    | iii   |
| ACKNOWLEDGEMENTS . . . . .                              | iv    |
| RÉSUMÉ . . . . .                                        | v     |
| ABSTRACT . . . . .                                      | vi    |
| TABLE OF CONTENTS . . . . .                             | vii   |
| LIST OF TABLES . . . . .                                | xi    |
| LIST OF FIGURES . . . . .                               | xiii  |
| LIST OF SYMBOLS AND ACRONYMS . . . . .                  | xviii |
| LIST OF APPENDICES . . . . .                            | xix   |
| CHAPTER 1 INTRODUCTION . . . . .                        | 1     |
| 1.1 Motivations . . . . .                               | 1     |
| 1.2 Problem statement and research objectives . . . . . | 2     |
| 1.3 Summary of contributions . . . . .                  | 4     |
| 1.4 Thesis structure . . . . .                          | 5     |
| CHAPTER 2 LITERATURE REVIEW . . . . .                   | 7     |
| 2.1 Gas To Liquid (GtL) Technology . . . . .            | 7     |
| 2.2 Syngas production unit . . . . .                    | 8     |
| 2.3 Fischer-Tropsch synthesis . . . . .                 | 11    |
| 2.3.1 Kinetic Modelling . . . . .                       | 11    |
| 2.3.2 Hydrodynamics . . . . .                           | 15    |
| 2.3.3 Heat transfer . . . . .                           | 18    |
| 2.4 Product upgrading . . . . .                         | 21    |
| 2.5 Process Safety and Risk Assessment . . . . .        | 22    |
| 2.6 Process control . . . . .                           | 22    |

|           |                                                                                                           |    |
|-----------|-----------------------------------------------------------------------------------------------------------|----|
| CHAPTER 3 | ARTICLE 1 : SAFETY ANALYSIS AND RISK ASSESSMENT OF A MICRO-GTL PLANT . . . . .                            | 26 |
| 3.1       | Introduction . . . . .                                                                                    | 27 |
| 3.2       | Micro-GTL Plant Unit . . . . .                                                                            | 29 |
| 3.2.1     | Process . . . . .                                                                                         | 29 |
| 3.2.2     | Process Control & Instrumentation . . . . .                                                               | 31 |
| 3.3       | Process Hazard and Risk Assessment . . . . .                                                              | 32 |
| 3.3.1     | Process Hazards Review . . . . .                                                                          | 32 |
| 3.3.2     | Risk Assessment . . . . .                                                                                 | 32 |
| 3.4       | Results and Discussion . . . . .                                                                          | 38 |
| 3.5       | Conclusion . . . . .                                                                                      | 50 |
| CHAPTER 4 | ARTICLE 2 : FEEDBACK CONTROL STRATEGY OF FISCHER-TROPSCH PROCESS IN A MICRO-GTL PLANT . . . . .           | 52 |
| 4.1       | Introduction . . . . .                                                                                    | 52 |
| 4.1.1     | Research gap/novelty . . . . .                                                                            | 54 |
| 4.2       | Process overview, operation objectives, and constraints . . . . .                                         | 54 |
| 4.3       | Simulation-based controller design approach . . . . .                                                     | 56 |
| 4.3.1     | Fischer-Tropsch Model . . . . .                                                                           | 57 |
| 4.3.2     | Residence time distribution (RTD) experiment . . . . .                                                    | 62 |
| 4.3.3     | Hydrodynamics . . . . .                                                                                   | 64 |
| 4.3.4     | Steady-state simulation . . . . .                                                                         | 67 |
| 4.3.5     | Dynamic simulation . . . . .                                                                              | 68 |
| 4.4       | Control design for FT reactor . . . . .                                                                   | 69 |
| 4.4.1     | Open-loop simulation . . . . .                                                                            | 69 |
| 4.4.2     | Controller design . . . . .                                                                               | 72 |
| 4.5       | Results and discussion . . . . .                                                                          | 73 |
| 4.5.1     | Hydrodynamics and RTD . . . . .                                                                           | 73 |
| 4.5.2     | Temperature controller . . . . .                                                                          | 75 |
| 4.5.3     | Closed-loop simulation for the step change in set point . . . . .                                         | 75 |
| 4.5.4     | Closed loop simulation for disturbance rejection . . . . .                                                | 78 |
| 4.5.5     | Robustness of the temperature controller . . . . .                                                        | 87 |
| 4.6       | Conclusion . . . . .                                                                                      | 91 |
| CHAPTER 5 | ARTICLE 3 : EXPERIMENTAL MODELING OF HEAT EXCHANGE FOR CONTROL DESIGN OF A FLUIDIZED BED SYSTEM . . . . . | 93 |
| 5.1       | Introduction . . . . .                                                                                    | 94 |

|           |                                                                                                    |     |
|-----------|----------------------------------------------------------------------------------------------------|-----|
| 5.2       | Method . . . . .                                                                                   | 95  |
| 5.2.1     | Process . . . . .                                                                                  | 95  |
| 5.2.2     | Experiment . . . . .                                                                               | 97  |
| 5.3       | Heat transfer analysis . . . . .                                                                   | 100 |
| 5.3.1     | Overall heat transfer coefficient . . . . .                                                        | 100 |
| 5.3.2     | Bed convective heat transfer coefficient . . . . .                                                 | 102 |
| 5.4       | Results and discussion . . . . .                                                                   | 103 |
| 5.4.1     | Single cooling coil . . . . .                                                                      | 103 |
| 5.4.2     | Double cooling coils . . . . .                                                                     | 107 |
| 5.4.3     | Bed convective heat transfer . . . . .                                                             | 112 |
| 5.4.4     | Cooling capacity . . . . .                                                                         | 114 |
| 5.5       | Dynamics and control of heat exchange . . . . .                                                    | 115 |
| 5.5.1     | System Identification . . . . .                                                                    | 115 |
| 5.5.2     | Controller design . . . . .                                                                        | 119 |
| 5.6       | Conclusion . . . . .                                                                               | 127 |
| CHAPTER 6 | GENERAL DISCUSSION . . . . .                                                                       | 129 |
| 6.1       | Risk assessment of micro-GtL plant . . . . .                                                       | 129 |
| 6.2       | Temperature Control . . . . .                                                                      | 130 |
| 6.3       | Pilot plant Startup . . . . .                                                                      | 131 |
| CHAPTER 7 | CONCLUSION . . . . .                                                                               | 132 |
| 7.1       | Summary of Works . . . . .                                                                         | 132 |
| 7.1.1     | Risk Assessment of the Micro-GtL plant . . . . .                                                   | 132 |
| 7.1.2     | Feedback Control Strategy of Fischer-Tropsch . . . . .                                             | 132 |
| 7.1.3     | Experimental Modeling of Heat Exchange for Control Design of a Flu-<br>idized Bed System . . . . . | 133 |
| 7.2       | Limitations . . . . .                                                                              | 133 |
| 7.2.1     | Process hazard review and risk assessment . . . . .                                                | 133 |
| 7.2.2     | Temperature control of Fischer-Tropsch process . . . . .                                           | 133 |
| 7.2.3     | Dynamics of the heat exchange . . . . .                                                            | 134 |
| 7.3       | Future Research . . . . .                                                                          | 134 |
| 7.3.1     | Safety and risk analysis of the process . . . . .                                                  | 134 |
| 7.3.2     | Temperature control of FTS . . . . .                                                               | 135 |
| 7.3.3     | Thermal performance of the process in terms of cooling design and<br>control . . . . .             | 135 |

|                      |     |
|----------------------|-----|
| REFERENCES . . . . . | 136 |
| APPENDICES . . . . . | 159 |

## LIST OF TABLES

|            |                                                                                                                                                                                                                                                                                                                                                          |    |
|------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Table 2.1  | Correlations available in the literature to predict the average heat transfer coefficient. . . . .                                                                                                                                                                                                                                                       | 20 |
| Table 3.1  | Severity table of incidents . . . . .                                                                                                                                                                                                                                                                                                                    | 33 |
| Table 3.2  | Quantified severity of incident . . . . .                                                                                                                                                                                                                                                                                                                | 34 |
| Table 3.3  | Mean probability of failures during 20 years . . . . .                                                                                                                                                                                                                                                                                                   | 34 |
| Table 3.4  | Risk level(%) . . . . .                                                                                                                                                                                                                                                                                                                                  | 36 |
| Table 3.5  | Design template of FMRD technique for a micro GtL unit. Elements are derived from the flowchart Figure 3.4. The header of the table includes project name, team members, the node and additional details about documentation for the project (P&ID number, revision number). The acceptable $R_r$ satisfies the conditional blocks of the flowchart. . . | 38 |
| Table 3.6  | Feasible technical and human causes of failure in MRU . . . . .                                                                                                                                                                                                                                                                                          | 39 |
| Table 3.7  | Feasible consequences of the process failure with estimated severity value                                                                                                                                                                                                                                                                               | 40 |
| Table 3.8  | Anticipated safeguards of the GtL process in MRU . . . . .                                                                                                                                                                                                                                                                                               | 41 |
| Table 3.9  | Spreadsheet NODE 1; Natural gas feed . . . . .                                                                                                                                                                                                                                                                                                           | 43 |
| Table 3.10 | Spreadsheet NODE 2; Air feed . . . . .                                                                                                                                                                                                                                                                                                                   | 44 |
| Table 3.11 | Spreadsheet NODE 3; CPOX Reactor . . . . .                                                                                                                                                                                                                                                                                                               | 45 |
| Table 3.12 | Spreadsheet NODE 4; Intercoolers . . . . .                                                                                                                                                                                                                                                                                                               | 45 |
| Table 3.13 | Spreadsheet NODE 5; Fischer-Tropsch Reactor . . . . .                                                                                                                                                                                                                                                                                                    | 46 |
| Table 3.14 | Spreadsheet NODE 6; Cooling water circuit . . . . .                                                                                                                                                                                                                                                                                                      | 47 |
| Table 3.15 | Spreadsheet NODE 7; Filter cleaning system by air . . . . .                                                                                                                                                                                                                                                                                              | 47 |
| Table 4.1  | Kinetics parameters data [94] . . . . .                                                                                                                                                                                                                                                                                                                  | 59 |
| Table 4.2  | Value of parameters for the chain growth probability evaluation, $T_0 = 573K$ . . . . .                                                                                                                                                                                                                                                                  | 60 |
| Table 4.3  | Kinetic parameters of the FTs reactions. Subscript r refers to the FT or WGS. . . . .                                                                                                                                                                                                                                                                    | 61 |
| Table 4.4  | Comparison of the fractional (LHHW) and Power law models in ASPEN plus with RIPI's experiment [94] . . . . .                                                                                                                                                                                                                                             | 62 |
| Table 4.5  | Parameters of the dispersion model for the experimental pilot reactor                                                                                                                                                                                                                                                                                    | 64 |
| Table 4.6  | Characteristics of the pilot FT reactor at Polytechnique Montreal and operating conditions . . . . .                                                                                                                                                                                                                                                     | 66 |
| Table 4.7  | Heat exchange parameters from steady-state simulation and hydrodynamics of the process for the powerlaw kinetics . . . . .                                                                                                                                                                                                                               | 68 |

|            |                                                                                                                                                                                                                                                                                                                                                         |     |
|------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Table 4.8  | Resulting parameters of RTD test and hydrodynamic regime . . . . .                                                                                                                                                                                                                                                                                      | 75  |
| Table 5.1  | Operating variables of the heat transfer test, $N = u_0/u_{mf}$ is the fluidization number and $u_0$ is the superficial gas velocity, $\dot{q}$ is the air flow rate at the actual conditions ( $T=300^\circ\text{C}$ , $P$ ), and $\dot{q}_{\text{NTP}}$ is the air flow rate at normal conditions ( $T=0^\circ\text{C}$ , $P=1\text{ bar}$ ). . . . . | 99  |
| Table 5.2  | Characterization of alumina catalyst. Skeletal density and pore volume were measured by BET method, respectively. . . . .                                                                                                                                                                                                                               | 101 |
| Table 5.3  | Constant coefficients of the heat capacity for air in $\text{J kg}^{-1} \text{K}^{-1}$ (Eqn. 5.5) [256]. The original molar based values in Eqn. 5.5 are divided by the molecular mass of the air, 29, to obtain the mass heat capacity. . . .                                                                                                          | 102 |
| Table 5.4  | Two paired t-test analysis of $U_m$ verses operating pressure of the fluidized bed to reject the null-hypothesis of mean values . . . . .                                                                                                                                                                                                               | 112 |
| Table 5.5  | Cooling water properties at $55^\circ\text{C}$ and $300\text{ kPa}$ . Data extracted from Aspen properties V12 . . . . .                                                                                                                                                                                                                                | 112 |
| Table 5.6  | Cooling water properties at $55^\circ\text{C}$ and $300\text{ kPa}$ . Data extracted from Aspen properties V12 . . . . .                                                                                                                                                                                                                                | 112 |
| Table 5.7  | Correlations available in the literature to predict the average heat transfer coefficient of fluidized bed. 1st correlation is applicable to heat transfer from vertical surfaces and the 2nd one is applied to both horizontal and vertical surfaces. . . . .                                                                                          | 113 |
| Table 5.8  | Comparison of experimental convective heat transfer coefficient with correlations in table 5.7. The operating conditions of each run is available in table 5.1. . . . .                                                                                                                                                                                 | 113 |
| Table 5.9  | Parameters of the cooling system transfer functions for both cooling scenarios. . . . .                                                                                                                                                                                                                                                                 | 117 |
| Table 5.10 | Characterizations of the PI and PIDf controllers. . . . .                                                                                                                                                                                                                                                                                               | 121 |
| Table 5.11 | Coefficients and constants of Eqns. 5.24 and 5.23. . . . .                                                                                                                                                                                                                                                                                              | 124 |

## LIST OF FIGURES

|            |                                                                                                                                                                                                                                                     |    |
|------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 2.1 | General Block Diagram of a GtL Plant . . . . .                                                                                                                                                                                                      | 8  |
| Figure 2.2 | ASF model for the prediction of hydrocarbon product distribution [60].                                                                                                                                                                              | 12 |
| Figure 2.3 | Input injection functions: the dirac delta-pulse is infinite at time zero, while the unit step function takes a value of 1 at zero, and the ideal pulse injection takes value of 1 between $-\Delta t < 0 < \Delta t$ [101]. . . . .                | 16 |
| Figure 3.1 | Preliminary overall P&ID of MRU. The Natural gas compressor, C-1, air compressor, C-2, and cooling water packages are not shown as those are at the battery limit of the main setup. . . . .                                                        | 30 |
| Figure 3.2 | Risk matrix; Top horizontal line is probability ( $P$ ) progress and left vertical line is severity level ( $S$ ) progress. The cross values are the products of $P$ and $S$ in %. . . . .                                                          | 35 |
| Figure 3.3 | Contour plot of risk surface based on probability of malfunction and severity of resulting incident . . . . .                                                                                                                                       | 36 |
| Figure 3.4 | Flow chart of combined HAZOP and risk analysis of risky scenarios — $P_m$ , $S$ , and $R = P_m \times S$ are estimated probability and severity and computed risk level respectively. Cnt is a counter. . . . .                                     | 37 |
| Figure 3.5 | Boundary of Node 1; Natural gas feeding stream with auxiliaries indicated by blue colour and Node 2; compressed air feeding with auxiliaries indicated in green, on the P&ID of MRU . . . . .                                                       | 43 |
| Figure 3.6 | Boundary of Node 3; CPOX reactor with auxiliaries including the furnace indicated in red and Node 4; intercoolers and interconnecting stream between reactors showing in purple, on the P&ID of MRU . . . . .                                       | 44 |
| Figure 3.7 | Boundary of Node 5; FT reactor, its auxiliaries, output stream and the gas analyzer are indicated by the brown colour and Node 6; cooling water circuit including the water pump and auxiliaries are indicated in cyan on the P&ID of MRU . . . . . | 46 |
| Figure 3.8 | Boundary of Node 7; Filter cleaning of FT reactor including the back-wash stream and the auxiliaries are indicated in dark red on the P&ID of MRU . . . . .                                                                                         | 47 |
| Figure 3.9 | Final P&ID of MRU with safety system. The modifications are indicated by the revision clouds . . . . .                                                                                                                                              | 49 |
| Figure 4.1 | Piping and instrumentation diagram of Fischer-Tropsch process . . . . .                                                                                                                                                                             | 56 |

|            |                                                                                                                                                                                                                                                                                                                                                                            |    |
|------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 4.2 | Flow chart diagram of simulation-based control for the Fischer- Tropsch process. O.L.Sim. refers to the open-loop simulation. Depending on the process, the hydrodynamics may contribute to both steady state and dynamic simulation or only the dynamic one. . . . .                                                                                                      | 57 |
| Figure 4.3 | Piping & Instrumentaion Diagram of the experimental setup at Polytechnique Montreal to determine the hydrodynamic regime inside the fluidized bed reactor. Simultaneous rotation of solenoid 4-way valves, S9 and S10, generates argon pulse injection. . . . .                                                                                                            | 63 |
| Figure 4.4 | Process flow diagram of Fischer-Tropsch process with temperature controller in Aspen Plus Dynamics V12. FT is the Fischer-Tropsch reactor, PR is the product stream, V1V4 are the manual valves to adjust steam flow rates that the dynamic simulator adapts the steady state flow rates on 50% valve opening automatically, and TC is the temperature controller. . . . . | 69 |
| Figure 4.5 | Open loop response of the reactor temperature against manipulating the coolant flow rate: (a) step change in flow from 1120 to 600 kg h <sup>-1</sup> . (b) Temperature variation from 300 to 336 °C. . . . .                                                                                                                                                              | 71 |
| Figure 4.6 | RTD of a pulse injection for FT entrance, cyan line, and FT exit, red line. The curve represents $Y = \frac{C_i}{\sum C_i}$ vs time. The actual gas flow rate is 0.35 L s <sup>-1</sup> at 10 bara and 150 °C corresponding $u_g = 6u_{mf}$ with $u_{mf} = 2 \text{ mm s}^{-1}$ . The graph is moved 2 minutes back to match injection at zero time. . . . .               | 74 |
| Figure 4.7 | Closed loop response of the process versus + 10 °C step change in set point, $T_s = 300^\circ\text{C}$ in Aspen Plus Dynamics V12: (a) Set point and measuring temperature of the process, (b) coolant flow rate, and (C), Vol. flow rate of $\text{C}_5^+$ in the product. . . . .                                                                                        | 76 |
| Figure 4.8 | Closed loop response of the process versus - 10 °C step change in set point, $T_s = 300^\circ\text{C}$ in Aspen Plus Dynamics V12: a) Set point and measuring temperature of the process, (b) coolant flow rate, and (C), Vol. flow rate of $\text{C}_5^+$ in the product . . . . .                                                                                        | 77 |
| Figure 4.9 | Closed loop response of the process versus increasing the syngas ratio from 1.8 to 2 in Aspen Plus Dynamics V12, $T_s = 300^\circ\text{C}$ and $F_{\text{syn},s} = 8.7 \text{ kmol h}^{-1}$ : (a) measured process temperature and set point value, (b)coolant flow rate, and (C)Vol. flow rate of $\text{C}_5^+$ in product. . . . .                                      | 79 |

|             |                                                                                                                                                                                                                                                                                                                                                            |    |
|-------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 4.10 | Closed loop response of the process versus decreasing the syngas ratio from 1.8 to 1.5 in Aspen Plus Dynamics V12, $T_s = 300^\circ\text{C}$ and $F_{\text{syn},s} = 8.7\text{ kmol h}^{-1}$ : (a) measured process temperature and set point value, (b) coolant flow rate, and (C) Vol. flow rate of $\text{C}_5^+$ in product . . . . .                  | 80 |
| Figure 4.11 | Closed loop response of the process versus %10 increase in syngas flow rate in Aspen Plus Dynamics V12, $T_s = 300^\circ\text{C}$ and the original $F_{\text{syn},s} = 8.7\text{ kmol h}^{-1}$ : (a) measured process temperature and set point value, (b) coolant flow rate, and (C) $\text{CO}_2$ and $\text{C}_5^+$ concentrations in product . . . . . | 82 |
| Figure 4.12 | Closed loop response of the process versus %10 decrease in syngas flow rate in Aspen Plus Dynamics V12, $T_s = 300^\circ\text{C}$ and the original $F_{\text{syn},s} = 8.7\text{ kmol h}^{-1}$ : (a) measured process temperature and set point value, (b) coolant flow rate, and (C) Vol. flow rate of $\text{C}_5^+$ in product . . . . .                | 83 |
| Figure 4.13 | Closed loop response of the process versus $50^\circ\text{C}$ increase in the feed temperature in Aspen Plus Dynamics V12, $T_s = 300^\circ\text{C}$ : (a) process temperature and set point, (b) coolant flow rate. . . . .                                                                                                                               | 85 |
| Figure 4.14 | Closed loop response of the process versus $50^\circ\text{C}$ decrease in the feed temperature in Aspen Plus Dynamics V12, $T_s = 300^\circ\text{C}$ : (a) process temperature and set point, (b) coolant flow rate. . . . .                                                                                                                               | 86 |
| Figure 4.15 | Closed loop response of the process against step change in set temperature for uncertainty of overall heat transfer coefficient, + % 20 increase in $UA$ : (a) process temperature and set point value, (b) coolant flow rate, and (c) coolant temperature. . . . .                                                                                        | 88 |
| Figure 4.16 | Open loop response of the reactor temperature against manipulating the coolant flow rate for the alternative kinetic model: (a) Step change in flow from $850$ to $500\text{ kg h}^{-1}$ . (b) Temperature variation from $300$ to $336^\circ\text{C}$ . . . . .                                                                                           | 89 |
| Figure 4.17 | Closed loop response of the control system for the model mismatch in Aspen Plus Dynamics V12; the kinetics follows the alternative (LHHW) model, $T_s = 300^\circ\text{C}$ (a) process temperature and $\pm 10^\circ\text{C}$ step change in set point (b) coolant flow rate. . . . .                                                                      | 90 |
| Figure 5.1  | The experimental pilot designed for mobile micro-refinery: (a) the setup originally located at Polytechnique Montreal. (b) 3D of fluidized bed reactor, RC-2, consisting the two internal 2-passes cooling coils. The total length of the longer coil in blue is $6.7\text{ m}$ and that of shorter coil in yellow is $5.3\text{ m}$ . . . . .             | 96 |

|             |                                                                                                                                                                                                                                                                                                                                                       |     |
|-------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 5.2  | Piping and instrumentation diagram of the experimental setup. Compressed air is heated up through the furnace, RC-1 before reaching the fluidized bed reactor, RC-2. The air flow rate and the pressure of the reactor are adjusted by MFCs and back pressure regulator respectively.                                                                 | 97  |
| Figure 5.3  | Air velocity vs $\Delta P$ of the alumina powder in a bench-scale ( $D = 8$ mm) and pilot plant ( $D = 0.2$ m) . Minimum fluidization velocity, $u_{mf}$ , is at the intersection of horizontal and slop lines on the backward measurement which is equal to $2.4 \text{ mm s}^{-1}$ . . . . .                                                        | 98  |
| Figure 5.4  | Dynamics of bed temperature for different superficial gas velocities through the bed in single coil scenario. (a) at 5 bara, (b) at 10 bara. At time zero, the cooling water control valve is open at 50% and the equivalent coolant flow is $13.8 \text{ L min}^{-1}$ . . . . .                                                                      | 104 |
| Figure 5.5  | Estimated overall heat transfer coefficients of heat exchange over time for different superficial gas velocities in single coil scenario. (a)at 5 bara, (b)at 10 bara. The cooling water control valve was 50% open and the equivalent coolant flow is $13.8 \text{ L min}^{-1}$ . . . . .                                                            | 106 |
| Figure 5.6  | Effect of pressure and fluidization numbers, $u/u_{mf}$ , on the average heat transfer coefficient, $U_m$ by running the single coil scenario. . . . .                                                                                                                                                                                                | 107 |
| Figure 5.7  | Dynamics of bed temperature for different superficial gas velocities through the bed in double coil scenario. (a)at 5 bara, (b)at 10 bara. At time zero, the cooling water control valve is open at 50% and the equivalent coolant flow is $13.8 \text{ L min}^{-1}$ . . . . .                                                                        | 108 |
| Figure 5.8  | Estimated overall heat transfer coefficients of heat exchange over time for different superficial gas velocities in double coil scenario. (a)at 5 bara, (b)at 10 bara. The cooling water control valve was 50% open and the equivalent coolant flow is $13.8 \text{ L min}^{-1}$ . . . . .                                                            | 110 |
| Figure 5.9  | Effect of pressure and fluidization numbers, $u/u_{mf}$ , on the average heat transfer coefficient by running the double-coils scenario. . . . .                                                                                                                                                                                                      | 111 |
| Figure 5.10 | Molar heat removal from the fluidized bed during the cooling operation at 10 bara and $u/u_{mf} = 10$ in single and double coil scenarios. . . . .                                                                                                                                                                                                    | 115 |
| Figure 5.11 | Open loop response of the bed temperature to a step change of coolant flow from no-flow to $13.8 \text{ L min}^{-1}$ , equivalent to 50% opening of cooling control valve. (a) Response temperature of the bed for single coil, ‘cyan’ and double coil ‘red’ scenarios. (b) Coolant flow rate from closed valve to equivalent of 50% opening. . . . . | 118 |

|             |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |     |
|-------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 5.12 | Block diagram of the control loop system for changing in bed temperature set point and disturbance rejection. $T_r(s)$ is the set point temperature, $d(s)$ is the disturbance, $u(s)$ is the input variable, here coolant flow rate ( $F_c$ ), and $e(s)$ is the error. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                | 119 |
| Figure 5.13 | Performance of the controller for step change in the set point of the fluidized bed temperature for both single and double coil scenarios. (a) Temperature set point changes from 305 °C to 285 °C. (b) Coolant flow rate variation to recover the temperature on its set value. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                        | 120 |
| Figure 5.14 | Performance of the modified controller ‘red’ and PIDf ‘orange’ against a step change in the temperature of the fluidized bed with the double coil system. (a) The set point of bed temperature changes from 305 °C to 285 °C. (b) Coolant flow rate variation to restore the temperature on its set point. . . . .                                                                                                                                                                                                                                                                                                                                                                                                              | 122 |
| Figure 5.15 | Temperature variation due to the disturbance of generating the heat of FT reaction in absence of cooling system. Solid line is the dynamics of adiabatic temperature at startup (Eqn. 5.25). Dash dot is the approximation of the reactor temperature’s dynamics with a ramp function until it reaches its maximum adiabatic temperature, 1205 °C. $SL$ is the slope of the ramp, 50 °C min <sup>-1</sup> . . . . .                                                                                                                                                                                                                                                                                                             | 125 |
| Figure 5.16 | Performance of the modified PI controller ‘red’ and PIDf ‘orange’ against a ramp disturbance in the temperature of the fluidized bed with double coil. For both controllers, the anti-reset windup technique is used to maintain the coolant flow within its feasible constraint. (a) Controller performance when the temperature ramps up + 50 °C min <sup>-1</sup> for 18 min and then stays at 1205 °C. The upper constraint, 400 °C, is the deactivation temperature of the catalyst. The lower constraint, 280 °C, is the minimum required temperature for dry operation. (b) Coolant flow rate variation to re-adjust the temperature on its set point. The maximum flow rate is $F_c = 60$ L min <sup>-1</sup> . . . . . | 126 |
| Figure C.1  | Closed loop response of the process against step change in set temperature for uncertainty of overall heat transfer coefficient, -10% increase in $UA$ : (a) process temperature and set point value, (b) coolant flow rate, and (c) coolant temperature. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 166 |

## LIST OF SYMBOLS AND ACRONYMS

|       |                                    |
|-------|------------------------------------|
| BET   | Brunauer–Emmett–Teller             |
| DOE   | Design of experiment               |
| CPOX  | Catalytic partial oxidation        |
| FOPTD | First order plus time delay        |
| FTS   | Fischer-Tropsch synthesis          |
| MRU   | Micro refinery unit                |
| PID   | Proportional-Integral-Derivative   |
| P&ID  | Piping and instrumentation diagram |

## LIST OF APPENDICES

|            |                                 |     |
|------------|---------------------------------|-----|
| Appendix A | Nomenclature for P&ID . . . . . | 159 |
| Appendix B | Nomenclature . . . . .          | 162 |
| Appendix C | Supporting Data . . . . .       | 165 |

## CHAPTER 1 INTRODUCTION

### 1.1 Motivations

The energy demand is going on to grow dramatically as the world's population keeps on to increase and economies proceed [1]. Since the capacity of the exploitable oil is decreasing, other virgin resources such as associated and stranded gas reservoirs are notably marked [2]. This kind of resources are practically unused as they are located in remote areas and conventional transferring of the gas to the end users by pipeline is economically unpractical [3]. Apart of this issue, associated gas as a mixture of hydrocarbons from methane to pentane, typically dissolved in crude oil at high pressure which escapes from the solution during the oil extraction. and according to Global Gas Flaring Reduction(GGFR), around 140 billion cubic meters per year of this gas is flared [4]. This amount of flaring discharges more than 300 million tons of  $\text{CO}_2$ , carbon monoxide (CO) and other air pollutants like  $\text{NO}_x$  and  $\text{SO}_2$  that negatively impact on the environment and health issues for people living in the vicinity of these oil regions [4–6]. In Alberta, even though numerous oil wells have been abandoned alone, flaring and venting at oil-treatment batteries continue resulting in an annual loss equivalent to 5500 barrels of oil [7]. Some prominent processes monetize these natural gas resources including liquefied natural gas (LNG), compressed natural gas (CNG) and gas to liquids (GtL) [2, 3]. Among these options, GtL has an outstanding place as it has the potential to transform the natural gas or associated gas into the value-added hydrocarbons as synthetic fuel. In particular, the liquid synthetic fuels are promising alternatives of oil-related transportation sector considering the fact that the price of crude oil gradually rises while its reservoirs are going to finish [8].

However, large scale industrial GTL plants are not always economical as in most cases, building a commercial plant needs a huge investment resulting in the plant to be infeasible [7]. Furthermore, in some areas, providing the industrial utilities such as water resource and electricity is limited or sometimes impossible.

In such cases, to exploit the gas reservoir and convert it to a synthetic fuel like green diesel, micro-scale GTL process or Micro Refinery Unit (MRU) is feasible as it needs a lesser investment and consumes lower utility as well.

The available MRU, designed in Prof. Patience group [4] contains a gauze reactor and a fluidized bed reactor to produce synthesis gas ( $\text{CO} + \text{H}_2$ ) from methane-containing gas and moderate- chain fuels from synthesis gas, respectively.

To generate synthesis gas or briefly 'syngas', a catalytic partial oxidation (CPOX) process is

applied as the produced syngas has the best composition ratio of hydrogen to carbon monoxide to obtain moderate carbon chain length of fuel and in the next step a high temperature Fischer-Tropsch synthesis (FTS) takes place in the fluidized reactor using iron catalysts to augment the production chance of gasoline range hydrocarbon in an environment with uniform heat and mass dispersion.

## 1.2 Problem statement and research objectives

The micro-GtL is an intensified process that comprises CPOX at 900 °C and 20 bar followed by FTS at 300 °C and the same pressure. Even though extensive researches on syngas production and Fischer-Tropsch process have been done so far, insufficient data is available about such a pilot scale plant. The mix of air and methane as the CPOX reactants are flammable as well as hydrogen of the syngas [9] which increases the risk of explosion. Moreover, CO is toxic and its emission to the environment makes high risk. Due to lack of information in academic literature about the potential hazardous scenarios on the pilot GtL, a precise process hazard review is required to modify the process design by adding protection layers to the system before running the setup. Furthermore, unpredictable operating conditions at the upstream well head and syngas generation causes disturbance resulting in unstable FT process. Both reactions are exothermic and FTS, in particular, generates huge amount of heat during the reaction. The generated heat may increase the process temperature rapidly and without a reliable temperature controller, it goes over the design temperature of catalyst, reactor and instruments. The over-temperature conditions deactivates the catalyst due to sintering and coking, runaways the reaction [10] and even makes thermal stress leading to incidents like cracking and reactor burst [11,12]. To design a credible controller, dynamics of the system either at the startup stage or at the normal operation is crucial. However, the kinetics of Fischer-Tropsch, hydrodynamics, and heat transfer rate of the pilot process in particular are the challenging parameters that are not addressed well in the academic literature. Moreover, ensuring adequate heat removal capacity is a crucial factor in the development of commercial FT reactors [10]. At the early stage of developing the micro-GtL technology, when the pilot setup has not run yet in the actual operating conditions, uncertainties and lack of knowledge about kinetics and hydrodynamics parameters as well as dangerous scenarios at startup, normal operation and shutdown make enormous issues leading to various losses. Hence the objectives of this research are summarized in three parts.

### Objective 1 : Process hazard review and risk analysis of micro-GtL unit

- Identify the risky scenarios

In the first part, we study the hazardous operability (HAZOP) of the MRU, compare the available methods of process safety, and select the efficient approach to identify all hazardous scenarios as designing the safety loop and risk assessment of this unit to handle the GTL process in a mobile setup located near an oil-gas field.

- **Development of a numerical analysis method to minimize the risk**

In the next step, we develop an appropriate risk assessment method to realize the risk level numerically before and after adding the safeguards which assists us to mitigate the risk as much as possible.

## **Objective 2 : Design a preliminary temperature controller for FT reactor**

- **Design a simulation-based temperature control system**

As the pilot setup is not run yet in actual conditions, no experimental data exists to specify the kinetics of the FT reaction. Therefore, we focus on FTS, select an experiment-based kinetics and propose a lumped kinetic model, and provide a heat exchange approach to identify the dynamics of the system resulting in the design of a preliminary temperature controller for the FT reactor.

- **Performance test of the controller against uncertainties and disturbances**

We test the performance of the controller in case of uncertainties in the kinetics and heat transfer parameters as well as possible disturbances that may happen in the FT process resulted from the former CPOX reactor or upstream source to ensure about its convenient application during the operation. Hence, we provide this opportunity to improve the controller during the operation without getting into the unstable conditions.

## **Objective 3: Integrate the cooling design and control of a fluidized bed system**

- **Impact of operating conditions and coil arrangement on the thermal performance of the reactor**

We propose a safe mode experiment to find out the impact of the operating pressure, feed gas flow rate and cooling coil arrangement on the dynamics of heat exchange between the fluidized bed and cooling coil.

- **Design a temperature controller applicable at startup and regular operation**

After identifying the most efficient scenario of cooling from the transient dynamics, we

designed a PI controller as well as a PID plus filter and tested their performances. This is a guideline to run the actual FT process. We also recognized the deficiencies of the cooling system and the required measures to improve it.

### 1.3 Summary of contributions

- **Safety Analysis and Risk Assessment of a Micro-GtL Plant**

Published in :

Journal of Loss Prevention in the Process Industries, vol. 83, p. 105071, 2023

We proposed a method called Failure Mode Risk Decision (FMRD) to review the inherent hazards of the MRU. This approach combines the Process Flow Failure Mode (PFFM) methodology as a systematic and reliable technique with a novel numerical risk assessment method to improve the analytical evaluation of hazardous conditions. The objective is to combine causes and consequences in a single metric, where scaled probability of evident causes and severity of consequences are used to derive a risk level measure. With the proposed metric, the magnitude of a potential hazard is directly correlated with the risk level. This mechanism identifies extra risk scenarios compared to the classical hazard analysis method and provides a straightforward comprehensive numerical assessment to represent the inherent and residual risks to facilitate justifying the hazardous scenarios. Accordingly, we designed a safety loop and supplied all the required facilities to remove the potential risks at the process plant. Not only the proposed methodology clarifies the risks of the MRU presented in this study, but can be extended to review the hazards of other chemical process plants [13].

- **Feedback Control Strategy of Fischer–Tropsch Process in a Micro-GtL Plant**

Submitted to :

Journal of Chemical Engineering and Processing–Process Intensification, September 2023

We proposed a simulation-based feedback controller design strategy to initially estimate the parameters of a proportional Integral (PI) controller. We applied a power law model to design the controller in Aspen V12 and tested its robustness with a fractional lumped model as an alternative. An excel ‘solver module’ estimated heat exchange parameters considering the fluidized bed hydrodynamics at steady state. Then, through dynamic simulation, we identified the parameters of a ‘first-order plus time delay’ model

via a step response of the reactor temperature to design the PI temperature controller. The controller parameters were characterized by the internal model control (IMC) approach, which is suitable to characterize kinetic model mismatch and heat exchange uncertainties.

- **Experimental Modeling of Heat Exchange for Control Design of a Fluidized bed System**

Submitted to :

Journal of Applied Thermal Engineering, October 2023

We designed a safe mode experiment for a coil-equipped fluidized bed reactor with single and double cooling coil scenarios using compressed air. In each scenario, we run the experiments at 5 and 10 bara, and superficial gas velocities from  $5u_{mf}$  to  $10u_{mf}$  to investigate the effect of operating conditions on the dynamics of the cooling. The result verifies that the dynamics of the cooling is faster at higher pressure and fluidization which favours the exothermic process. The estimated cooling rate for both scenarios also reveals that the surface area of double coil is capable to remove the equivalent heat to the enthalpy of FT reaction. Finally, we identified the parameters of the experimental heat transfer model for both cooling scenarios and designed a PI and a PID controller plus filter (PIDf) separately using internal mode control (IMC) approach based on the double coil model as it cools down the process faster than the single one and then tested the performance of both controllers for a step change and disturbance rejection of the bed temperature in the reactor. Based on the results, the performance of the PIDf controller is better than the PI, as it smoothly restores the bed temperature to its set point. Thus, we proposed a cooling strategy at startup and during the normal operation which involves the double coils coupled with its PIDf controller.

## 1.4 Thesis structure

This proposal contains seven chapters and three annexes. Chapter 1 presents an introduction. Chapter 2 presents literature review on each objective. Chapter 3 gives the first contribution entitles ‘Safety analysis and risk assessment of a micro-GtL plant’. Chapter 4 offers the second contribution ‘Feed-back control strategy of Fischer-Tropsch reactor in a micro refinery plant’. Chapter 5 presents the third contribution ‘Experimental Modeling of Heat Exchange for Control Design of a Fluidized bed System’. Chapter 6 briefly explains the main procedures of risk assessment, testing the controller performance in simulator as well as startup of the

pilot plant and eventually chapter 7 offers the conclusion, limitations and future works. Annex A contains the nomenclature as well as the abbreviations and the symbols of the piping & instrumentation diagram (P&ID) of the plant. Annex B is the nomenclature, and Annex C covers the supporting data.

## CHAPTER 2 LITERATURE REVIEW

Considering all the essential aspects of this research, illuminates the lack of information about the process resulting in procedures to achieve the final targets. Therefore, the sequential structures of this review are: study the available technologies, chemistry of each process, safety issues and risk process hazard review of chemical plants, modelling and control of the FT process and finally heat transfer of the fluidized bed systems.

### 2.1 Gas To Liquid (GtL) Technology

Even though Gas-to-liquid (GtL) mostly emerges a process getting involve with Fischer-Tropsch synthesis (FTS) to produce liquid fuels and petrochemical products from natural gas [4, 14], it also includes the synthesis of oxygenates [4, 14, 15]. These higher value liquid products obtained from synthesis gas (syngas) are hydrocarbons via FTS and oxygenates such as methanol and Dimethyl ether (DME). In the GtL processes, feedstocks may be natural gas, or generated gas from gasification of biomass or coal [4].

Some predictions represent that world's inquiry to diesel may increase from 25 million barrels a day in 2011 to around 40 million barrels a day by the year 2035. In this regard, GtL technologies have a promising contribution to envisage the increasing demand for transportation fuels [1].

Excluding of feedstock pre-treatment and purification [16, 17], the GtL process basically consists of three main sectors (Fig. 2.1) [3, 16–20].:

1. Syngas production unit to produce syngas with proper ratio  $H_2/CO$ .
2. FTS unit to synthesis the fuels from syngas.
3. Separation and upgrading unit to reach the marketable liquid fuels via hydro-processing and cracking operations.

The treatment of feedstock, either non-associated or associated natural gas, includes removal and recovering of natural gas liquids (NGL or LPG) and /or gas sweetening to mitigate the concentration of  $CO_2$  and sulphur components [16, 21]. In following, each unit is briefly explained.

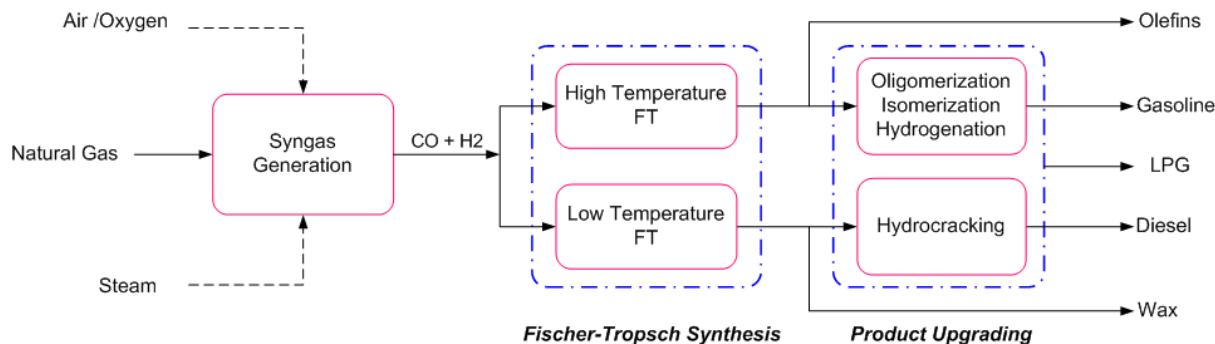


Figure (2.1) General Block Diagram of a GtL Plant

## Compact GtL units

The dominant privilege of GtL technologies is that they decline the affinity of transportation fuels to crude oil. However, the technologies are complicated and costly and in particular, a few companies have the know-how of the process which might be a limiting factor to build large-scale plants [1]. GtL manufacturing is also affected by both of oil and gas price risks since its economical justification relies on the difference between the gas feed cost and oil-derived fuel prices [1]. For these reasons, small GtL plants consuming associated gas in remote onshore and offshore oil fields are really preference. These units not only address to flaring reduction [1] but also require low investment. In this regard, some companies have started to develop this technology in micro-scale of industrial plant. One of them is UK-based company CompactGtL [1, 22, 23]. Here, associated gas is converted to syngas through the steam methane reformer and syngas is then fed into FT reactor to generate syncrude [1, 2], water and a tail gas consisting of hydrogen, carbon monoxide and light gases. Next, the main synthetic oil is sent to a refinery for post-treatment [1]. Another design refers to a share work of Velocys and Toyo Engineering and Mitsui Ocean Development & Engineering Co. They commercialized Micro-GtL unit for small capacity gas reservoirs. They constructed with Petrobras a unified small scale consuming associated gas [2].

## 2.2 Syngas production unit

Synthesis gas is produced from various feed sources such as natural gas, coal, biomass, naphtha, residual oil, and petroleum coke. However, natural gas especially low-value natural gas, is notably one of the desirable feedstocks [16, 17]. To produce the syngas, commercial technologies including steam methane reforming (SMR), non-catalytic partial oxidation (POX), and auto-thermal reforming (ATR) are available and also some alternative methods like cat-

alytic partial oxidation (CPOX) [16,24,25] and carbon dioxide reforming [16] are being tested. SMR is a highly endothermic process which normally occurs at 25 bar to 45 bar and 900 °C catalysed by nickel [16,26,27]. The advantages of this method are summarized in no need for oxygen plant to supply the oxygen feed, and syngas ratio,  $H_2/CO$  of about 3 [16] deserving it for  $H_2$  production purposes [25]. However, it needs high steam to carbon (S/C) ratios as the feed to prevent the carbon formation on the catalyst [25] and it is accordingly applicable where plenty of water at low cost is available [16,28].

POX, as another commercialized technology, is based on the exothermic non-catalytic reactions of methane and oxygen that takes place in a combustion module [25]. In this technology, oxygen obtained from air separation unit (ASU), reacts with natural gas at 20-150 bar and the generated syngas has a ratio about 1.6-1.9 [16,29] which may not be favorable in GtL application [25,30–32].

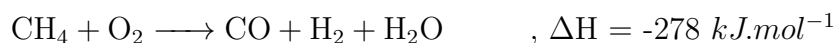
This approach has some priorities; it is tractable to wide range of feedstocks from natural gas to petroleum coke [25,30] and the process is insensitive to coke formation as no catalyst is used for the reaction [25]. However, operating temperature of reformer is near 1400 °C to get the high conversions of methane. Furthermore, some soot likely formed during this process that must be separated next to the reactor [16,28,32].

Another substantial technology of syngas generation for GtL is ATR since the produced syngas ratio is match more with the stoichiometry of the Low temperature Fischer-Tropsch [24,25]. In fact, ATR combines partial oxidation with steam reforming in the same reactor [16,33,34]. The reactor operates at 20 bar to 40 bar [16] and comprises of a burner to provide well mixing of feed, a combustion chamber and a catalytic fixed bed part in a refractory lined pressure vessel [16,25]. In general, produced gases from partial oxidation burner are blended with steam and sent to the steam reformer and providing auto-thermal conditions along the process. The generated heat from partial oxidation supplies the heat for steam reforming [1]. The catalyst bed which preferably is nickel-based supported on either alumina ( $\alpha-Al_2O_3$ ) or magnesium alumina spinel ( $MgAl_2O_4$ ) operates nearly adiabatic at temperature 1100 °C to 1300 °C [16]. Indeed, its relative compactness, and economical issues such as lower capital investment, excel ATR as a dominant industrial process [16,35].

Along with modifying the current technologies, some prominent investigations are going on to develop new technologies concentrated to reduce the costs of syngas production and consequently the total investment of the GtL unit. Catalytic partial oxidation (CPOX), as one of the feasible alternatives, carries out in a catalytic reactor without a burner [16,24,25]. As this reaction is exothermic, it would save much more energy rather than the steam reforming. Oxidation reactions are also notably faster than the reforming reactions leading to a single stage syngas generation, smaller reactor and a higher throughput [16].

### *Catalytic Partial Oxidation of Methane*

Although almost all the syngas production technologies are based on SMR, ATR or POX, catalytic partial oxidation (CPOX) has a dominant potential to be integrated with Fischer-Tropsch synthesis to obtain fuel from natural gas. Through the main reaction of partial oxidation, synthesis gas with 2:1 ratio of hydrogen to carbon monoxide is produced from interaction of methane to oxygen according to the following stoichiometry: [36]:



Partial oxidation has some advantages in comparison with other processes:

- As the oxidation reaction is exothermic, the process would save much more energy.
- Through the main reaction of CPOX, synthesis gas with a  $\text{H}_2/\text{CO}$  close to 2 is produced which is proper for Fischer-Tropsch process.
- As the oxidation reactions are faster than reforming, its promising a smaller reactor and higher throughput of feedstocks leading to lower capital cost [4, 36–39].
- Since the reaction consumes low amount of oxygen, it can serve directly compressed air instead of installation of air separation unit which reduces the capital investment and operating costs [7].

### *Catalysts*

Among various supported metal catalyst from group VIII i.e. Fe, Co, Ni, Ru, Rh, Pd, Ir and Pt tested in CPOX process, both Ni and Rh-based catalysts have been the best one since noble metals are much more expensive despite high activity and better performances [37]. Although Nickel is cheaper than the others, it tends to form coke. Due to this fact, researchers focus to synthesis catalysts not only have a high stability and activity also well resistant to carbon formation [25, 37, 40–45].

In addition, running the CPOX at high pressure is a challenging issue due to insufficient selectivity of methane to CO and  $\text{H}_2$  and high selectivity towards coke [40]. Patience et al. have developed a new generation of catalysts promoting the methane conversion to syngas while reducing the coke formation [40, 41] and recently they are attempting to modify the

catalyst attributes to magnify the methane conversion and suppress the carbon formation [41].

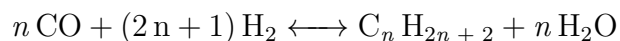
## 2.3 Fischer-Tropsch synthesis

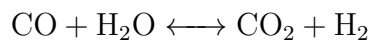
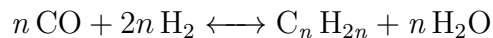
The Fischer-Tropsch process is known as the catalytic hydrogenation of carbon monoxide to produce a range of hydrocarbon products from oxygenated hydrocarbons to high quality diesel fuel and gasoline as well as linear chemicals including 1-alkenes and alkenes [16, 46]. The Fischer-Tropsch reaction is highly exothermic with an enthalpy domain of  $165 \text{ kJ mol}^{-1}$  to  $180 \text{ kJ mol}^{-1}$  of converted CO (related to exact product composition). Consequently, specification of all FT reactors is maximum heat removal. Insufficient cooling would otherwise lead to deactivation of catalyst, reduction of selectivity to desired products and even run-away reaction [16, 17]. The commercial Fischer-Tropsch (FT) reactors may be classified as four types: fixed bed, slurry phase, fluidized bed and circulating fluidized bed reactor [47–52]. The operating pressure of process is 18 bar to 45 bar and in terms of operating temperature, FT reactors are high temperature (HTFT) and low temperature (LTFT). The main difference between these two class is that in HTFT no liquid phase forms around the catalyst particles. In other words, liquid formation in HTFT reactors will result in severe problems because of the particle agglomeration and missing of fluidization [16, 18]. To synthesis of the Fischer-Tropsch catalysts, four metals (Fe, Co, Ni, and Ru) from group VIII are highly active to hydrogenate the carbon monoxide [16]. However, cobalt and iron are commercial due to the fact that ruthenium is a scarce and accordingly expensive metal which is non-economical for industrial application [16]. Nickel also generates much more methane than cobalt and iron and produces volatile carbonyls leading to loss of the metal at industrial operating conditions even if it is cheap and a powerful hydrogenating catalyst [16].

### 2.3.1 Kinetic Modelling

In general, kinetic modelling is the main part of the Fischer-Tropsch reaction for the industrial process design, simulation, scale-up and optimization [53].

FTS is the substantial technology to reach liquid fuels from coal, biomass and specially natural gas. The overall FTS reaction can be summarized as the combination of paraffin and olefin formation accompanied by water gas shift (WGS) reaction [54]:





In the view of FTS as polymerization process, the synthesis consists of three steps; initiation of chains, competing chain propagation and chain termination [55]. Based on this frame, the products tend to follow the Anderson-Shultz-Flory (ASF) chain-length statistical distribution [55–58]. The mathematical expression of the ASF distribution is as follows [59]:

$$W_n = n \cdot \alpha^{n-1} (1 - \alpha)^2 \quad (2.1)$$

where  $\alpha$  is the chain growth probability factor, and  $W_n$  is the mass fraction of hydrocarbon with the carbon number of  $n$ . Figure 2.2 shows the ASF product distribution [60]. Based on this model, the product selectivity depends on the chain growth probability ( $\alpha$ ), so that the the model has a substantial role in maximum selectivity toward the final product [56]. Al-

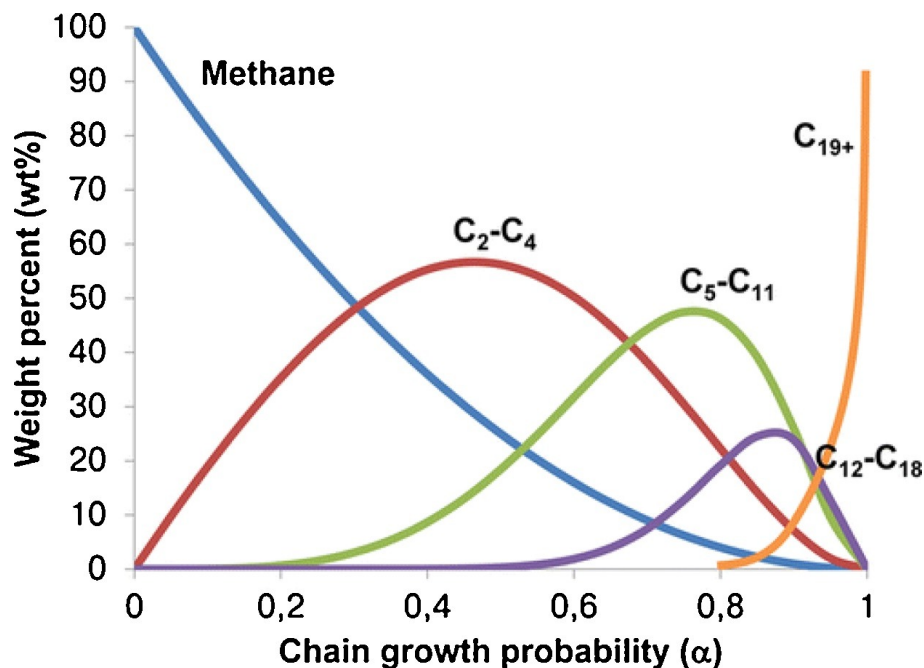


Figure (2.2) ASF model for the prediction of hydrocarbon product distribution [60].

though the ASF distribution is feasibly an acceptable estimation of the hydrocarbon product, it is not always true, and deviations from this theory was reported many times [47, 58, 61–63].

Theories for ASF deviations focus on the superposition of the two ASF distributions and relay in the dual active sites theory [61,63–66], secondary chain growth of re-adsorbed alkenes theory [58,61,62,67], and the dual mechanism of chain growth theory [68,69]. Iron catalysts are more likely to follow the dual mechanism pattern of chain growth [55]. The chain growth probability depends on the temperature and the partial pressure of the syngas components. Fischer-Tropsch technology mainly divided into two LTFT and HTFT processes. LTFT normally operates in temperature lower than 250°C to minimize unwanted methane production and maximize the wax selectivity as well as avoiding the hydrocracking of the wax [70]. On the other hand, the operating temperature of HTFT is 300-350°C and the process operates by iron-based catalysts [71]. Sie and Krishna [50], developed some equations to show that the operating temperature to be higher than 280 °C so that the gas-solid fluidized FT processes meet the dry operating conditions and obtain a relatively light product of low  $\alpha$  value. Product mainly consist of light hydrocarbons that are almost linear paraffins or with a low degree of branching. The oil is substantially rich in olefinic chemicals, especially linear  $\alpha$ -olefins but low in aromatics and naphthenics (cyclo-paraffins and cyclo-olefins) [57]. Iron is capable to inspire WGS which is substantial in case of low  $H_2/CO$  content as it converts excess carbon monoxide to hydrogen to improve the syngas ratio [47, 72, 73]. Adding an alkali promoter such as potassium to iron can also increase the dissociative adsorption of CO leading to improve accordingly the carbonization and hinder methane formation [72,74–76]. Furthermore, iron catalyst is more productive than cobalt in more severe conditions such as higher space velocities and higher reactor pressures [47].

Selection of appropriate reactor depends on the expected products such as light olefin, gasoline, diesel or heavy hydrocarbons including wax [77,78]. In addition, as the FT process is highly exothermic [50], adapting an appropriate cooling system to the reactor is critical to obtain the optimum temperature gradient in catalyst-bed and remove hot-spot creation [54]. In this regard, fluidized bed reactor is the excellent one for high temperature FT as donates a high conversion and selectivity for precious chemicals with an economically feasible process in multi-phase reactions [79,80]. In fact, fluidized bed reactor is specified by higher heat and mass transfer rate as a result of effective contacting and mixing properties compare to other plug flow reactors [54,81].

The major difficulty of developing an accurate model over a range of experimental carbon numbers is the detailed construction of FTS mechanism [82–84]. FT using iron-based catalyst is challenging since the catalyst is dual function that produces both paraffin and light olefin. Furthermore, it arises the water gas shift reaction which makes the FT complex as in one hand it produces more  $H_2$  that is required for progress of the FT reaction and on the other hand, it consumes the CO to hinder the FT reaction. The main benefits of iron catalysts

over cobalt are:

- Cost much less than cobalt catalyst [85,86].
- Display higher activity in the water-gas shift reaction and high selectivity towards olefins which is stable in converting the high  $H_2/CO$  syngas [85,86].
- Operability under a wide range of temperatures and ratios of  $H_2/CO$  resulting in low selectivity to methane [87].
- Improve the syngas conversion from raw materials such as biomass with low  $H_2/CO$  because of the high activity of the WGS reaction [87,88].

The kinetics expressions developed for both iron- and cobalt-based catalysis are mechanistic equations of Langmuir-Hinshelwood-Hougen-Watson (LHHW) and empirical power law forms [88]. The power law kinetic models developed with iron catalyst are function of partial pressures of reactants, and products. Since this kinetics does not address the reaction mechanisms in detail, its application is limited to the industrial cases [88]. Another model uses the Langmuir's theory to express the competition among  $CO$ ,  $CO_2$ ,  $H_2$ , and  $H_2O$  to adsorb on the catalyst's sites [89]. This model has insufficient accuracy in predicting a wide range of hydrocarbons. LHHW-based models consider the elementary step of forming monomer as the rate-determining step where various active sites are involved for water gas shift reaction, paraffins and 1-olefins formation [90]. These models contribute the partial pressures of  $H_2$  and  $Co$  in the initial rate of carbon dioxide and various hydrocarbons. However, those are limited to the ideal chain growth probability model and each model can handle a limited range of operating conditions, for example some work for syngas ratio of 3 and higher and some works for constant pressure and narrow range of temperature ( $220^\circ C$  to  $260^\circ C$ ) [90,91]. More complex models are based on the overall consumption rate of  $CO$ , the hydrocarbon distribution model, and olefin re-adsorption which cites the paraffins and olefins formation

Among the available kinetic models for iron catalysts, only a few are valid in a range of temperatures above  $260^\circ C$  and pressures above 15 bar [92–94] and some models are, in particular, limited to a constant temperature without estimating the activation energy of the both FT and WGS reactions [55,95,96]. The kinetic models are targeted to be developed based on a widespread data set and operating conditions. However these models have complex catalytic mechanism, statistical uncertainties on the kinetic constants and challenging assumptions to generalize [88,97].

Furthermore, the major problem of the most fractional kinetic models is that they do not address the enthalpy variation over time and because of limitations on their spatial bound-

aries, their coefficient, and initial conditions they fail in the dynamic simulation or result in inverse temperature behaviour with time meaning the temperature of the reactor increases with removing more heat instead of decrease [95, 96, 98]. Considering all these issues, we selected two models, power law and fractional, which are not only reliable on desired operating conditions of fluidized bed FTS also flexible on time variation domain that makes them appropriate for the dynamic simulation.

### 2.3.2 Hydrodynamics

Even though the back-mixing and inefficient contacting in fluidized bed reactors may reduce the performance and/ or negatively impacts on the conversion and selectivity, these reactors have substantial advantages for industrial operations like; rapid solid mixing maintains the conditions close to isothermal leading to simple and reliable controlled operation, resists to quick temperature variations and slows down the abrupt changes in operating conditions which reduces the likelihood of temperature runaway for highly exothermic reactions, high heat and mass transfer between gas and particles compared to other modes, and high heat transfer rate between a bed and immersed tubes of heat exchanger [99]. In fluidized beds, when the pressure drop exceeds the weight of the bed, the bed continues to expand with increasing gas velocity, and bubble frequency increases [100].

Extensive vertical motion of porous particles in catalytic reactors moves up and down the adsorbing reactants within the bed which decreases the conversion and selectivity. Thus, we need to know the amount of back mixing, how to model it mathematically to predict the concentrations, and what tools are applicable to reduce this motion. To increase the conversion and selectivity of the catalyst to the desired product, placing horizontal and vertical tubes within the reactor is effective as it improves the temperature control, decreases the gulf circulation of solids, reduces the bubble size, rises the emulsion voidage and increases the overall residence time of reactants in the bed [99]. Particle size and density (Geldart group) with fluid properties determine the flow regime. For example, group A powders are aeratable, their  $d_p$  is around  $70\mu\text{m}$  with bulk density of  $1000\text{ kg m}^{-3}$ . This group powders begin to bubble at velocities around  $2u_{mf}$  and higher while group B powers immediately transit from the fixed bed to the bubbling regime [100]. The bubbling fluidized bed is considered at moderate gas velocities,  $u_0 < 10u_{mf}$ . At higher velocities more particles are conducted into the freeboard above the bed, some of them return to the bed and the rest move out of the bed which makes the bed surface agitated. The terminal velocity,  $u_t$  of the small particles is theoretically  $78u_{mf}$  and for large particles,  $u_t = 9.2u_{mf}$  [99]. The onset of turbulent fluidization,  $u_k$ , is beyond  $u_t$  and for fine particles,  $u_k/u_t = 8 - 13$  which decreases

with pressure increase. Fast fluidization occurs at higher gas velocity,  $u_0 > 20u_t$  when the solid particles are pushed into the bottom of the column [99].

### Residence time distribution (RTD)

One of the applicable tools to characterize the experimental and industrial fluidized beds in order to identify the flow pattern and back-mixing and to quantify kinetics is residence time distribution (RTD) using step or pulse injection techniques [101]. First, detector of gas chromatograph (GC) records the signal over time and the pick position with respect to the residence time of a component that has little or no affinity to the column. The shape of the these peaks depends on eddy diffusion, longitudinal diffusion, and mass transfer between the mobile and stationary phases [101,102]. RTD measurement to study the hydrodynamics of the vessels relies on non-reactive, non-absorbing tracer with a pulse input that injects a certain amount of tracer in a time shorter than the vessel residence time. If the pulse injection is narrower than RTD, it is approximated as Dirac  $\delta$  – *pulse*. Even though achieving this pulse is more crucial, its mathematics is simpler than a ideal pulse [103]. Another injection technique is step tracer input, which is a constant rate of tracer is added to the feed at  $t = 0$  while before this time, no tracer existed and the concentration of tracer in the feed to the reactor is maintained at this level until the concentration in the effluent is equal to that of the feed (Fig. 2.3).

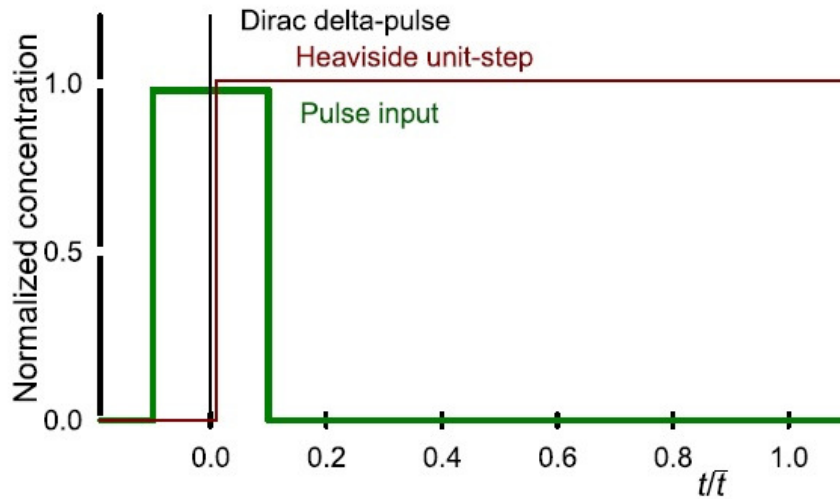


Figure (2.3) Input injection functions: the dirac delta-pulse is infinite at time zero, while the unit step function takes a value of 1 at zero, and the ideal pulse injection takes value of 1 between  $-\Delta t < 0 < \Delta t$  [101].

Although it is easier to carry out practically than the pulse test and we do not need to know the amount of tracer in the feed, it has disadvantages. It is sometimes tough to keep a constant tracer concentration in the feed. Estimating the RTD in this way also involves differentiation of the data resulting in large errors. Moreover, significant amount of tracer in this test, particularly when it is very expensive make it costly compare to cost-efficient pulse test [103]. The RTD function,  $E(t)$  expresses the time that the tracer stays in the reactor [103]. In fact  $E(t)$  is the probability that a tracer that enters the reactor at  $t = 0$  leaves it at  $t$  [104]:

$$\int_0^\infty E(t)dt = 1 \quad (2.2)$$

Hence the first moment is the mean residence time (Eqn. 4.19) and the second moment is the variance ( $\sigma^2$ ) representing the spread of the curve and that how much the tracer deviates from plug flow regime (Eqn. 4.20) [105].

$$\bar{t}_{\text{pulse}} = \frac{\int_0^\infty tC(t)dt}{\int_0^\infty C(t)dt} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \quad (2.3)$$

$$\sigma_{\text{pulse}}^2 = \frac{\int_0^\infty t^2 C(t)dt}{\int_0^\infty C(t)dt} - \bar{t}_{\text{pulse}}^2 = \frac{\sum t_i^2 C_i \Delta t_i}{\sum C_i \Delta t_i} - \bar{t}_{\text{pulse}}^2 \quad (2.4)$$

### Axial dispersion model

One dimensional axial dispersion model is a measure of prevailing hydrodynamic regime. The model considers the plug flow and inside the vessel and merges the effects of back-mixing and axial diffusion inside the reactor [105,106] with assuming negligible radial gradients [107]. To characterize the experimental data, we adopt the axial dispersion model for the pulse injection (Eqn. 4.21):

$$\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial \xi} = \frac{1}{N_{\text{Pe}}} \frac{\partial^2 C}{\partial \xi^2} \quad (2.5)$$

where  $\theta = tu/Z$  (non-dimensional time),  $\xi = z/Z$  (non-dimensional length),  $N_{\text{Pe}} = uZ/D$ , is the Peclet number,  $Z$  is the system length,  $D$  is the axial dispersion, and  $u$  is the tracer gas velocity. The Peclet number and the moments are related to each other [108]:

$$N_{\text{Pe}} = \frac{8}{\sqrt{8\sigma^2/\bar{t}^2 + 1} - 1} \quad (2.6)$$

Depending on various boundary conditions; open-open, closed-open, and closed-closed, Equation 2.5 has different solutions and for the closed-open system, the exact analytical solution for the bolus-pulse is [109]:

$$G'(\theta) = G(\theta) - H(\theta - \eta)G(\theta - \eta) \quad (2.7a)$$

$$H(\theta - \eta) = \begin{cases} 0 & , \theta \leq \eta \\ 1 & , \theta > \eta \end{cases} \quad (2.7b)$$

$$G(\theta) = \frac{1}{2} \left[ \text{erfc} \sqrt{\frac{N_{\text{Pe}}}{4\theta}}(1 - \theta) + e^{N_{\text{Pe}}} \text{erfc} \sqrt{\frac{N_{\text{Pe}}}{4\theta}}(1 + \theta) \right] \quad (2.7c)$$

where  $\eta = (V_{\text{loop}}/\dot{V})(u/Z)$  is the non-dimensional time length of the pulse injection,  $V_{\text{lp}}$  is the volume of the sample loop,  $\dot{V}$  is volumetric flow rate.

Continuous stirred tank reactors,  $n_{\text{CSTR}}$  assumes perfect mixing for each tank in series and its model is approximately equal to dispersion model and they are related by [107]:

$$n_{\text{CSTR}} = N_{\text{Pe}}/2 + 1 \quad (2.8)$$

Fitting the RTD curve to axial dispersion model identifies diffusion and back-mixing, high Peclet numbers ( $N_{\text{Pe}} > 20$ ) represents plug flow and  $N_{\text{Pe}} < 10$  shows back-mixed phenomena [101].

### 2.3.3 Heat transfer

#### Heat transfer coefficient

One of the main advantages of a fluidized bed is maintaining a uniform temperature throughout the bed. The moving solid particles in the bed act as heat carriers and facilitate the heat transfer in the bed and make a nearly uniform temperature profile [110]. Therefore, a good understanding of the flow and heat transfer characteristics is fundamental to design and con-

trol a fluidized bed particularly when it applies to a chemical reactor [111]. Considering the system as a heat exchanger to take or remove the heat and that the convection of heating or cooling fluid is generally high ( $> 1000 \text{ W m}^{-2} \text{ K}^{-1}$ ), the determining portion of the overall heat transfer coefficient is the bed convection. Hence, over the last few decades, the heat transfer from a fluidized bed to immerse tubes has been broadly studied [112,113] to improve this parameter. According to the literature, following factors impact on the heat transfer coefficient [114–118]:

- Physical properties of the gases and the solid particles inside the bed such as particle size, density, specific heat capacity, and thermal conductivity as well as gas density, viscosity and thermal conductivity.
- Operating conditions including temperature, pressure, and superficial gas velocity.
- Design of gas distributor, heat transfer surfaces; geometry, location and the orientation of the internals.

However, most of the available database of fluidized bed heat transfer are at atmospheric pressure [119,120]. Researchers also worked on both of immersed horizontal [112,121,122] and vertical tubes within the fluidized beds [118,123,124]. In bubbling fluidized bed, increasing the gas velocity boosts the heat transfer coefficient and when it approaches the transition region, slows down the increase of heat transfer coefficient and in the turbulent regime,  $h_b$  slightly decreases [124]. Table (2.1) summarizes the mostly used correlations of convective heat transfer according to the coil orientation:

Table (2.1) Correlations available in the literature to predict the average heat transfer coefficient.

| Ref.  | Correlation                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | Application                      |
|-------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------|
| [125] | $\frac{hd_p}{k_g} = 0.525 Re_p^{0.75}$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | Vertical surfaces                |
| [122] | $\frac{hD_t}{k_g} = 1.754 Re_p^{0.556} Pr^{0.3}$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | Horizontal surfaces              |
| [126] | $\frac{hD_t}{k_g} = 0.66 Pr_g^{0.3} \left( \frac{\rho_s(1-\varepsilon)}{\rho_g \varepsilon} \right)^{0.44} Re_D^{0.44}$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | Horizontal surfaces              |
| [127] | $\frac{hD_t}{k_g} = 900(1-\varepsilon) \left( \frac{\rho_s}{\rho_g} Pr_g \left( \frac{\mu_g^2}{g \rho_s^2 d_p^3} \right) \right)^{0.3} Re_D^{0.3}$                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Horizontal surfaces              |
| [128] | $\frac{hd_p}{k_g} = 0.74 Ar^{0.1} \left( \frac{\rho_s}{\rho_g} \right)^{0.14} \left( \frac{c_{ps}}{c_{pg}} \right)^{0.24} (1-\varepsilon)^{2/3} + 0.46 Re_p Pr_g \frac{(1-\varepsilon)^{2/3}}{\varepsilon}$                                                                                                                                                                                                                                                                                                                                                                                                                  | Vertical and horizontal surfaces |
| [129] | $\frac{hl_1}{k_g} = \frac{0.125(1-\varepsilon_{mf})}{a_1[1+a_2(k_g/2c_{ps}\mu_g)]} + 0.165 Pr_g^{1/3} \left( \frac{\rho_g}{\rho_s-\rho_g} \right)^{1/3} \left( \frac{1}{a_3} \right)$<br>$a_1 = 1 + 33.3 \left[ \left( \frac{u_e \rho_p c_{ps}}{u_{mf} g k_g} \right)^{1/3} u_e \right]^{-1}$<br>$a_2 = 1 + 0.28(1-\varepsilon_{mf})^2 u_e u_{mf} \left( \frac{\rho_g}{\rho_p-\rho_g} \right)^{1/2} \left( \frac{\rho_p c_{ps}}{g k_g} \right)^{2/3}$<br>$a_3 = 1 + 0.05 \left( \frac{u_{mf}}{u_e} \right)$<br>$l_1 = \left( \frac{\mu_g}{\rho_s-\rho_g} \right)^{2/3} \left( \frac{1}{g} \right)^{1/3}, u_e = u_0 - u_{mf}$ | Vertical and horizontal surfaces |

Inserting the vertical immersed heat exchanging tubes within the gas-solid fluidized bed has some advantages compare to horizontal ones. It minimizes the pressure drop, slugging, bed height fluctuations, and particles erosion which improve the heat transfer in the beds [130–132]. Furthermore, vertical internals reduce the bubble size resulting in better mass and heat transfer rates inside the bed [118]. One of the critical hydrodynamic parameters in design, performance and scale-up is the gas holdup which is defined as the gas volume fraction because it not only determines the hydrodynamics and transport phenomena, but also affects the performance of chemical reaction. Almost all the researches focus on measuring the heat convection of the powder bed in fancy operating conditions i.e. the bed does not contact with a cooling coil. Thus, they do not clearly address the sensitivity of the overall heat transfer coefficient to the practical operating conditions. The experiments were also conducted in steady state conditions meaning that the temperature of the fluidized bed is nearly constant over time. Furthermore, we observed a notable uncertainties between the experimental convective coefficients and those estimated by predictive models even in similar conditions. As a result, researchers developed their own correlations and justified that the former correlations ignored the effect of operating conditions, coil configuration, and specific parameters such as bubble frequency and local gas holdup [118]. One of the contributions

of this work is to measure the overall heat transfer coefficient and convection heat transfer coefficient through the bubbling fluidized regime while the system is in operation to estimate the cooling capacity and thermal efficiency of the fluidized bed vessel which would be a guideline to improve the heat transfer through the FT reactor in the actual operation.

### **Coolant characterization**

The design of cooling coil and coolant properties are the critical parameters of FT reactors. The type of coolant and its operating conditions, in particular, is crucial in thermal and even production efficiency. In the large-scale FT, manufacturers do not reveal the details of the cooling circuits. However, in fluidized bed reactors, the coolant is circulated through internal heat exchangers [34]. The coolants and their operating conditions are different according to the design of the reactor. It might be a high-pressure water [10] or boiling water [34,49,70,133] passing through the tubes or surrounding the catalyst-filled tubes [50], steam [70] and cooling oil [48,134,135]. High pressure water facilitates the isothermal conditions in the reactor, while heat transfer oil has lower risk of evaporation / phase change. A few studies have considered the coolant properties in the modelling and design of the large scale reactor. To the best of our knowledge, the detail information about the cooling system of the pilot-scale is unavailable which makes difficulties in the research and development of this system.

## **2.4 Product upgrading**

Fischer-Tropsch products include a mixture of hydrocarbons which is not primarily usable for the customer or downstream industries. In fact, the composition of the FT product (HTFT and LTFT products) determines the process design of treatment [136]. The essential liquid product treatment basically begins with removing of light hydrocarbons and dissolved gases so that the remaining hydrocarbons can be stored at ambient pressure [20]. The syncrude from HTFT synthesis is rich in olefins, oxygenates and consists of aromatics [25, 83, 137]. Thus, olefins are removed from the straight run liquid product to use as chemical feedstocks. Major fraction of LTFT products, on the other hand, are wax and hydrocarbons consisting of linear paraffins with a small contents of olefins and oxygenates which means that the olefin content is not expected being high enough to merit the olefin extraction and thus upgrading just consists of hydro-processing and separation [20]. In upgrading step, hydrogenation of olefin and oxygenate as well as hydrocracking of the wax to naphtha and diesel can be taken place at gentle conditions [28]. The upgrading section can be done in a refinery unit aside of GtL plant especially in case of small GtL units.

## 2.5 Process Safety and Risk Assessment

The developing scale and complexity of process industries have brought safety and environmental concerns to the leading edge [138]. Safety of personnel, facilities, and operations is crucial to continue economic viability and without safety measures in place, a company may face severe financial consequences such as loss of income, legal fines and damage to its credibility [139]. Thus, adopting proactive risk reduction strategies (RRSs) is essential for daily operation and is also a key factor for a long-term economic success [138, 140]. Most chemicals are hazardous by nature and often make the processes unsafe. Moreover, chemical accidents are more destructive than other types [141]. Despite the substantial development in automation and risk analysis, still catastrophic incidents continue to occur in small and large chemical plants as evidenced by Bhopal in 1984, Longford in 1998, Deepwater Horizon 2010 [142] and recently ExxonMobil's refinery at Baytown, Texas as well as Niquan GtL plant just one month after reopening in 2021. Pilot plant operations are not exceptional than other commercial plants and hazard and operability (HAZOP) study is an important section of the design before the new process can be run [143, 144]. Hazard identification, is the first major step of risk management to mitigate the accidents and other losses related to the unit operation [142]. In fact, the goal of hazard identification is defining all the feasible scenarios or sequences of events so that a dangerous issue will expose people, assets and environment to risks [145]. Many disasters are the consequence of a scenario that no one discovered [145]. To the best of our knowledge, no detail information or data is available in the literature about process hazard review and risk assessment of micro-GtL technology which distinguishes this part of research.

## 2.6 Process control

Process control is an inseparable part of every chemical plant. The main tasks of control systems for chemical reactions are providing uniform quality, high product yields, low energy consumption and minimal impacts on the environment [146]. The nonlinear behaviour of exothermic reactors comes from the interplay between heat generation removal and non-monotonic kinetics [147] which reveals limit cycling, multiplicity of steady-state (SS), structural instability and strong parametric sensitivity [147–149]. Hence, the aim of a control design scheme is to achieve a closed-loop operation with an adequate trade-off between safety, operability, productivity, and quality based on investment operation costs [147].

Particularly in GtL process, the Fischer-Tropsch reaction is highly exothermic leading to increase the temperature inside the reactor. Thus, an appropriate feedback control is essential to keep the temperature constant not only to prevent runaway reaction, but also to give a uniform composition of product. The control of batch reactor differs from that of continuous processes and different techniques are required for each one [150, 151]. In batch and semi-batch reactors, thermal runaway (temperature increase) occurs for highly exothermic reactions due to the limited cooling capacity of this type of reactor [152]. As the operation of these processes is sequential heating and rapid cooling, the conventional feedback control approaches are deficient since they act to the deviation of controlled variable and set point with delay that is unpleasant to the nature of the process [150]. Industrial practice mostly employs cascade configuration to control the temperature of jacketed continuous stirred tank reactors [150, 153]. These reactors are basically controlled by manipulating the exit flow and coolant flows driven by linear-decentralized volume and temperature PI loops [154, 155]. Extensive model-based novel control studies (non linear model predictive and feedforward-state feedback (FF-SF) combined with nonlinear state observer) have concentrated on exothermic reactors [155]. In particular, model predictive control (MPC) maintains the input and output variables of the system within their constraints. It is also capable to optimize the control action while considering the limits of selected variables which ensures the safety, stability and performance within predefined boundaries. Moreover, it controls as many process variables as possible even if a sensor or actuator is unavailable [?, 156]. However, an accurate reaction kinetics model is essential to design these kinds of controllers [157]. Furthermore, real-time data is required to compare the output variable(s) of experiment with those from the model. On the other hand, the proportional integral (PI) controller is simple, robust and widely applicable in the regulatory control layer in industrial cases [158]. Even though in wide range of PID controllers, the derivative action is unused, tuning the other two adjustable parameters is inconvenient and major controllers are poorly set since weary tests are needed to determine the improved controller settings [158]. Most tuning techniques are based on open-loop process model which is basically specified in terms of its gain ( $k$ ), time constant ( $\tau$ ) and time delay ( $\theta$ ). Having the process model, direct synthesis is a suitable approach to design the controller [156, 159]. This technique has good results for set point changes. On the other hand, its response to load disturbances is slow for lag-dominant processes with  $\tau/\theta$  larger than 10. To amend the load disturbance test, Skogestad developed modified SIMC method to reduce the large values of constant times [160]. This approach has one setting parameter called closed-loop time constant  $\tau_c$  chose equal to  $\theta$  for ‘fast and robust’ control. However, this method also needs the open-loop model of the process which has limitation since providing adequate process data needs an open-loop experiment which is time consuming and

sometimes result in objectionable deviations [158]. Thus, the easiest way is to directly tune the controller from the closed-loop test regardless of dealing with process model like Ziegler-Nichols method which gives the ultimate controller gain ( $K_u$ ) and period of oscillations ( $P_u$ ) only from a unique experiment [158, 161]. The disadvantages of Ziegler-Nichols method or the the modified technique by Tyreus and Luyben [162] is that they are not applicable to all process dynamics and also they bring the system to the limit of instability in order to get the sustained oscillation for which a couple of trial and errors happens [?]. Hence, a novel technique proposed by Shamsuzzoha and Skogestad which is simply able to tune the controller parameters from the closed-loop data via a set-point step test called ‘set point overshoot method’ [158]. The advantage of this method is that it obtains reliable setting for the PI controller for various types of process dynamics including the standard first-order plus time delay (FOPTD), integrating, high-order, inverse response, unstable and oscillating processes. This technique needs to roughly estimate the controller parameters prior of running the experiment. Hence, reliable kinetics and heat exchange equations are required to model the dynamic behaviour of the FT reactor and obtain the theoretical parameters of a PI controller. Depending on the process, sometimes we need to consider the derivative parameter of the controller. In particular, PID is recommended for slow processes such as noise-free temperature loops. The derivative mode improves the controller performance by making a faster response and reducing overshoot and oscillations around the set point. In processes with noise, using derivative action amplifies the noise and should be avoided [?]. In these cases, we can add a filter to eliminate the noise by applying the internal model control (IMC) technique [163]. One of the important and realistic problems in the process control is the reset windup which is common in processes when an unusual large disturbance changes the output variable [?]. For example, in Fischer-Tropsch when the reaction starts, it releases a huge amount of heat which rises the temperature largely. This condition makes the process unstable when the integration mode of the controller maintain the output variable saturated for a long time even if the controlled variable has been restored towards its set point. Hence, anti-reset windup algorithm protects the system by limiting the integration to its limits [164].

## Overview

- *Process safety of the micro-GtL plant*

Even though advanced techniques have been developed within the recent decades to analyze the risk, they are inapplicable or inefficient for such a pilot unit with sorts of uncertainties that has not been started yet at its actual operation. We also recognized a lack of confidence in classical process hazard review and qualitative risk analysis that

needs to be addressed well. It leads to proposing a simple and reliable quantitative approach to mitigate the potential risks of the plant.

- *Temperature control of the FTS*

Advanced control strategies like MPC, might be a good solution for this complex process with multiple variables and uncertainties. However, those methods are inapplicable at this stage since it was not being run in actual conditions and no real-time data is available to predict the output variable and modify or re-tune the controller parameters online. Hence, a robust method that serves PID controller based on the simulation with least knowledge about process is required to design a preliminary PI / PID controller and engage it in the system to adjust the temperature of the process.

- *Thermal performance of the Fischer-Tropsch reactor*

To the best of our knowledge, a few studies were found in the literature to address the thermal issues and heat exchange within the FTS. Even the operating conditions and chemical- physical properties of the powders inside the reactor are quite different in the experimental tests to estimate the thermal efficiency of the fluidized bed system. Hence, an appropriate strategy is to run the experiment in safe mode (without the reaction) to measure the cooling rate, investigate the impact of operating conditions on improving the heat exchange, identify the heat exchange parameters and design a primary controller accordingly.

## CHAPTER 3    ARTICLE 1 : SAFETY ANALYSIS AND RISK ASSESSMENT OF A MICRO-GTL PLANT

Mahdi Sharifian, Federico Galli, Bill Timbers, Nicolas Hudon, Gregory S. Patience

Published in :

Journal of Loss Prevention in the Process Industries, vol. 83, p. 105071, April 28, 2023

---

### Abstract

Laboratory hydrogen generators, medical oxygen, and micro-breweries are examples of modular and micro technologies that are commercial successes. Researchers, patients, and unskilled workers operate these facilities but more complex processes require highly qualified personnel to ensure they operate safely. Modular-micro processes that run in remote locations meet economic objectives only when operated remotely to minimize personnel expenses. Mitigating the risk requires a comprehensive hazards analysis with advanced control systems particularly for explosive and toxic compounds. Here, we propose a method called Failure Mode Risk Decision (FMRD) to review the inherent hazards of a micro-refinery unit (MRU) that converts flared and wasted natural gas to long chain hydrocarbons. This approach combines the Process Flow Failure Mode (PFFM) methodology as a systematic and reliable technique with a novel numerical risk assessment method to improve the analytical evaluation of hazardous conditions. The objective is to combine causes and consequences in a single metric, where scaled probability of evident causes and severity of consequences are used to derive a risk level measure. With the proposed metric, the magnitude of a potential hazard is directly correlated with the risk level. This mechanism identifies extra risk scenarios compared to the classical hazard analysis method and provides a straightforward comprehensive numerical assessment to represent the inherent and residual risks to facilitate justifying the hazardous scenarios. Accordingly, we design a safety loop and supply all the required facilities to remove the potential risks at the process plant. Not only the proposed methodology clarifies the risks of the MRU presented in this study, but can be extended to review the hazards of other chemical process plants.

---

### 3.1 Introduction

Process intensification increases the efficiency of chemical processes by delivering higher energy per volume to chemical reactions compared to traditional processes [165]. To achieve process improvement through intensification, engineers either introduce new equipment or operate the process at minimum or maximum allowable operating conditions (pressure, temperature, etc) [166]. However, dealing with exothermic reactions and dangerous (flammable or toxic) substances at high pressure and high temperature augments the risk of hazardous operation. In general, risk analysis is a difficult apply to provide as no prior experience or similar cases are available to retrieve the require safety information [167]. As a result, designing or operating such chemical processes triggers the need for new and robust hazard evaluation methods to mitigate the risks of process failures.

To assess the potential risks and risk modulation, safety engineers apply methods such as checklist (CL), what-if (WI) analyses, failure modes and effects analyses (FMEA), fault tree analyses (FTA), and hazard and operability (HAZOP) studies [166, 168–170]. Generally, the HAZOP analysis is divided into knowledge-based and model-based approaches. The former has recently received more attention as it determines the value and the duration of deviations in addition to their existence. However, this method is limited by the reliability of the mathematical model [166]. Even though the integration of simulators with HAZOP identifies unexpected deviations and reduces the time of the hazard identification procedure, the absence of experimental data when developing new processes generates inaccuracy in the final hazard analysis. Hence, to study a chemical process at start-up and during operation, the model-based HAZOP approach might be impractical. Knowledge-based methods, on the other hand, apply large databases of information about the failure modes, causes, and consequences of various process units and equipment. Advances in computer technology mitigate the weak points of conventional techniques of process hazard analysis, [166, 171]. Automated HAZOP procedures combine sophisticated knowledge-based with a fault-propagation engine to apply deviations and propagate their effects throughout the complex plant networks. However, these techniques are complex since they need to convert the system drawings such as piping and instrumentation diagrams (P&IDs) into a certain format which is hard and costly. Furthermore, some scenario in a fully automated analysis needs conservative judgments. Hence the assessment requires further review after completion to reject the incorrect automated reports [172] which implies that the human expert team remains at the core for any HAZOP study [166]. In particular, applying automated HAZOP procedures is unnecessary and inefficient for pilot plants consisting of a limited number of scenarios and predictable outcomes. In addition, an inadequate identification of deviations

in classical HAZOP results in confusion [173]. Hence, an appropriate alternative method to HAZOP is the Process Flow Failure modes (PFFM) analysis [174]. It is basically a structured, systematic ‘what-if’ method following the direction of flow. Classical HAZOP was only capable of analyzing half of the scenarios compared to PFFM [175]. PFFM identifies catastrophic scenarios better than HAZOP [176]. Furthermore, it is straightforward since it integrates the cause of two or more deviations as a result of one failure mode, which is a robust short-cut technique to facilitate the hazards review. The conventional HAZOP considers the deviations of each scenario and uses guide-words to define the deviations and consequently recognizes the relevant cause and effects. Process Flow Failure Mode (PFFM) is more efficient as it covers both the deviation and the cause of the deviation and it recognizes extra incidents that deviation-wise technique are incapable of detecting. For example, a HAZOP has a limited framework to consider underlying causes as it reports low-flow, no-flow etc. In PFFM, an electrical storm is the cause of the malfunction and thus deviation—it recognizes inherent causes better than a conventional HAZOP. Techniques to quantify the risk of each scenario include proportional risk-assessment (PRAT) [177, 178], decision matrix risk-assessment (DMRA) [179–181], quantitative risk measures of societal risk [182], quantitative risk-assessment (QRA) tool [183], quantitative assessment of domino scenarios (QADS) [184], clinical risk and error analysis (CREA) [185], predictive epistemic approach (PEA) [186] and weighted risk analysis (WRA) [187, 188]. Among these techniques, DMRA has the advantage that it discriminates risks to promote decision making and also improves the consistency and basis of decision. Moreover, this graphical method assists to prioritize and manage the key risks [179, 189].

Layer of protection analysis (LOPA) is a semi-quantitative method that provides the factors and the rationale of risk decisions to demonstrate how the risk levels are lowered to satisfy the tolerable criteria [190]. It incorporates prevention and mitigation criteria [191] to illustrate safeguards and initiating events [190]. However, this method is time consuming [191] and needs special skill to source the likelihood numbers, discriminate which numbers to engage and format them [192]. In addition, finding the LOPA figures is difficult and requires specialized skills. The numbers are also based on educated guesses that leads to false sense of confidence since the final value gives the order of magnitude analysis rather than a more accurate estimate [192]. We apply the PFFM technique to analyze the safety of a micro refinery unit (MRU) that produces fuel ( $C_5^+$ ) from associated natural gas via gas-to-liquid (GtL) technology. The plant includes catalytic partial oxidation of natural gas and operates at extreme conditions (1000 °C and 2 MPa). We also modify the DMRA as a new quantitative risk assessment approach and combine it with the PFFM to reach a quantitative evaluation of the process risks. For any new, untested process, our approach (FMRD–failure mode risk

decision) detects extra scenarios compared to the conventional HAZOP, which translates to increased safety. Also, our numerical risk assessment estimates the inherent risk of each scenario because it is supported by the experimental database for failure probability and explicit asset loss-based severity, which guides making appropriate decisions and considering further actions to reduce the risk. Our methodology is similar to LOPA in terms of defining the frequency of the hazardous event and making an explicit comparison against the risk criteria. However, this approach is more conservative than LOPA since instead of considering the control system as a protection layer or safeguard, it involves the safety when a controller fails or operates improperly. It is also based on detecting the failure of equipment and instruments rather than deviations which reveals all the hazardous scenarios. It facilitates executing of the risk assessment and gives a precise dimensionless risk value according to the probability of the failure and the severity magnitude. Another difference is that FMRD is more straightforward and clearer than LOPA and does not require interpreting the result to make the final decision. FMRD is intuitive and develops the scenario based on a feasible cause, then it extends to likely consequences and checks whether more controls are necessary to minimize the chance of a loss of containment event (LoC—the severest process safety category). We designed a nonlinear platform to evaluate risk and mitigation numerically to help guide the evaluation process for experienced and inexperienced safety personnel to recognize hazardous conditions and determine the efficacy of the safeguards based on residual hazards (the hazard levels remaining after adding the safeguards). In the section Micro-GTL Plant Unit, we present the basic control equipment. The proposed methodology combining process flow failure modes analysis and a numerical risk assessment method is detailed in Section 3.3. The analysis of the Micro GtL unit and the obtained results is discussed in Section 5.4. Conclusions and potential extensions of the proposed methodology are given in Section 3.5.

## 3.2 Micro-GTL Plant Unit

### 3.2.1 Process

The MRU produces gasoline and diesel from stranded gas via a Gas-to-Liquid (GtL) process in intensified operating conditions: pressures from 1.5 MPa to 2.0 MPa and temperatures from 300 °C to 1000 °C. MRU consists of catalytic partial oxidation (CPOX) reactor, intermediate coolers, and Fischer–Tropsch (FT) reactor (Fig.3.1). The unit is mounted in a trailer therefore is mobile. This unit treats associated gas from oil well head or natural gas (pure methane) from pipelines as feedstock. A filter-included reciprocating compressor (Atlas Copco, 180 L min<sup>-1</sup> at 3 MPa Max.) feeds air to the CPOX reactor together with compressed natural gas (NG) as the main reactants to generate the synthesis gas (syngas), a mixture of

The diagram illustrates a Fischer-Tropsch synthesis process. Reactants (FHA, filtered air, natural gas) are fed into a CPOX reactor (RC-1) which is heated by an electrical heater. The effluent from RC-1 is cooled in heat exchanger E-1 and then enters a FT Reactor (RC-2). The effluent from RC-2 is cooled in heat exchanger E-2 and then separated into a liquid phase (Fuel Product) and a gas phase (Vent). A cooling water loop (P-1) is used to maintain the temperature of the heat exchangers. The diagram also shows a sample line for GC-MS analysis and a PC interface.

carbon monoxide and hydrogen. To start up, an electrical heater rises the CPOX reactor temperature to  $400^{\circ}\text{C}$ , which is required for the partial oxidation of natural gas. The heater has two sections with a heating power of 13.5kW including its own temperature controller as well as temperature limit in case of overheating. During start-up, natural gas flow is established into the reactor while electrical heating is turned on and flared until the inside temperature of the reactor reaches the set point. Then, the electrical heater is turned off and air is fed to the reactor. We adjust the air to methane ratio at 2.5 to reach a desirable conversion and selectivity of syngas product [193,194]. The outlet product passes across two double pipe heat exchangers (intercoolers) that reduce the gas temperature to the operating temperature of Fischer-Tropsch (FT) reactor ( $300^{\circ}\text{C}$ ). The FT reactor is filled with iron catalyst and operates in fluidized bed regime. Hydrogen reacts with carbon monoxide at the catalyst surface and hydrocarbon products including paraffins and olefins leave the reactor from top. At the top section of FT reactor two filters separate catalyst particles from products. We considered a sequential cleaning procedure for the filters. Thus, when a filter blocks, the pressure drop across it reaches a certain set point (2kPa) and therefore process solenoid valve, S6 or S8, (depending on the filter) closes and at the same time backflush valve, S5 or S7 (corresponding solenoid valve, Fig. 3.1) opens to clean the filter for a certain time duration (2s).

### 3.2.2 Process Control & Instrumentation

In the CPOX reactor, the likelihood of forming an explosive mixture of methane and air increases with high temperature and pressure since those conditions expand the explosion limit [195,196]. The exothermic reactions also form a nonlinear process so that a safe start-up is essential [197]. A ratio controller adjusts the required air flow when mixing with methane and a gradual controlled-heat furnace on the body of CPOX reactor provides the required temperature ( $400^{\circ}\text{C}$ ) to start the reaction. In addition, a PI control loop adjust the internal temperature of the FT reactor. This system consists of three temperature sensors along the catalytic bed of the FT reactor (T1, T2, T3), a PI controller and a control valve(TV5) to adjust the coolant flow rate though the internal coil of the reactor. Finally, a back pressure regulator at the outlet of FT reactor(PV1) regulates the internal pressure of the system (Fig. 3.1). Having the proper controllers does not guarantee the safety of the plant, particularly in case of failure of the control system or operator's faults. Thus an extended logic would be necessary to protect the whole system.

### 3.3 Process Hazard and Risk Assessment

#### 3.3.1 Process Hazards Review

The first step in the proposed approach, FMRD, is breaking down the P&ID to sections or nodes (with specified flows in different colours). Then, all the potential causes of hazard scenarios that emerge from failures within the process are identified. These failures include technical deficiencies or limitations of instruments, (mis-calibrated flow meter, for example), equipment (leaking through a mechanical seal), piping (crack or break), and operator's errors that upset the process in the flow direction which are tabulated in a master list. A mechanical failure of a pump or compressor are causes that are different than the signal and power failure of these devices. Then, using engineering principles and technical vision, we develop a list of all possible consequences. For instance, failure of the water pump (P-1) in the cooling Node of the FT reactor stops the pump resulting in temperature increase inside the reactor, thereby overheating and possible reactor damage. Due to this failure, water flow through the coil is interrupted and the heat from the reactor could vaporize any remaining fluid inside the coil and cause a rupture. Reviewing each Node starts with the first element - where the flow begins. For example, the cooling circuit Node of the FT reactor starts with the water pump (P-1) and continues with the rotameter flow gauge (FI1) and the internal cooling coil and ends with the temperature control valve (TV5) (Fig. 3.1). Then, by following this procedure, we inspect the scenarios in every Node to analyze the risk of each. In the next step, through the assessment meeting, the team investigates all the possible causes. If the cause table has missed any, the team adds the causes in the order of process flow then the assessment of potential consequences. Finally, the team considers the necessary controls (safeguards and barriers such as check valves, rupture disks or pressure relief valves and so on) and adds a note or recommendation if required. Then it proceeds to the next item.

#### 3.3.2 Risk Assessment

As a second step in the proposed approach, we integrate the process hazard with risk analysis to mitigate or remove the hazardous conditions including fire, explosion and emission of toxic gases ( $\text{CO}$  and  $\text{H}_2$ ) [198,199]. The standard table of severity (Table 3.1) [198] ranks the severity of consequence values and authority levels of responsibility in a commercial plant from 0 to 5.

Table (3.1) Severity table of incidents

| Severity | Personnel                   | Assets                       | Environment | Reputation                 | Responsibility   |
|----------|-----------------------------|------------------------------|-------------|----------------------------|------------------|
| 0        | No injury                   | No damage                    | No effect   | No impact                  | Shift Supervisor |
| 1        | Slight injury,<br>first aid | Slight,<br><\$10k            | Slight      | Slight                     | Group Manager    |
| 2        | Minor injury,<br>lost time  | Minor<br>\$10k to \$100k     | Minor       | Limited                    | Section Manager  |
| 3        | Major injury                | Localized<br>\$ 100k to \$1M | Localized   | Considerable,<br>community | General Manager  |
| 4        | Single fatality             | Major<br>\$1M to \$10M       | Major       | State                      | Plant Manager    |
| 5        | Multiple fa-<br>talities    | Expensive<br>>\$10M          | Massive     | National                   | Headquarters     |

We consider the cost of damage for the assets (the third column of Table 3.1) as a numerical indicator of the severity. However, the costs in this table proposed for commercial plants and are inapplicable to pilot plants like the Micro GtL unit. Thus, we consider a factor of 0.01 to convert the commercial costs to pilot unit costs and apply a factor of 1% to account for the difference in scale. It means that we compare the price of our pilot setup to a roughly price of a commercial refinery unit giving a ratio of 1% to scale down the cost table and adapt it rationally to our setup losses. Further, to reflect the magnitude of the damages as the representative of the asset losses, we scale the severity levels from 0 (negligible) to 1 (severe) as the ratio of the logarithm of the damage cost to its maximum value (Eqn.3.1).

$$S = \frac{\log[c_d]}{\log[c_{d,\max}]} \quad (3.1)$$

where  $c_d$  is the cost of damage at each level and  $c_{d,\max}$  is the maximum cost of damage corresponding to the last level of severity.

To compute  $S$ , the lower limit of cost in each level of severity are considered as the main criteria and also the lower cost of “No damage” starts from \$1 (level 0) (Table 3.2).

Table (3.2) Quantified severity of incident

| Rank | Assets                      | $c_d$ , \$ | S   |
|------|-----------------------------|------------|-----|
| 1    | No damage                   | 1          | 0   |
| 2    | Slight, <\$100              | 10         | 0.2 |
| 3    | Minor, \$100 to \$1000      | $10^2$     | 0.4 |
| 4    | Localized, \$ 1000 to \$10K | $10^3$     | 0.6 |
| 5    | Major, \$10K to \$100K      | $10^4$     | 0.8 |
| 6    | Expensive, >\$100K          | $10^5$     | 1   |

The probability of equipment/instruments malfunction is also specified based on frequency of occurrence per year (Table 3.3) [200]. Here, we adopt a mathematical expression for transforming the failure frequency (rate) to probability (Eqn.3.2).

$$P(t) = 1 - \exp(-ft) \quad (3.2)$$

where  $P(t)$  is the failure probability at time  $t$  in years and  $f$  is the failure frequency of a system at  $t = 0$ . [201, 202]. The constant failure frequency is credible during the useful-life period [201]. Then we define the term ' $P_m$ ' as the mean probability to develop to avoid dealing with time proceeding. (Eqn.3.3)

$$P_m = \frac{\int_0^t P(t) dt}{\int_0^t dt} = \frac{t - \frac{1}{f}(1 - \exp(-ft))}{t} \quad (3.3)$$

where  $P_m$  is the average failure probability of a device during the time  $t$ . Here, we assume that the useful-life of the unit including the equipment and instruments is 20 years. During this period, the failure frequency is considered constant and the unit of frequency is  $y^{-1}$ .

Table (3.3) Mean probability of failures during 20 years

| Description                                 | Failure frequency, $y^{-1}$ | $P_m$ |
|---------------------------------------------|-----------------------------|-------|
| Extremely unlikely (1/10,000 years or less) | $10^{-4}$                   | 0.001 |
| Unlikely (1/1,000 to 1/10,000 years)        | $10^{-3}$                   | 0.01  |
| Rare (1/100 to 1/10,000 years)              | $10^{-2}$                   | 0.094 |
| Occasional (1/10 to 1/100 years)            | $10^{-1}$                   | 0.568 |
| Likely (1/year to 1/10 years)               | 1                           | 0.95  |
| Frequently (1/year or more)                 | 10                          | 0.995 |

In the next step, we determine the risk level to recognize how much each risk scenario is

close to a hazardous situation and make a proper decision to reduce the risk. Employing the numerical values for severity and probability help us to assess the risk quantitatively. The risk level ( $R$ ) is defined as the product of severity of an incident consequence ( $S$ ) and the probability of occurrence ( $P$ ) [189,203]:

$$R = 100 \cdot S \cdot P_m \quad (3.4)$$

Hence, the higher value of  $R$  means the relevant scenario is more risky. From Equation 3.4, we obtain the overall frame of risk representing how the frequency of technical problems in equipment or instruments and the severity of incident/losses directly affect the risk (Fig. 3.2). To analyze the risk numerically, we transform the discrete risk matrix to a continuous “Risk surface” (Fig.3.3). The acceptable level (risk target) is identified by the HAZOP team based on the confidence policy and authorities’ requirements and considering the numerical discrete risk matrix (Fig. 3.2). Here, we classify and indicate the risk levels of less than 0.5% by green, risks between 0.5% and 5% by yellow, between 5% and 50% by orange and higher than 50% by the red colour to visually represent the intensity of risk (Table 3.4). The structure of this fabricated risk matrix is close to the standard qualitative form [204].

| $\begin{matrix} P_m \\ S \end{matrix}$ | 0.001 | 0.01 | 0.1 | 0.57 | 0.95 | 1   |
|----------------------------------------|-------|------|-----|------|------|-----|
| 1                                      | 0.1   | 1    | 10  | 57   | 95   | 100 |
| 0.8                                    | 0.08  | 0.8  | 8   | 45.6 | 76   | 80  |
| 0.6                                    | 0.06  | 0.6  | 6   | 34.2 | 57   | 60  |
| 0.4                                    | 0.04  | 0.4  | 4   | 22.8 | 38   | 40  |
| 0.2                                    | 0.02  | 0.2  | 2   | 11.4 | 19   | 20  |
| 0                                      | 0     | 0    | 0   | 0    | 0    | 0   |

Figure (3.2) Risk matrix; Top horizontal line is probability ( $P$ ) progress and left vertical line is severity level ( $S$ ) progress. The cross values are the products of  $P$  and  $S$  in %.

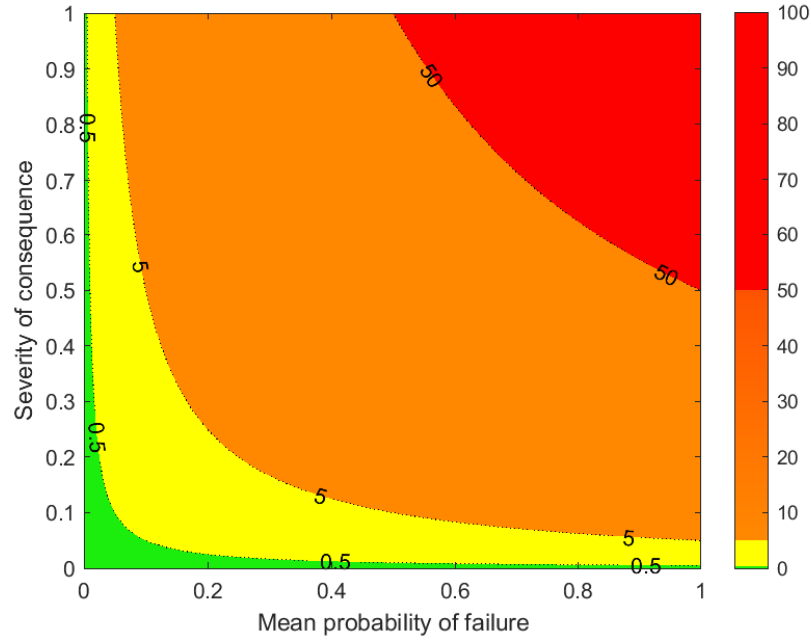


Figure (3.3) Contour plot of risk surface based on probability of malfunction and severity of resulting incident

Table (3.4) Risk level(%)

| Risk level        | Description                                              |
|-------------------|----------------------------------------------------------|
| $0 < R \leq 0.5$  | Acceptable, no modification required                     |
| $0.5 < R \leq 5$  | Acceptable with controls                                 |
| $5 < R \leq 50$   | Unacceptable, Risk mitigation required                   |
| $50 < R \leq 100$ | Intolerable, Temporary mitigation and permanent solution |

From the technical background of industrial plants, the frequency of destruction of process devices are determined giving the real value of their probability function. In the next step, we combine the PFFM technique as the modified HAZOP with numerical risk analysis according to the flow chart (Fig. 3.4) to mitigate the possible risks of each scenario to an acceptable level. We designed this flow chart based on the “hazard identification and risk assessment procedure” [205–207] and call this hybrid technique FMRD.

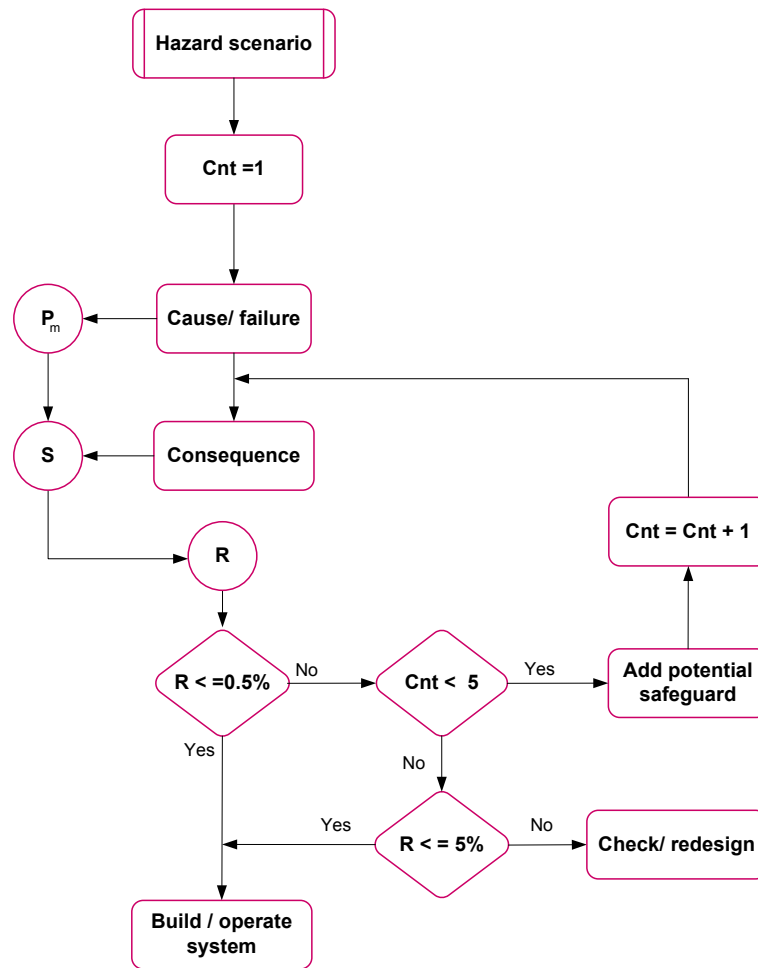


Figure (3.4) Flow chart of combined HAZOP and risk analysis of risky scenarios —  $P_m$ ,  $S$ , and  $R = P_m \times S$  are estimated probability and severity and computed risk level respectively. Cnt is a counter.

Table (3.5) Design template of FMRD technique for a micro GtL unit. Elements are derived from the flowchart Figure 3.4. The header of the table includes project name, team members, the node and additional details about documentation for the project (P&ID number, revision number). The acceptable  $R_r$  satisfies the conditional blocks of the flowchart.

| column                              | item                                                                                |             |                  |       |       |           |       |        |
|-------------------------------------|-------------------------------------------------------------------------------------|-------------|------------------|-------|-------|-----------|-------|--------|
| 1                                   | scenario number                                                                     |             |                  |       |       |           |       |        |
| 2                                   | failure type, <i>e.g.</i> FWP—tag #, Table 3.6                                      |             |                  |       |       |           |       |        |
| 3                                   | possible consequences, Table 3.7                                                    |             |                  |       |       |           |       |        |
| 4                                   | allocates the mean probability to each cause, $0 \leq P_m < 1$                      |             |                  |       |       |           |       |        |
| 5                                   | severity for each of the consequence with the highest severity, $0 \leq S_i \leq 1$ |             |                  |       |       |           |       |        |
| 6                                   | inherent risk, $R_i = P_m \cdot S_i \cdot 100$                                      |             |                  |       |       |           |       |        |
| 7                                   | safeguards, Table 3.8                                                               |             |                  |       |       |           |       |        |
| 8                                   | severity after implementing safeguard(s), $0 \leq S_f \leq 1$                       |             |                  |       |       |           |       |        |
| 9                                   | residual risk, $R_r = P_m \cdot S_f \cdot 100$                                      |             |                  |       |       |           |       |        |
| <b>Risk analysis:</b>               |                                                                                     |             | <i>micro-GtL</i> |       |       | P&ID #    |       | Rev. # |
| Team members: <i>list</i>           |                                                                                     |             |                  |       |       | Sheet #   |       |        |
| <b>Node</b> ( <i>number: name</i> ) |                                                                                     |             |                  |       |       | Date      |       |        |
| Scenario                            | Cause                                                                               | Consequence | $P_m$            | $S_i$ | $R_i$ | Safeguard | $S_f$ | $R_r$  |
|                                     |                                                                                     |             |                  |       | %     |           |       | %      |
| 1                                   | 2                                                                                   | 3           | 4                | 5     | 6     | 7         | 8     | 9      |
| 1                                   | Failure type                                                                        | CSQ No.     | $v_1$            | $w_1$ | $x_1$ | SG No.    | $y_1$ | $z_1$  |
| $i$                                 | Failure type                                                                        | CSQ No.     | $v_i$            | $w_i$ | $x_i$ | SG No.    | $y_i$ | $z_i$  |

### 3.4 Results and Discussion

The overall Piping and Instrumentation Diagram (P&ID) of MRU includes the process equipment, instruments and logic interlocks of the system (Fig. 3.1). Here, we divide the process into seven nodes to investigate precisely all possible scenarios. Each node is highlighted with a specific colour. Then we create the relevant spreadsheets consisting of the safety and numerical risk analysis. During the completion of hazards review, we recognize all the possible technical and human causes of failure to determine the hazard conditions. In the next step we also estimate the probability of failure / malfunction according to their frequency available in literature [208] and then all these data are summarized (Table 3.6).

Table (3.6) Feasible technical and human causes of failure in MRU

| Cause                                           | Symbol | Frequency<br>$y^{-1}$ | Probability |
|-------------------------------------------------|--------|-----------------------|-------------|
| Failure of air operated valve & fully open      | AVO    | $7.5 \times 10^{-4}$  | 0.007       |
| Failure of air operated valve & fully close     | AVC    | $7.5 \times 10^{-4}$  | 0.007       |
| Flow control valve open by operator             | CVO    | $9 \times 10^{-4}$    | 0.009       |
| Flow control valve close by operator            | CVC    | $9 \times 10^{-4}$    | 0.009       |
| Failure of solenoid valve & permanently open    | SVO    | $1.6 \times 10^{-4}$  | 0.002       |
| Failure of solenoid valve & permanently close   | SVC    | $1.6 \times 10^{-4}$  | 0.002       |
| Pipe leakage due to crack                       | FLB    | $5 \times 10^{-6}$    | 0.00005     |
| Fastening problem in reactor/piping             | FLF    | $5 \times 10^{-6}$    | 0.00005     |
| Leakage due to corrosion                        | FLC    | $2.4 \times 10^{-3}$  | 0.024       |
| Wrong setting of pressure regulator             | RVS    | $9 \times 10^{-4}$    | 0.009       |
| Pressure regulator failure & Fully open         | RVO    | $9 \times 10^{-4}$    | 0.009       |
| Pressure regulator failure & Fully close        | RVC    | $9 \times 10^{-4}$    | 0.009       |
| Back pressure regulator failure & Fully close   | BVC    | $9 \times 10^{-4}$    | 0.009       |
| Air compressor failure (reciprocating)          | FAC    | $1 \times 10^{-3}$    | 0.014 [209] |
| Gas compressor failure (reciprocating)          | FGC    | $1 \times 10^{-3}$    | 0.014 [209] |
| Electrical signal failure                       | FES    | $8 \times 10^{-2}$    | 0.501 [210] |
| Manual valves failure of opening/closing        | MVO/S  | $9 \times 10^{-4}$    | 0.009       |
| Valve clogging                                  | VCL    | $9.6 \times 10^{-5}$  | 0.001       |
| Orifice or Nozzle clogging due to impurities    | ONC    | $1.75 \times 10^{-4}$ | 0.002       |
| Blockage of filters                             | FBF    | 0.85                  | 0.94        |
| Failure of water pump, flow switch low          | FWP    | $5 \times 10^{-4}$    | 0.005       |
| Cooling coil malfunction due to dirty surface   | FCC    | $1.3 \times 10^{-2}$  | 0.12        |
| Runaway reaction due to heat generation         | FRR    | 0.5                   | 0.900       |
| Flow transmitter failure to High/Low output     | FFH/L  | $6.3 \times 10^{-4}$  | 0.006       |
| Temperature transmitter failure output          | FTH/L  | 0.263                 | 0.811       |
| Pressure transmitter failure to High/Low output | FPH/L  | $3.7 \times 10^{-4}$  | 0.004       |
| DCS operation mistake                           | FDC    | $2.1 \times 10^{-2}$  | 0.183       |
| Insufficient operation monitoring               | IOM    | $5 \times 10^{-2}$    | 0.368       |

\* PLC : Programmable Logic Controller

Regarding the blockage of internal filters of FT reactor, the same frequency as that of impurities was postulated since no references determined the expected value of that. We also summarized all the feasible consequences obtained from the detailed review of the process and allocate a pre-defined value of severity to each one based on the weight factor that the team agrees on. value to each one severity value of each consequence (Table 3.7)

Table (3.7) Feasible consequences of the process failure with estimated severity value

| Consequence                                                     | Consequence<br>number | Severity |
|-----------------------------------------------------------------|-----------------------|----------|
| No consequence of concern                                       | CSQ-1                 | 0        |
| Incomplete oxidation                                            | CSQ-2                 | 0.2      |
| High concentration of Natural gas                               | CSQ-3                 | 0.4      |
| Formation of explosive mixture                                  | CSQ-4                 | 0.8      |
| Gas leakage to the environment leads to fire and/or explosion   | CSQ-5                 | 1        |
| Air leakage to the environment                                  | CSQ-6                 | 0        |
| High pressure resulting in reactor burst                        | CSQ-7                 | 0.8      |
| Gas transmit to the cooling side                                | CSQ-8                 | 0.6      |
| High temperature                                                | CSQ-9                 | 0.6      |
| Minor gas leak to environment due to reverse flow               | CSQ-10                | 0.6      |
| Tube burst                                                      | CSQ-11                | 0.6      |
| Filter blockage by wax due to over-cooling                      | CSQ-12                | 0.6      |
| Reactor damage due to overheating                               | CSQ-13                | 0.8      |
| Filter damage due to high $\Delta P$                            | CSQ-14                | 0.2      |
| Explosion when gas composition operates above LEL or below HEL  | CSQ-15                | 1        |
| Sparger blockage due to catalyst agglomeration by waxy products | CSQ-16                | 0.6      |
| Reverse flow of NG/Air that damages instrument                  | CSQ-17                | 0.4      |
| Thermal expansion of the pipe / coil                            | CSQ-18                | 0.8      |

In order to protect the system and mitigate hazardous conditions as much as possible, we design safeguards (Table 3.8), each of which is indicated by ‘SG’ followed by a number.

Table (3.8) Anticipated safeguards of the GtL process in MRU

| Description                                                               | Safeguard number |
|---------------------------------------------------------------------------|------------------|
| No Safeguard                                                              | SG-0             |
| Trigger the HH pressure CPOX safety interlock                             | SG-1             |
| Trigger the HH pressure FT safety interlock                               | SG-2             |
| Trigger the HH temperature CPOX safety interlock                          | SG-3             |
| Trigger the HH temperature FT safety interlock                            | SG-4             |
| Activation of the low/no flow CPOX safety interlock                       | SG-5             |
| Pressure safety valve of the CPOX reactor                                 | SG-6             |
| Rupture disc of the CPOX reactor                                          | SG-7             |
| Pressure safety valve of the FT reactor                                   | SG-8             |
| Rupture disc of the FT reactor                                            | SG-9             |
| Activation of safety interlock in the absence of a signal from instrument | SG-10            |
| Open solenoid valve from CPOX reactor to flare                            | SG-11            |
| Check valve on the NG line                                                | SG-12            |
| Check valve on the air line                                               | SG-13            |
| Check valve on the water line                                             | SG-14            |
| Check valve on the product line                                           | SG-15            |
| Check valve on the filter backflush line                                  | SG-16            |
| Control valve fail open                                                   | SG-17            |
| Control valve fail close                                                  | SG-18            |
| LEL detector for CH <sub>4</sub>                                          | SG-19            |
| H <sub>2</sub> & CO detectors                                             | SG-20            |
| Fire eye detector                                                         | SG-21            |
| Pressure relief valve on the line of cooling water return                 | SG-22            |
| Cooling water control valve full opens to suppress the overheat           | SG-23            |
| Low temperature alarm in FT reactor                                       | SG-24            |
| High pressure alarm in CPOX reactor                                       | SG-25            |
| High pressure alarm in FT reactor                                         | SG-26            |
| High temperature alarm in CPOX reactor                                    | SG-27            |
| High temperature alarm in FT reactor                                      | SG-28            |
| High temperature alarm on intercoolers                                    | SG-29            |
| High temperature switch (thermostat) on the reactor                       | SG-30            |
| Emergency shut down button                                                | SG-31            |
| High O <sub>2</sub> content alarm on GC analyzer                          | SG-32            |
| Triggering the safety interlock by high-high O <sub>2</sub>               | SG-33            |

To compute the risk level of each scenario, we apply the corresponding values of cause and consequence from Tables (3.6) and (3.7) with equation (3.4). Each scenario follows the risk algorithm. In these node tables  $R_i$  and  $R_r$  are inherent risk and residual risk, respectively.

In the classical HAZOP and LOPA, the likelihood of evidence (consequence) is affected by the safeguard. In our approach, on the other hand, the concept of likelihood is different as it is defined and formulated based on the probability of failure which is precisely measurable. In FMRD method, to assess the initial (inherent) risk, the likelihood of failure is identical to the likelihood of the evidence. However, adding the safeguard does not impact on the probability of the failure of equipment, instrument, or personnel's mistake since those happen due to inherent faults such as mechanical and electrical problem of the device or the lack of knowledge, focus or confidence. Preventive maintenance and training personnel are measures to avoid failure but are not considered safeguards. During operation, safeguards are activated in the case of a failure to mitigate catastrophic consequences. In our formulation, because the only representative parameter of consequence is its severity, we introduce the likelihood level of consequence in its severity. It means that although the inherent severity of a consequence does not change, its chance level decreases by adding a safeguard. It is interpreted as reducing the severity level of a scenario which makes the analysis simpler in practice. Thus, safeguards just impact severity levels rather than failure probability. Furthermore, once a cause results in more than one consequence, the one with higher severity is considered in computing the risk level. Based on defined concepts, we consider these assumptions to calculate the residual risk:

- The maximum number of safeguards (safety layers) are five based on the total number of the intervals amongst the severity layers (Table 3.2).
- The minimum reduced severity after considering the safeguard is zero as the cost less than \$100 and is negligible.
- Safety interlock reduces the severity at least 2 levels (*e.g.*, from 1 to 0.6) since it is a powerful logic which triggers the plant total shut down and typically consists of multiple sensors, logic processors and final elements with a very low failure on demand [211].
- Pressure safety valves reduces the severity at least 2 levels as a powerful safeguard (*e.g.*, from 1 to 0.6) since it immediately releases the pressure to the original operating conditions. Its average failure on demand is in the order of  $10^{-3}$  [211] and we couple it with a rupture disk to minimize its risk (double failure scenario). However, the rupture disk alone does not impact on the severity as it is just a second safety layer for the PSV.
- Each remaining safeguard routinely reduce the severity by one level (*e.g.*, from 1 to 0.8) since it would be the least impact of an appropriate layer of protection.

- Achieving the yellow region ( $0.5\% < R \leq 5\%$ ) after considering the possible safeguards satisfies the safety issues.

We eventually developed a spreadsheet based on the flowchart (Fig. 3.4) and the template (Table 3.5) to investigate each scenario within the NODE.

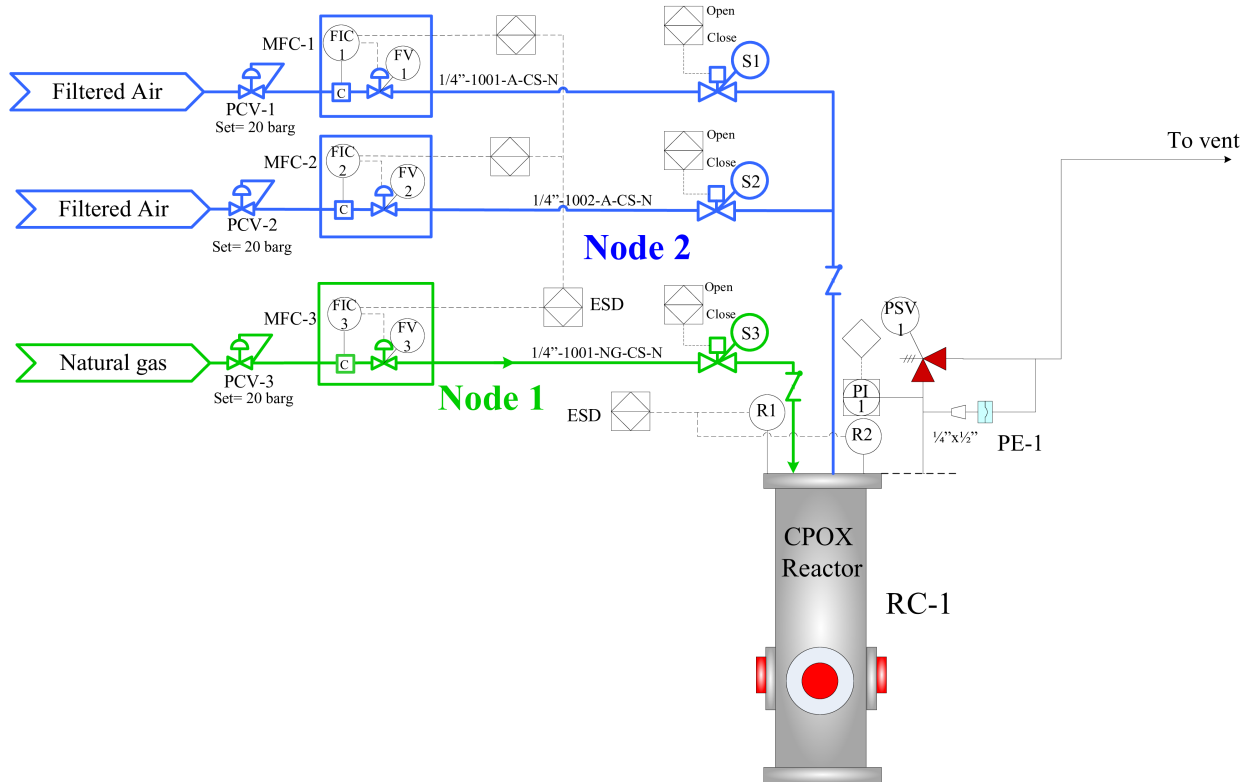


Figure (3.5) Boundary of Node 1; Natural gas feeding stream with auxiliaries indicated by blue colour and Node 2; compressed air feeding with auxiliaries indicated in green, on the P&ID of MRU

Table (3.9) Spreadsheet NODE 1; Natural gas feed

| Scenario | Cause    | Cons.   | $P_m$   | $S_i$ | $R_i, \%$ | Safeguard | $S_f$ | $R_r, \%$ |
|----------|----------|---------|---------|-------|-----------|-----------|-------|-----------|
| 1        | CVO-MFC3 | CSQ-2   | 0.009   | 0.2   | 0.18      | SG-0      | 0.2   | 0.18      |
| 2        | CVC-MFC3 | CSQ-4   | 0.009   | 0.8   | 0.72      | SG-5      | 0.4   | 0.36      |
| 3        | FGC-C-1  | CSQ-4   | 0.014   | 0.8   | 1.1       | SG-5      | 0.4   | 0.5       |
| 4        | RVC-PVC3 | CSQ-4   | 0.009   | 0.8   | 0.72      | SG-5      | 0.4   | 0.36      |
| 5        | RVO-PVC4 | CSQ-7   | 0.009   | 0.8   | 0.72      | SG-1,6,7  | 0.0   | 0.0       |
| 6        | FLB      | CSQ-5   | 0.00005 | 1.0   | 0.005     | SG-19     | 0.6   | 0.003     |
| 7        | FLF      | CSQ-5   | 0.00005 | 1.0   | 0.005     | SG-19     | 0.6   | 0.003     |
| 8        | VCL      | CSQ-4,8 | 0.001   | 0.8   | 0.08      | SG-0      | 0.8   | 0.08      |
| 9        | FES-C-1  | CSQ-4   | 0.501   | 0.4   | 20.0      | SG-5      | 0.0   | 0.0       |

Table (3.10) Spreadsheet NODE 2; Air feed

| Item | Cause      | Cons.   | $P_m$   | $S_i$ | $R_i$ , % | Safeguard | $S_f$ | $R_r$ , % |
|------|------------|---------|---------|-------|-----------|-----------|-------|-----------|
| 1    | CVO-MFC1/2 | CSQ-4,9 | 0.009   | 0.8   | 0.72      | SG-3,12   | 0.2   | 0.18      |
| 2    | CVC-MFC1/2 | CSQ-1   | 0.009   | 0     | 0         | SG-0      | 0     | 0.0       |
| 3    | FAC-C-2    | CSQ-17  | 0.014   | 0.4   | 0.56      | SG-13     | 0.2   | 0.28      |
| 4    | FLB        | CSQ-6   | 0.00005 | 0     | 0         | SG-0      | 0.0   | 0         |
| 5    | FLF        | CSQ-6   | 0.00005 | 0     | 0         | SG-0      | 0.0   | 0         |
| 6    | RVC-PCV1/2 | CSQ-17  | 0.009   | 0.4   | 0.36      | SG-13     | 0.2   | 0.18      |
| 7    | RVO-PCV1/2 | CSQ-7   | 0.009   | 0.8   | 0.72      | SG-1,6,7  | 0.2   | 0.18      |
| 8    | VCL        | CSQ-8   | 0.001   | 0.06  | 0.1       | SG-1      | 0.6   | 0.06      |
| 9    | FES-C-2    | CSQ-17  | 0.501   | 0.4   | 20        | SG-5      | 0.0   | 0         |

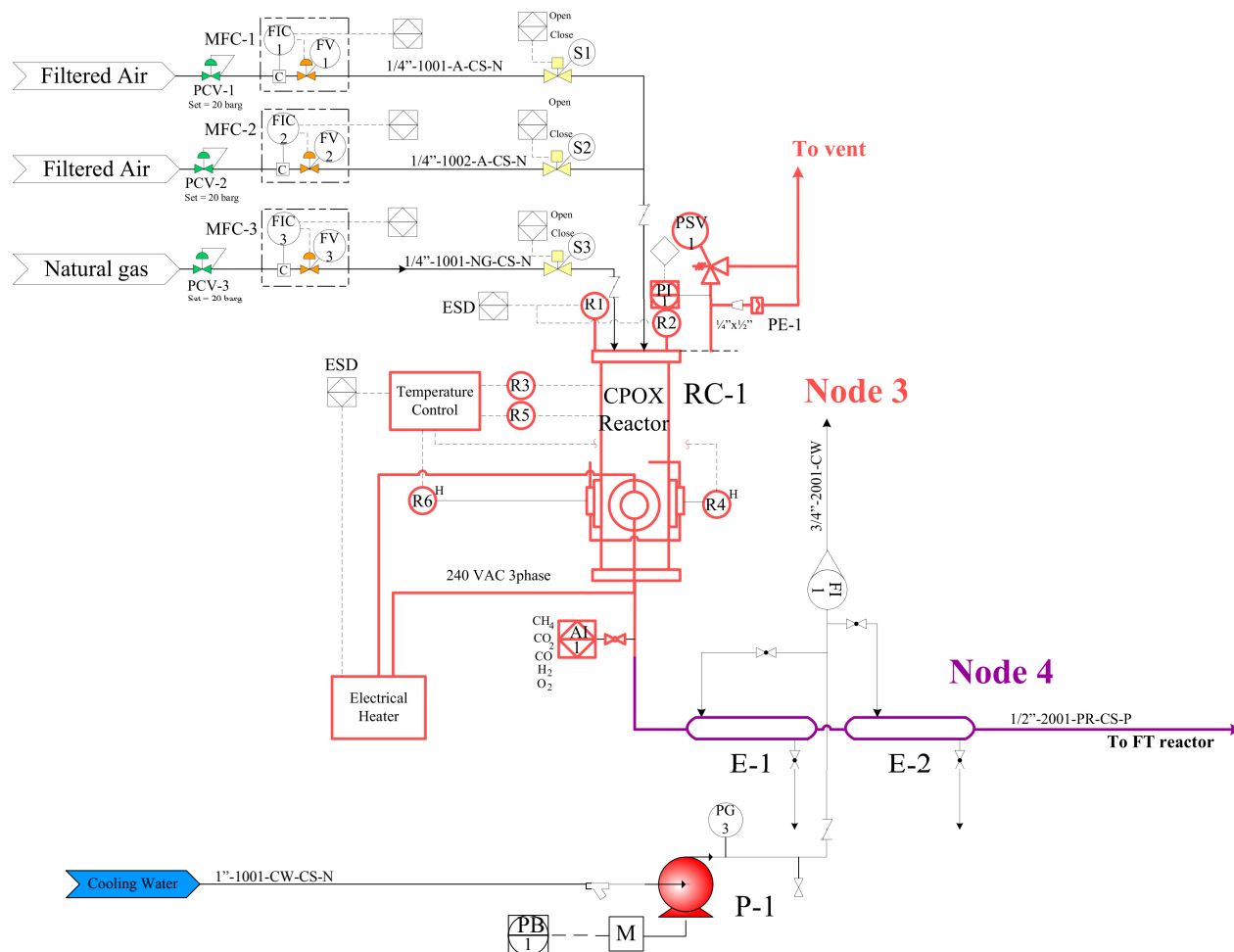


Figure (3.6) Boundary of Node 3; CPOX reactor with auxiliaries including the furnace indicated in red and Node 4; intercoolers and interconnecting stream between reactors showing in purple, on the P&ID of MRU

Table (3.11) Spreadsheet NODE 3; CPOX Reactor

| Item | Cause       | Cons.      | $P_m$ | $S_i$ | $R_i, \%$ | Safeguard     | $S_f$ | $R_r, \%$ |
|------|-------------|------------|-------|-------|-----------|---------------|-------|-----------|
| 1    | FTH/L-R1/R2 | CSQ-9      | 0.811 | 0.6   | 48.7      | SG-10,11      | 0     | 0         |
| 2    | FPL-P1      | CSQ-7      | 0.004 | 1.0   | 0.4       | SG-0          | 1.0   | 0.4       |
| 3    | ONC         | CSQ-7      | 0.002 | 1.0   | 0.2       | SG-0          | 1.0   | 0.2       |
| 4    | FRR-RC-1    | CSQ-9      | 0.9   | 0.6   | 54        | SG-3,11       | 0.0   | 0.0       |
| 5    | FDC         | CSQ-7,9,13 | 0.183 | 1.0   | 18.3      | SG-1,3,11,6,7 | 0.0   | 0.0       |
| 6    | IOM-P1/P2   | CSQ-7      | 0.368 | 0.8   | 29.4      | SG-25,1,11    | 0.0   | 0.0       |
| 7    | IOM-R1/R2   | CSQ-9,13   | 0.368 | 0.8   | 29.4      | SG-27,3,11    | 0.0   | 0.0       |
| 8    | FES-P1/P2   | CSQ-7      | 0.501 | 1.0   | 50.1      | SG-10,11,6    | 0.0   | 0.0       |
| 9    | FES-R1/R2   | CSQ-9      | 0.501 | 0.6   | 30.1      | SG-10,11      | 0.0   | 0.0       |

Table (3.12) Spreadsheet NODE 4; Intercoolers

| Item | Cause   | Cons. | $P_m$   | $S_i$ | $R_i, \%$ | Safeguard | $S_f$ | $R_r, \%$ |
|------|---------|-------|---------|-------|-----------|-----------|-------|-----------|
| 1    | FCC-E-1 | CSQ-9 | 0.12    | 0.6   | 7.2       | SG-29     | 0.4   | 4.8       |
| 2    | FCC-E-2 | CSQ-9 | 0.12    | 0.6   | 7.2       | SG-29     | 0.4   | 4.8       |
| 3    | FLB     | CSQ-8 | 0.00005 | 0.6   | 0.003     | SG-0      | 0.6   | 0.003     |

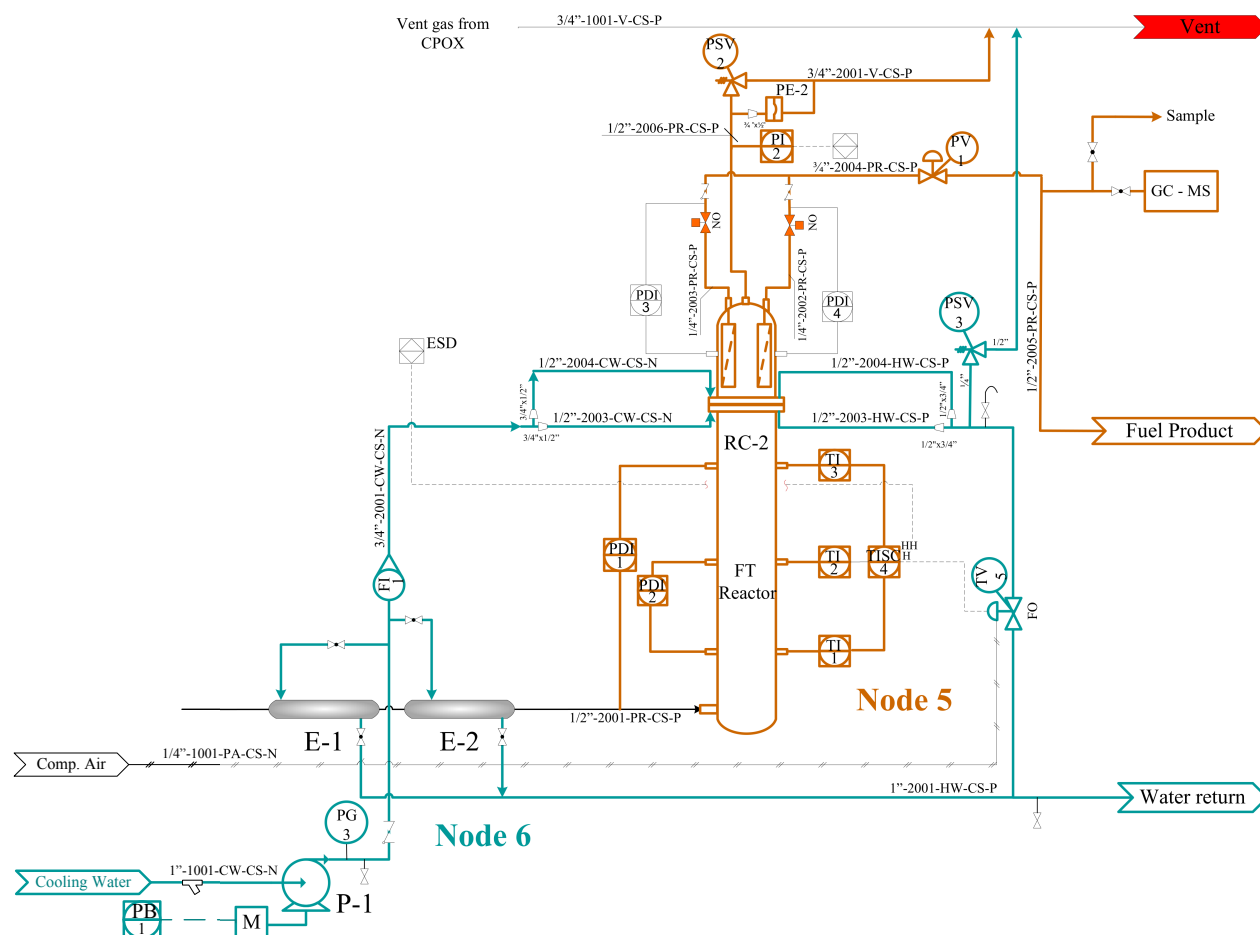


Figure (3.7) Boundary of Node 5; FT reactor, its auxiliaries, output stream and the gas analyzer are indicated by the brown colour and Node 6; cooling water circuit including the water pump and auxiliaries are indicated in cyan on the P&ID of MRU

Table (3.13) Spreadsheet NODE 5; Fischer-Tropsch Reactor

| Item | Cause      | Cons.       | $P_m$ | $S_i$ | $R_i, \%$ | Safeguard     | $S_f$ | $R_r, \%$ |
|------|------------|-------------|-------|-------|-----------|---------------|-------|-----------|
| 1    | FBF        | CSQ-7,14    | 0.94  | 0.8   | 75.2      | SG-26,2,8,9   | 0.0   | 0.0       |
| 2    | BVC-PV1    | CSQ-7       | 0.009 | 0.8   | 0.72      | SG-26,2,8,9   | 0.0   | 0.0       |
| 3    | FTL-T1 ~T3 | CSQ-9       | 0.811 | 0.6   | 48.7      | SG-30,23      | 0.0   | 0.0       |
| 4    | FTH-T1~T3  | CSQ-7,12,16 | 0.811 | 0.8   | 64.9      | SG-26,2,8,9   | 0.0   | 0.0       |
| 5    | FPL-P2     | CSQ-7       | 0.004 | 0.8   | 0.32      | SG-0          | 0.8   | 0.32      |
| 6    | FRR-RC-2   | CSQ-13      | 0.9   | 0.8   | 72        | SG-28,23,4    | 0.0   | 0.0       |
| 7    | IOM-T1~T3  | CSQ-9,13    | 0.368 | 0.8   | 29.4      | SG-28,2,23    | 0.0   | 0.0       |
| 8    | FDC        | CSQ-7,9,13  | 0.183 | 0.8   | 14.6      | SG-2,4,8,9,23 | 0.0   | 0.0       |

Table (3.14) Spreadsheet NODE 6; Cooling water circuit

| Item | Cause   | Cons.     | $P_m$ | $S_i$ | $R_i, \%$ | Safeguard  | $S_f$ | $R_r, \%$ |
|------|---------|-----------|-------|-------|-----------|------------|-------|-----------|
| 1    | AVO-TV5 | CSQ-12,7  | 0.007 | 0.8   | 0.56      | SG-24,2    | 0.2   | 0.14      |
| 2    | AVC-TV5 | CSQ-13    | 0.007 | 0.8   | 0.56      | SG-28,3    | 0.0   | 0.14      |
| 3    | AVC-TV5 | CSQ-18    | 0.007 | 0.8   | 0.56      | SG-23      | 0.4   | 0.28      |
| 4    | FWP-P-1 | CSQ-13,18 | 0.005 | 0.8   | 0.4       | SG-23      | 0.4   | 0.2       |
| 5    | FLC     | CSQ-4     | 0.024 | 0.8   | 1.92      | SG-22,31   | 0.2   | 0.48      |
| 6    | VCL     | CSQ-13    | 0.001 | 0.8   | 0.08      | SG-0       | 0.8   | 0.08      |
| 7    | FES-P-1 | CSQ-9,18  | 0.501 | 0.8   | 40.1      | SG-28,23,4 | 0.0   | 0.0       |

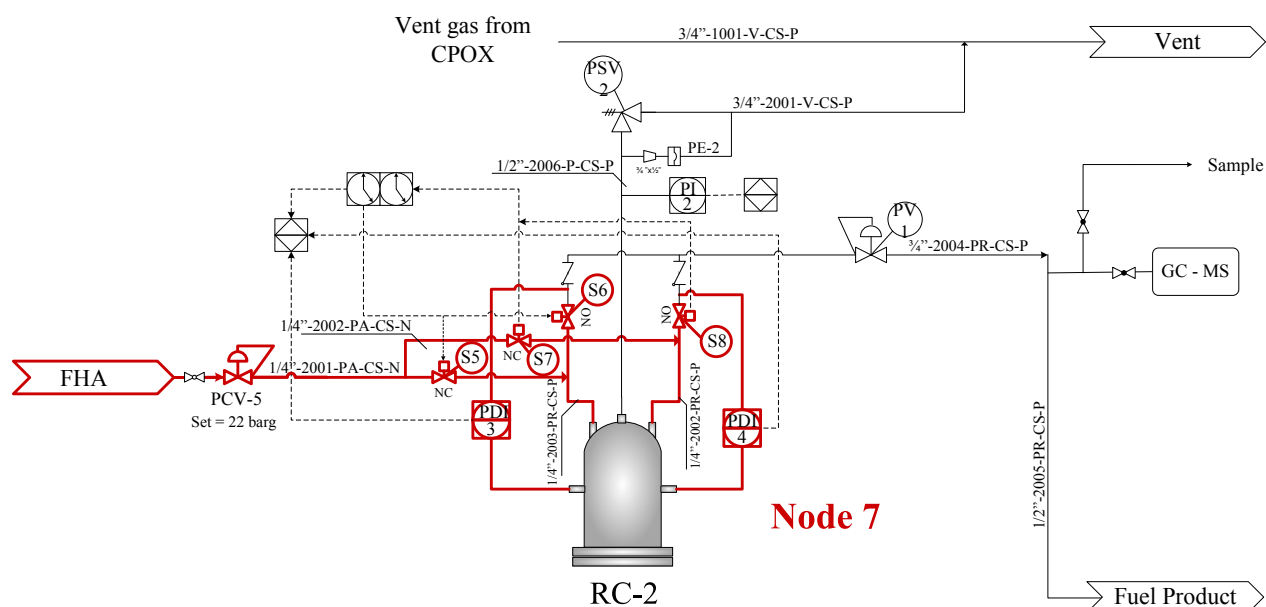


Figure (3.8) Boundary of Node 7; Filter cleaning of FT reactor including the backwash stream and the auxiliaries are indicated in dark red on the P&amp;ID of MRU

Table (3.15) Spreadsheet NODE 7; Filter cleaning system by air

| Item | Cause     | Cons.     | $P_m$ | $S_i$ | $R_i, \%$ | Safeguard   | $S_f$ | $R_r, \%$ |
|------|-----------|-----------|-------|-------|-----------|-------------|-------|-----------|
| 1    | RVO-PCV4  | CSQ-1     | 0.009 | 0.0   | 0.0       | SG-0        | 0.0   | 0.0       |
| 2    | RVC-PCV4  | CSQ-7,14  | 0.009 | 0.8   | 0.72      | SG-26,2     | 0.4   | 0.36      |
| 3    | SVO-S5/S7 | CSQ-15    | 0.002 | 1.0   | 0.2       | SG-0        | 1.0   | 0.2       |
| 4    | SVO-S6/S8 | CSQ-14    | 0.002 | 0.2   | 0.04      | SG-0        | 0.2   | 0.04      |
| 5    | SVC-S5/S7 | CSQ-14    | 0.002 | 0.2   | 0.04      | SG-0        | 0.2   | 0.04      |
| 6    | SVC-S6/S8 | CSQ-4,15  | 0.002 | 1.0   | 0.2       | SG-0        | 1.0   | 0.2       |
| 7    | FAC       | CSQ-14,15 | 0.014 | 0.4   | 0.56      | SG-26,2     | 0.0   | 0.0       |
| 8    | FDC-S6/8  | CSQ-4     | 0.183 | 0.8   | 14.6      | SG-26,32,33 | 0.0   | 0.0       |
| 9    | FES-S5/7  | CSQ-7,14  | 0.501 | 0.8   | 40.1      | SG-26,2,8,9 | 0.0   | 0.0       |
| 10   | FES-S6/8  | CSQ-7,14  | 0.501 | 0.8   | 40.1      | SG-26,2,8,9 | 0.0   | 0.0       |

To control the temperature of the FT reactor in particular during the start-up, the operator prefers to bypass the closed loop control and do it manually. Node 6, items 1, 2, 3 identify the likely incidents when the operator completely open or close the cooling water control valve by mistake. In case of water pump failure (node 6, item 4), although the resulting risk is acceptable ( $R = 0.5\%$ ), a few safeguards are suggested to minimize it. In case of leakage in cooling coil of FT reactor due to the thermal stress, item 5 of node 6 (Table 3.14), the hydrocarbon gas penetrates into water and consequently escapes to the environment from the water reservoir if it is an open circulating system which is a potential source of explosion. Hence, we conservatively assume that the cause of coil leakage is similar to the corrosion leakage (Table 3.6) and compute the risk. We recommend to add a pressure relief valve (PSV 3) on the line of cooling return with a set pressure of 1.5 times higher than the maximum working pressure of the water pump. Thus in case of gas leakage from process side into the coil, the pressure rapidly rises and reaches the set value to open the PSV into the flare with a pop-up sound and announces the operator to stop the operation. Another consequence of pump failure or wrong closure of control valve is the thermal expansion of water inside the coil. Thus considering the PSV 3 as the safeguard will also release the excess pressure. In the filter cleaning operation, node 7, item 8 (Table 3.15), if the operator wrongly keep close the outlet process valves, S6 or S8 while the backflush valves are working properly, the cleaning air will enter the FT reactor intermittently and without sufficient output, it may increase the formation of an explosive mixture. Items 9 and 10 in this node also represent the scenarios that electrical signals of process or backflush solenoid valves fail and make them stay on their normally open (NO) or close (NC) position respectively (Fig. 3.1). In both cases, the cleaning air is not allowed to enter the reactor which causes the filters to clog and eventually increases the pressure inside the reactor. Hence, proper protections will prevent these incidents. Although alarms are considered a protection layer in risk assessments [212] to reduce the severity of the consequences, in practice, we do not use it alone as a risk-mitigating factor because in some cases, the operator has insufficient time to take a proper action against critical circumstances. The appropriate protection layers would be high, high-high, low, and low-low interlocks. For each node, the entire predictable failures such as equipment, instrument and personnel were investigated. All the tabulated malfunction probability, consequences and safeguards were developed and classified based on the process hazard analyses of the nodes and finally we characterized the mechanism of safety interlock and chose the required safety mechanisms and devices to protect the system even in cases of natural disasters and terrorist attack. The activation of safety interlock leading to emergency shut down (ESD) consists of :

- Automatic closing of the feed valves to CPOX reactor

- Automatic opening of the outlet valves on FT reactor
- Turning off the heating element of CPOX reactor
- Turning off the natural gas and air compressors

Another notable issue is selecting the value of risk level as the decision criteria to determine if a scenario needs safeguard or not. Here, we assumed that  $R = 0.5\%$  is enough strict and conservative for safety as the upper limit of “Acceptable” risk level (Table 3.4). However to apply this method to the other processes, the engineering team may change the risk thresholds upon the required confidence. Although our pilot MRU is not working all day long, we assumed that it operates continuously for all the year which comes to overestimating the failure probability due to the lack of data for the pilot unit. To define the automatic sequence of operation, record the online operating parameters (temperature, pressure, flow rate) and trigger the safety interlock of emergency shut down, we applied the LabVIEW software integrated to the PLC. The final P&ID (Fig. 3.9) includes all the required safeties for the process.

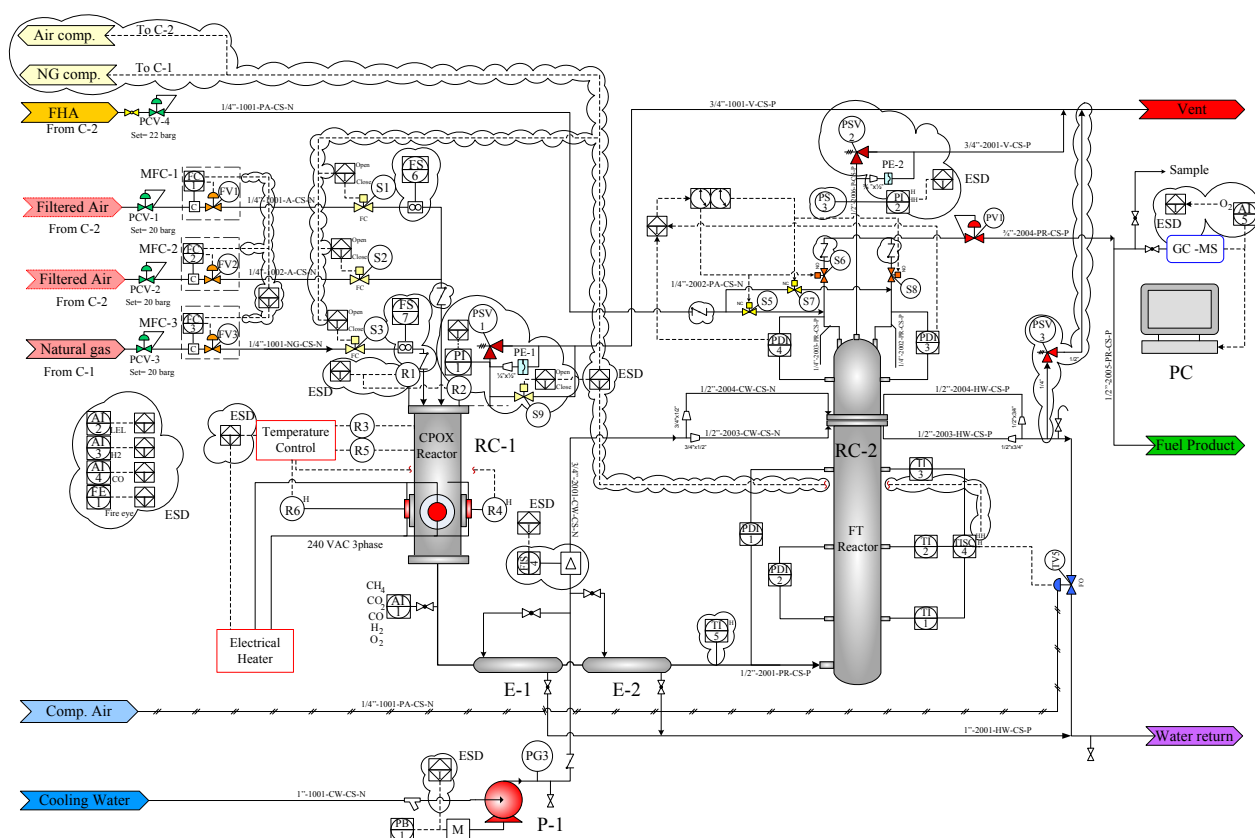


Figure (3.9) Final P&ID of MRU with safety system. The modifications are indicated by the revision clouds

### 3.5 Conclusion

We proposed a new approach to safety and risk analysis for novel chemical processes by combining PFFM with risk quantification. This failure mode risk decision approach led to the definition of a new metric to be used in the design and development of chemical processes operating at or near critical conditions. The proposed methodology was applied to a Micro GtL plant. Compared to classical HAZOP, we identified excess hazardous scenarios in terms of equipment and instrument failure as well as operator mistake. The numerical analysis not only shows the value of risk but also is able to precisely evaluate the residual risk after adding each safeguard since the probability and severity functions have not necessarily equal weight percent. Finally, we designed the safety interlock in the PLC and considered all required components and instruments to protect MRU against the expected risky conditions. This approach has a few limitations. Here, we collected the frequency of almost all the instrument and equipment failure as well as personnel mistake to translate into the failure likelihood. However for complex processes with specialized equipment and/or instruments, failure frequency data may be unavailable. Furthermore, although we provided the mean value of the failure probability for over 20 y of operation, the site location and the climate variation may affect the accuracy of the failure frequency. We have scaled and evaluated the severity table by considering the financial loss of the equipment as it is the easiest metric to approximate the consequence value. However, the contribution of personnel injuries/accidents and the environmental deterioration were ignored. Future studies may consider these factors in calculating severity. Also, the severity scale is evaluated at discrete intervals and the resulting inherent and residual risks vary over the tie-lines on the risk contour plot. However, adopting the cost of the damage of any consequence would convert the severity scale to a continuous function. In the risk assessment, to distinguish the concept of pure/ inherent severity of a consequence from its chance level impacted by safeguard(s), we recommend defining ‘apparent severity’. This term would be a function of pure severity of a consequence ( $S$ ) and the reduction factor of likelihood of that consequence. In the risk formulation, it would be an arithmetic operator or logic corresponding to the reduction factor of a safeguard that explicitly reflects its impact on the chance or likelihood of the consequence. Hence, without safeguard, this operator has no impact on the severity while adding a safeguard decreases its value depending on the intensity of that protection layer. The team has a critical role to conduct the analysis and must include people with experience and a varied background to identify the various scenarios, assess failure modes, assign consequences, understand the chemistry, set the minimum residual risk, and identify deficiencies to finalize the assessment. If final residual risk of a scenario is still a bit higher than the upper limit of the acceptable

range, their task is to decide whether it is conditionally accepted or more safeguards must be added to meet the criteria. They may even recommend further safeguards even when the inherent risk or residual risk is within the acceptable range. Although this hybrid technique requires some basic knowledge about process and safety issues, it is simple, robust and convenient for the industry. It also provides a systematic approach to improve the process design stepwise meaning that after adding each safeguard layer, it recalculates the residual risk and compare it with the numerical decision pattern to reach the safe side. In addition, the applied numerical analysis of risk gives a quantitative sense to this process which is potentially applicable to other industrial chemical and petrochemical plants. It is also flexible for the safety and design authorities to change the thresholds of decision pattern and revise the severity levels upon their required confidence.

## CHAPTER 4 ARTICLE 2 : FEEDBACK CONTROL STRATEGY OF FISCHER-TROPSCH PROCESS IN A MICRO-GTL PLANT

Mahdi Sharifian, Nicolas Hudon, Ergys Pahija, Gregory S. Patience

Submitted to :

Journal of Chemical Engineering and Processing-Process Intensification, September 17, 2023

---

### Abstract

Gas-to-liquid technology monetizes flared natural gas to produce green fuel while reducing carbon emissions. In the first step, oxygen reforms methane to CO and H<sub>2</sub> followed by Fischer-Tropsch synthesis (FTS), which is highly exothermic and requires a tight temperature control to avoid thermal runaway. Bench-scale units are insufficient to generate basic data to design dynamic control systems for pilot-plants, particularly for intensified processes, because of uncertainties related to heat losses and the spatial and temporal reaction rates. Here, we propose a simulation-based feedback controller design strategy to initially estimate the parameters of a proportional Integral (PI) controller. We applied a power law model to design the controller in Aspen V12 and tested its robustness with a fractional lumped model as an alternative. An excel ‘solver module’ estimated heat exchange parameters considering the fluidized bed hydrodynamics at steady state. Then, through dynamic simulation, we identified the parameters of a ‘first-order plus dead time’ model via a step response of the reactor temperature to design the PI temperature controller. The controller parameters were characterized by the internal model control (IMC) approach, which is suitable to characterize kinetic model mismatch and heat exchange uncertainties.

---

### 4.1 Introduction

Gas-to-Liquid (GtL) technology converts associated natural gas from oil fields, bio-gas, land-fill gas and gas from water treatment facilities to value-added hydrocarbons as synthetic fuel [8]. Existing commercial processes are economical at the very large scale  $> 35\,000\text{ bbl d}^{-1}$  with conventional processes for which the investment costs are on the order of  $15\,000\text{ \$ bbl}^{-1}$  of oil capacity. Total capital investment cost decreases with smaller facilities but the capital

investment cost per barrel of synthetic crude produced increases. For example, capital cost of a  $500 \text{ bbl d}^{-1}$  unit will be  $80\,000 \$ \text{ bbl}^{-1}$  of installed capacity (\$40 million). Moreover, providing industrial utilities such as water and electricity is limited in remote areas, thus limiting the deployment of the technology. Intensified processes together with mass manufacturing for distributed facilities reduces the excessively high capital costs when scaling-down [213]. For a capacity of  $< 100 \text{ bbl d}^{-1}$ , a micro-scale GtL plant can be built at lower investment costs  $> 100\,000 \text{ bbl d}^{-1}$  and requires limited infrastructure [4]. However, one challenge for this process is the Fischer–Tropsch reaction as it is extremely exothermic [10,214]. The major concerns for this reaction are its safe start-up and operation with variable natural gas feed rates, which is characteristic of oil field production [197].

Regardless of the choice reactor configuration—fixed bed, fluidized bed, or slurry reactor—the FT reaction requires a robust temperature controller [215,216]. Appropriate feedback control is essential to prevent runaway reaction, which deactivates catalyst [150,217]. Adequate temperature control is also required for start-up and ramping up to steady-state operation. Process hazards assessment requires a detailed plan to mitigate the potential of runaway reactions and other risks before operating a unit. These analyses are less arduous for experimental reactors as the impact is much smaller compared to pilot facilities with huge volumes of natural gas, CO, and H<sub>2</sub>.

The Process Intensification community recognizes that process control is one of the pillars in the chemical engineer’s toolbox (area 3) [218]. Furthermore, it generates new options to apply hardware and process schemes. Heat and mass transfer, fluid mechanics, and reaction engineering are in Area 2 of toolbox, which are basic concepts independent of process intensification. However, to apply design and operate, an intensified process requires basic data to be able to operate it and apply new process control schemes and hardware. This data is unavailable as the uncertainties at the bench scale are too large (like heat losses, global reaction kinetics, gas/solids flow distribution), and thus could compromise operations at the larger scale. Even for continuous bioprocessing with reaction rates orders of magnitude lower than catalytic processes, control and operational challenges hinder the adoption of bioprocess intensification [219,220]. Furthermore, a driving force of process intensification is to minimize the footprint, which might also entail reducing any engineering allowances. Thus, one huge challenge is to design a feedback controller with these uncertainties [221]. One approach is applying a model-based feedback controller using a dynamic simulation model of a chemical process under structural and parametric uncertainties.

### 4.1.1 Research gap/novelty

Here, the overall objective is to develop an effective temperature control strategy for a process at the *design stage*. Just as control challenges limit bioprocess intensification uptake, they present an obstacle while designing pilot plant processes and controllers from bench scale experiments. Although the literature suggests reactor designs to improve heat transfer rates in FT processes, few studies focus on the design of a temperature controller [222], which is particularly important for start-up (since the reaction is highly exothermic) and in the case of process upset, like unforeseen changes in gas flowrates due to a perturbation in the syngas reactor, for example. Moreover, micro-GtL processes as intensified systems [23, 223] are insufficiently covered in the open literature, so the aim of this paper is to propose and illustrate a methodology to develop feedback control strategies using dynamic simulation models.

Dynamic simulation is a promising approach for both industrial applications and as a research field [224, 225]. We first develop a dynamic simulation of the process with literature kinetics and hydrodynamic models. With this simulation, we then generate information required to design a feedback temperature controller. The choice of the simulation platform is motivated by the fact that Aspen is versatile and allows users to monitor the dynamic responses [226, 227]. In the present context, one can benefit from Aspen’s physical properties database, while implementing user-defined kinetics. Using the developed simulation platform, open-loop simulations are then performed to characterize the temperature dynamics in the reactor as first-order plus delay transfer functions. A conservative temperature feedback Proportional-Integral (PI) controller is designed using the direct synthesis methodology [156]. Within closed-loop simulations under various scenarios, the proposed controller performs well in the nominal case, and in cases where kinetics and hydrodynamics parameters differ from the nominal ones. Furthermore, the proposed controller performs well when the kinetic formulation is different than the one used to develop the control strategy. This is due, in part, to the properties of PI controller designed using the direct synthesis method. To the best of our knowledge, this is the first study that combines hydrodynamic tests, validated at the pilot scale, and reaction kinetics to initially characterize the controller as a part of design strategy.

## 4.2 Process overview, operation objectives, and constraints

The Micro Refinery Unit (MRU), designed in our group [4], consists of catalytic partial oxidation (CPOX) to convert the natural gas to syngas at 20 bar and 900 °C followed by

Fischer-Tropsch synthesis to transform the syngas into diesel range fuel at the same pressure and 300 °C [13].

The process starts with CPOX to generate CO+H<sub>2</sub> (syngas) which is the ideal composition to produce moderate carbon chain length of fuel. In practice, an oil free reciprocating compressor package (Atlas Copco) provides the filtered air and Sulphur-free natural gas (more than 95% methane) supplied from an oil well is pressurized to 20 bar. The syngas is fed into a fluidized bed FT reactor so that the syngas well mixed with the iron catalyst particles at 300 °C and 20 bar and chain reactions of Fischer-Tropsch as well as water gas shift reaction (WGS) take place. Here, pressurized sub-cooled water flowing through internal coils of the FT reactor removes the heat of reaction. Industrial reactors are often cooled by pressurized saturated steam [222,228]. We intend to design an automatic temperature controller in order to keep the temperature and consequently the composition of the product constant inside the FT reactor by manipulating the coolant flow rate. Such a control system is expected to attenuate the disturbances such as varying the natural gas composition, gradual deactivation/coking of CPOX and FT catalysts or instability of the syngas temperature coming from CPOX into the FT reactor (Fig.4.1). The hot water returns to a cooling package consisting of an auto tuned air-cooled heat exchanger to remove the excess heat from the water and to make a constant temperature for the water supply returning to the internal coils. Finally an MS-GC measures the light contents of the riched-fuel product before entering a three phase condenser to separate the green diesel from water and light hydrocarbons. All the signals from indicators, safety instruments and control valves are connected to a programmable logic controller, PLC, and is monitored via the LabVIEW.

The experimental tuning of the controller parameters is problematic because the FTS is highly exothermic and local hot spots deactivate the catalyst by carbon deposition, and makes the operation unstable [134,229]. Furthermore, as the operating temperature of the FT process (290 °C to 300 °C) is close design temperature of the reactor (350 °C), a well-tuned controller is expected to minimize the failure risk of the reactor and the auxiliary instruments. However, the main challenges to design a controller for FT reactor are:

- Having no functional process yet
- Risky conditions of open-loop startup of the unit particularly when the CPOX reactor is at the upstream of the Fischer-Tropsch one.

An appropriate technique to solve these issues is to develop a feed back controller based on the simulation and then improve the controller parameters practically while the operation is

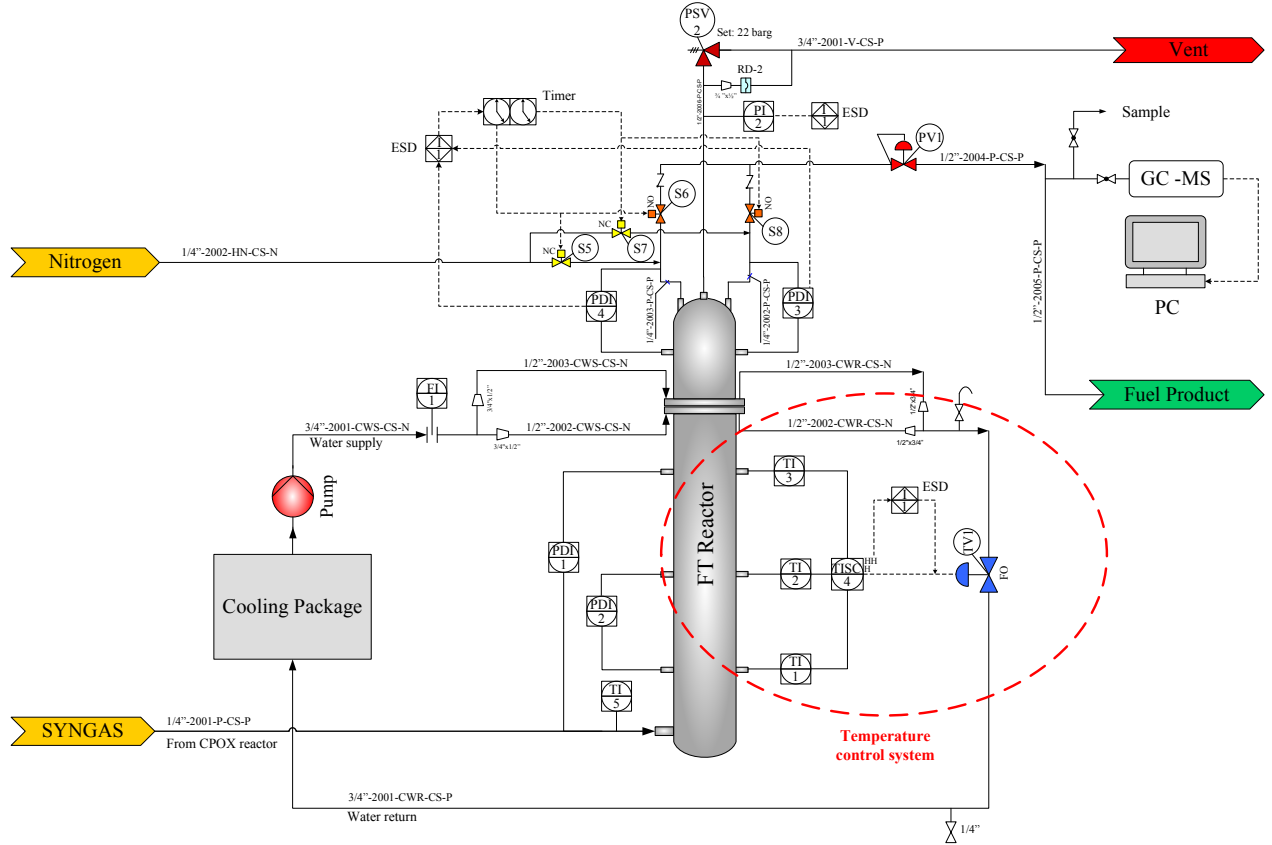


Figure (4.1) Piping and instrumentation diagram of Fischer-Tropsch process

running.

### 4.3 Simulation-based controller design approach

We propose a methodology to design a controller based on the simulation (Fig.4.2). Having the experimental data, a well-adapted kinetic model is used in the steady state simulation. Then the steady state point is adopted as the initial conditions in the dynamic mode to obtain the open-loop response of the process variable, temperature versus the input variable; here the coolant flow rate. The parameters of the PI controller are then adjusted based on the transfer function of the system which finally gives the response of the closed-loop system against the step changes in set point and possible disturbances.

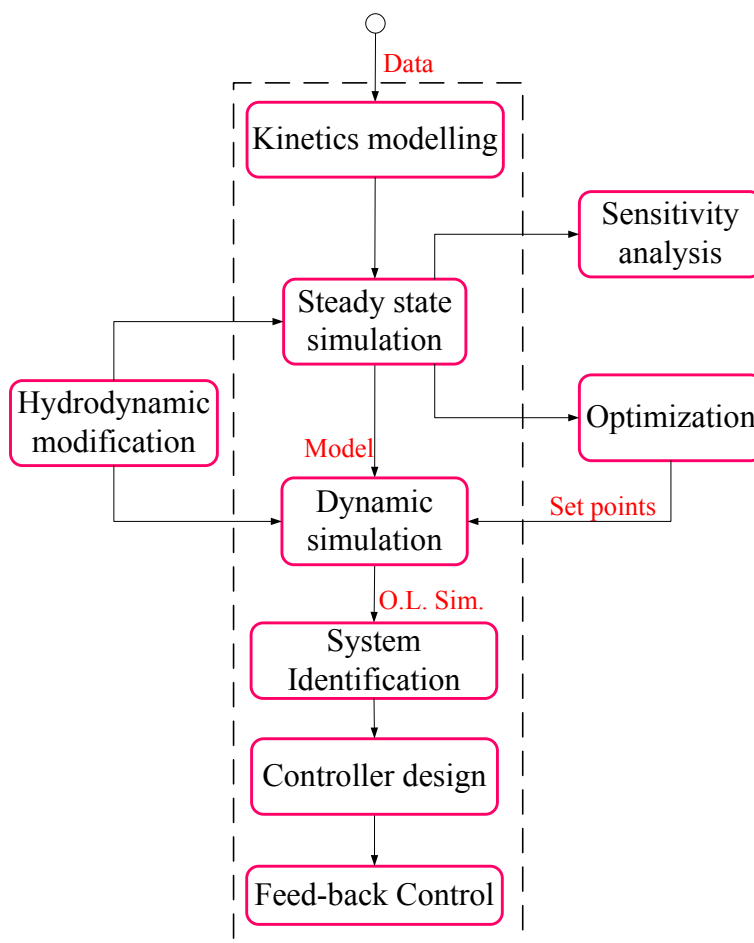


Figure (4.2) Flow chart diagram of simulation-based control for the Fischer- Tropsch process. O.L.Sim. refers to the open-loop simulation. Depending on the process, the hydrodynamics may contribute to both steady state and dynamic simulation or only the dynamic one.

Based on this flow chart, the kinetic model is developed from experimental data and then a hydrodynamic model consisting of mass and heat transfer correlations contributes to build the steady state simulation. The results are then applied to simulate the process dynamically. From the open loop simulation and by adopting a proper model, the parameters of the system are identified obtaining the controller parameters. Finally, the performance of the controller is tested in a closed-loop system and if it is unacceptable, we need to redo the procedure from beginning.

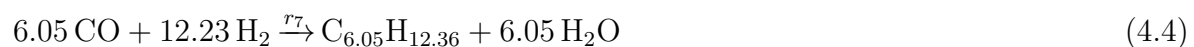
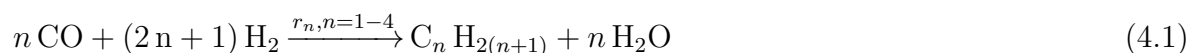
#### 4.3.1 Fischer-Tropsch Model

One of the main challenges of the Fischer–Tropsch synthesis is kinetic modeling since this process is a polymerization reaction involving step-wise chain growth [71, 92]. Furthermore,

the iron-based catalysts have two types of active sites (bi-functional) which are selective to both paraffin and olefin products [55, 214]. Hence, the chemistry does not follow a unique mechanism and people attempt to develop detailed mathematical models to match better the product distribution to the experimental results [88, 230]. Furthermore, some models do not meet the thermodynamics points meaning that the syngas conversion is not compatible with the enthalpy progress by varying the temperature [92, 98] or some are isotherm i.e. are valid only at one temperature but fail at others since no activation energy was assigned [95]. To study the dynamic behaviour of the reactor, we considered powerlaw equations for the kinetics since it is one of the most reliable models adopted to the lab-scale as well as industrial FT over our required operating range. We also applied Langmuir-based model as the alternative approach.

### Power law kinetics model

The following reactions were considered as leading FTS reactions on the bi-functional Fe–HZSM<sub>5</sub> catalyst [94]:



The parameter  $j$  is 1 for paraffins and 0 for olefins. The below kinetic equation [93], followed by the parameters of each reaction rate (Table 4.1) represents the concentration of each

component in the reactor.

$$r_i = 2.278 \times 10^{-4} k_i \exp \left[ \frac{-E_{a,i}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] P_{\text{CO}}^{v_i} P_{\text{H}_2}^{w_i} \quad [\text{mol g}^{-1} \text{s}^{-1}] \quad (4.6)$$

The kinetic model is valid over 290 °C to 310 °C, 15 bar to 23 bar, and syngas ratio of 0.76

Table (4.1) Kinetics parameters data [94]

| Reaction no. | $v_i$ | $w_i$ | $k_{i,573 \text{ K}}$ | $E_{a,i}$ |
|--------------|-------|-------|-----------------------|-----------|
| 1            | -1.1  | 1.6   | 0.0035                | 83        |
| 2            | -0.56 | 1.3   | 0.00072               | 50        |
| 3            | 0.41  | 0.66  | 0.00031               | 35        |
| 4            | 0.47  | 1.14  | 0.000014              | 28        |
| 5            | 0.82  | 0.5   | 0.0000038             | 26        |
| 6            | 0.76  | 0.072 | 0.000061              | 65        |
| 7            | 0.59  | 0.6   | 0.00016               | 24        |
| 8            | 0.57  | 0.71  | 0.0018                | 59        |

to 1.82 [93,228]. The hydrocarbon  $\text{C}_{6.05}\text{H}_{12.36}$  called  $\text{C}_5^+$  is defined as a pseudocomponent in Aspen Plus and we approximated the required properties (Normal Boiling Point (NBP) and density) equal to those of n-hexane. To make sure that no liquid forms inside the reactor, Soave-Redlich-Kwong (SRK) equation of state is selected as the property package since it involves the VLE thermodynamics of multicomponents [231].

### Langmuir kinetics model

The Fischer-ropsch synthesis over Iron catalyst is approximated as a combination of series - parallel FT and water gas shift (WGS) reactions (eqn.4.7,4.8) [232]:



To estimate the properties of hydrocarbons from FT reactor, we consider a virtual component as the main product of FTS containing the average carbon numbers over the defined range of operating conditions called  $\text{C}^*$ . The hydrogen usage is calculated based on the olefin to paraffin distribution ratio  $\gamma_{FT}$  which is here assumed as 0.35 [233]. Thus,  $m$  in the Eqn. 4.7

is:

$$m = 2n + \frac{2}{1 + \gamma_{FT}} \quad (4.9)$$

To develop the model, we determine the properties of the C\* by using the experimental data from the RIPI pilot [93]. For each run, the chain growth probability of the mixture was calculated based on the operating conditions (eqn.4.10) [234]

$$\alpha = \frac{K_{\alpha,1}P_{CO}}{K_{\alpha,1}P_{CO} + K_{\alpha,2}P_{H_2} + K_{\alpha,3}} \quad (4.10)$$

where the  $k_i$  parameters are given by 4.2:

$$K_{\alpha,i} = k_i(T_0) \cdot \exp \left[ -\frac{E_i}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (4.11)$$

Table (4.2) Value of parameters for the chain growth probability evaluation,  $T_0 = 573K$

| parameter | Value                  |
|-----------|------------------------|
| $k_1$     | $1.22 \times 10^{-10}$ |
| $k_2$     | $1.05 \times 10^{-11}$ |
| $k_3$     | $2.36 \times 10^{-6}$  |
| $E_1$     | 0                      |
| $E_2$     | 94.5                   |
| $E_3$     | 132.3                  |

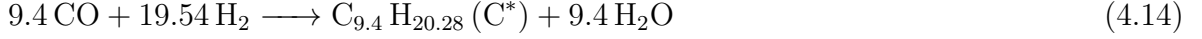
Then we obtain the average carbon number of C\* by assuming that the hydrocarbon distribution is  $C_1$  to  $C_{60}$ , computing the molar fraction of each component in the mixture and finally estimating the total carbon number of the mixture over the whole operational domain of the experiment (eqn. 4.12).

$$n = \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^{60} n_{j,i} \cdot M_{j,i} \quad (4.12)$$

where  $N$  is the number of experimental runs (24) [93],  $j$  is the number of carbon atoms in each component and  $M_j$  is the mole fraction of each component (eqn. 4.13) [235]:

$$M_{j,i} = \alpha_i^{j-1} (1 - \alpha_i) \quad (4.13)$$

The overall equation of FT reaction consequently is:



To develop the simulation, we select a generalized Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model proposed by Zimmerman and Bukur [232] with the parameters in Table 4.3.

$$r_{FT} = K_{FT} \frac{P_{\text{H}_2} P_{\text{CO}}}{P_{\text{CO}} + a_{FT} P_{\text{H}_2\text{O}} + b_{FT} P_{\text{CO}_2}} \quad (4.15)$$

$$r_W = K_W \frac{P_{\text{CO}} P_{\text{H}_2\text{O}} - \frac{P_{\text{H}_2} P_{\text{CO}_2}}{K_P}}{P_{\text{CO}} + a_W P_{\text{H}_2\text{O}} + b_W P_{\text{CO}_2}} \quad (4.16)$$

where

$$K_r = k_r^0 \exp \left[ -\frac{E_{a,r}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (4.17)$$

$$\ln(K_P) = \frac{4578}{T} - 4.33 \quad (4.18)$$

Table (4.3) Kinetic parameters of the FTs reactions. Subscript r refers to the FT or WGS.

| parameter   | Value                  |
|-------------|------------------------|
| $k_{FT}^0$  | 0.085                  |
| $E_{a,FT}$  | 86                     |
| $a_{FT}$    | $1.25 \times 10^{-7}$  |
| $b_{FT}$    | $7 \times 10^{-6}$     |
| $k_{WGS}^0$ | 9330                   |
| $E_{a,WGS}$ | 132                    |
| $a_{WGS}$   | $2.78 \times 10^{-6}$  |
| $b_{WGS}$   | $1.227 \times 10^{-5}$ |

To validate the model, eqs. (4.10) to (4.18), we compare its prediction with the practical data from pilot reactor of RIPI [94] (Tab. 4.4). We define the  $C^*$  in ASPEN PLUS as a pseudocomponent by assigning the molecular weight of  $\text{C}_{9.4}\text{H}_{20.28}$  ( $133 \text{ g mol}^{-1}$ ). Its NBP and density are obtained from a linear regression between those of  $\text{C}_9$  and  $\text{C}_{10}$ . We use the

SRK package again to ensure that no liquid phase is inside the reactor. To represent the fixed bed reactor, we apply the RPlug module on the software, assigned the constant cooling temperature and implement all of the characteristics of the RIPI pilot plant [94].

Table (4.4) Comparison of the fractional (LHHW) and Power law models in ASPEN plus with RIPI's experiment [94]

| parameter                                 | LHHW | Power law | Experiment |
|-------------------------------------------|------|-----------|------------|
| CO conversion, %                          | 98   | 91        | 93         |
| H <sub>2</sub> conversion, %              | 84   | 83        | 78         |
| CO <sub>2</sub> selectivity <sup>†</sup>  | 349  | 331       | 339        |
| H <sub>2</sub> O selectivity <sup>†</sup> | 95   | 100       | 120        |

<sup>†</sup> g m<sup>-3</sup> syngas (NTP)

One reason for the model deviation from RIPI experiment is that the component fraction of the Zimmerman's catalyst (100Fe/0.3Cu/0.2K) is different than that applied by RIPI (100Fe/5Cu/5K<sub>2</sub>O/25SiO<sub>2</sub>). Another reason is the Lumped modelling method which gives the product as an average over all the experiments using  $\alpha$  correlation and directly impacts on the selectivity.

Since this model adequately captures the experimental data, we adopt it to implement in the steady-state simulation of the pilot FT reactor of MRU. This short-cut modelling initially estimates the products from a FT reactor meaning that this approach may assist engineers in the preliminary design of the reactor, without requiring advanced kinetic models [92, 134].

#### 4.3.2 Residence time distribution (RTD) experiment

To study the flow regime of the gas-solid mixture inside the FT reactor and assign a proper reactor model into the simulation, we designed an RTD experiment on the real setup using air, argon as the tracer gas and a mass spectrometer to monitor the argon concentration. The reactor was loaded by 75  $\mu$ m alumina catalyst support. MFC-1,2 set the compressed air flow at 3 L s<sup>-1</sup>(STP) and then air passes through the furnace, RC-1 to reach 150 °C to reach the FT reactor, RC-2. Lateral heating tapes keep the bed temperature constant. The superficial gas velocity at this condition is 6 times greater than the minimum fluidization velocity confirming the bubbling fluidized regime. To generate a pulse injection for the RTD, we arrange two solenoid 4-way valves, S9, S10, that are connected to two sample loops, A and B, with identical configuration: equal volume of the loop (1.2 L) and the same number of valve ports.

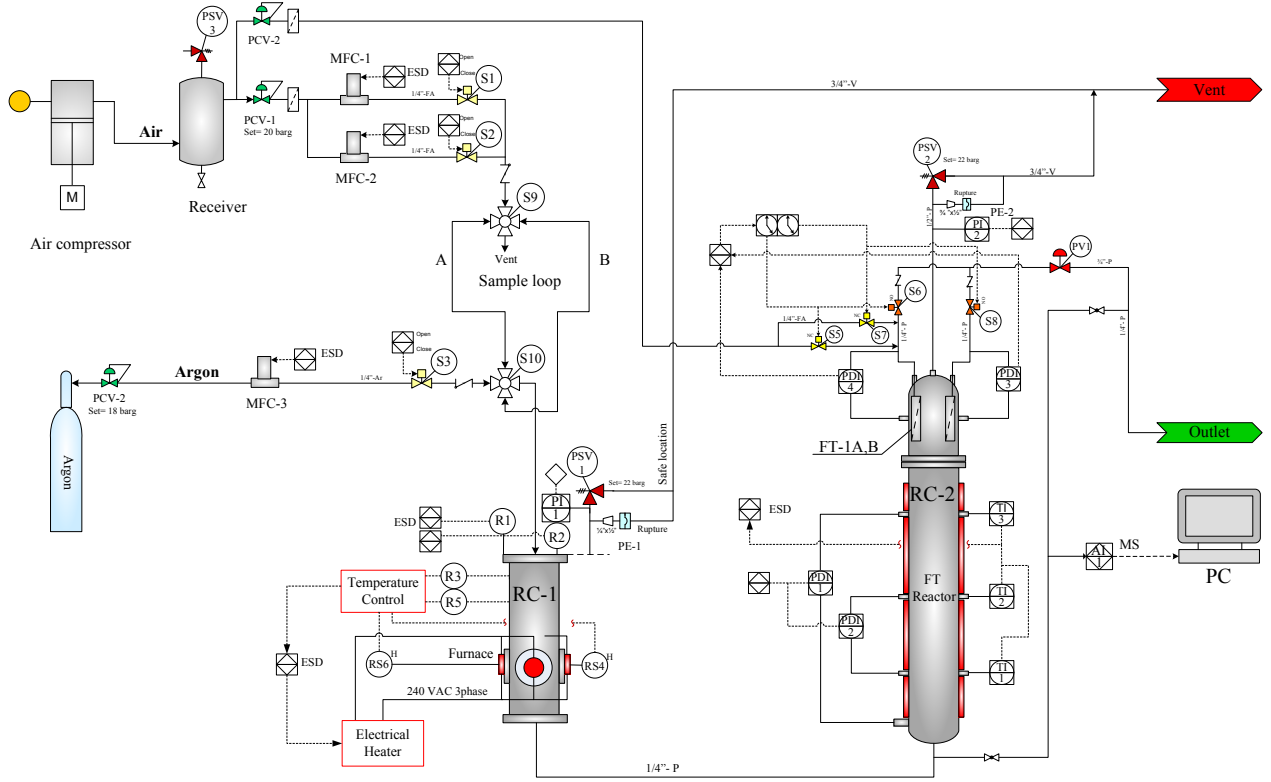


Figure (4.3) Piping & Instrumentaion Diagram of the experimental setup at Polytechnique Montreal to determine the hydrodynamic regime inside the fluidized bed reactor. Simultaneous rotation of solenoid 4-way valves, S9 and S10, generates argon pulse injection.

At time  $t = 0$ , we turned the MS on while the air passes through one sample loop, A, leading to the reactor/furnace (RC-1) and Ar as the tracer fills the second loop, B, and evacuates to exhaust (Fig. 4.3). At  $t = 120$  s, we rotate both S9 and S10 simultaneously so that the air flushes the second loop with Ar and sweeps it into the reactor making an Ar pulse injection. We measure the RTD once at the FT entrance and another time at the FT exit by connecting the MS detector to the inlet and exit lines of the FT reactor respectively and repeat the test for each experiment. The following equations estimate the mean residence time and the variance [101].

$$\bar{t}_{\text{pulse}} = \frac{\int_0^\infty tC(t)dt}{\int_0^\infty C(t)dt} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \quad (4.19)$$

$$\sigma_{\text{pulse}}^2 = \frac{\int_0^\infty t^2 C(t)dt}{\int_0^\infty C(t)dt} - \bar{t}_{\text{pulse}}^2 = \frac{\sum t_i^2 C_i \Delta t_i}{\sum C_i \Delta t_i} - \bar{t}_{\text{pulse}}^2 \quad (4.20)$$

To characterize the experimental data, we adopt the axial dispersion model for the pulse injection (eqn. 4.21):

$$\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial \xi} = \frac{1}{N_{\text{Pe}}} \frac{\partial^2 C}{\partial \xi^2} \quad (4.21)$$

where  $\theta = tu/Z$  (non-dimensional time),  $\xi = z/Z$  (non-dimensional length), and  $N_{\text{Pe}} = uZ/D$  is the Peclet number. The exact analytical solution for the bolus-pulse is:

$$G'(\theta) = G(\theta) - H(\theta - \eta)G(\theta - \eta) \quad (4.22a)$$

$$H(\theta - \eta) = \begin{cases} 0 & , \theta \leq \eta \\ 1 & , \theta > \eta \end{cases} \quad (4.22b)$$

$$G(\theta) = \frac{1}{2} \left[ \text{erfc} \sqrt{\frac{N_{\text{Pe}}}{4\theta}} (1 - \theta) + e^{N_{\text{Pe}}} \text{erfc} \sqrt{\frac{N_{\text{Pe}}}{4\theta}} (1 + \theta) \right] \quad (4.22c)$$

where  $\eta = (V_{\text{lp}}/\dot{V}) (u/Z)$  is the non-dimensional time length of the pulse injection,  $V_{\text{lp}}$  is the volume of the sample loop,  $\dot{V}$  is air volumetric flow rate and  $Z$  is the bed length (Table 4.5).

Table (4.5) Parameters of the dispersion model for the experimental pilot reactor

| Spec, unit                    | Value |
|-------------------------------|-------|
| $u$ , mm s <sup>-1</sup>      | 12    |
| $Z$ , mm                      | 1600  |
| $V_{\text{lp}}$ , L           | 1.2   |
| $\dot{V}$ , L s <sup>-1</sup> | 0.35  |

Having the Peclet number,  $N_{\text{Pe}}$ , the number of CSTR is:

$$n_{\text{CSTR}} = N_{\text{Pe}}/2 + 1 \quad (4.23)$$

### 4.3.3 Hydrodynamics

The hydrodynamics of fluidization involves in both steady-state and dynamic simulation. In the steady state mode, the catalytic bed voidage,  $\varepsilon$ , integrates into the mass balance equation

to obtain the product concentrations. The superficial gas velocity of the feed is ten times higher than the  $u_{mf}$  of the catalyst [100] (Table 4.6) pointing out that the hydrodynamics is in the fluidized regime. Hence, we estimate the bed voidage [236, 237] and the minimum fluidization velocity ( $u_{mf}$ ) for the so-called Fe catalyst by using the Archimedes number [100], characteristics of the operation, diameter of the catalyst [228] and its density [228].

$$Ar = \frac{d_p^3 \rho_g (\rho_p - \rho_g) g}{\mu_g^2} \quad (4.24)$$

$$u_{mf} = \left( \frac{\mu_g}{\rho_g d_p} \right) (\sqrt{27.2^2 + 0.0408 Ar} - 27.2) \quad (4.25)$$

$$\varepsilon_e = \varepsilon_{mf} + 0.00061 \exp \left( \frac{u_0 - u_{mf}}{0.262} \right) \quad (4.26)$$

$$\varepsilon_b = 0.784 - 0.139 \exp \left( -\frac{u_0 - u_{mf}}{0.272} \right) \quad (4.27)$$

$$\delta = 1 - \exp \left( -\frac{u_0 - u_{mf}}{0.62} \right) \quad (4.28)$$

$$\varepsilon = (1 - \delta) \varepsilon_e + \delta \varepsilon_b \quad (4.29)$$

where  $\varepsilon_{mf}$  is equal to 0.56 for Fischer–Tropsch catalyst [99]. To approximate the overall heat transfer coefficient,  $U$ , and the outlet temperature of the cooling water from the coil of reactor as key parameters for the dynamic mode, we also determine the maximum convective heat coefficients of the bed,  $h_{b,max}$  and of the coolant,  $h_c$ . Many correlations may approximate the heat convection from the catalytic bed to the internal coil [123, 238]. However, we used Eqn. 4.30 as it is valid over a wide range of particle-gas properties and pressures ( $0.1 \leq d_p \leq$

Table (4.6) Characteristics of the pilot FT reactor at Polytechnique Montreal and operating conditions

| <b>Spec</b>                           | <b>Value</b>           |
|---------------------------------------|------------------------|
| Reactor dimensions (mm)               | $\phi 200 \times 1600$ |
| Coil diameter, $D_c$                  | 0.019                  |
| Coil length (m)                       | 10                     |
| $\rho_p$                              | 1290                   |
| $\varepsilon$                         | 0.6                    |
| GHSV                                  | 3150                   |
| $d_p$                                 | $2 \times 10^{-4}$     |
| $P_t$                                 | 1800                   |
| $T_f$                                 | 573                    |
| Feed flow rate (mol h <sup>-1</sup> ) | 8700                   |
| Syngas ratio                          | 1.8                    |
| N <sub>2</sub> mol%                   | 0.45                   |
| $u_0$                                 | 0.2                    |
| $u_{mf}$                              | 0.015                  |

6 mm,  $0.1 \leq P \leq 10$  MPa,  $293 \leq T \leq 1713$  K) [112, 128].

$$Nu_{\max} = \frac{h_b d_p}{k_g} = 0.4 Ar^{0.16} \left( \frac{\rho_p}{\rho_g} \right)^{0.14} \left( \frac{C_{ps}}{C_{pg}} \right)^{0.30} + 0.0013 Ar^{0.63} Pr_g \quad (4.30)$$

Assuming the fully developed turbulent flow of the coolant inside the coil,  $h_c$  is determined by ‘Colburn equation’ as follows [239]:

$$Nu_c = \frac{h_c D_c}{k_c} = 0.023 Re_c^{0.8} Pr_c^{0.4} \quad (4.31)$$

Since the thermal resistance of the coil tube is negligible and the inner and outer surfaces of the tube are almost identical, we used the simplified form of ‘U’:

$$U = \left( \frac{1}{h_b} + \frac{1}{h_c} + R_f \right)^{-1} \quad (4.32)$$

Where  $R_f$ , fouling resistance of the cooling side is  $0.0002 \text{ m}^2 \text{ K W}^{-1}$ . The heat exchange between the cooling coil and the reactor bed and the heat dissipation through the coil were obtained as follows:

$$Q = UA\Delta T_{lm} = \dot{m}_c C_{pc} (T_{c,o} - T_{c,i}) \quad (4.33)$$

$$\Delta T_{lm} = [(T_b - T_{c,i}) - (T_b - T_{c,o})] / \ln [(T_b - T_{c,i}) / (T_b - T_{c,o})] \quad (4.34)$$

An air-cooled heat exchanger removes the absorbed heat from the coolant because it is able to widely cool down the fluids. To determine the inlet temperature of coolant to the coil of reactor, we consider the maximum dry bulb of the air 31 °C as the highest temperature of the year in Canada and the approach temperature of coolant is 14 °C [205, 240, 241] both result in the minimum inlet temperature of the coolant to the coil of reactor as 45 °C.

#### 4.3.4 Steady-state simulation

The pilot FT reactor is a fluidized bed with a superficial gas velocity of  $0.2 \text{ m s}^{-1}$  ( $P = 20 \text{ bar}$ ,  $T = 300 \text{ °C}$ ) [7]. Simulators such as Aspen plus and HYSYS estimate these reactors using CSTRs in series [242, 243] or by combining CSTR and plug flow reactors to represent the gas flow through the emulsion and through the bubbles phases respectively [244, 245]. Aspen plus V12 is applied to simulate the process in the steady state mode. This simulator has a fluidized bed module which is designed for circulating fluidized bed vessels. However, it not only needs precise information of solid particles and solid flow rates but also does not function in dynamic mode. Therefore, we approximated the system behaviour in Aspen plus by a CSTR considering the RTD analysis and with the following assumptions:

- Reactions in bubble phase are negligible.
- The reactor is well mixed, thus axial heat and mass gradients are negligible.
- The radial temperature gradient between the coil and the bed is negligible as the cooling coils are within the bed.
- The bed porosity does not change with the particle size of catalyst.

The mass balance of MRU determined the feed specification by considering the maximum verified syngas ratio, 1.8. As the main components of the feed from syngas generation are  $\text{H}_2$ ,  $\text{CO}$  and  $\text{N}_2$ , we normalized the feed composition based on them (Table. 4.6). After running the steady state simulation and as the last step, we determine the parameters of heat exchange between the bed and the internal cooling coil at the steady state conditions. Having the reactor duty,  $Q$ , from the steady-state simulation of the power law kinetics, the inlet temperature of coolant supply as well as the dimensions of the reactor and solving Eqns. 4.30 to 4.34 simultaneously by the ‘data solver’ in MS.Excel, we obtain the  $U$ , coolant

flow rate  $\dot{m}_c$ , and the temperature of coolant return from the coil  $T_{c,o}$  which is represented as an approach temperature in the dynamics sheet of the reactor in the Aspen Plus (Table 4.7). Aspen property package gives all the needed physical parameters of the process gas and cooling water. For the gas side, we estimated the heat exchange based on the mean (average) properties of the syngas feed and product. In the temperature control of the reactor, the heat transfer between the catalytic bed and the coolant is a crucial phenomena. To compute the heat exchange, we also consider two constrains in the solver; the lower limit of coolant inlet temperature is 45 °C as it is the design factor of the air-cooled exchanger and ( $Re \geq 1 \times 10^4$ ) to meet the turbulent regime inside the cooling coil which gives the maximum  $\Delta T$  on the cooling side. The later constraint, not only satisfies a proper heat transfer within the coolant but also avoids scale formation due to a low velocity inside the cooling coil.

Table (4.7) Heat exchange parameters from steady-state simulation and hydrodynamics of the process for the powerlaw kinetics

| Input         |                                               | Result      |                                        |
|---------------|-----------------------------------------------|-------------|----------------------------------------|
| Spec          | Value                                         | Spec        | Value                                  |
| $Q$           | 75 kW                                         | $\dot{m}_c$ | 1120 kg h <sup>-1</sup>                |
| $A$           | 0.75 m <sup>2</sup>                           | $Re_c$      | $1.12 \times 10^5$                     |
| $\varepsilon$ | 0.6                                           | $Ar$        | 1340                                   |
| $C_{ps}$      | 1.06 kJ kg <sup>-1</sup> K <sup>-1</sup> [99] | $Pr_g$      | 0.6                                    |
| $C_{pc}$      | 4.4 kJ kg <sup>-1</sup> K <sup>-1</sup>       | $Pr_c$      | 1.1                                    |
| $C_{pg}$      | 1.5 kJ kg <sup>-1</sup> K <sup>-1</sup>       | $h_{b,max}$ | 798 W m <sup>-2</sup> K <sup>-1</sup>  |
| $\rho_g$      | 8.6 kg m <sup>-3</sup>                        | $h_c$       | 9550 W m <sup>-2</sup> K <sup>-1</sup> |
| $\mu_g$       | $2.5 \times 10^{-4}$ s Pa                     | $U$         | 610 W m <sup>-2</sup> K <sup>-1</sup>  |
| $k_g$         | 0.068 W m <sup>-1</sup> K <sup>-1</sup>       | $T_{c,i}$   | 95 °C                                  |
|               |                                               | $T_{app}$   | 150 °C                                 |

#### 4.3.5 Dynamic simulation

To perform the dynamic simulation, we add the required information of heat exchange (results in table 4.7) in the dynamic sheet of FT reactor, select the dynamic mode and re-run the simulation in Aspen Plus. Thus, the simulator computes  $UA$  which is very close to what is obtained from Excel solver. Aspen transfers the result of the steady-state to the dynamic module by exporting the simulation to ‘Aspen plus dynamic’. In this step, we selected the pressure-driven export which is more realistic in practice compared to flow-driven [227]. We assume that the radial and axial temperature gradients through the catalytic bed are

negligible because the internal coils in the reactor are well in contact with the whole catalytic particles and back-mixing is the governing regime.

#### 4.4 Control design for FT reactor

To design a temperature controller, we obtain the open-loop response of the system and determine its transfer function. Then the controller parameters are characterized based on it.

##### 4.4.1 Open-loop simulation

To eliminate the off-set of the process system, a proportional-integral (PI) control is an appropriate type [156]. Hence, we apply a PI controller module in ‘ASPEN Plus Dynamics’ and connect the reactor temperature and the coolant flow as the controlled variable and controller output respectively to it (Fig. 4.4).

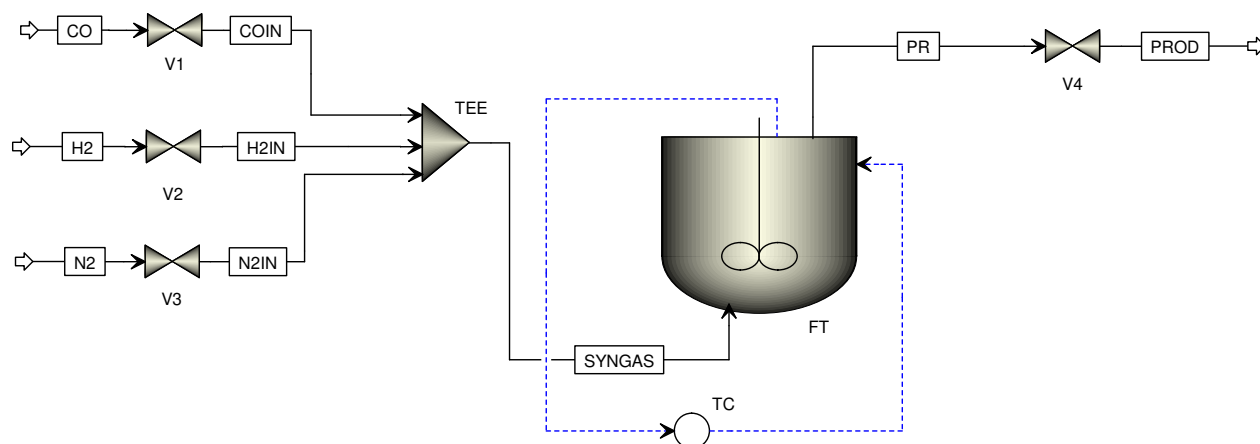
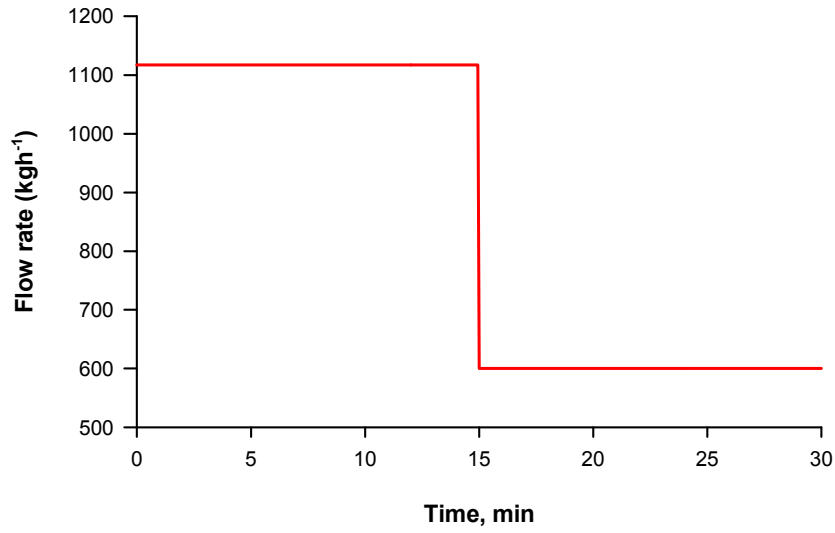


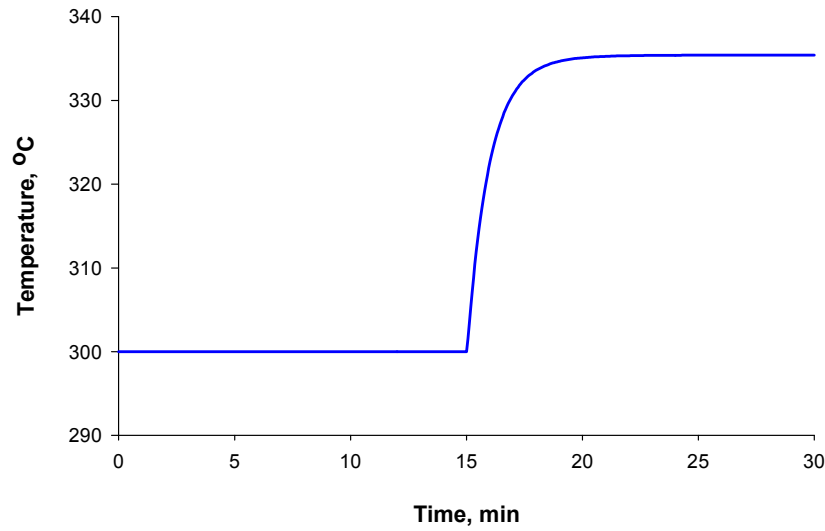
Figure (4.4) Process flow diagram of Fischer-Tropsch process with temperature controller in Aspen Plus Dynamics V12. FT is the Fischer-Tropsch reactor, PR is the product stream, V1-V4 are the manual valves to adjust steam flow rates that the dynamic simulator adapts the steady state flow rates on 50% valve opening automatically, and TC is the temperature controller.

Aspen dynamics has some auto-tuning methods in open and closed loops. Tuning methods such as Ziegler-Nichols and Cohen-Coon make undesired results in terms of disturbance rejection, optimally and robustness [246]. Further, since we avoid obtaining oscillatory response, these approaches along with Tyreus-Luyben are inapplicable. Other predefined techniques such as integral of the absolute value of the error (IAE), integral of the squared error (ISE),

and integral of the time-weighted absolute error (ITAE) provide aggressive settings [156] which are inappropriate. Instead, we use the internal model control (IMC) as a reliable method since its design is simple and intuitive [246], and the resulting controller provides convenient and satisfactory performance [247]. The controller in Aspen dynamics takes manual and automatic actions. To study the open-loop response of the system, we put the controller action on the manual and track the dynamic response of the temperature by changing the coolant flow rate. We decrease the coolant flow rate as the input variable by around 50% ( $1120 \text{ kg h}^{-1}$  to  $600 \text{ kg h}^{-1}$ ) and record the variation of the reactor temperature with the time (Fig. 5.11). As expected, reducing the coolant flow increases the internal temperature of the reactor because the reaction is exothermic.



(a)



(b)

Figure (4.5) Open loop response of the reactor temperature against manipulating the coolant flow rate: (a) step change in flow from 1120 to 600 kg h<sup>-1</sup>. (b) Temperature variation from 300 to 336 °C.

The open-loop response (Fig. 4.5b), determines the transfer function of the FT process by the empirical method [156] as follows (eqs. (4.35) to (4.39)).

$$K = \frac{\Delta T}{\Delta \dot{m}_c} = \frac{T_0 - T_\infty}{\dot{m}_{c,0} - \dot{m}_{c,\infty}} \quad (4.35)$$

$$\tilde{t}_1 = t : T_1 = T_0 + 0.28\Delta T \quad (4.36)$$

$$\tilde{t}_2 = t : T_2 = T_0 + 0.63\Delta T \quad (4.37)$$

Hence, the specifications of the FT process are:

$$\tau = \frac{3}{2}(\tilde{t}_1 - \tilde{t}_2) \quad (4.38)$$

$$\varphi = \frac{1}{2}(3\tilde{t}_1 - \tilde{t}_2) \quad (4.39)$$

And the process is approximated as a first-order plus time-delay system:

$$G_p(s) = \frac{-0.07e^{0.02s}}{s + 1} \quad (4.40)$$

where  $-0.07$  is the gain in  $^{\circ}\text{C min L}^{-1}$  and 1 and 0.02 are time constant and time delay in ‘minutes’ respectively. The small time constant of the system,  $t = 1$  min, represents the rapid variation of the reactor temperature which verifies the acceptable range of overall heat transfer coefficient.

#### 4.4.2 Controller design

We apply the internal model control method [156] to tune the controller parameters from the transfer function of the process (Eqn. 4.41, 4.42)

$$\tau_I = \tau \quad (4.41)$$

$$K_c = \frac{\tau}{K(\tau + \varphi)} \quad (4.42)$$

Therefore, the equation of PI controller is:

$$T(t) = T_0 + K_c \left( e(t) + \frac{1}{\tau_I} \int_0^t e(t^*) dt^* \right) \quad (4.43)$$

where  $K_c = -14.3$  and  $\tau_I = 1$  min.

## 4.5 Results and discussion

### 4.5.1 Hydrodynamics and RTD

To analyze the Ar pulse injection and investigate the flow regime inside the FT, we first normalize the Ar concentration curve with time for both entrance and exit experiments. We also apply the exponential smoothing function from excel data analysis module with a damping factor of 0.95 for the exit signal to remove its noises (Fig. 4.6).

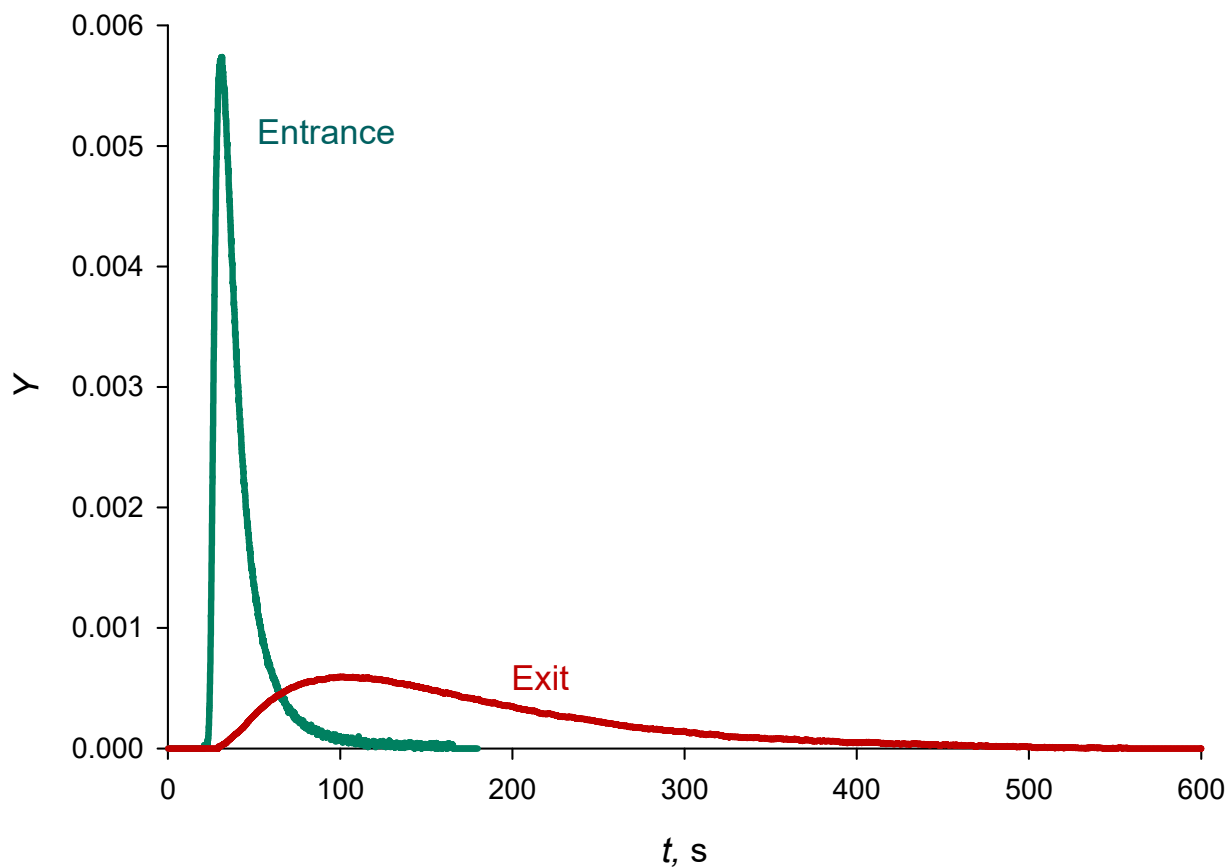


Figure (4.6) RTD of a pulse injection for FT entrance, cyan line, and FT exit, red line. The curve represents  $Y = \frac{C_i}{\sum C_i}$  vs time. The actual gas flow rate is  $0.35 \text{ L s}^{-1}$  at 10 bara and  $150^\circ\text{C}$  corresponding  $u_g = 6u_{mf}$  with  $u_{mf} = 2 \text{ mm s}^{-1}$ . The graph is moved 2 minutes back to match injection at zero time.

Then we subtract  $t_m$  of entrance and exit tests obtained from Eqn. 4.19 to find the mean residence time inside the fluidized reactor. To determine the flow regime, we adopt the dispersion model (eqn. 4.22) by varying the Peclet number and minimizing the least square error of model and experimental data set which eventually gives  $n_{\text{CSTR}}$  (Table 4.8).

Table (4.8) Resulting parameters of RTD test and hydrodynamic regime

| parameter                                             | value               |
|-------------------------------------------------------|---------------------|
| $\bar{t}_{m,in}$                                      | 21 s                |
| $\bar{t}_{m,out}$                                     | 151 s               |
| $\bar{t}_m$                                           | 130 s               |
| $\sigma_m^2 \dagger$                                  | 8530 s <sup>2</sup> |
| $N_{Pe}$                                              | 4                   |
| $n_{CSTR}$                                            | 3                   |
| $\dagger \sigma_m^2 = \sigma_{in}^2 - \sigma_{out}^2$ |                     |

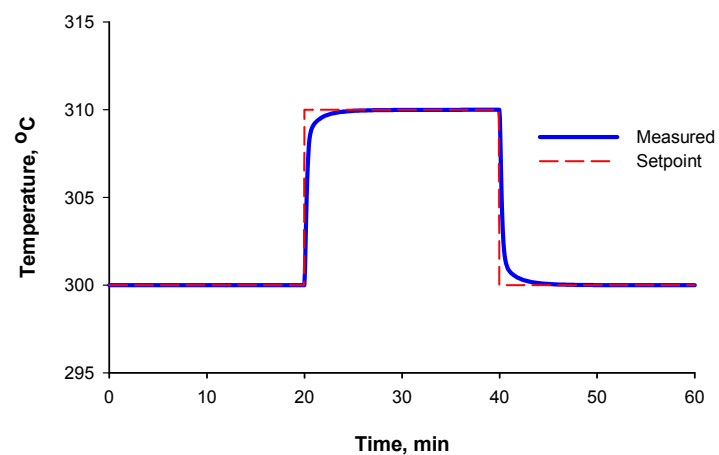
A hydrodynamic model assuming  $3n_{CSTR}$  and accounting for the contribution of FT entrance and exit, fits the experimental breakthrough curve best. As  $N_{Pe} < 10$ , the back-mixing phenomena is notable through the bubbling fluidized regime [101]. In the experiment, the superficial gas velocity is 6 times greater than the minimum fluidization velocity ( $u = 6u_{mf}$ ) corresponding to  $3n_{CSTR}$ . In the theoretical operating conditions ( $u = 0.2$  m and  $u_{mf} = 0.015$  m),  $u = 12u_{mf}$  means the back-mixing is even higher than experimental conditions and the flow regime is closer to a CSTR model. Hence, we applied a CSTR reactor in the simulation.

#### 4.5.2 Temperature controller

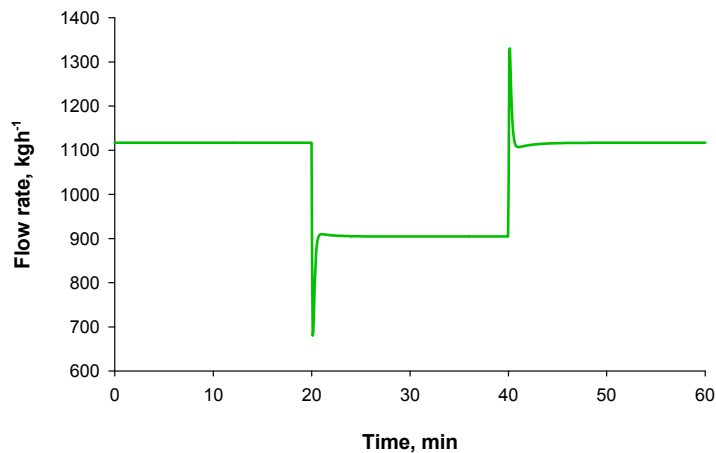
To gauge the performance of the temperature controller, we consider the closed loop response of the system for different scenarios. Hence, section 4.5.3 represents the controller action for step set point. Section 4.5.4, displays the closed loop response against the disturbances in syngas ratio, syngas flow rate and feed temperature and eventually, section 4.5.5 examines the robustness of the controller in terms of uncertainty in overall heat transfer coefficient ‘ $UA$ ’ and model mismatch when the alternative kinetic model is applied.

#### 4.5.3 Closed-loop simulation for the step change in set point

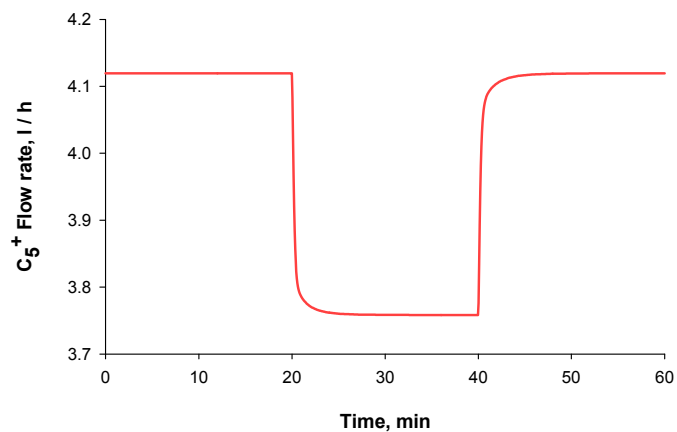
Variation of operating temperature is applicable in studying the optimization and sensitivity analysis. Thus the control system must handle it in a safe mode. To test the performance of the controller, we obtained the closed loop response for the temperature  $300^\circ\text{C} \pm 10$  (Fig. 4.7 and 4.8 ) followed by switching from manual to automatic on controller screen.



(a)

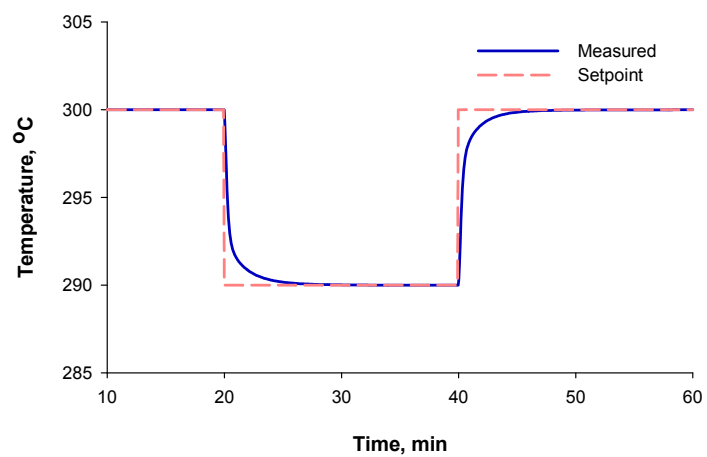


(b)

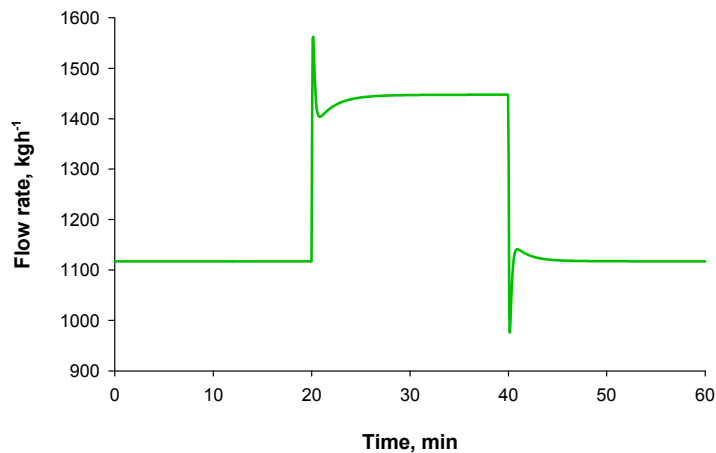


(c)

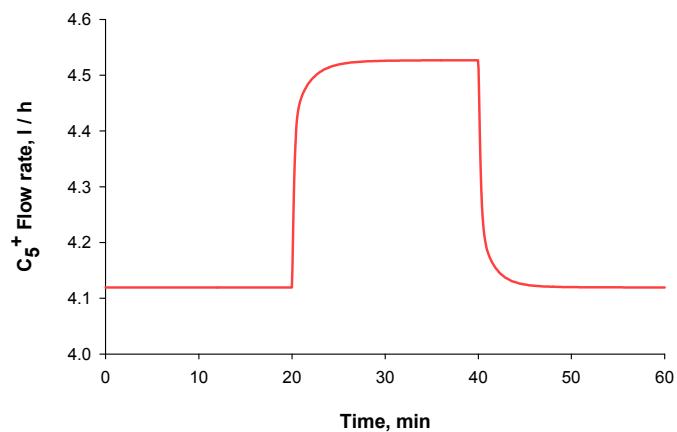
Figure (4.7) Closed loop response of the process versus + 10 °C step change in set point,  $T_s = 300^\circ\text{C}$  in Aspen Plus Dynamics V12: (a) Set point and measuring temperature of the process, (b) coolant flow rate, and (C), Vol. flow rate of  $\text{C}_5^+$  in the product.



(a)



(b)



(c)

Figure (4.8) Closed loop response of the process versus - 10 °C step change in set point,  $T_s = 300$  °C in Aspen Plus Dynamics V12: a) Set point and measuring temperature of the process, (b) coolant flow rate, and (C), Vol. flow rate of C<sub>5</sub><sup>+</sup> in the product

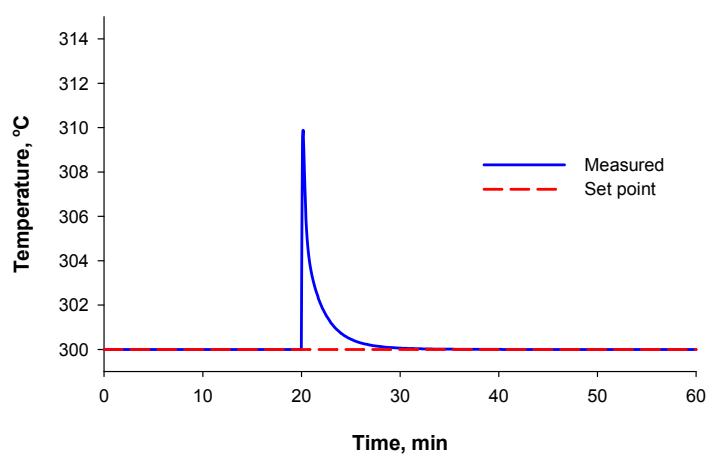
To increase the bed temperature from 300 °C to 310 °C, the controller throttles the cooling valve and accordingly reduces the coolant flow rate. This temperature increase, also reduces the probability of making the higher chain hydrocarbon which results in lower selectivity and lower flow rate of  $C_5^+$ . To decrease the bed temperature from 300 °C to 290 °C, the controller opens the cooling control valve to increase the coolant flow rate. Decreasing the temperature will increase the  $C_5^+$  selectivity and its flow rate. The results reveal that the controller is capable to properly adjust the temperature to its set point (300 °C to 310 °C and 300 °C to 290 °C) in around 5 minutes and as the result, the  $C_5^+$  production rate is smoothly controlled.

#### 4.5.4 Closed loop simulation for disturbance rejection

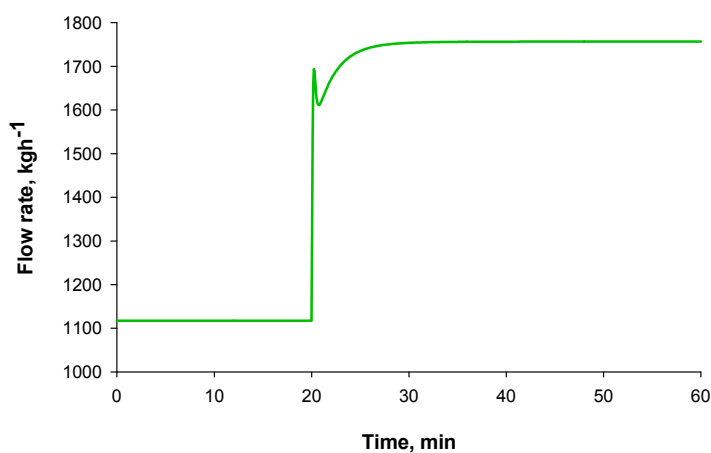
To study the performance of the controller against the disturbances, we consider the changes in the syngas ratio, syngas flow rate and inlet temperature of the syngas to FT reactor.

##### Disturbance in syngas ratio

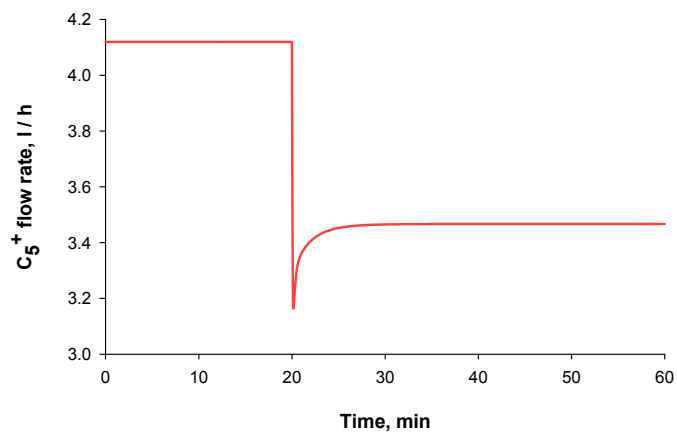
The syngas ratio is changed due to variation of the natural gas to air ratio [248] or coke formation on the CPOX catalyst [194] at the upstream of FT reactor. In the dynamic simulator, we consider separate line and feeding valve for CO,  $H_2$  and  $N_2$  as the main components of the syngas, to be able to change the syngas ratio by opening or closing each of the stream valves. Hence, upon running the dynamic simulation in the closed-loop configuration, once the  $H_2$  valve ( $V_2$ ) opens by % 5 (from %50 to %55) and  $N_2$  valve ( $V_3$ ) closes by %5 (from %50 to %45) to change the ratio from 1.8 to 2 with the same feed flow rate and another time  $V_2$  closes by %8 (%50 to %42) and  $V_3$  opens by %6 (%50 to %56) to increase the ratio from 1.8 to 2 to record the response of the system. (Fig. 4.9, 4.10).



(a)

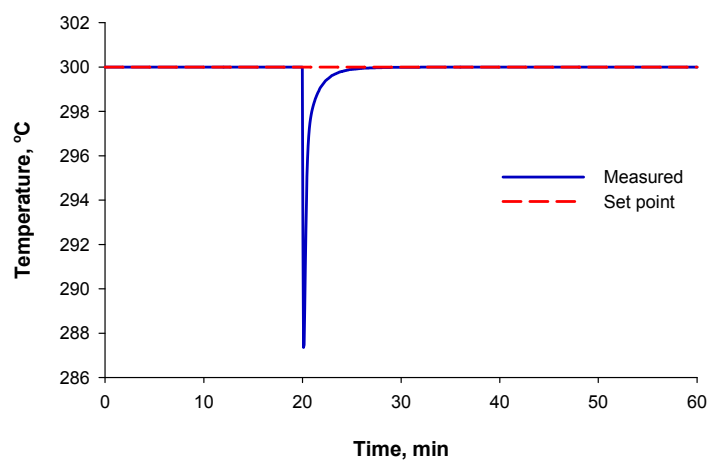


(b)

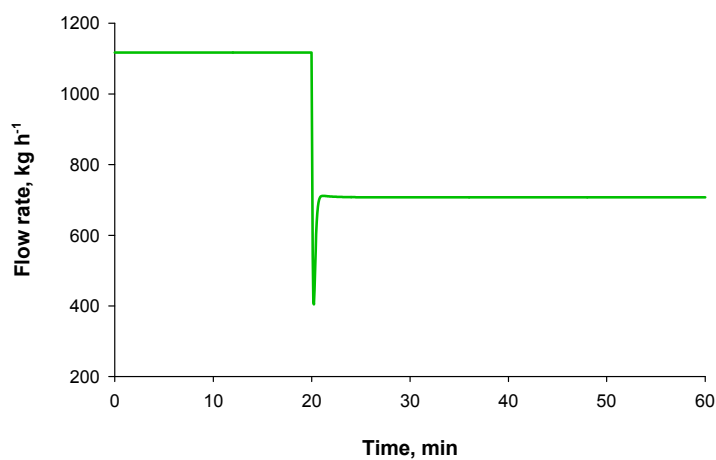


(c)

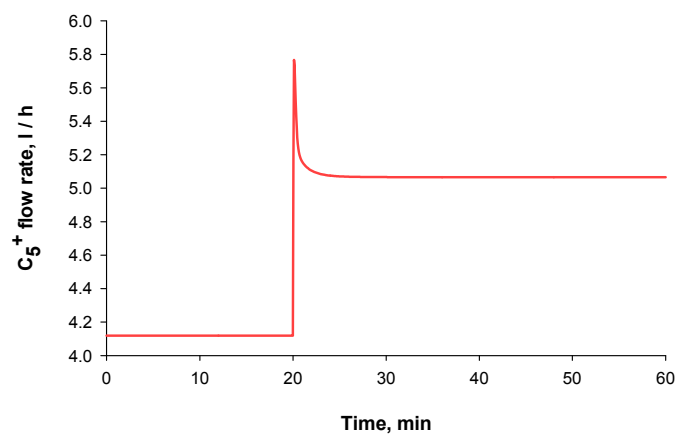
Figure (4.9) Closed loop response of the process versus increasing the syngas ratio from 1.8 to 2 in Aspen Plus Dynamics V12,  $T_s = 300^\circ\text{C}$  and  $F_{\text{syn},s} = 8.7 \text{ kmol h}^{-1}$ : (a) measured process temperature and set point value, (b) coolant flow rate, and (C) Vol. flow rate of C<sub>5</sub><sup>+</sup> in product.



(a)



(b)



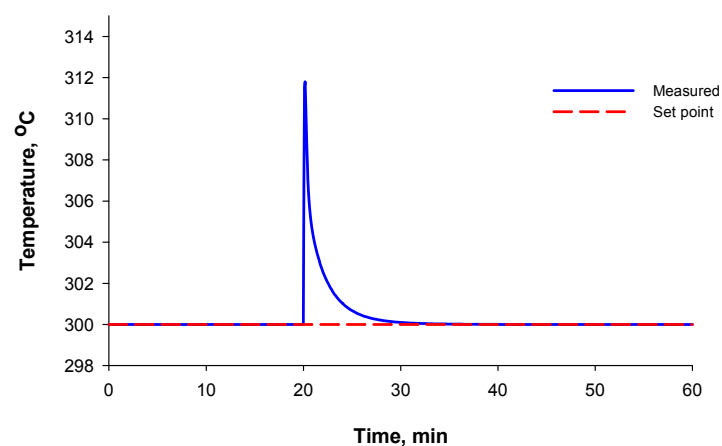
(c)

Figure (4.10) Closed loop response of the process versus decreasing the syngas ratio from 1.8 to 1.5 in Aspen Plus Dynamics V12,  $T_s = 300^\circ\text{C}$  and  $F_{\text{syn},s} = 8.7 \text{ kmol h}^{-1}$ : (a) measured process temperature and set point value, (b) coolant flow rate, and (C) Vol. flow rate of  $\text{C}_5^+$  in product

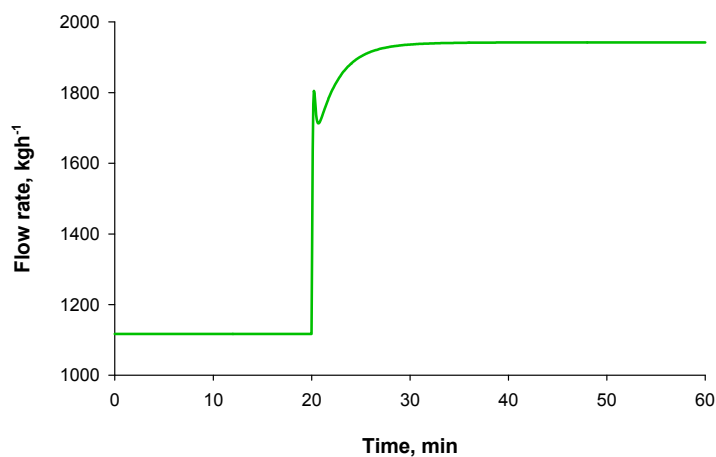
As expected, increasing the ratio boosts the syngas conversion and heat of reaction which consequently rises the temperature. Thus, the controller opens the cooling valve to return the temperature to its set value. Inversely, a decrease in syngas ratio reduces the conversion which decreases the heat generation and the temperature. Ultimately, the controller decreases the coolant flow to adjust the temperature on its set point when the syngas ratio decreases. In both cases, although the PI controller recovers the process temperature, the production rate of fuel is the function of syngas ratio. Hence, it follows the governing chemistry of the reaction and does not return to its original value.

### **Disturbance in the syngas flow rate**

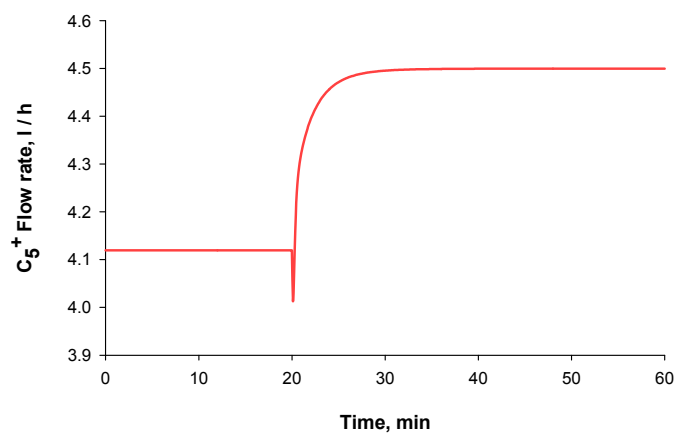
To investigate the performance of the controller against the disturbance in the feed flow rate into the FT reactor, we decrease and increase the syngas flow rate by %10 by closing and opening the inlet valves respectively.(Fig. 4.11, 4.12).



(a)

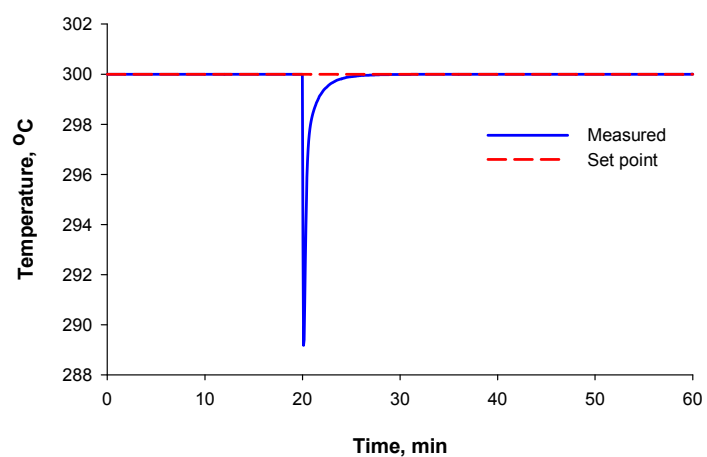


(b)

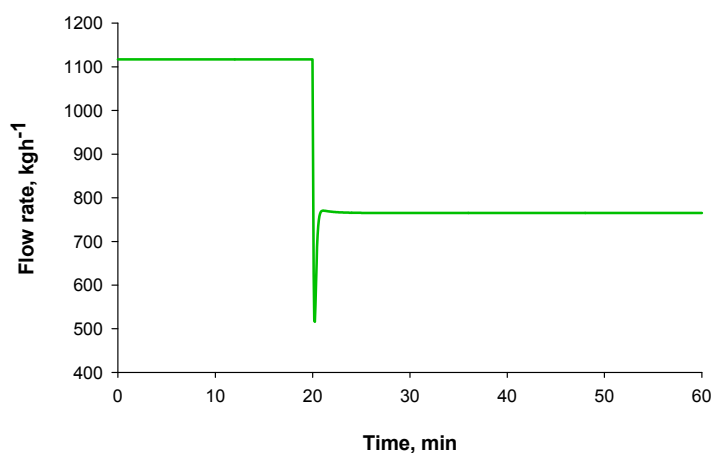


(c)

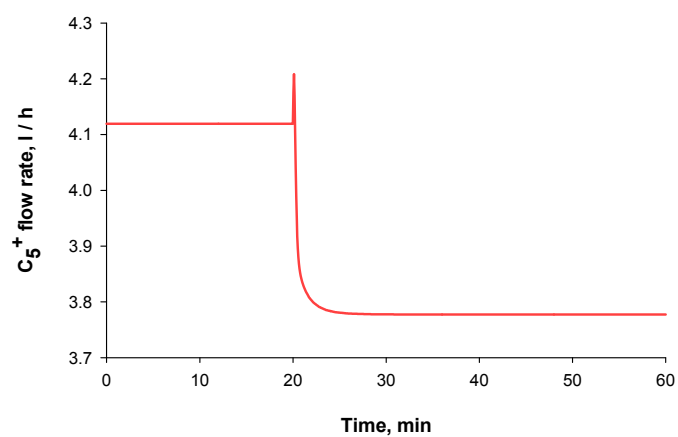
Figure (4.11) Closed loop response of the process versus %10 increase in syngas flow rate in Aspen Plus Dynamics V12,  $T_s = 300^\circ\text{C}$  and the original  $F_{\text{syn},s} = 8.7 \text{ kmol h}^{-1}$ : (a) measured process temperature and set point value, (b) coolant flow rate, and (C)  $\text{CO}_2$  and  $\text{C}_5^+$  concentrations in product



(a)



(b)



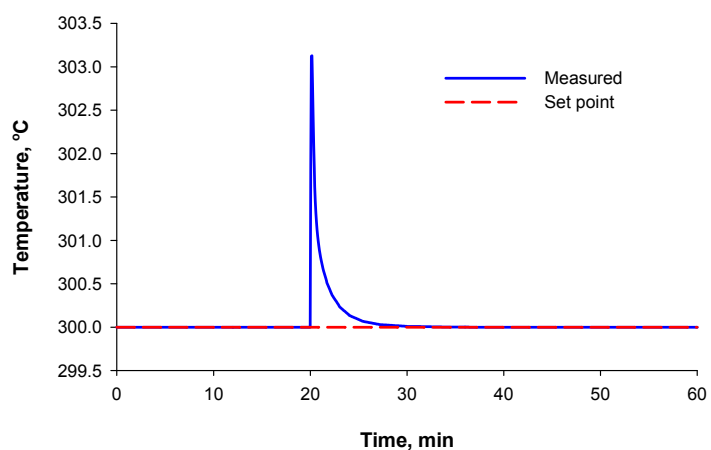
(c)

Figure (4.12) Closed loop response of the process versus %10 decrease in syngas flow rate in Aspen Plus Dynamics V12,  $T_s = 300^\circ\text{C}$  and the original  $F_{\text{syn},s} = 8.7\text{ kmol h}^{-1}$ : (a) measured process temperature and set point value, (b) coolant flow rate, and (C) Vol. flow rate of C<sub>5</sub><sup>+</sup> in product

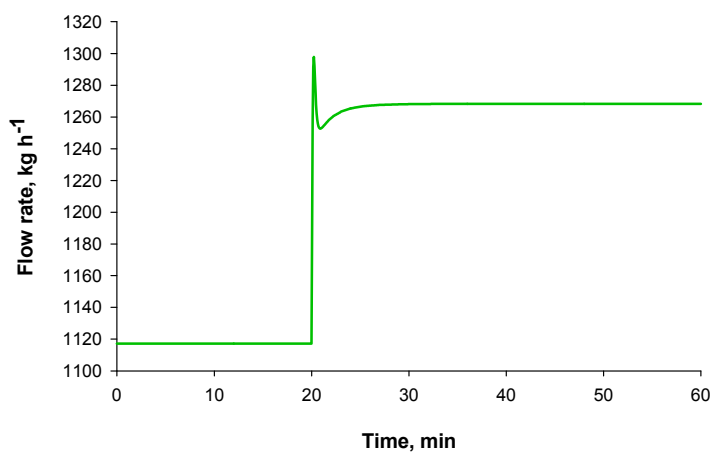
Figure 4.11 represents that excess syngas flow rate moves the total reaction towards the products which generates more heat followed by temperature increase. Hence, the control valve of the coolant is open more to reduce the temperature. The fuel flow rate increases by %10 (from 4.1 to 4.5 L h<sup>-1</sup>) which is in consistent with the feed increase. In case of decreasing the syngas flow rate, the control valve acts inversely and throtles the coolant to recover the set temperature. In addition, the fuel flow is declined around %10 as the result of feed decrease.

### **Disturbance of the feed temperature**

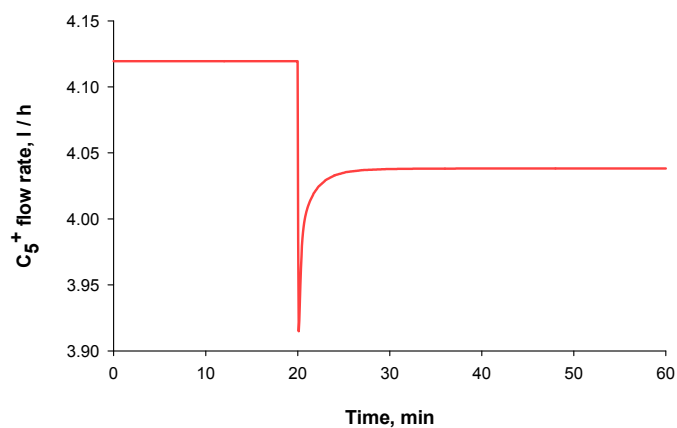
In the micro-GtL plant, the syngas is a product of the CPOX reactor. Thus, the feed temperature relies on the efficiency of the CPOX as well as the passive intercooler between CPOX and FT reactors. This variation has a remarkable impact on the safety and product distribution from FT reactor as it may change the feed temperature. First we investigate the performance of the PI controller when the feed temperature reaches 350 °C. This temperature is the upper limit for FT operation since overheating may destroy the catalyast at exposure spot to the feed which reduces its operational lifetime [134,228] (Fig. 4.13). On the opposite side, over-cooling the syngas feed is not in favor of the process because forming the liquid wax in lower than 280 °C [50], disturbs the two-phase fluidization by agglomerating the catalyst particles. Hence, we assume that the minimum allowable feed temperature is 250 °C and monitor the controller performance facing this disturbance (Fig. 4.14).



(a)

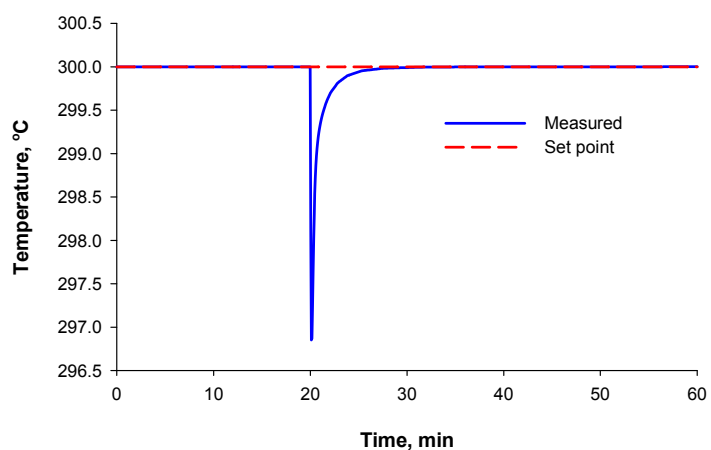


(b)

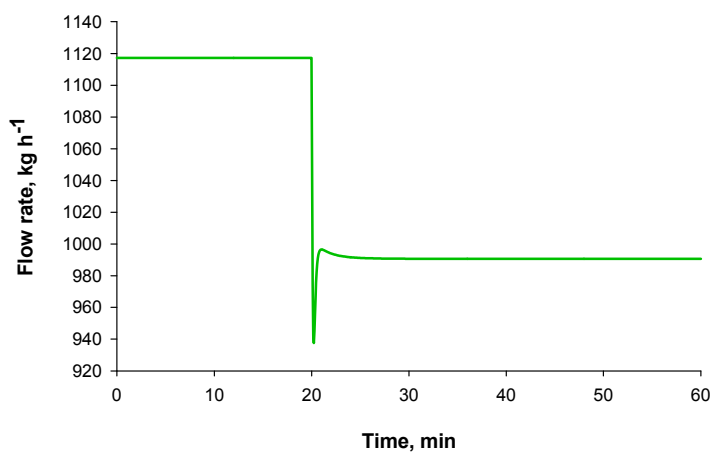


(c)

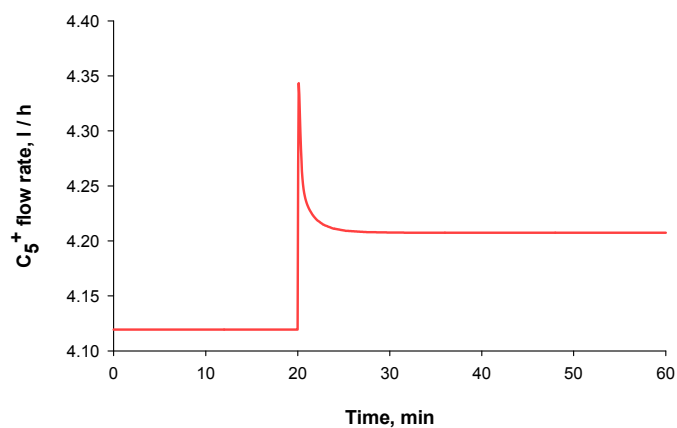
Figure (4.13) Closed loop response of the process versus 50 °C increase in the feed temperature in Aspen Plus Dynamics V12,  $T_s = 300$  °C: (a) process temperature and set point, (b) coolant flow rate.



(a)



(b)



(c)

Figure (4.14) Closed loop response of the process versus 50 °C decreases in the feed temperature in Aspen Plus Dynamics V12,  $T_s = 300$  °C: (a) process temperature and set point, (b) coolant flow rate.

The results indicate that the control system is able to adjust the process temperature against the feed temperature increase or decrease by 50 °C.

#### 4.5.5 Robustness of the temperature controller

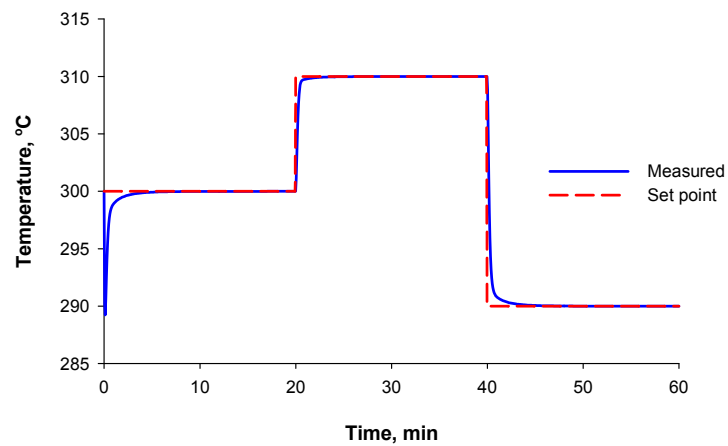
FT process has uncertainties in the overall heat transfer coefficient and kinetic model. Hence, we inspected the robustness of the controller against changing of these cases.

##### Overall heat transfer coefficient

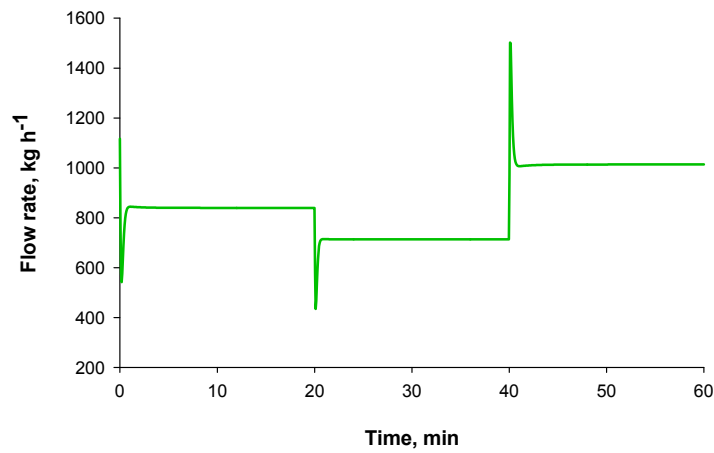
Since the FT reaction occurs at temperature lower than 500 °C, the radiation is negligible in computing of the bed convective heat transfer [238]. However, empirical  $h_b$  (eqn. 4.30) could still deviate from its real experimental value due to neglecting the heat transfer of lean gas phase [238] and uncertainties in determining the dense particle phase [118, 123]. Here, we examined the controller performance against % 20 increase in  $U$  (Fig.4.15) for various set points. In this case, the controller also restores quickly the temperature to its set point and the coolant temperature deviates around 15 °C as the result of changes in the  $U$ <sup>1</sup>. As the UA is increased, the coolant outlet temperature is initially increased from 150 °C to 167 °C and its flow rate decreases accordingly since it removes the same heat from the bed.

---

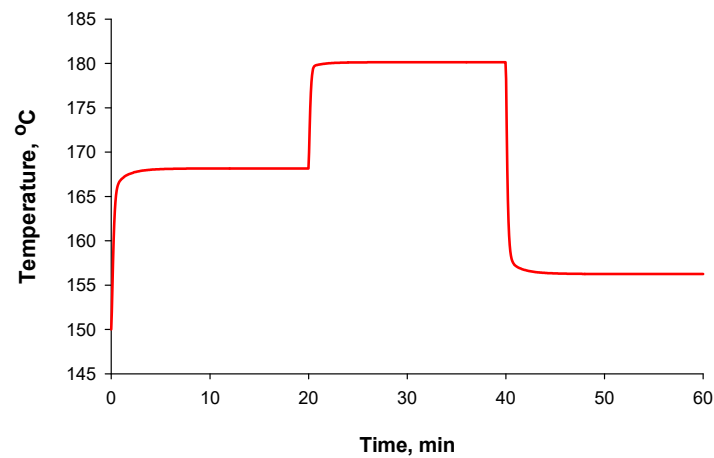
<sup>1</sup>Supplementary data is available in annex C



(a)



(b)

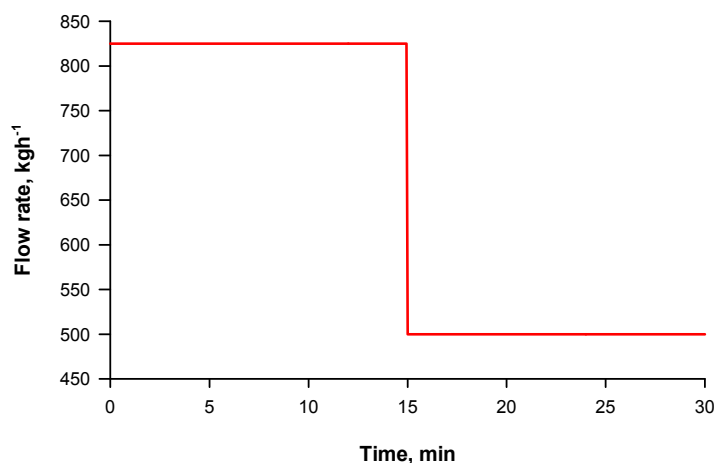


(c)

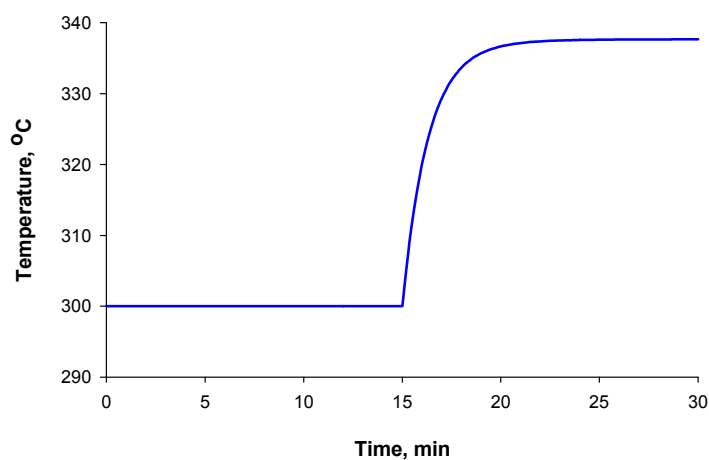
Figure (4.15) Closed loop response of the process against step change in set temperature for uncertainty of overall heat transfer coefficient, + % 20 increase in  $UA$ : (a) process temperature and set point value, (b) coolant flow rate, and (c) coolant temperature.

## Model mismatch

Due to the complexity of Fischer-Tropsch process, no certain kinetic model has been provided so far. Thus, various kinetic models result in different concentration of products and conversion followed by different enthalpies of reaction. The transfer function that resulted from the open-loop response of the alternative model, *LHHW*, represents its deviation from the main model, powerlaw (Fig. 4.16, Eqn. 4.44).



(a)

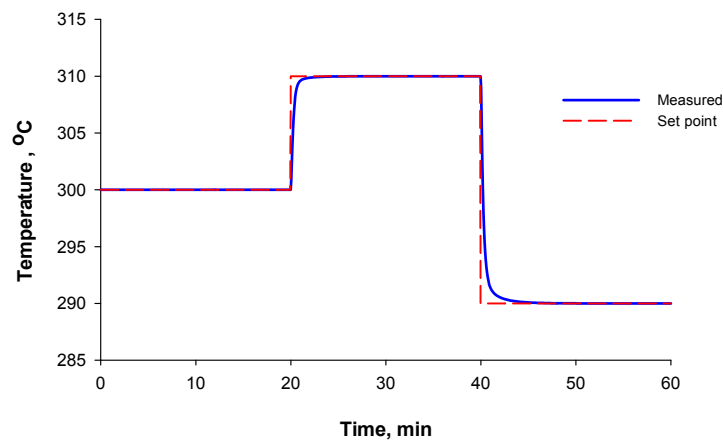


(b)

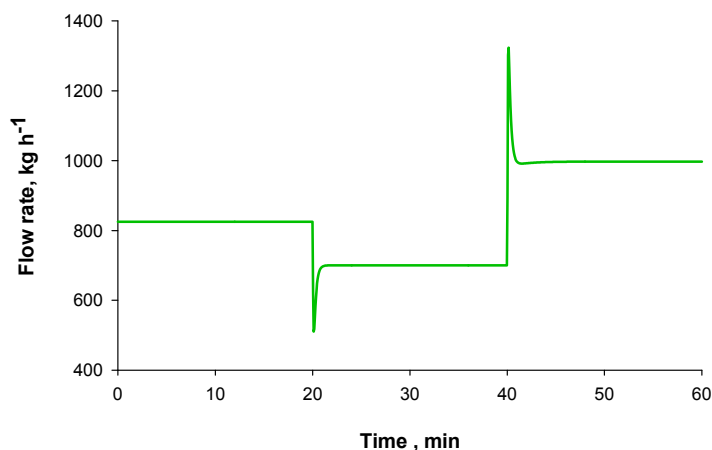
Figure (4.16) Open loop response of the reactor temperature against manipulating the coolant flow rate for the alternative kinetic model: (a) Step change in flow from 850 to 500  $\text{kg h}^{-1}$ . (b) Temperature variation from 300 to 336  $^{\circ}\text{C}$ .

$$G_l(s) = \frac{0.12e^{-0.01s}}{1.3s + 1} \quad (4.44)$$

We applied our alternative model to analyze the performance of the controller for a completely different model (Fig. 4.17).



(a)



(b)

Figure (4.17) Closed loop response of the control system for the model mismatch in Aspen Plus Dynamics V12; the kinetics follows the alternative (LHHW) model,  $T_s = 300^\circ\text{C}$  (a) process temperature and  $\pm 10^\circ\text{C}$  step change in set point (b) coolant flow rate.

The PI controller is able to adjust the temperature to the set point values,  $310^\circ\text{C}$  from 20 to 40 min and  $290^\circ\text{C}$  from 40 to 60 min (Fig. 4.17a). If the LHHW kinetics is the governing

model, the steady-state coolant consumption is  $860 \text{ kg h}^{-1}$  which is less than  $1120 \text{ kg h}^{-1}$  as the required coolant flow for the powerlaw kinetics (Fig.4.5b). This is true because the heat duty of LHHW model is  $60 \text{ kW}$  which is 20% less than that of powerlaw model ( $75 \text{ kW}$ ). We obtained the transfer function of the system relying on LHHW model by applying the openloop response of the system and applying the same evaluating rules. In the design stage, since the cooling system works based on the pressurized hot water, we suggest to select the hot water feed pump with the head of over 35 m at its best efficient point (BEP) to ensure that the water remains in the subcooled region since the saturated water temperature at 35 m is  $150^\circ\text{C}$  which is well above the maximum temperature of returning water from the coil of FT reactor. The heat sink capacity of the air cooler must be also %25 excess than the calculated duty of the reactor. Hydrodynamics and the kinetics of reaction are two crucial parameters in dynamic simulation of the Fischer-Tropsch process. Hydrodynamics determines the heat exchange between the catalytic bed and cooling coil and kinetics represents the outlet composition and the finally the heat that must be removed from the reactor to keep the temperature constant. The designed controller is able to encounter the changes in temperature set point and properly damps the possible disturbances of the process.

Its performance also remains acceptable despite model mismatch or underestimating the overall heat transfer coefficient. We try to represent the performance of the controller in the startup operation. However, due to the bound limitations of the model parameters and unknown variations of  $U$  in transient state, it is not able to capture this phenomena. Furthermore, in the hydrodynamic modeling,  $U$  is assumed constant i.e. it does not change by the process variables since its average value involves in the simulation and its functionality to the fluid velocity and temperature is ignored which is a limitation of this methodology. Since the CSTR model simplifies the complex nature of the fluidized bed system, the concentrations may not be accurate enough which needs to be verified in practice. We also assume that the axial temperature gradient along the fluidized bed reactor is negligible and instead use the average value. However, in practice, a slight gradient is expected which needs a detailed space-time modelling.

## 4.6 Conclusion

In our Micro-GtL technology, the high temperature Fischer-Tropsch process is one of the critical sections as the reaction is strongly exothermic generating a huge amount of heat in the FT reactor. We developed a procedure to design a temperature controller for this reactor. We used a powerlaw kinetics model as the main model and involved the heat transfer correlations through the fluidized bed to estimate the heat exchange between the bad and

the cooling coil. Next, we designed a PI temperature controller in Aspen Plus Dynamic v12 and investigated the performance of this controller against the step changes in temperature set point and disturbances in feed temperature and flow rate, syngas composition ratio.

We also track the controller performance in terms of model mismatch and uncertainties in overall heat transfer coefficient. To observe the model mismatch, we proposed a novel LHHW-based model and simulated the process in the steady-state and dynamic mode of Aspen Plus and then implemented the so-called controller on this model and monitored its closed loop response to the step change in the temperature set point. The result represents that the controller is able to adjust the temperature properly. This approach provides a preliminary controller to run a safe and stable close-loop process which eventually enable us to modify the controller performance during the operation by online re-tuning techniques like ‘set point overshoot method’ [158]. Next, we increased the  $U$  by % 20 of its original calculated value and implemented the same step change in the temperature which shows that the controller is again able to properly adjust the temperature on its set point.

ASPEN considers the overall heat transfer coefficient as constant value and varies the outlet temperature of the cooling coil while in practice, the  $U$  varies over the changing of process temperature and the coolant flow rate. Since the sub-cooled water is used to control the temperature of the FTS and uncertainty of underestimating the  $U$  may increase the outlet temperature of the coolant up to 180 °C, we recommend to operate the cooling water system above 10 bar to avoid saturated vapor or two-phase cooling water inside the coil. In order to have a smooth operation regardless of coolant  $\Delta T$ , we recommend to simulate the process with pressure control configuration of saturated steam as the coolant medium and compare its results with the present work. Although the available procedure is promising to predict the dynamic behaviour of a system from steady-state point, it is not able to monitor the transient conditions during the startup because of the limitations of the process parameters. However, it is recommended to initially run the experiment at low capacity (% 10 of maximum feed flow rates) and after ensuring that the reaction and the temperature are under control, gradually increase the feed flow in a step-wise method.

## CHAPTER 5 ARTICLE 3 : EXPERIMENTAL MODELING OF HEAT EXCHANGE FOR CONTROL DESIGN OF A FLUIDIZED BED SYSTEM

Mahdi Sharifian, Nicolas Hudon, Gabin Sarpy, Ergys Pahija, Gregory S. Patience

Submitted to :

Journal of Applied Thermal Engineering, October 22, 2023

### Abstract

Fluidized bed reactors are suitable alternatives for high temperature Fischer-Tropsch (FT) process because of their efficient heat and mass transfers and low pressure drop. However as the reaction is extremely exothermic, even in these systems, insufficient heat removal makes an unstable non-uniform condition resulting in reaction runaway, catalyst deactivation and mechanical damage. Removing the heat from the system particularly at the startup of pilot and large scale units is critical and running a stable and safe process requires a proper temperature control strategy. Hence, heat exchange is one of the key characteristics of the process operation resulting in design of a convenient cooling strategy coupled with a preliminary control system. Here, we designed a safe mode experiment for a coil-equipped fluidized bed reactor with single and double cooling coil scenarios using compressed air. In each scenario, we run the experiments at 5 and 10 bara, and superficial gas velocities from  $5u_{mf}$  to  $10u_{mf}$  to investigate the effect of operating conditions on the dynamics of the cooling. The result verifies that the dynamics of the cooling is faster at higher pressure and fluidization which favours the exothermic process. The estimated cooling rate for both scenarios also reveals that the surface area of double coil is capable to remove the equivalent heat to the enthalpy of FT reaction. Finally, we identified the parameters of the experimental heat transfer model for both cooling scenarios and designed a PI and a PID controller plus filter (PIDf) separately using internal mode control approach based on the double coil model as it cools down the process faster than the single one and then tested the performance of both controllers for a step change and disturbance rejection of the bed temperature in the reactor. Based on the results, the performance of the PIDf controller is better than the PI, as it makes smoother, and faster response in the fluidized bed temperature. Thus, we proposed a cooling strategy that employs double coils coupled with its PIDf controller to startup and operate the pilot reactor.

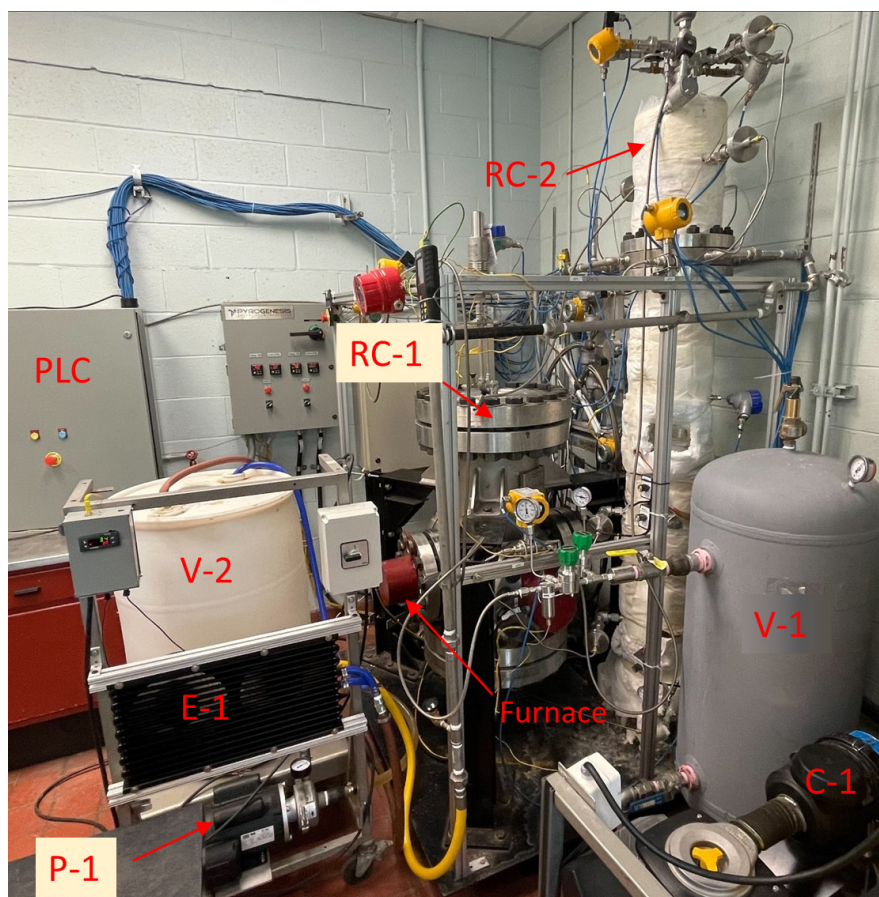
## 5.1 Introduction

Gas-to-liquid (GtL) technology is one of the dominant alternatives to monetize the shale/natural gas to the synthetic fuels [8,249]. In this process, Fischer-Tropsch synthesis (FTS) is a key component to produce synthetic fuels [71]. In the development of FTS reactors, adapting an adequate cooling method to reach the uniform temperature gradient in the catalyst bed is important [54] to guarantee a safe, stable and smooth operation. Fluidized bed reactors meet this criteria because they improve the heat and mass transfer rates by effective contacting and mixing properties compared to fixed beds [54,250–252]. However, FTS is extremely exothermic and a reliable configuration of cooling system coupled with the temperature controller is necessary to avoid runaway phenomenon [222]. Startup operation is further challenging as the cooling system must allow the reaction to light off without quenching it, but must control the exothermic behaviour to minimize the sintering due to high temperature [150]. In order to improve the heat transfer rate in fluidized bed systems, studies have examined experimentally and numerically the effect of immersed tube configurations through the bed [123,253] as well as operating conditions [112,254,255]. However, have not yet addressed to sensitivity analysis of heat transfer from the fluidized bed in the transient conditions. Furthermore, due to the lack of data in the academic literature [150], controlling the FTS temperature is controversial. Here, we developed a series of safe mode experiments in an exothermic fluidized bed reactor to design an integrated cooling and preliminary temperature control system to address this issue. This controller then will be re-tuned during the actual process [158]. This strategy moves one step forward to propose a global approach for running the exothermic systems in the early stage of operation. In section 5.2, we explained the process and experimental method. Section 5.3, is about the theory of heat transfer analysis. In section 5.4, we analyzed the data to investigate the effect of cooling coil design, operating pressure, and superficial gas velocity, on the dynamics of the heat exchange and heat transfer coefficient. And in section 5.5, we identified the system parameters from the dynamic data, and finally developed PI and PIDf temperature controllers to efficiently remove the heat from the process.

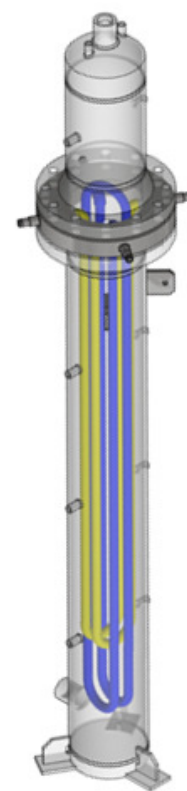
## 5.2 Method

### 5.2.1 Process

The GtL pilot plant is originally designed to convert flared gas to green fuel and consists of catalytic partial oxidation (CPOX) followed by FTS. Since the FTS is extremely exothermic, the generated heat abruptly rises the internal temperature of the reactor which may sinter and deactivate the catalyst. Thus, heat transfer rate and dynamics of the cooling mechanism is a guideline to design, startup, and control the temperature of the reactor. The system includes a reciprocating air compressor, C-1 (Atlas Copco, model LT3), its receiver tank, V-1, and four mass flow controllers (MFC) (Bronkhorst) to adjust the flow rate between 0 and  $180 \text{ L min}^{-1}$ . A furnace preheats the air up to  $300^\circ\text{C}$  through the reactor RC-1 that is filled with ceramic beads,  $D = 60 \text{ mm}$  and  $H = 1 \text{ m}$ . The furnace has 8 ceramic heaters and operates at  $11.8 \text{ kW}$  and an electrical power-control panel adjusts the element temperatures up to  $1000^\circ\text{C}$ . The pressure and the temperature of RC-1 are measured by pressure transducer, P1 and thermocouples, R1 and R2 (COMHAS, type K,  $0 - 1000^\circ\text{C}$ ), respectively. The hot air then reaches the FT reactor, RC-2 via a quarter inch fiberglass insulated tube. Thermocouple, TI0 measures the gas temperature at the entrance of this reactor. RC-2 is a pressurized vessel ( $D = 0.2 \text{ m}$ ,  $H = 1.8 \text{ m}$ ) with two internal cooling coils with nominal diameter of  $d = 3/4 \text{ in.}$ . Each coil is a 2-pass U-tube,  $6.7 \text{ m}$  and  $5.3 \text{ m}$  long (Fig. 5.1b)



(a)



(b)

Figure (5.1) The experimental pilot designed for mobile micro-refinery: (a) the setup originally located at Polytechnique Montreal. (b) 3D of fluidized bed reactor, RC-2, consisting the two internal 2-passes cooling coils. The total length of the longer coil in blue is 6.7 m and that of shorter coil in yellow is 5.3 m.

These separate coils are connected to a circulating water system and a proportional-integral (PI) controller functions in automatic or manual modes to adjust the reactor temperature (Fig. 5.2). Thermocouples, TI1, TI2, TI3 (COMHAS, PT-100, 0 – 400°C), measure the bed temperature at 0.30 m, 0.75 m, and 1.20 m above the gas distributor respectively and the maximum value is considered as the process variable in the control algorithm to adjust the opening of control valve, TV-5, and water flow rate accordingly. Furthermore, two differential pressure transducers, PDI1 and PDI2, measure the pressure drop along the bed. At the bottom of the reactor, a seamless porous tube sparger (Mott series 2300-A) is installed to distribute the gas uniformly into the reactor bed. The reactor is loaded with 36 kg alumina particles ( $d_{50} = 75 \mu\text{m}$ ) so that the vertical coils are submersed in the bed. At the top section of RC-2, two internal filters separate catalyst particles from the exit gas/product. A back-

pressure regulator at the exit stream, PV1, adjusts the pressure of the vessel (Fig. 5.2) [13]. To heat up the catalytic bed, 5 heat tapes (McMaster-Carr, 2.5 cm wide, 120 V AC) are wrapped along RC-2, which are insulated by 2.5 cm Fiberglass sheets. The cooling system consists of water pump (Johnbrooks), P-1, that delivers up to  $3.6 \text{ m}^3 \text{ h}^{-1}$  and 2.0 barg, an external air-cooled heat exchanger, E-1 (capacity 2.5 kW), to remove the heat from cooling water, and a supply tank, V-2. Thermocouples, TI5 and TI6 (McMaster-Carr K-type) measure the inlet temperature of the coolant in the supply tank and the outlet temperature at the cooling coil exit, respectively.

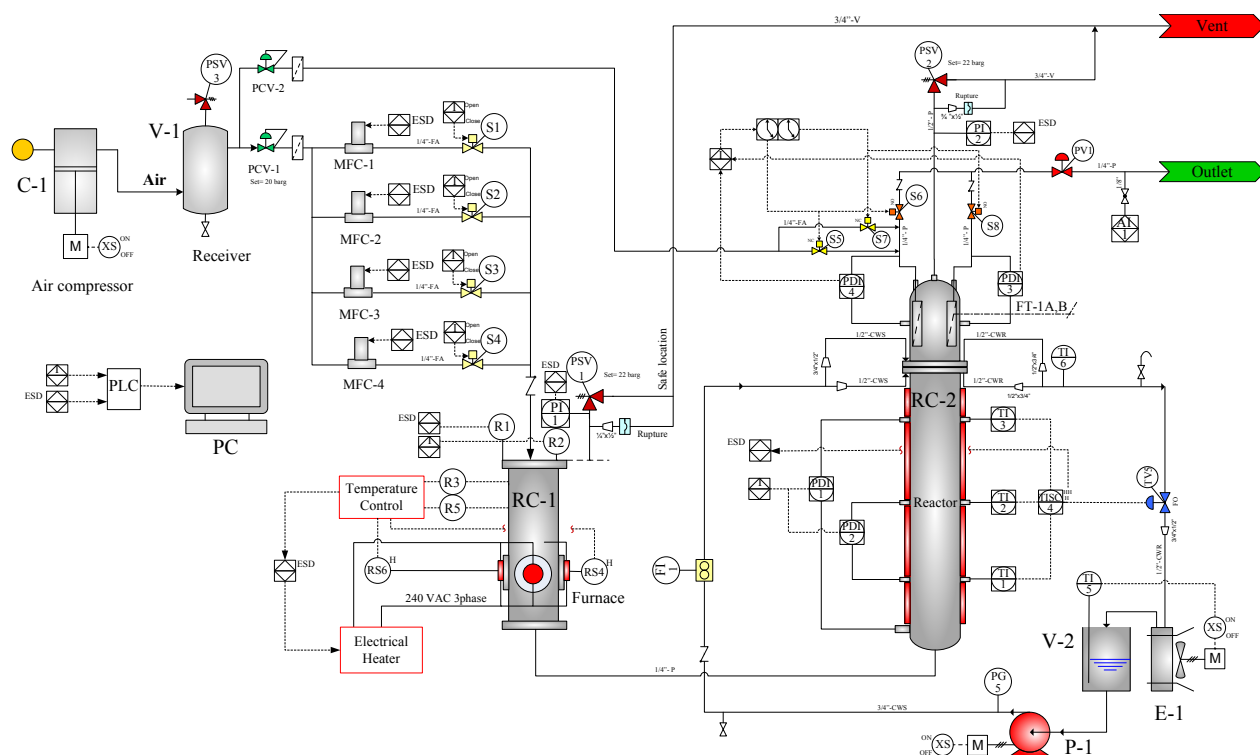


Figure (5.2) Piping and instrumentation diagram of the experimental setup. Compressed air is heated up through the furnace, RC-1 before reaching the fluidized bed reactor, RC-2. The air flow rate and the pressure of the reactor are adjusted by MFCs and back pressure regulator respectively.

## 5.2.2 Experiment

We designed a safe mode experiment to simulate the cooling rate of exothermic processes such as Fischer–Tropsch, model the heat exchange and analyze the its dynamic during the cooling operation. The aim is to characterize the transfer function of the system regarding the heat exchange at startup. We injected hot air into the reactor filled by alumina particles. Five heating tapes wrapped around the reactor, heat it up laterally. We measured the minimum

fluidization velocity,  $u_{mf}$ , of air through the alumina powder in a 8 mm tube as  $2.4 \text{ mm s}^{-1}$  which is confirmed by the pilot plant , RC-2 (Fig. 5.3). The measuring procedure is available in detail [100].

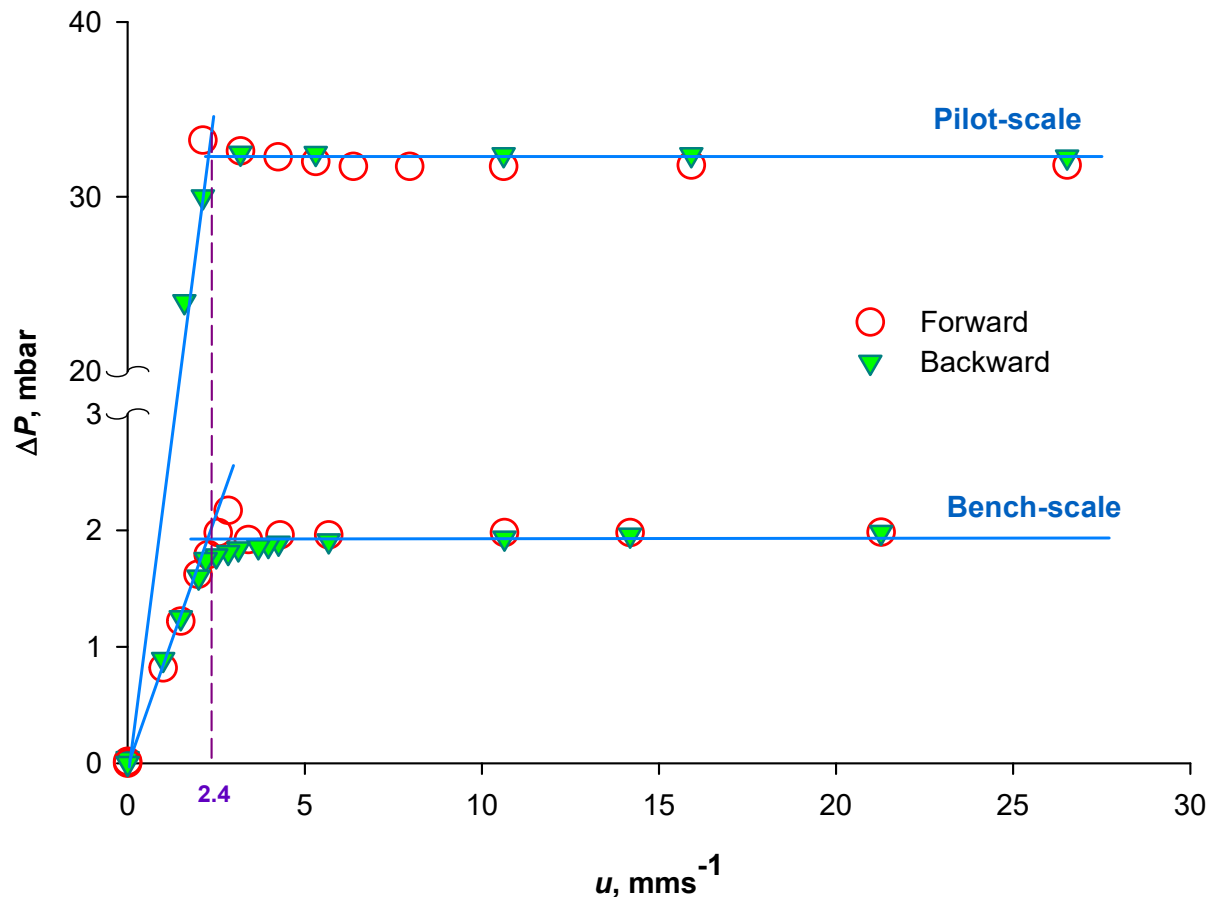


Figure (5.3) Air velocity vs  $\Delta P$  of the alumina powder in a bench-scale ( $D = 8 \text{ mm}$ ) and pilot plant ( $D = 0.2 \text{ m}$ ) . Minimum fluidization velocity,  $u_{mf}$ , is at the intersection of horizontal and slop lines on the backward measurement which is equal to  $2.4 \text{ mm s}^{-1}$

Thus, the air flow rate is adjusted such that its superficial velocity across the bed is higher than its  $u_{mf}$  and also meets values of DOE table. (Table 5.1). The air temperature at the entrance of RC-2 reaches  $300^\circ\text{C}$  based on the flow rate and the tape heaters are set at the maximum of  $650 \text{ W}$ , in total  $3250 \text{ W}$  which was continuously measured by power meters. The thermal conductance of the exterior insulation was  $1.5 \text{ W m}^{-2} \text{ K}^{-1}$  and we used  $1.4 \text{ m}^2$  Fiberglass to insulate the reactor body + heating tapes at  $350^\circ\text{C}$  from the ambient temperature at  $25^\circ\text{C}$  which makes a heat loss of  $680 \text{ W}$ . Hence, the heat source accordingly provides net heat of  $2570 \text{ W}$  to the reactor bed. We reached the inlet temperature of the air at  $300^\circ\text{C}$

Table (5.1) Operating variables of the heat transfer test,  $N = u_0/u_{mf}$  is the fluidization number and  $u_0$  is the superficial gas velocity,  $\dot{q}$  is the air flow rate at the actual conditions ( $T=300^\circ\text{C}$ ,  $P$ ), and  $\dot{q}_{\text{NTP}}$  is the air flow rate at normal conditions ( $T=0^\circ\text{C}$ ,  $P=1$  bar).

| Run | $P$<br>bar | $N$ | $u_0$<br>$\text{cm s}^{-1}$ | $\dot{q}$<br>$\text{L min}^{-1}$ | $\dot{q}_{\text{NTP}}$<br>$\text{L min}^{-1}$ |
|-----|------------|-----|-----------------------------|----------------------------------|-----------------------------------------------|
| 1   | 5          | 5   | 1.2                         | 20                               | 45                                            |
| 2   | 5          | 7.5 | 1.8                         | 30                               | 67.5                                          |
| 3   | 5          | 10  | 2.4                         | 40                               | 90                                            |
| 4   | 10         | 5   | 1.2                         | 20                               | 90                                            |
| 5   | 10         | 7.5 | 1.8                         | 30                               | 135                                           |
| 6   | 10         | 10  | 2.4                         | 40                               | 180                                           |

by setting up the furnace temperature of the RC-1 and also adjust the temperature of FT at  $300^\circ\text{C}$  by the power of heating tapes. We completed two sets of experiments. In the first set, we only involve the big coil and in the second set, both cooling coils are involved to determine the effect of increasing the heat transfer area on the dynamics of the heat exchange. In each run, the pressure is adjusted with a needle valve at the exit and the volumetric flow rate is set by the MFCs. The bed temperatures, T1, T2, T3 and the reactor pressures, P1 and P2 are recorded automatically on the PC. The coolant inlet temperatures,  $T_{\text{c,in}}$  and  $T_{\text{c,out}}$  are measured manually by a digital reader every 30 second. At the beginning of startup, we put TV-5 on manual mode, 50% and at time 0 turn on the water pump, P-1 to start recirculating the water. The water enters into the cooling coil and before completely filling the coil and establishing the re-circulation, a complex phenomena occurs; the cooling water reaches hot tube at  $300^\circ\text{C}$  and get partially vaporized until it recirculates and turns to liquid and get fully developed regime. This time duration is recognizable by reading the outlet temperature. We also noted the time that the saturated vapour turns to the liquid water as it needs to be excluded from the results due to the its unknown impacts and complexity. During this transient zone, the coolant temperature immediately drops, approaches to its final steady state value and nearly remains constant while the water inlet temperature start raising to reach its final value.

### 5.3 Heat transfer analysis

#### 5.3.1 Overall heat transfer coefficient

To estimate the instantaneous overall heat transfer coefficient over time in each experiment, we also model the spatial (transient) energy balance around the fluidized bed:

$$(m_s c_{ps} + \rho_g V_g c_{pg}) \frac{dT_b}{dt} = Q_h + \dot{m}_g c_{pg} (T_{g,in} - T_{g,out}) - U(t) A (T_b - T_{cf}) \quad (5.1a)$$

$$V_g = \varepsilon V_b = \varepsilon \left[ \frac{m_s}{(1 - \varepsilon) \rho_p} \right] \quad (5.1b)$$

We excluded the effect of temperature isothermal inertia of the cooling coils. The assumptions are:

- The bed temperature is uniformly constant in axial and radial direction consistent with the measurements. Because the bubbling fluidized regime forms back-mixed flow which minimizes the axial gradient of temperature and the coil tubes well-distributed across the reactor to remove both axial and radial temperature gradients. This assumption was proved during the experiment as the temperature difference along the reactor was less than 10 °C.
- The heat loss from the bed to the free board gas is negligible.
- The specific heat capacity of the air only changes with the temperature.
- The gas temperature at the boundary of the bed and free board,  $T_{g,out}$  is the same as bed temperature at each time step since the powder bed was well-mixed.

Re-arranging the discrete form of equation 5.1a gives the  $U_i$  where  $i$  corresponds to  $t_i$ . The specific heat capacity of the air,  $c_{pg}$  varies with time since it is a function of its temperature [256] and void fraction of the bed is calculated from the air-solid properties at actual and minimum fluidization conditions [236]. We measured the particle size of the catalyst support and also estimated the particle density from measuring its skeletal density,  $\rho_s$  and pore volume,  $\hat{v}_{pore}$  (Eqn. 5.2) [257]. The other specifications of alumina powder come from literature [99] (Table 5.2).

$$\rho_p = \frac{\rho_s}{\hat{v}_{pore} \rho_s + 1} \quad (5.2)$$

Table (5.2) Characterization of alumina catalyst. Skeletal density and pore volume were measured by BET method, respectively.

| Spec, unit                                             | Value                |
|--------------------------------------------------------|----------------------|
| $\rho_s, \text{ kg m}^{-3}$                            | 3470                 |
| $\hat{\nu}_{\text{pore}}, \text{ m}^3 \text{ kg}^{-1}$ | 376                  |
| $\rho_p, \text{ kg m}^{-3}$                            | 1510                 |
| $d_p, \text{ m}$                                       | $7.5 \times 10^{-5}$ |
| $c_{\text{ps}}, \text{ J kg}^{-1} \text{ K}^{-1}$      | 910                  |
| $\varepsilon_{\text{mf}}$                              | 0.50                 |

$$U_i = \frac{1}{A(T_{b_i} - T_{\text{cf}_i})} \left[ Q_h + \dot{m}_g c_{\text{pg}_i} (T_{g,\text{in}} - T_{b_i}) + \alpha_i (T_{b_{i-1}} - T_{b_i}) / \Delta t \right] \quad (5.3a)$$

$$\alpha = m_s \left( c_{\text{ps}} + \frac{\varepsilon \rho_g}{(1 - \varepsilon) \rho_p} c_{\text{pg}} \right) \quad (5.3b)$$

$$T_{\text{cf}_i} = \frac{1}{2} (T_{\text{c,out}} + T_{\text{c,in}})_i \quad (5.4)$$

$$c_{\text{pg}} = a_1 + a_2 \left[ \frac{a_3/T}{\sinh(a_3/T)} \right]^2 + a_4 \left[ \frac{a_5/T}{\cosh(a_5/T)} \right]^2 \quad (5.5)$$

$$\rho_g = PM_g/RT \quad (5.6)$$

$$\varepsilon_e = \varepsilon_{\text{mf}} + 0.00061 \exp \left( \frac{u_0 - u_{\text{mf}}}{0.262} \right) \quad (5.7)$$

$$\varepsilon_b = 0.784 - 0.139 \exp \left( -\frac{u_0 - u_{\text{mf}}}{0.272} \right) \quad (5.8)$$

$$\delta = 1 - \exp\left(-\frac{u_0 - u_{mf}}{0.62}\right) \quad (5.9)$$

$$\varepsilon = (1 - \delta)\varepsilon_e + \delta\varepsilon_b \quad (5.10)$$

Table (5.3) Constant coefficients of the heat capacity for air in  $\text{J kg}^{-1} \text{K}^{-1}$  (Eqn. 5.5) [256]. The original molar based values in Eqn. 5.5 are divided by the molecular mass of the air, 29, to obtain the mass heat capacity.

| Coefficient | value |
|-------------|-------|
| $a_1$       | 9985  |
| $a_2$       | 3228  |
| $a_3$       | 3012  |
| $a_4$       | 2614  |
| $a_5$       | 1484  |

Finally,  $U_m$  for each experiment is an average of  $U_i$  over time (Eqn. 5.11)

$$U_m = \frac{\sum_0^n U_i \Delta t_i}{\sum_0^n \Delta t_i} = \frac{1}{n} \sum_0^n U_i \quad (5.11)$$

### 5.3.2 Bed convective heat transfer coefficient

To estimate the convective heat transfer coefficient of the bed,  $h_b$ , we applied an indirect classical method. First, we determine the convective coefficient of the coolant,  $h_c$  from its information at the average temperature and measured flow rate and using correlations. To compute the  $h_c$  through the cooling coil, we applied the Gnielinski's correlation (Eqn. 5.12) since the error  $< 10\%$  for both transitional and turbulent regimes ( $0.5 \leq Pr_c \leq 2000$  and  $3 \times 10^3 < Re_c < 5 \times 10^6$ ) [258,259]. Then, we determine  $h_b$  knowing  $U_m$  and  $h_c$  (Eqn. 5.14).

$$Nu = \frac{(f/8)(Re_c - 1000)Pr_c}{1 + 12.7(f/8)^{0.5}(Pr_c^{2/3} - 1)} \quad (5.12)$$

Friction factor as the function of relative roughness ( $\epsilon/D$ ) is calculated as [260]:

$$\frac{1}{\sqrt{f}} = -1.8 \log \left[ \frac{6.9}{Re_c} + \left( \frac{\epsilon/D}{3.7} \right)^{1.11} \right] \quad (5.13)$$

where  $\epsilon$  is 0.002 mm for stainless steel pipes. Thus,  $h_b$  is:

$$h_b = \frac{1}{1/U_m - 1/h_c} \quad (5.14)$$

This approach, also evaluates the order of magnitude of convective heat transfer on both hot fluidized bed side and cooling side and reveals the limited resistance during the heat exchange.

## 5.4 Results and discussion

To determine the impact of coil design of the cooling dynamics, we classified the experimental data based on the involved heat transfer area. Because of the complexity of heat exchange mechanism at the beginning of the startup including the phase change, filling up the entire coil with liquid water and establishing the fully developed regime, we excluded the first 2 minutes of cooling. However, the whole operation is involved in studying the dynamics to determine the transfer function of the system.

### 5.4.1 Single cooling coil

The initial tests excluded the smaller of the two cooling coils. After opening the cooling water control valve to 50% and leaving it at the same position, the bed temperature started decreasing (Fig. 5.4).

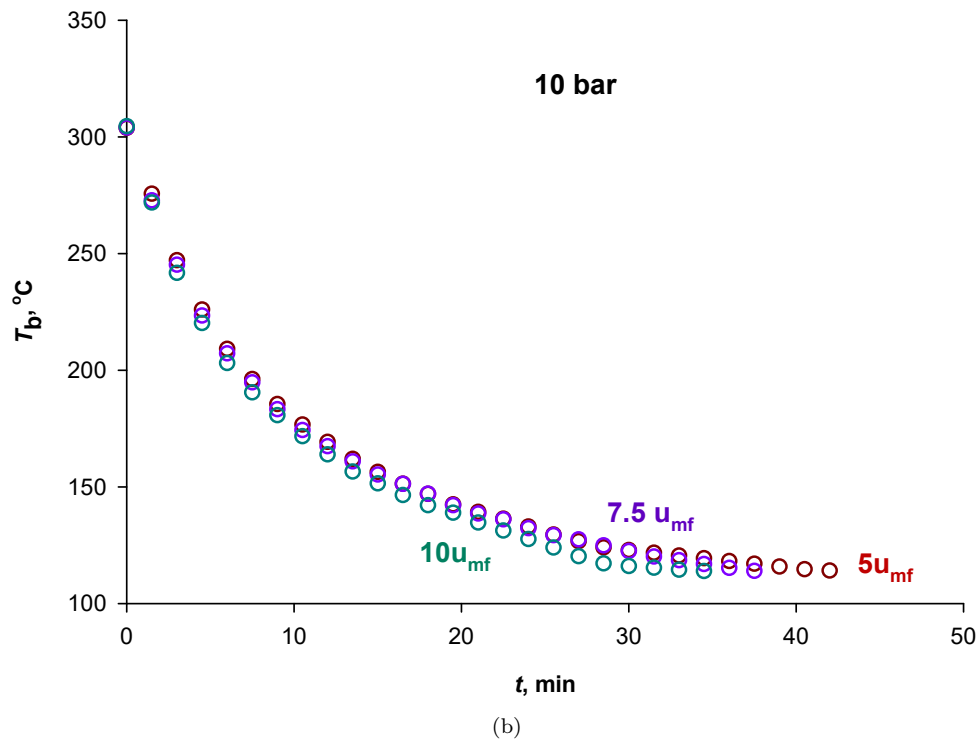
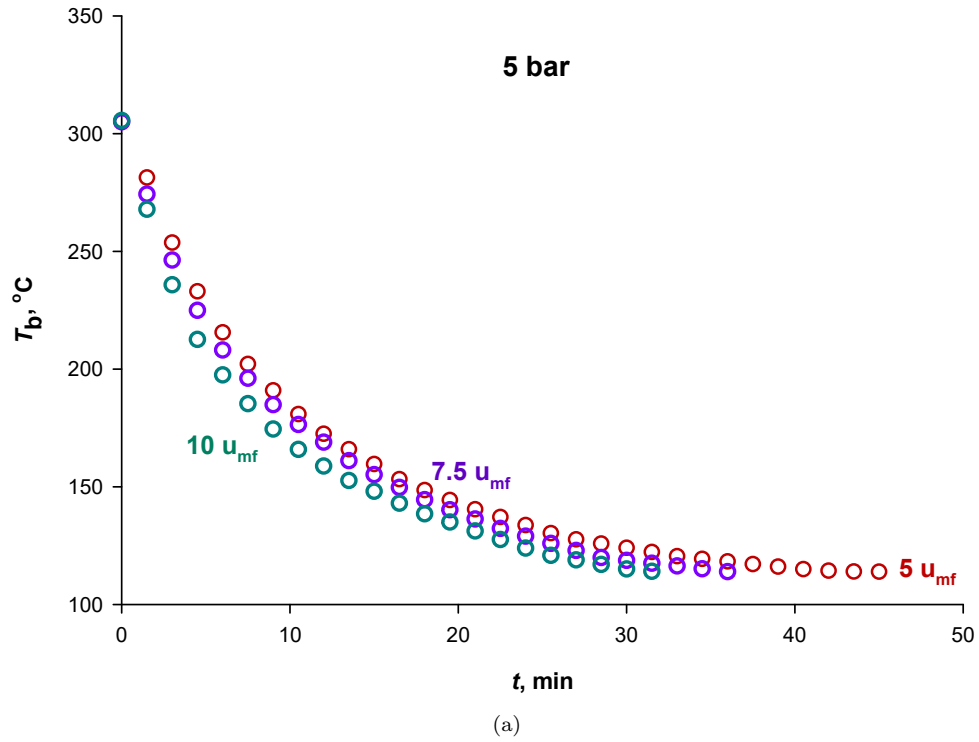


Figure (5.4) Dynamics of bed temperature for different superficial gas velocities through the bed in single coil scenario. (a) at 5 bara, (b) at 10 bara. At time zero, the cooling water control valve is open at 50% and the equivalent coolant flow is  $13.8 \text{ L min}^{-1}$

We employed Eqns. (5.3)–(5.10) to compute the instantaneous overall heat transfer coefficients at various gas velocities and pressures (Fig. 5.5).

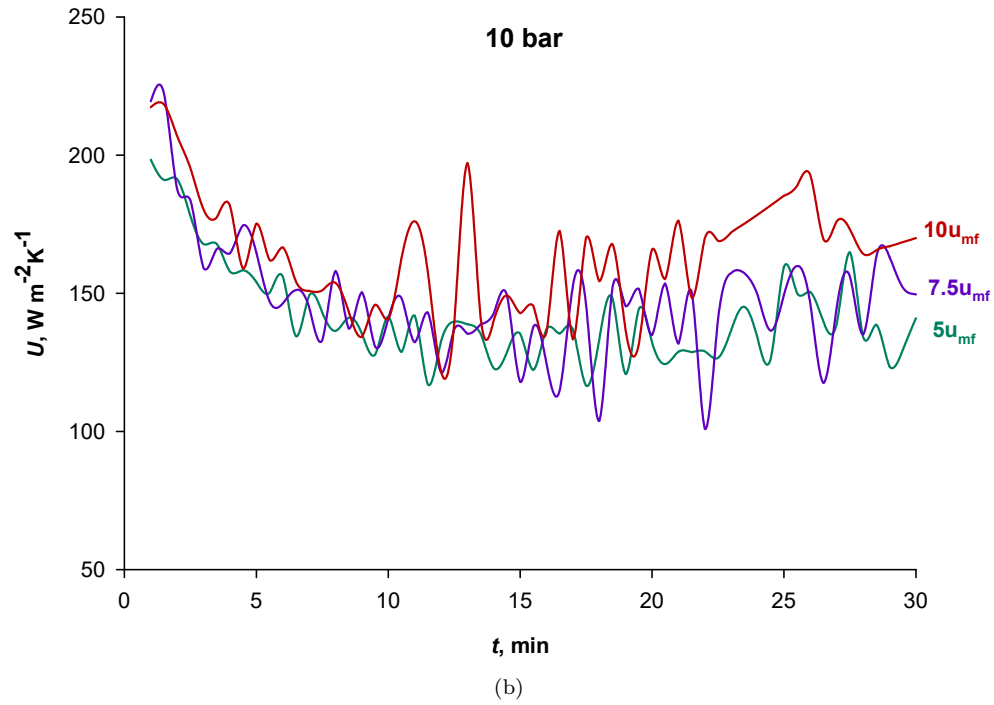
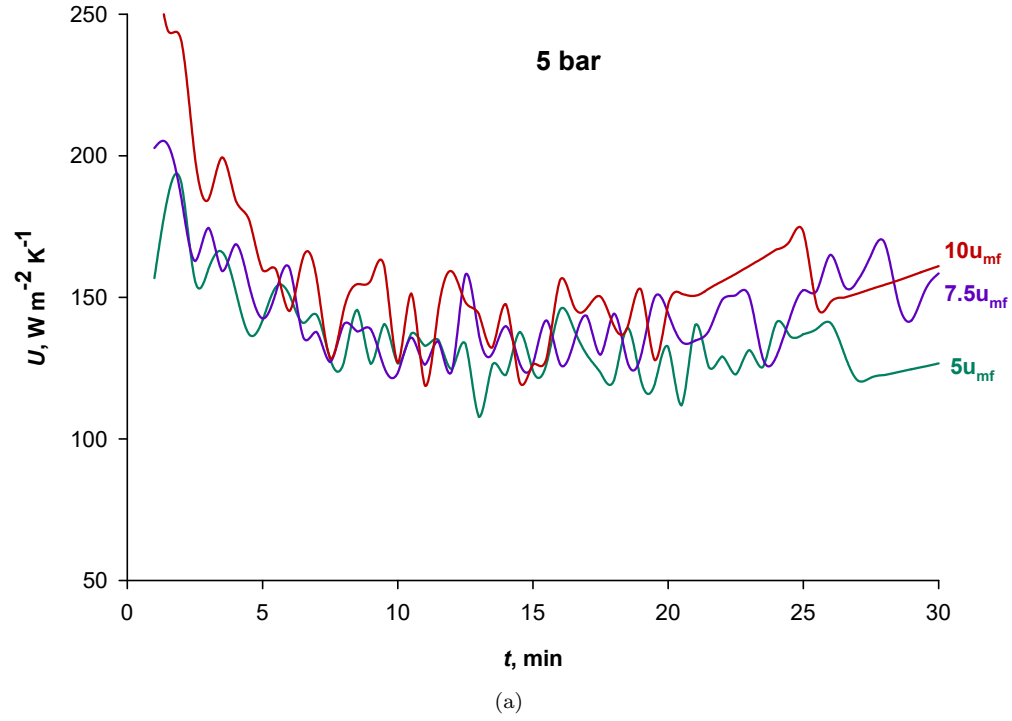


Figure (5.5) Estimated overall heat transfer coefficients of heat exchange over time for different superficial gas velocities in single coil scenario. (a) at 5 bara, (b) at 10 bara. The cooling water control valve was 50% open and the equivalent coolant flow is  $13.8 \text{ L min}^{-1}$

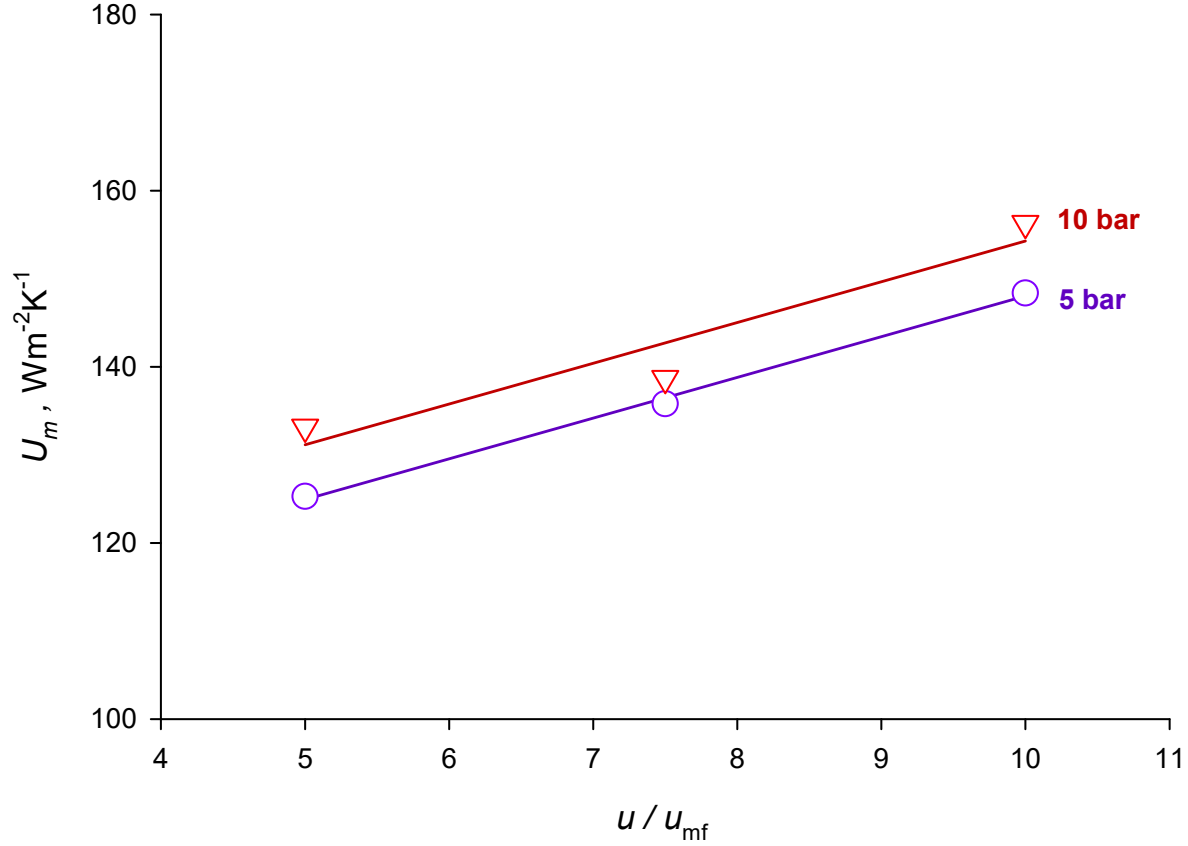
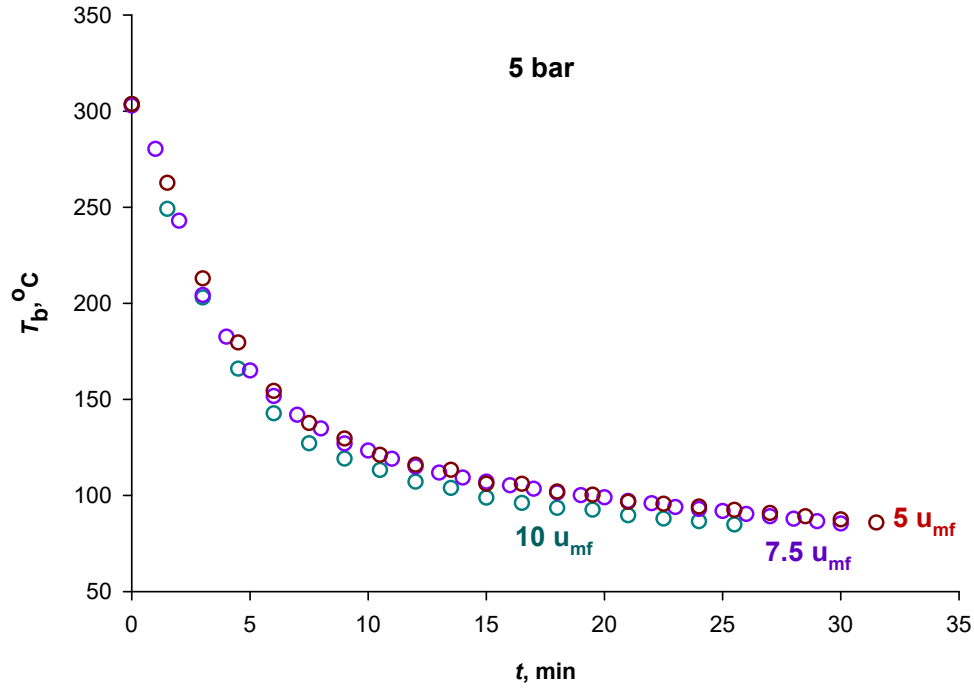


Figure (5.6) Effect of pressure and fluidization numbers,  $u/u_{mf}$ , on the average heat transfer coefficient,  $U_m$  by running the single coil scenario.

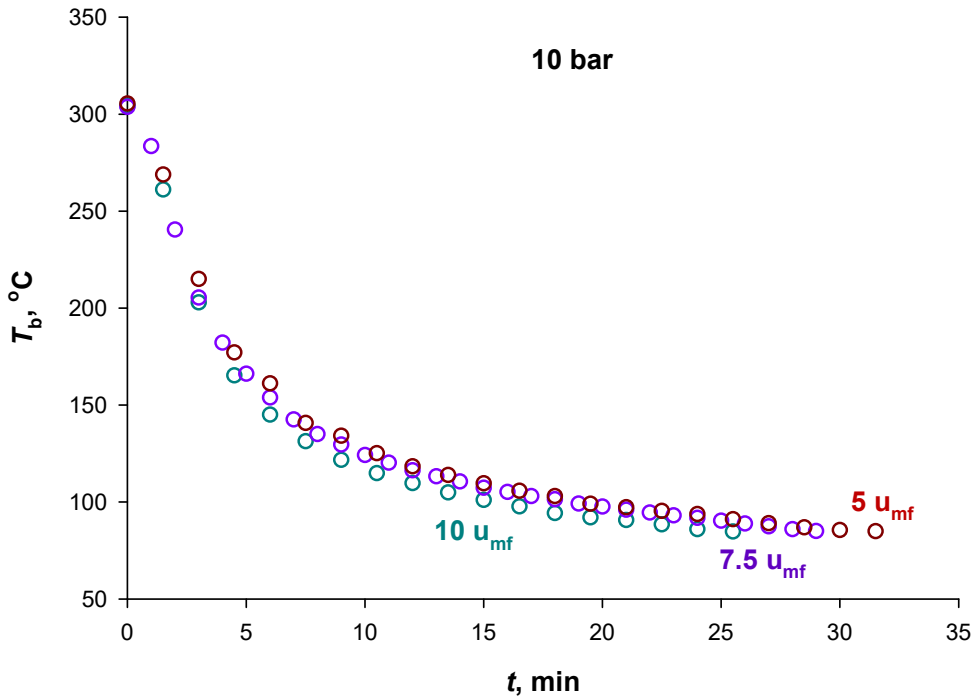
Hence, increasing the superficial gas velocity, reduces the cooling time (Fig. 5.4) which means that the cooling operation is faster and accordingly the average heat transfer coefficient, ' $U_m$ ' is higher, as expected (Fig. 5.6).

#### 5.4.2 Double cooling coils

In the next step, we brought also the smaller cooling coil into service to study the impact of effective area on the dynamics of the heat transfer. Compared to the single coil, having both coils in service, drops the bed temperature more, during the same period confirming that increasing the surface area improves the heat transfer rate (Fig. 5.7).



(a)



(b)

Figure (5.7) Dynamics of bed temperature for different superficial gas velocities through the bed in double coil scenario. (a) at 5 bar, (b) at 10 bar. At time zero, the cooling water control valve is open at 50% and the equivalent coolant flow is  $13.8 \text{ L min}^{-1}$

To precisely determine the impact of pressure and superficial gas velocity on the cooling dynamics, again we estimated the average heat transfer coefficients at different operating conditions (Fig. 5.9). The dynamic tests confirm that increasing the superficial gas velocity from  $5u_{mf}$  to  $10u_{mf}$  marginally increases the heat transfer rate (35%) which is consistent with [110, 129, 261, 262] who reported a 30–40% over the same range.

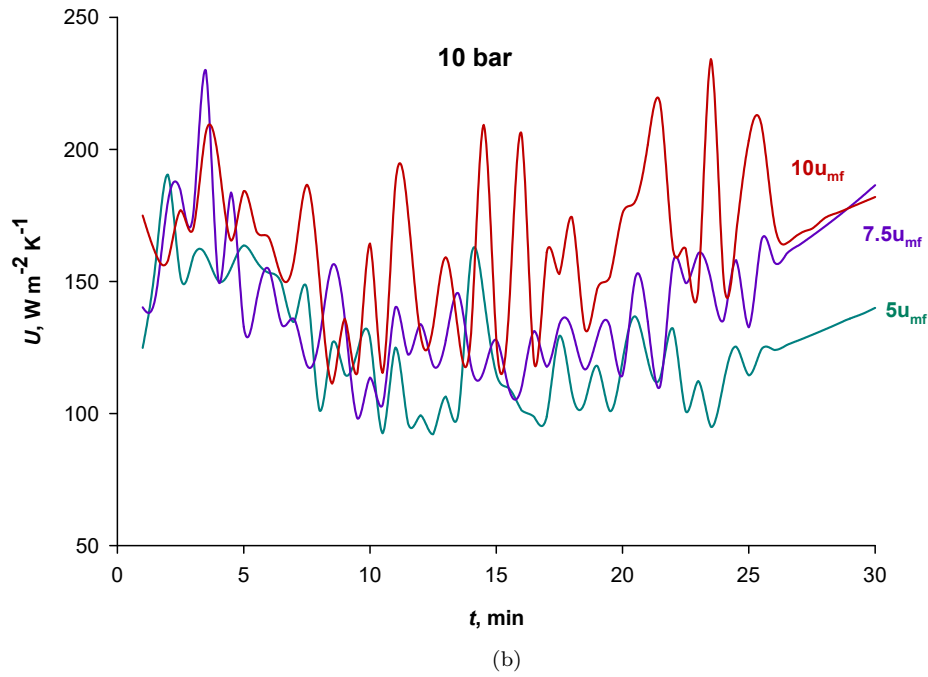
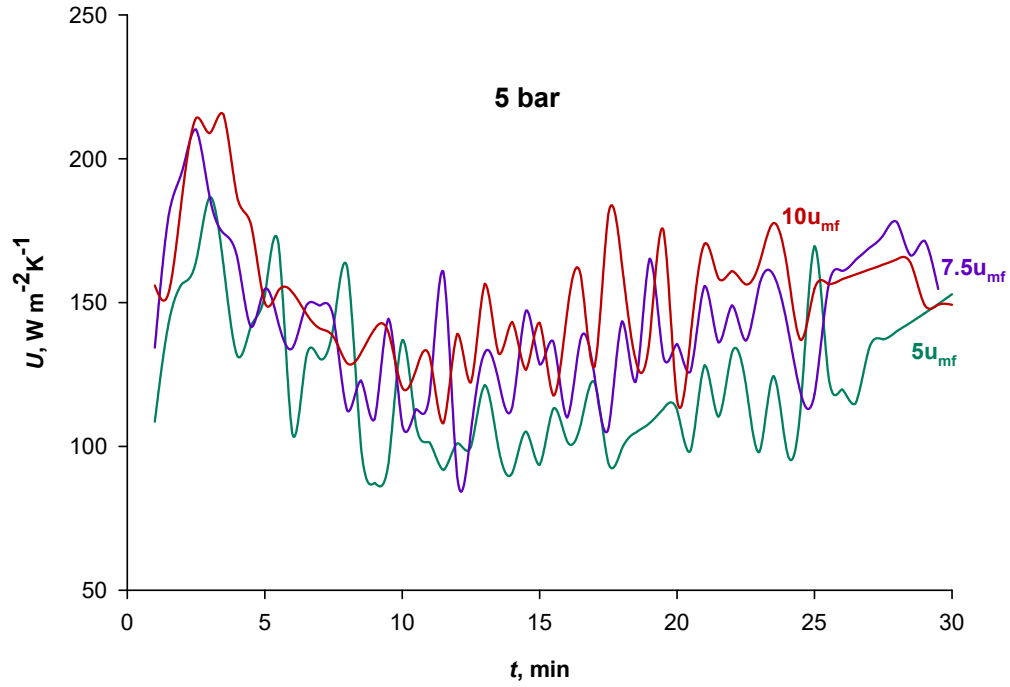


Figure (5.8) Estimated overall heat transfer coefficients of heat exchange over time for different superficial gas velocities in double coil scenario. (a) at 5 bara, (b) at 10 bara. The cooling water control valve was 50% open and the equivalent coolant flow is  $13.8 \text{ L min}^{-1}$

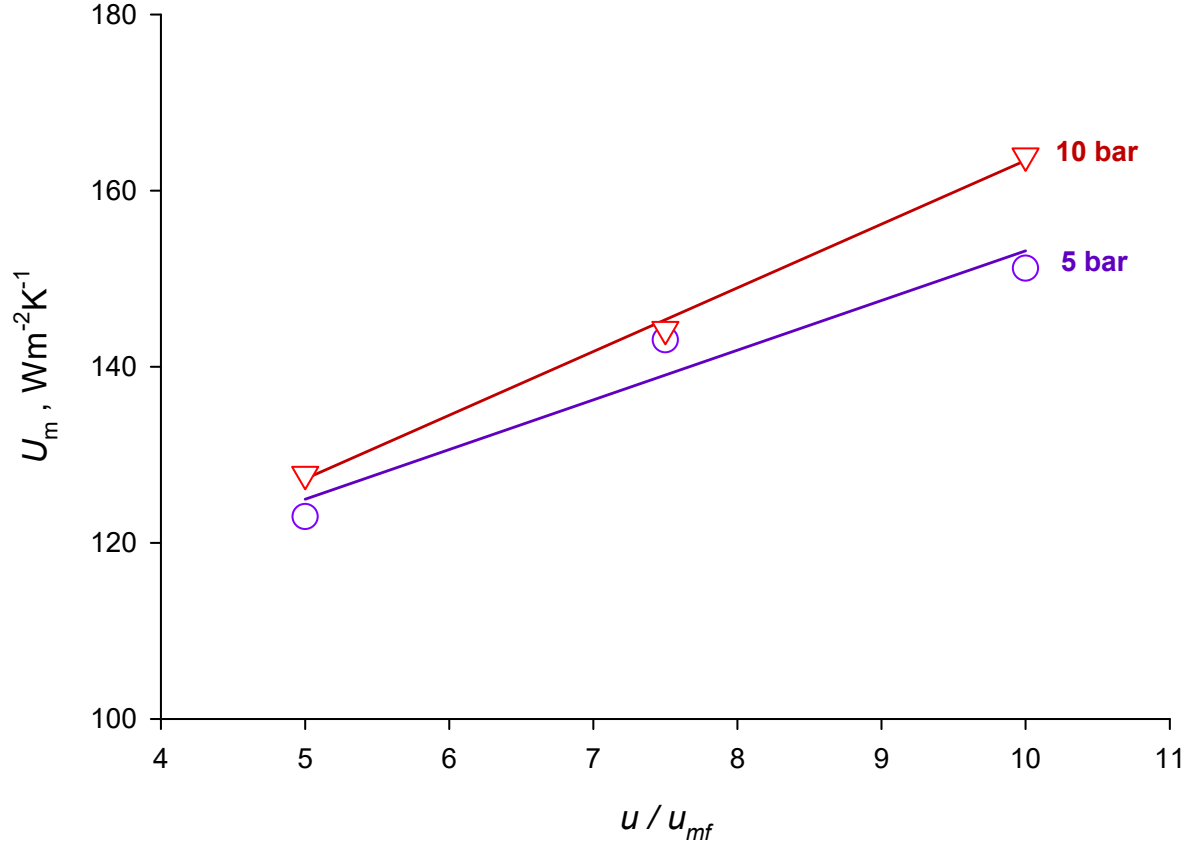


Figure (5.9) Effect of pressure and fluidization numbers,  $u/u_{mf}$ , on the average heat transfer coefficient by running the double-coils scenario.

For the single coil and double coils, increasing the air velocity improves the heat transfer coefficients (Fig. 5.6 and 5.9) and accordingly makes the cooling dynamics faster (Fig. 5.4, and 5.7) because higher gas velocities increase the particle-wall collisions per unit time [128]. To investigate the impact of operating pressure of the fluidized bed on the heat transfer coefficient, we made a paired t-test analysis for  $U_m$  with pressure at a given gas velocity (Table. 5.4). Since the P-values for both scenarios is higher than 0.05, the test fails to reject the null hypothesis representing that the pressure has no meaningful effect on the overall heat transfer coefficient. Even though the higher throughput, gas velocity, improves the heat removal efficiency and practically assists the safety during the startup and normal operation, the system still needs a temperature control to avoid thermal disruptions during the operation. Comparing the  $U_m$  of both scenarios at the same pressures and gas velocities (Fig. 5.6 and 5.9) also confirms that although changing the heat transfer area as a design parameter, changes the dynamics of the heat exchange, it is independent from heat transfer

Table (5.4) Two paired t-test analysis of  $U_m$  verses operating pressure of the fluidized bed to reject the null-hypothesis of mean values

| $u/u_{mf}$             | Single coil |        | Double coil |        |
|------------------------|-------------|--------|-------------|--------|
|                        | 5 bar       | 10 bar | 5 bar       | 10 bar |
| 5                      | 125         | 133    | 123         | 128    |
| 7.5                    | 136         | 139    | 143         | 144    |
| 10                     | 148         | 156    | 151         | 165    |
| $P(T \leq t)$ two-tail | 0.07        |        | 0.21        |        |

coefficient as they were not changed meaningfully with switching from single- to double coil scenario.

### 5.4.3 Bed convective heat transfer

In all the experiments, the water temperature varies between 25 °C and 85 °C. Hence, to evaluate the  $h_c$  of the cooling water, we extracted its physical properties at 55 °C as the mean temperature using Aspen properties V12 (Table 5.5). In all the experiments, the

Table (5.5) Cooling water properties at 55 °C and 300 kPa. Data extracted from Aspen properties V12

| Property, unit                                | value              |
|-----------------------------------------------|--------------------|
| $c_{pc}$ , J kg <sup>-1</sup> K <sup>-1</sup> | 4325               |
| $k_c$ , W m <sup>-1</sup> K <sup>-1</sup>     | 0.6485             |
| $\mu_c$ , Pa s                                | $5 \times 10^{-4}$ |

cooling control valve, TV5 is open on 50% and the corresponding water flow is the same, the coolant velocity on single coil scenario is double that of the both coils which means single-coil makes higher convective heat on the cold side (Table 5.6). The values of  $h_c$  (Table 5.6) and

Table (5.6) Cooling water properties at 55 °C and 300 kPa. Data extracted from Aspen properties V12

| No.                                       | 1           | 2            |
|-------------------------------------------|-------------|--------------|
| Scenario                                  | Single coil | Double coils |
| $Re_c$                                    | 33215       | 16320        |
| $Pr_c$                                    | 3.3         | 3.3          |
| $h_c$ , W m <sup>-2</sup> K <sup>-1</sup> | 3200        | 5900         |

Eqn.5.14 verify that the limiting resistance during the cooling relies on the fluidized bed

side. To evaluate the convective heat transfer coefficient of the bed obtained from the above indirect method, we applied two correlations from literature to predict the convective heat of the bed and compare the estimated average  $h_b$  from experiment with them (Table 5.7).

Table (5.7) Correlations available in the literature to predict the average heat transfer coefficient of fluidized bed. 1st correlation is applicable to heat transfer from vertical surfaces and the 2nd one is applied to both horizontal and vertical surfaces.

| No.        | Correlation                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |
|------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1<br>[125] | $\frac{hd_p}{k_g} = 0.525 Re_p^{0.75},$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |
| 2<br>[129] | $\frac{hl_1}{k_g} = \frac{0.125(1-\varepsilon_{mf})}{a_1[1+a_2(k_g/2c_{ps}\mu_g)]} + 0.165 Pr_g^{1/3} \left(\frac{\rho_g}{\rho_s-\rho_g}\right)^{1/3} \left(\frac{1}{a_3}\right)$ $a_1 = 1 + 33.3 \left[ \left(\frac{u_e \rho_p c_{ps}}{u_{mf} g k_g}\right)^{1/3} u_e \right]^{-1}$ $a_2 = 1 + 0.28(1 - \varepsilon_{mf})^2 u_e u_{mf} \left(\frac{\rho_g}{\rho_p - \rho_g}\right)^{1/2} \left(\frac{\rho_p c_{ps}}{g k_g}\right)^{2/3}$ $a_3 = 1 + 0.05 \left(\frac{u_{mf}}{u_e}\right)$ $l_1 = \left(\frac{\mu_g}{\rho_s - \rho_g}\right)^{2/3} \left(\frac{1}{g}\right)^{1/3}, u_e = u_0 - u_{mf}$ |

Table (5.8) Comparison of experimental convective heat transfer coefficient with correlations in table 5.7. The operating conditions of each run is available in table 5.1.

| Run                 | $P$ , bar | $u_0$ , cm s <sup>-1</sup> | $h_b$ , W m <sup>-2</sup> K <sup>-1</sup> |          |          |
|---------------------|-----------|----------------------------|-------------------------------------------|----------|----------|
| Single cooling coil |           |                            | Experiment                                | Model(1) | Model(2) |
| 1                   | 5         | 1.2                        | 129                                       | 51       | 238      |
| 2                   | 5         | 1.8                        | 140                                       | 70       | 251      |
| 3                   | 5         | 2.4                        | 153                                       | 85       | 263      |
| 4                   | 10        | 1.2                        | 137                                       | 80       | 271      |
| 5                   | 10        | 1.8                        | 143                                       | 105      | 284      |
| 6                   | 10        | 2.4                        | 162                                       | 135      | 298      |
| Double cooling coil |           |                            |                                           |          |          |
| 7                   | 5         | 1.2                        | 129                                       | 50       | 233      |
| 8                   | 5         | 1.8                        | 152                                       | 70       | 246      |
| 9                   | 5         | 2.4                        | 161                                       | 82       | 258      |
| 10                  | 10        | 1.2                        | 135                                       | 83       | 271      |
| 11                  | 10        | 1.8                        | 153                                       | 112      | 284      |
| 12                  | 10        | 2.4                        | 175                                       | 138      | 298      |

According to table 5.8, the experimental and predicted heat transfer coefficients are quite different, so that the first correlation estimates lower values while the 2nd correlation gives higher compared to the experiment. The reason is that correlation (1) does not involve the impact of the hydrodynamic parameters such as void fraction and particle density. Correlation (2) which is applicable to the wide range of particular physical properties and operating conditions also overestimated the results on the vertical tubes [129]. Furthermore, in our cases the complex configuration of vertical tube bundles affect the estimation of the  $U_m$  and  $h_b$ . Taking the mean values with time is also an error. Thus, all these factors reveal the uncertainties of the heat transfer coefficient which is still a challenging point in the heat transfer community. Besides the uncertainties, the big difference between the bed temperature and coolant temperature over the time is a decreasing factor of  $U_i$ . It means that keeping the coolant temperature at higher range improves the heat transfer coefficient. For example, the coil can still remove the same amount of energy with the same  $\Delta T_c$  but smaller  $T_b - T_{cf}$ . This phenomena is not addressed in the predictive models since their results are based on a few non-involved coolant experiments.

#### 5.4.4 Cooling capacity

To evaluate the cooling capacity, we divided the heat exchange by the molar flow rate of the feed air at maximum pressure and fluidization number (10 bara and  $u/u_{mf} = 10$ ) for both scenarios (Fig. 5.10).

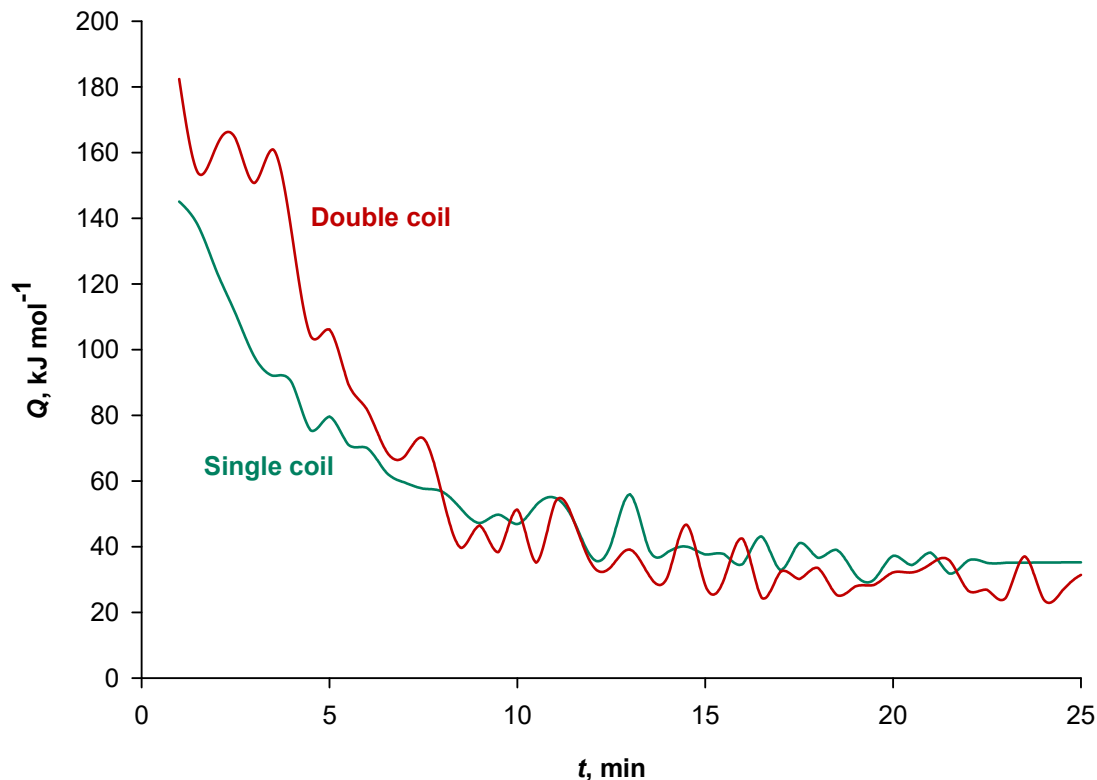


Figure (5.10) Molar heat removal from the fluidized bed during the cooling operation at 10 bara and  $u/u_{mf} = 10$  in single and double coil scenarios.

At the beginning of operation when the bed temperature is around  $300^{\circ}\text{C}$ , the cooling capacity of double coil is higher than equivalent enthalpy of FT reaction ( $\Delta H_{\text{rxn}} = 165 \text{ kJ mol}^{-1}$ ) [50, 231]. It verifies that the coil area is capable to remove this amount of heat from the fluidized bed when the real FT will be in operation. The heat exchange decreases with time since the bed temperature decreases in absence of heat of reaction as a powerful heat source and the driving force declines accordingly. Heat removal of the single coil is lower ( $145 \text{ kJ mol}^{-1}$ ) and has the same behaviour over the time. Although one coil area is capable to remove a huge amount of heat, it is risky to involve it only at the startup and even during the normal operation of FT, it should be served under supervision.

## 5.5 Dynamics and control of heat exchange

### 5.5.1 System Identification

In order to design a controller for this exothermic system, we characterized the transfer function of the system, temperature response to the step change in coolant flow rate as the

input variable. Among the 6 experimental runs in each single- and double coil scenario, the responses of more intensive operating conditions, 10 bar and  $10u_{mf}$ , were selected as the general criteria to obtain the transfer function since their  $U_m$  is higher and cooling dynamics is faster accordingly (Fig. 5.11). We identified the parameters of the system by a ‘first order’ and ‘first order plus time delay’ (FOPTD) for the single coil and double coil respectively [263]:

$$K = \frac{\Delta T}{\Delta \dot{m}_c} = \frac{T_\infty - T_0}{\dot{m}_{c,\infty} - \dot{m}_{c,0}} \quad (5.15)$$

- Transfer function of single coil cooling:

$$\tau_s = t : T = T_0 + 0.63\Delta T \quad (5.16)$$

$$G_s(s) = \frac{K_s}{\tau_s s + 1} \quad (5.17)$$

- Transfer function of double coil cooling:

$$\tilde{t}_1 = t : T_1 = T_0 + 0.28\Delta T \quad (5.18)$$

$$\tilde{t}_2 = t : T_2 = T_0 + 0.63\Delta T \quad (5.19)$$

$$\tau_d = \frac{3}{2}(\tilde{t}_2 - \tilde{t}_1) \quad (5.20)$$

$$\theta = \frac{1}{2}(3\tilde{t}_1 - \tilde{t}_2) \quad (5.21)$$

$$G_d(s) = \frac{K_d \exp(-\theta s)}{\tau_d s + 1} \quad (5.22)$$

The main reason that the first order transfer function was assigned to the single coil cooling

system is that the calculated time delay is close to zero. In practice, the dead time of the single coil is faster at the beginning because the same coolant flow is recirculated through one coil instead of splitting between two coils.

Table (5.9) Parameters of the cooling system transfer functions for both cooling scenarios.

| Parameter      | Scenario    |              |
|----------------|-------------|--------------|
|                | single coil | double coils |
| $K$ , °C min/L | -13.9       | -16          |
| $\tau$ , min   | 8.8         | 4.2          |
| $\theta$ , min | -           | 0.3          |

The parameters of both transfer functions (Table 5.9) represent that the double-coils cooling scenario is significantly faster and more effective than the single-coil one.

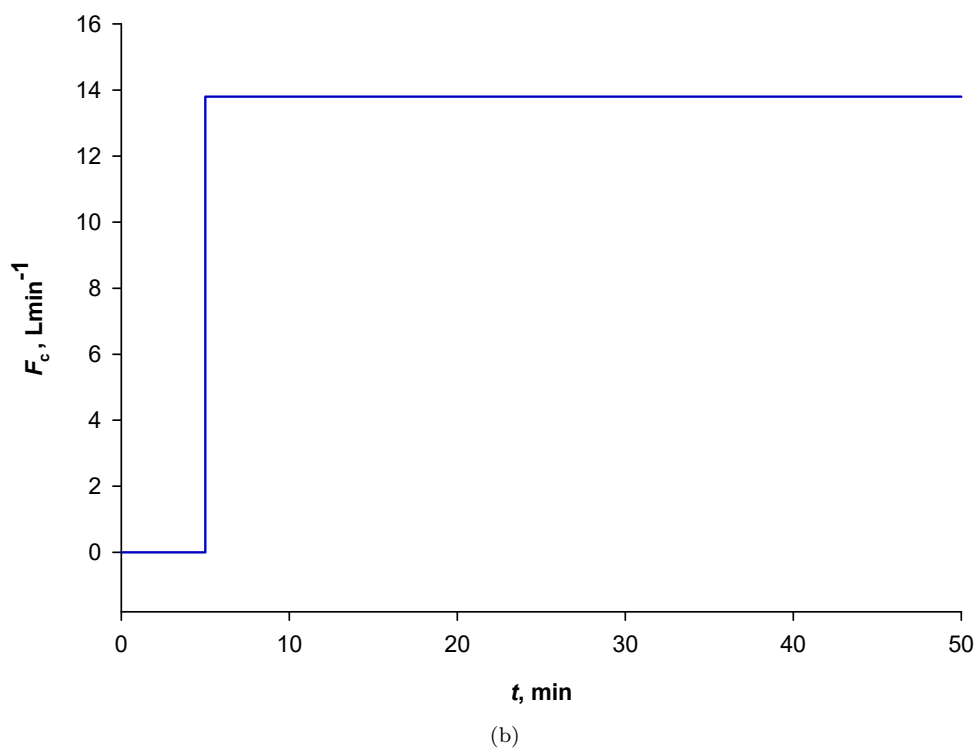
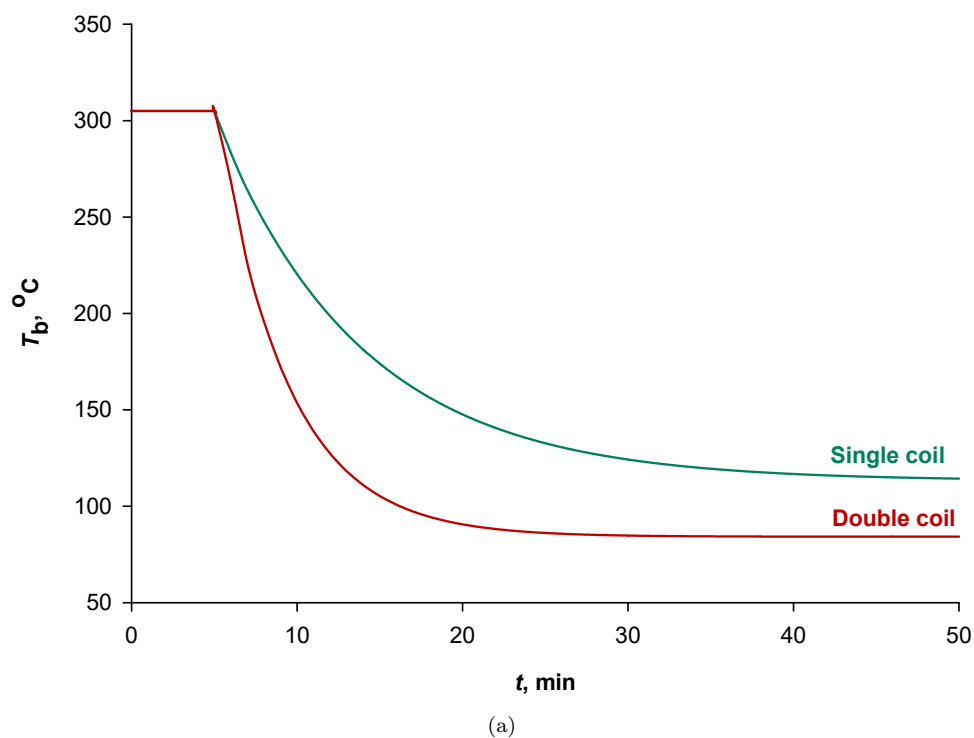


Figure (5.11) Open loop response of the bed temperature to a step change of coolant flow from no-flow to 13.8 L min<sup>-1</sup>, equivalent to 50% opening of cooling control valve. (a) Response temperature of the bed for single coil, 'cyan' and double coil 'red' scenarios. (b) Coolant flow rate from closed valve to equivalent of 50% opening.

### 5.5.2 Controller design

In general, cooling dynamics with longer time constant is more conservative to design the temperature controller as it leads to smoother control performance and better stability of the system. However, the faster cooling dynamics gives a more aggressive control actions and faster response time which is more convenient for the startup conditions. Thus, double coil scenario was selected to design the control system. We characterized the controller parameters by the internal model control (IMC) approach, which is suitable in the case of uncertainties and the resulting controller provides a satisfactory performance [247]. Figure 5.12 represents the general block diagram of the control loop system including the disturbance.

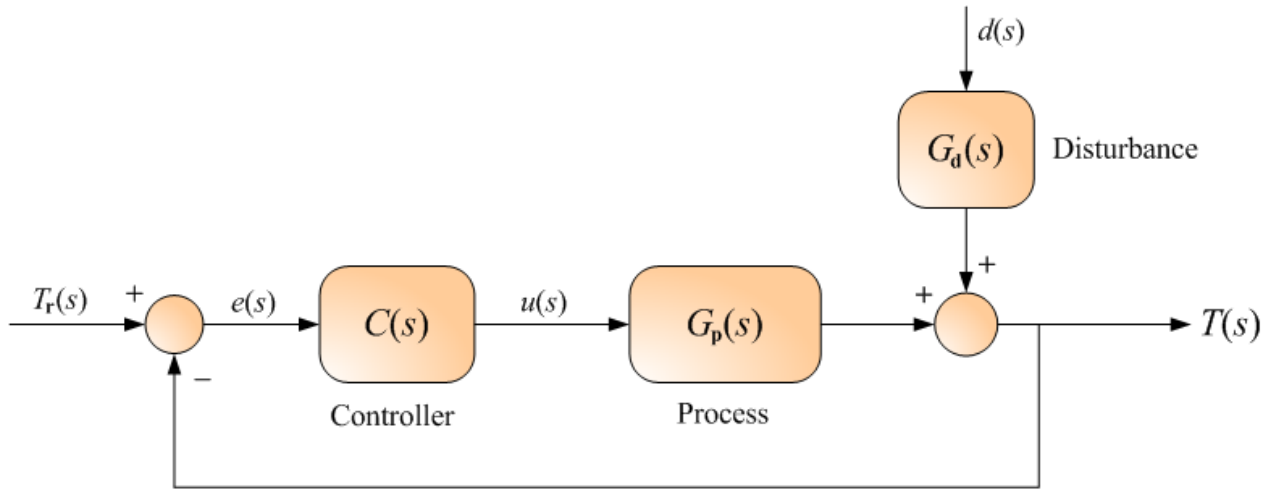


Figure (5.12) Block diagram of the control loop system for changing in bed temperature set point and disturbance rejection.  $T_r(s)$  is the set point temperature,  $d(s)$  is the disturbance,  $u(s)$  is the input variable, here coolant flow rate ( $F_c$ ), and  $e(s)$  is the error.

Hence, the controller parameters are tuned from the transfer function of the system (Table 5.10) [264] Finally, having considered  $\lambda = \tau$ , the parameters of the Proportional - Integral (PI) controller are  $K_c = -0.06 \text{ L min}^{-1} \text{ } ^\circ\text{C}^{-1}$  and  $\tau_I = 4.2 \text{ min}$ .

#### Step change in set point

To test the controller performance, we designed a closed loop system in SIMULINK <sup>®</sup> 2023 for a  $-20^\circ\text{C}$  step change in the set temperature ( $305^\circ\text{C}$  to  $285^\circ\text{C}$ ) for both single- and double coil scenarios (Fig. 5.13).

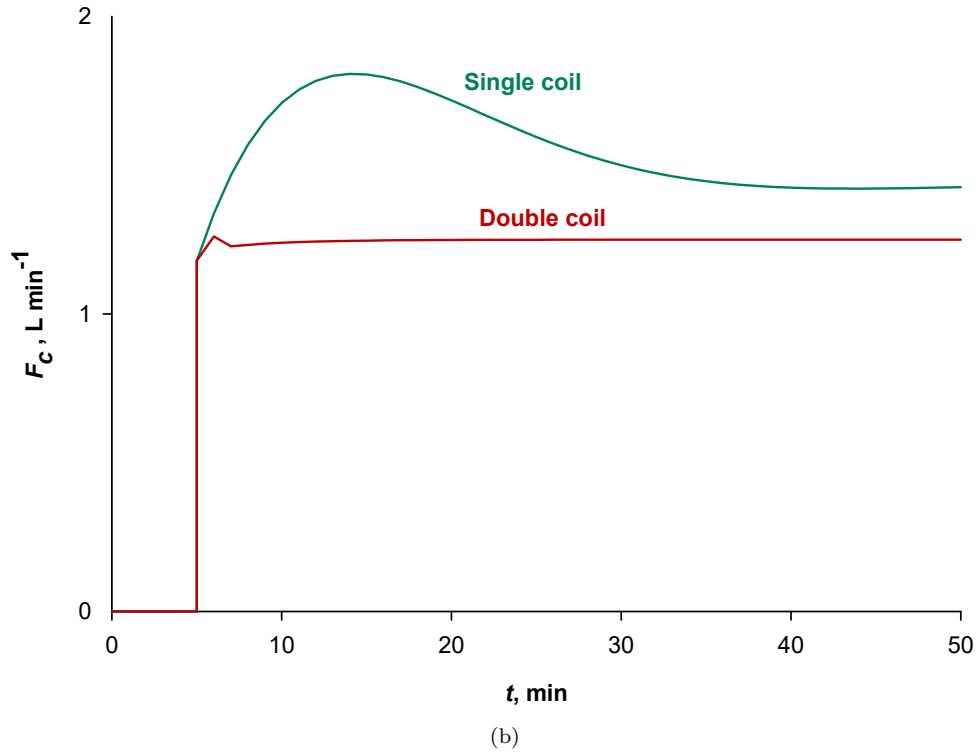
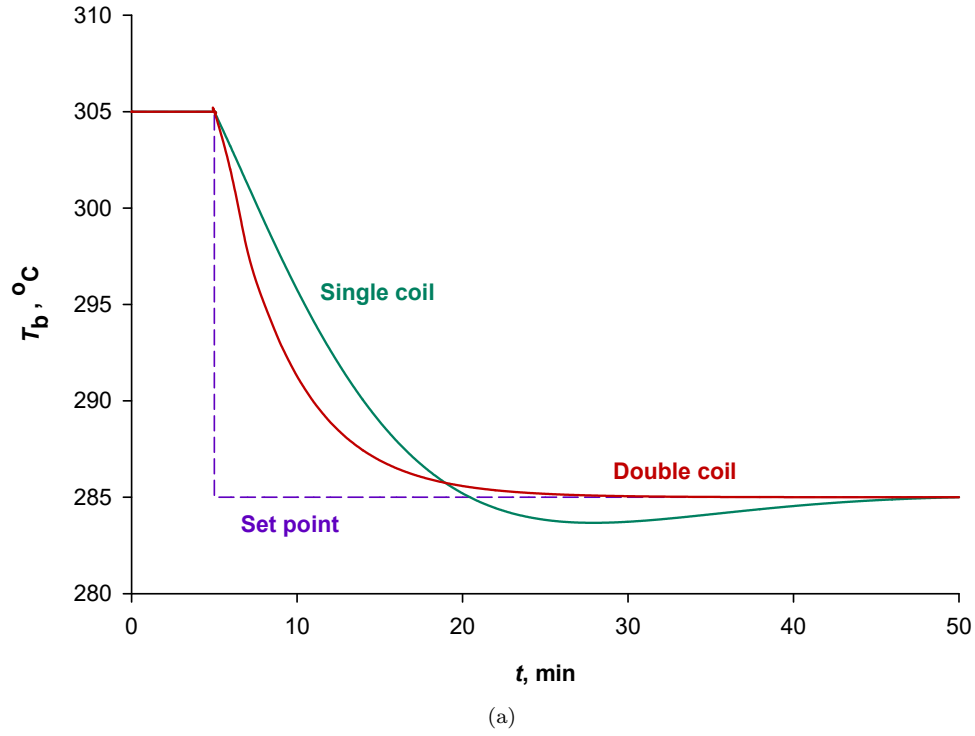


Figure (5.13) Performance of the controller for step change in the set point of the fluidized bed temperature for both single and double coil scenarios. (a) Temperature set point changes from 305  $^{\circ}\text{C}$  to 285  $^{\circ}\text{C}$ . (b) Coolant flow rate variation to recover the temperature on its set value.

The controller has a better performance with the double coil scenario compared to the single coil. However, it has a sluggish dynamics to restore the temperature to the desired set point which reduces the process efficiency. Hence we improved the controller to accelerate the cooling procedure by increasing the gain of the PI controller ( $\lambda = \tau/7$ ). Although the modified PI makes the cooling faster, the response exhibits oscillation to reach its set point. Then, we designed a PID controller + filter (PIDf) (Table 5.10) [163] and tested its performance for the same step change which gives a smooth response within the same time frame as modified PI (Fig. 5.14).

Table (5.10) Characterizations of the PI and PIDf controllers.

| Type     | PI [264]                                  | PIDf [163]                                                                                               |
|----------|-------------------------------------------|----------------------------------------------------------------------------------------------------------|
| $C(s)$   | $K_c \left(1 + \frac{1}{\tau_I s}\right)$ | $K_c \left(\frac{\tau_I \tau_D s^2 + \tau_I s + 1}{\tau_I s}\right) \left(\frac{1}{\tau_F s + 1}\right)$ |
| $K_c$    | $\frac{\tau}{K(\lambda + \theta)}$        | $\frac{\tau + \theta/2}{K(\theta + \lambda)}$                                                            |
| $\tau_I$ | $\tau$                                    | $\tau + \theta/2$                                                                                        |
| $\tau_D$ | —                                         | $\frac{\tau \theta}{2\tau + \theta}$                                                                     |
| $\tau_F$ | —                                         | $\frac{\lambda \theta}{2(\lambda + \theta)}$                                                             |

Then the parameters of PIDf controller are :  $K_c = -0.3 \text{ L min}^{-1} \text{ }^\circ\text{C}^{-1}$ ,  $\tau_I = 4.35 \text{ min}$ ,  $\tau_D = 0.15 \text{ min}$ ,  $\tau_F = 0.13 \text{ min}$

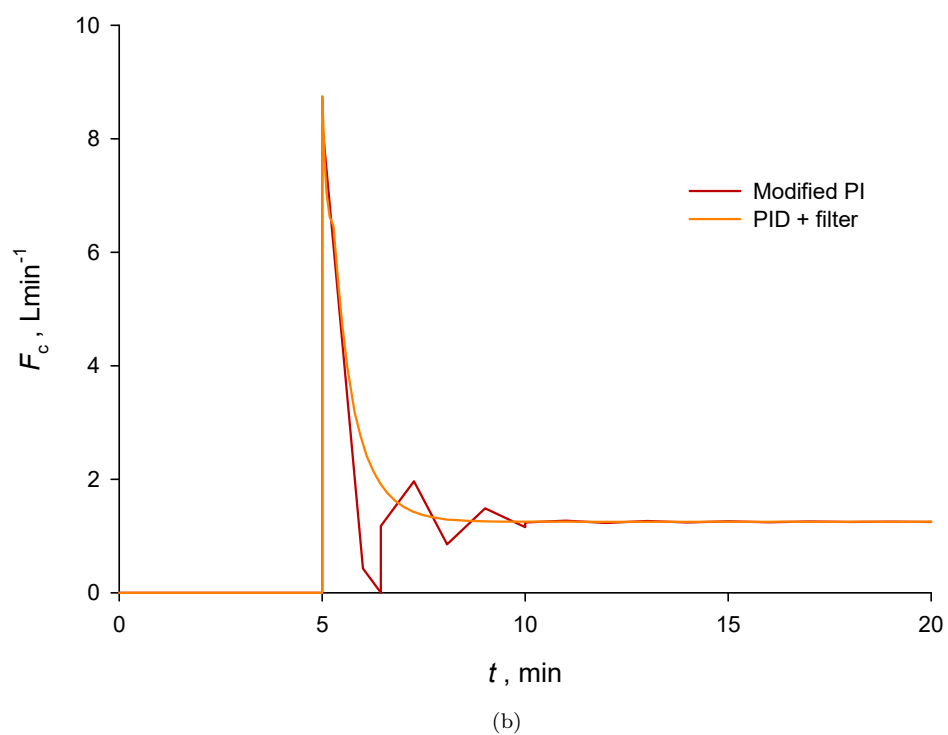
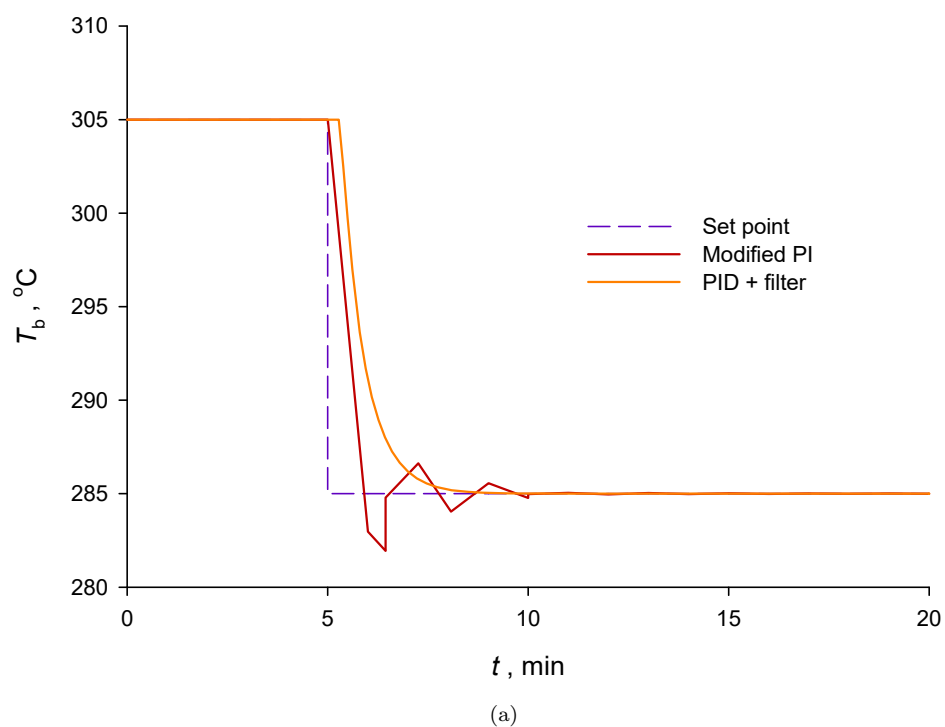


Figure (5.14) Performance of the modified controller ‘red’ and PIDf ‘orange’ against a step change in the temperature of the fluidized bed with the double coil system. (a) The set point of bed temperature changes from 305  $^{\circ}\text{C}$  to 285  $^{\circ}\text{C}$ . (b) Coolant flow rate variation to restore the temperature on its set point.

## Disturbance rejection

The main concern of the startup and operation for FTS is a fast increase in the reactor temperature due to releasing the huge heat of reaction. Hence, we tested the performance of the controller against the heat disturbance with considering a ramp increase in the bed temperature. At the beginning of FTS, when the catalyst is super active, and in absence of cooling system, the temperature rises quickly. The worse case scenario is when the bed temperature maintains ramping up with a constant rate until it reaches the adiabatic temperature of the reaction. The dynamic and steady state energy balance for FT reactor obtain the changing rate of reactor temperature and its adiabatic temperature, respectively (Eqns. 5.24, 5.23):

$$\frac{dT_b}{dt} + \left( \frac{\dot{m}_{mx} c_{p_{mx}}}{\alpha} \right) T_b = \frac{1}{\alpha} \left( \dot{n}_{CO} X_{CO} \Delta H_{FTS} + \dot{m}_{sg} c_{p_{sg}} T_{sg} \right) \quad (5.23)$$

$$T_{ad} = \frac{1}{\dot{m}_{mx} c_{p_{mx}}} \left( \dot{m}_{sg} c_{p_{sg}} T_{sg} + \dot{n}_{CO} X_{CO} \Delta H_{FTS} \right) \quad (5.24)$$

where  $T_{ad}$  is the adiabatic temperature in K,  $t$  is time in s,  $\dot{m}_{mx}$  is mass flow rate of hydrocarbon mixture,  $c_{p_{mx}}$  is heat capacity of mixture,  $\dot{m}_{sg}$  is the mass flow rate of the syngas feed ( $CO+H_2$ ),  $c_{p_{sg}}$  is heat capacity of syngas,  $T_{sg}$  is the temperature of the syngas feed to the reactor,  $\dot{n}_{CO}$  is the molar flow rate of carbon monoxide,  $X_{CO}$  is the conversion of carbon monoxide, and  $\alpha$  is the heat capacity of the solid-gas (Eqn. 5.3b) assuming that the gas phase in contact with catalyst is hydrocarbon mixture. Since the reactor is continuous,  $\dot{m}_{mx} = \dot{m}_{sg}$ . Furthermore,  $H_2/CO = 2$  as the syngas is the product of partial oxidation of methane [4]. We assumed that  $X_{CO} = 1$  to reach the maximum adiabatic temperature. We also approximated the properties of hydrocarbon mixture in FT product at 20 bar and 300 °C with that of n-pentane based on the theory of chain growth probability and hydrocarbon distribution [90]. The theoretical mass balance of the pilot GtL determined the flow rate of syngas and carbon monoxide at actual conditions, 20 bar and 300 °C (Table 5.11).

Table (5.11) Coefficients and constants of Eqns. 5.24 and 5.23.

| Spec, unit                                                                 | value      |
|----------------------------------------------------------------------------|------------|
| $\dot{m}_{\text{sg}}, \text{ kg s}^{-1}$                                   | 0.008      |
| $\dot{n}_{\text{CO}}, \text{ mol s}^{-1}$                                  | 0.24       |
| $c_{\text{psg}}$ at $300^\circ\text{C}$ , $\text{J kg}^{-1} \text{K}^{-1}$ | 1050 [256] |
| $\Delta H_{\text{rxn}}, \text{ J mol}^{-1} \text{K}^{-1}$                  | 165000     |
| $T_{\text{sg}}, \text{ K}$                                                 | 573        |

Considering the initial bed temperature equal to  $300^\circ\text{C}$  when the reaction starts, the analytical solution of Eqn. 5.23 is:

$$T_{\text{b}}(t) = 1205 [1 - 0.75 \exp(-0.001t)] \quad (5.25)$$

Solving equation 5.24 gives  $T_{\text{ad}} = 1205^\circ\text{C}$  which is equal to the result of Eqn. 5.25 at steady state ( $t$  approaches  $\infty$ ). Eqn. 5.25 was arranged so that it obtains the reactor temperature in  $^\circ\text{C}$  (Fig. 5.15).

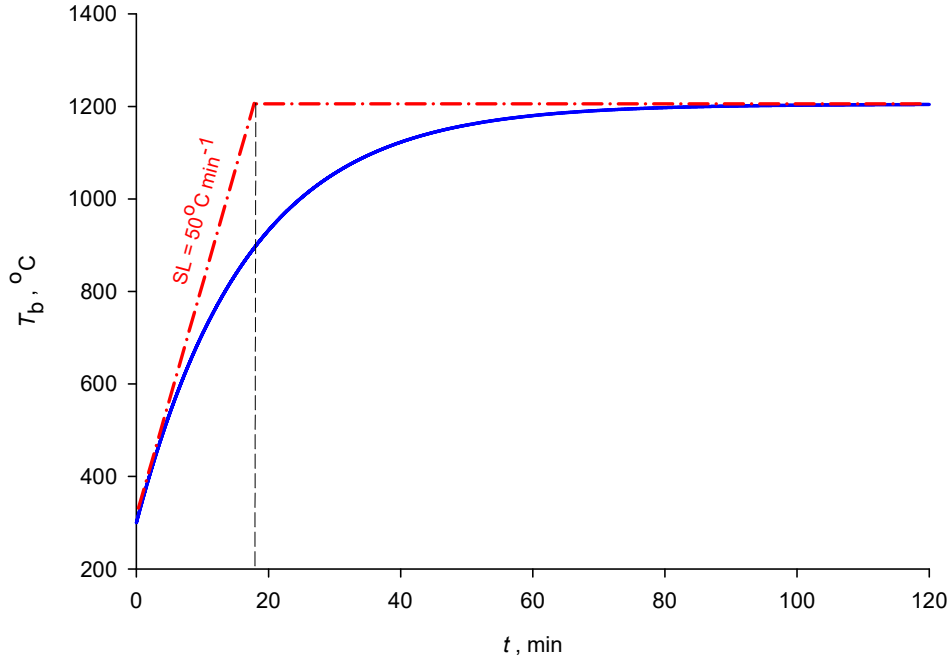
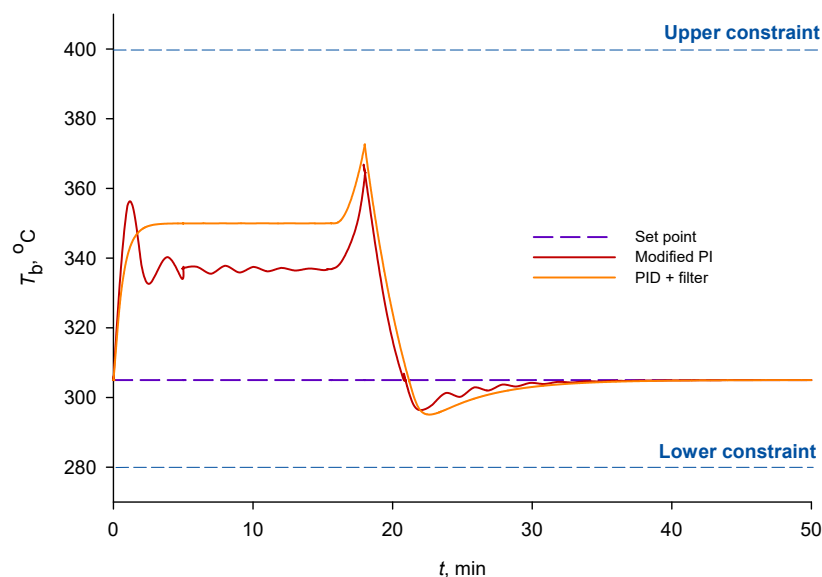
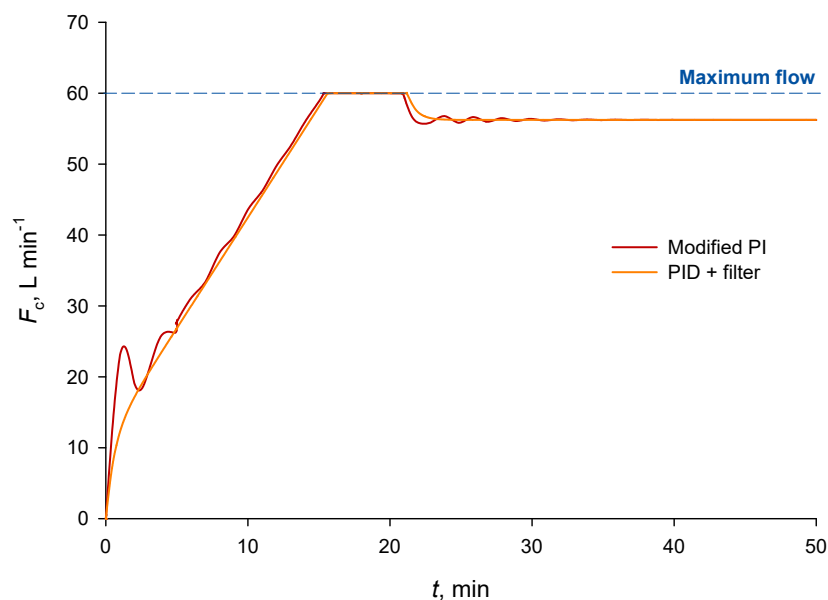


Figure (5.15) Temperature variation due to the disturbance of generating the heat of FT reaction in absence of cooling system. Solid line is the dynamics of adiabatic temperature at startup (Eqn. 5.25). Dash dot is the approximation of the reactor temperature's dynamics with a ramp function until it reaches its maximum adiabatic temperature, 1205 °C.  $SL$  is the slope of the ramp,  $50^{\circ}\text{C min}^{-1}$ .

This temperature is consistent with [50, 265]. Eqn. 5.24 also verifies that the adiabatic temperature depends to the syngas ratio and amount of the catalyst. To test the performance of the designed controller in terms of rejecting the heat generation disturbance, we defined a worst case scenario via approximating the dynamics of temperature increase (Eqn. 5.25) with a ramp function until it achieved the maximum adiabatic temperature at  $t = 18$  minute and then it stayed there (Fig. 5.15). Hence, we considered this temperature ramp up as a disturbance of the process. The upper and lower constraints on the bed temperature are the deactivation temperature of the catalyst [266] and minimum dry operation temperature [50], respectively. We also included the constraint of flow rate ( $60 \text{ L min}^{-1}$ ), according the capacity of the cooling water pump and control valve and applied the anti-reset windup method [164] so that the coolant remains within its limits.



(a)



(b)

Figure (5.16) Performance of the modified PI controller ‘red’ and PIDf ‘orange’ against a ramp disturbance in the temperature of the fluidized bed with double coil. For both controllers, the anti-reset windup technique is used to maintain the coolant flow within its feasible constraint. (a) Controller performance when the temperature ramps up  $+ 50^{\circ}\text{C min}^{-1}$  for 18 min and then stays at  $1205^{\circ}\text{C}$ . The upper constraint,  $400^{\circ}\text{C}$ , is the deactivation temperature of the catalyst. The lower constraint,  $280^{\circ}\text{C}$ , is the minimum required temperature for dry operation. (b) Coolant flow rate variation to re-adjust the temperature on its set point. The maximum flow rate is  $F_c = 60 \text{ L min}^{-1}$ .

Even though the PIDf gives a larger undershoot compared to the modified PI (Fig. 5.16b), it behaves smoothly to return the bed temperature to its set point. Hence, considering the responses of the controllers to the step change and disturbance, the PIDf had a better performance than the modified PI and was selected as a reliable preliminary controller for the FTS. A conservative startup is to run the FTS process with reducing the feed to lower than 15% of nominal capacity [267] and then involve the cooling system with controller in closed loop mode which brings the operation to a safe margin. Hence, the system stays away from the upper constraint on the catalyst temperature while ensuring that the maximum coolant flow rate is feasible.

## 5.6 Conclusion

We developed a safe mode experiment to investigate the cooling dynamics for an exothermic fluidized bed system and accordingly designed a temperature controller at the initial stage of the startup operation. We also studied the effect of system pressure and superficial velocity of the air as the main operating conditions on the heat exchange between the cooling coil and the hot bed. The results confirm that increasing the superficial gas velocity improves the mean overall heat transfer coefficient which assists the heat removal of the Fischer-Tropsch process while impact of pressure on the heat transfer is negligible. Comparing the single coil and double coil scenarios also reveals that the surface area of double coil is sufficient to handle the required cooling rate of FT reaction and it removes the excess heat faster than single coil. We also identified the parameters of the single and double coil scenarios with adopting the FOPTD model to the experimental data and designed a PI controller by serving IMC method for the later scenario since its cooling rate is more efficient. As the closed loop response of the PI controller is sluggish, we modified the PI by increasing its gain, also designed a PIDf and tested their performance separately for a step change and ramp-up disturbance in the bed temperature. Anti-reset windup method was also applied to include the constraint of the maximum coolant flow rate. Based on the results, not only does the PIDf controller lead to a faster cooling compared to the original PI, but it also has a smoother response to the temperature variations compared to the modified PI which makes it a reliable preliminary controller for the FTS operation. In this study, we ignored the effect of coil heat inertia since we had no temperature measure on the tube wall to verify the data. Moreover, all the analysis are based on average values. We also ignored the axial and radial temperature gradient through the bed which increases the uncertainties and errors in the data analysis. To estimate the instantaneous overall heat transfer coefficient,  $U_i$ , in the energy balance of the bed, we also ignored the effect of coil configuration which results in underestimating the

$U$ . Thus, the more precise technique is to install one or more thermocouples on the tube wall of both cooling coil, measuring online the wall temperatures and directly compute the convective heat transfer coefficient,  $h_b$ . To avoid phase change at the early stage of operation, water might be replaced with high-boiling fluids such as concentrated solution of ethylene glycol or DAW-therm oil.

## CHAPTER 6 GENERAL DISCUSSION

### 6.1 Risk assessment of micro-GtL plant

The flow chart of FMRD (Fig. 3.4), represents the FMRD steps and sequences. First, the P&ID of the process is called and the PHR goes with the direction of process flow until it approaches to the first device and its failure. The mean probability is computed from the failure frequency. Then, it recognizes the consequence of this failure and allocates a proper severity to it. Then the initial risk of scenario is estimated by equation 3.4. If the risk is within acceptable criteria ( $R \leq 0.5\%$ ), the scenario successfully passed the analysis, and it restarts for the next scenario. Otherwise, we need to add a proper safeguard which reduces the chance of severity of consequence and the new severity leads to recalculate the residual risk. The counter limit is 5 since the chance of severity can be reduced from 1 to 0 by maximum 5 levels. After considering the possible safeguards, if the residual risk is within the ‘acceptable with control’ criteria ( $R \leq 5\%$ ), it means the scenario already passed the assessment. If not so, the team leader should make the final decision to stop the procedure with the existing safeguards or recommend improving the process design in case of any possibilities. Amongst the nodes of the pilot plant, Fischer-Tropsch reactor has a notable place to discuss. The FT reactor and its cooling system are highlighted as Node 5 and Node 6, respectively (Fig. 3.7). One of the high-risk issues in FT reactor is the filter blockage with a high frequency of failure which results in high pressure inside the reactor and high pressure drop across the filter. To remove the risk and protect the reactor, we added the high-pressure alarm, high-high pressure safety interlock, and PSV, respectively. These safeguards finally reduce the chance of severity to zero and the residual risk goes to zero. Another issue which is not recognizable in classical HAZOP is the Failure of temperature transmitters of the reactor (FTL & FTH) which leads to high temperature and reactor damage. To deal with this issue, we added a temperature switch (thermostat) and cooling water control valve fully opens (SG-30, 23). All scenarios of FT reactor are indicated in table 3.13. Adding the safeguard only reduces the chance of severity of the consequence but has no impact on the failure frequency of equipment, instruments, or personnel’s mistake. The failure frequency varies with the uneven maintenance. The frequency data (table 3.6) are based on regular preventive maintenance (PM) of process devices and trained personnel.

## 6.2 Temperature Control

To test the performance of the designed controller in ASPEN Dynamics, we made the following procedure:

Having the parameters of the PI controller, we filled the values in the automatic sheet of the controller through the simulator environment, and then switched from the manual tab to automatic one just by clicking on its icon. After running the simulation in automatic (closed-loop mode) for 20 minutes, we stopped the run and changed the set point value and run it again. To test the performance of the controller against the disturbances, we run the simulation in automatic mode for 20 minutes. However this time we stopped the simulation and changed the flow rates or syngas ratio by varying the opening percentage of the feeding valves ( $V1 - V3$ ) and continue running (Fig. 4.4). To test the performance of the controller for the uncertainties in the kinetic model, we run the steady state simulation for the fractional kinetic model and exported it to the Aspen plus dynamics to run it in dynamic mode. Then we connected the PI controller with its original parameters that developed based on power law model and run the dynamic simulation in automatic mode. The dynamic response of the closed-loop system for step changes in the temperature set point reveals the successful performance of the controller in this scenario. Finally, to test the performance of the controller for heat transfer uncertainties, we changed the UA in the reactor sheet of Aspen plus dynamics and run the simulation in closed loop (automatic) mode with step changes in set point that explained earlier. The results represent that the controller is capable to properly readjust the temperature even if the heat transfer coefficient, UA is 20% underestimated. However, its performance is limited in case that UA is overestimated beyond 10% since the control valve gets saturated, fully open, and the bed temperature has offset from its set point. The experimental based controller is expected to perform properly around  $300^{\circ}\text{C}$  within its constraints since in the startup operation, we need to increase the bed temperature up to  $300^{\circ}\text{C}$  by heating tapes to initiate the reaction while the cooling system is not run yet. The power law kinetics in chapter 4, is valid within  $290^{\circ}\text{C}$  to  $310^{\circ}\text{C}$ . Hence, both theoretical and experimental controllers can work acceptably around the startup/ operating temperature,  $300^{\circ}\text{C}$ . The comparison between the dynamics of heat exchange in absence of FT reaction and that of actual condition reveals that the reaction significantly reduces the gain of the system. In other words, variation of bed temperature to coolant flow rate when the reaction is involved is lower compared to that in 'no reaction' case ( $|K| = 0.07^{\circ}\text{C min L}^{-1}$  with reaction and  $|K| = 16^{\circ}\text{C min L}^{-1}$  without reaction). Furthermore, the average overall heat transfer coefficient obtained from the experiment,  $U_m = 175 \text{ W m}^{-2} \text{ K}^{-1}$  is lower than the theoretical value in table 4.7,  $U = 610 \text{ W m}^{-2} \text{ K}^{-1}$  which increases the time constant of the system i.e.,

from 1 minutes to 4.2 minutes. These phenomena approve how the exothermic nature of the reaction and heat transfer impact on the dynamics of the bed temperature leading to design an appropriate controller. To sum up, the preference is using the theoretical PI controller to run the experiment since it considers both kinetics and hydrodynamic models which makes it more conservative than the experimental one to deal with the actual reaction. We recommend redesigning the cooling system by considering the experimental value of the overall heat transfer coefficient, simulate the process in chapter 4 with the new  $U$ , and re-evaluate the performance of the experimental PIDf controller with the new model (kinetics + modified heat transfer) in ASPEN Plus Dynamic.

### 6.3 Pilot plant Startup

The startup is a crucial step to run the process and experiment. The CPOX reaction takes place in a cyclic sequence. In order to avoid the explosion limit of methane / air mixture, first, methane (flare gas) enters the CPOX reactor with the flow rate of 10% of its nominal capacity and fills it while the furnace heats it up to reach  $800^{\circ}\text{C}$  required for starting the partial oxidation. It is purged at the outlet of CPOX to the flare. Then the air is injected to the reactor with the flow rate of 2.5 times that of methane while the furnace has been turned off. The syngas analyzer at CPOX outlet detects the composition of the product. As soon as the syngas ( $\text{CO}+\text{H}_2$ ) is produced and oxygen will get the lowest concentration, syngas is conducted to FT reactor. At this stage, heating tapes on FT reactor keep the bed temperature around  $300^{\circ}\text{C}$  so that hydrogen reduces the catalyst which takes couple of hours before the reaction begins. At this step, the cooling system is off to avoid quenching of the catalytic bed. Once the FTS starts and we monitor the first traces of  $\text{C}_5^{+}$  via gas chromatography, the cooling system will be running to remove the generated heat of reaction. The cooling control valve is initially opened at 10% and before bringing the cooling system in service, we run the closed-loop control with preliminary temperature controller. Once the temperature of the bed is stabilized on its set point,  $300^{\circ}\text{C}$ , we increase the feed flow rates and repeat this procedure step by step.

## CHAPTER 7 CONCLUSION

### 7.1 Summary of Works

#### 7.1.1 Risk Assessment of the Micro-GtL plant

We proposed a new structure on process safety and numerical risk analysis to recognize the potential hazardous scenarios of the micro-GtL pilot and prevent their happening. The advantage of this approach compare to available techniques is its simplicity to implement and to understand and also providing a clear image of risk before and after adding the safeguards or protection layers. This method gives an alter perspective to the process hazard review since it is founded on the failure mode methodology which is capable to recognize scenarios that are hidden in the classical deviation-wise HAZOP. Another notable advantage of this approach is that it avoids under- and over-estimating dangerous scenarios by quantifying their risk and assists the responsible team to make the final decision with enough confidence. We believe that this technique and its defined framework can be readily used in numerical risk assessment of other chemical plants regardless of their size and complexity. Based on this research, we prepared a process hazard review for the mobile MRU and equipped the system with required safeguards.

#### 7.1.2 Feedback Control Strategy of Fischer-Tropsch

Even though we considered sufficient logic and protective instruments, there was no guarantee on the proper operation of the Fischer-Tropsch reactor due to its strong exothermic nature. Because the generated heat of reaction extremely affects the bed temperature which results in the catalyst deterioration and reactor damage. Furthermore, Designing and tuning a temperature controller after running the open loop Fischer-Tropsch process is critical. To ensure safe and stable operation, design a preliminary PI temperature controller based on simulation and available knowledge of the process prior to actual operation. We also tested the robustness of this controller for various disturbances and uncertainties in the kinetic and heat transfer parameters. This initial controller provides a baseline level of temperature regulation and safety. As the process unfolds and more data is gathered through experimentation and operation, the controller tuning can be refined and improved. This iterative approach allows for a gradual optimization of the control system, ultimately enhancing the efficiency and safety of the Fischer-Tropsch synthesis process over time.

### 7.1.3 Experimental Modeling of Heat Exchange for Control Design of a Fluidized Bed System

Due to uncertainties in the hydrodynamics and heat transfer during the cooling procedure particularly at the beginning of the operation, and to investigate the cooling capacity, we designed a safe-mode experiment to study the dynamics of the heat exchange between the fluidized bed and internal cooling coils. Finally we selected the best efficient cooling scenario and designed a temperature controller for it which could be served as the preliminary control strategy. We also concluded that increasing the working range of the coolant in the coil temperature improves the average overall heat transfer coefficient,  $U_m$ , and accordingly cooling efficiency which also favours the process in terms of preventing reaction disruption near the cooling coil.

To recapitulate, we believe that all these measures improve the performance of the Fischer-Tropsch process within the micro-GtL; minimize risk and loss, and contribute in the process development of the GtL technology to run the pilot plant safely.

## 7.2 Limitations

### 7.2.1 Process hazard review and risk assessment

In the Failure mode risk decision method (FMRD), lack of information about failure frequency of a few equipment and instruments may increase the uncertainties since we have to use the data of similar devices or situations to determine the failure probability. Another factor is the topology and climate variation which may affect the failure accuracy. Furthermore, in our methodology, the only parameter of consequence is its severity. Thus, to compute the residual risk we need to involve a hidden parameter called likelihood level of consequence in its severity after adding the safeguard which may create a bit challenge in this procedure.

### 7.2.2 Temperature control of Fischer-Tropsch process

To design an appropriate controller we have uncertainties on the kinetic models and hydrodynamics. In the literature, almost all the kinetic models are applicable on the limited range of operating conditions, in particular, temperature and flow regime. Also, insufficient knowledge about the interaction of hydrodynamics and heat transfer on the process kinetics increases the uncertainties. Moreover, the kinetic models are developed for the steady state conditions and cannot predict the process parameters such as heat generation or concentrations of chemicals at the startup and transient conditions. Consequently, the model-based

controller performs properly around the steady state point assuming that a disturbance or change in the set point varies the stable conditions of the process. Since the real catalyst was unavailable at the time of writing this manuscript, we were unable to run the real process and test the preliminary controller.

### 7.2.3 Dynamics of the heat exchange

The main limitation was simulating the actual operating conditions of FTs as an exothermic process because the heating tapes around the FT reactor provide low energy for the process, so we were not able to maintain the bed temperature high ( $250^{\circ}\text{C}$  -  $300^{\circ}\text{C}$ ) while the cooling system was running to study the heat exchange and cooling dynamics in this range. It also limited us to easily study the effect of the cooling flow variations on the response of the bed temperature. Further, these conditions slow down the test runs by decreasing the number of experiment per day since after finishing each run, it took around 10 h to recover the temperature to its steady state ( $300^{\circ}\text{C}$ ) and prepare it for the next run. Moreover, low pressure (3 bar) cooling water made some difficulties at the beginning of the startup since we were unable to track and interpret the heat transfer rate during the phase change. Although the air compressor delivers up to 30 bar, we could not run the experiment for pressures beyond 10 bar because the available flow meters are working on normal flow rate and cannot provide the same actual flow at higher pressures that we defined in the DOE. For example, four flow meters deliver in total  $180\text{ L min}^{-1}$  at 1 bar and  $273\text{ K}$  while running an experiment for  $5u_{mf}$  and  $10u_{mf}$  at 20 bar needs  $190\text{ L min}^{-1}$  and  $380\text{ L min}^{-1}$ , respectively.

## 7.3 Future Research

### 7.3.1 Safety and risk analysis of the process

- To improve the risk analysis, we can evaluate the other aspects of the severity numerically and scale them in their own category by using the same method for the cost of damage and involve them in the severity by taking the arithmetic average or assigning a weight factor to each and then take the average to reach the final severity. Although it adds more calculations, the results will be more accurate. Implementing the Macro in excel sheets also makes the results faster.
- We would also recommend to replace the severity with ‘apparent severity’ and explicitly involve the term ‘likelihood level’ into it to distinguish it from the failure probability and in case of estimating the residual risk, manipulate this term to vary the apparent severity accordingly.

### 7.3.2 Temperature control of FTS

- To modify the performance of the preliminary controller, we may replace the kinetic models with the one derived for the lab-scale FTS in our group and adopt the controller with that as the governing kinetics in the pilot-scale will be the same.
- The controller must be tested in practice simply by changing the set temperature and then its parameters be re-tuned by available closed-loop techniques such as overshoot method.
- To startup the actual FT process in safe mode, two ways are suggested [267]: Decreasing the syngas feed ratio ( $\text{H}_2/\text{CO}$ ) below 0.25 which completely removes the multiple steady states out of the feasible region, and reducing the feed mass flux at least 85%. Since, the syngas generation is at the upstream of FTS in the micro-refinery, setting up the syngas ratio is critical since it is CPOX that governs the ratio and it is difficult or impossible to reach this ratio from there considering the CPOX constraints. Hence, to rationally start-up the process, the simplest way is maintaining the low feed flow (0.1 nominal capacity) to provide the safe condition, so that we reach the target temperature by the automatic preliminary controlling the coolant flow and then we gradually (step-wise) increase the feed mass flow.

### 7.3.3 Thermal performance of the process in terms of cooling design and control

- Increasing the operating temperature of the coolant is highly recommended. It can be achieved in a closed loop circulation instead of taking the coolant back to the tank and using a high pressure pump with best efficient point (BEP) of  $45 \text{ L min}^{-1}$  to  $50 \text{ L min}^{-1}$  at minimum 10 bar for water or the so-called flow at 3 bar for cooling oil.
- For the actual operation of the FT process, we also recommend to improve the cooling capacity by replacing the air cooler with the higher capacity which is consistent to the enthalpy of the reaction per mole of CO ( $1.25 \times 75 \text{ kW}$  based on energy balance).
- Adding another flow meter with the capacity of  $180 \text{ L min}^{-1}$  calibrated for air is highly recommended not only for the high pressures up to 20 bar but also for the required capacity of the micro-GtL plant.
- Running the experiment with steam, instead of hot water, is also another alternative since operating temperature of the coolant increases and there is also a possibility to integrate the energy with generating the electricity in a small thermodynamic cycle.

## REFERENCES

- [1] D. A. Wood, C. Nwaoha, and B. F. Towler, “Gas-to-liquids (gtl): A review of an industry offering several routes for monetizing natural gas,” *Journal of Natural Gas Science and Engineering*, vol. 9, pp. 196–208, 2012.
- [2] M. Ostadi *et al.*, “Conceptual design of an autonomous once-through gas-to-liquid process—comparison between fixed bed and microchannel reactors,” *Fuel processing technology*, vol. 139, pp. 186–195, 2015.
- [3] S. Al-Sobhi and A. Elkamel, “Simulation and optimization of natural gas processing and production network consisting of lng, gtl, and methanol facilities,” *Journal of Natural Gas Science and Engineering*, vol. 23, pp. 500–508, 2015.
- [4] Z. Ma *et al.*, “A micro-refinery to reduce associated natural gas flaring,” *Sustainable cities and society*, vol. 27, pp. 116–121, 2016.
- [5] A. Acocella *et al.*, “System and market analysis of methanol production using compact engine reformers,” in *ASME 2014 8th International Conference on Energy Sustainability collocated with the ASME 2014 12th International Conference on Fuel Cell Science, Engineering and Technology*. American Society of Mechanical Engineers Digital Collection, 2014.
- [6] C. Grant, “7th world congress of chemical engineering: a review,” *Chemical Engineering Research and Design*, vol. 83, no. 12, pp. 1345–1360, 2005.
- [7] G. Pauletto *et al.*, “Techno economic analysis of a micro gas-to-liquid unit for associated natural gas conversion,” *Renewable and Sustainable Energy Reviews*, vol. 150, p. 111457, 2021.
- [8] M. Sudiro and A. Bertucco, “Production of synthetic gasoline and diesel fuel by alternative processes using natural gas and coal: Process simulation and optimization,” *Energy*, vol. 34, no. 12, pp. 2206–2214, 2009.
- [9] D. A. Crowl and Y.-D. Jo, “The hazards and risks of hydrogen,” *Journal of Loss Prevention in the Process Industries*, vol. 20, no. 2, pp. 158–164, 2007.
- [10] X. Zhang *et al.*, “Effect of the operation parameters on the fischer–tropsch synthesis in fluidized bed reactors,” *Chinese journal of chemical engineering*, vol. 26, no. 2, pp. 245–251, 2018.

- [11] O. P. Oladijo *et al.*, “High-temperature properties of metal matrix composites,” 2021.
- [12] J. Douin *et al.*, “Influence of the elastic stress relaxation on the microstructures and mechanical properties of metal–matrix composites,” *Composites Part A: Applied Science and Manufacturing*, vol. 33, no. 10, pp. 1397–1401, 2002.
- [13] M. Sharifian *et al.*, “Safety analysis and risk assessment of a micro-gtl plant,” *Journal of Loss Prevention in the Process Industries*, vol. 83, p. 105071, 2023.
- [14] T. Fleisch, R. Sills, and M. Briscoe, “A review of global gtl developments,” *journal of natural gas chemistry*, vol. 11, pp. 1–14, 2002.
- [15] T. Fleisch *et al.*, “Market led gtl: The oxygenate strategy,” in *Studies in Surface Science and Catalysis*. Elsevier, 2001, vol. 136, pp. 423–428.
- [16] J. A. Velasco *et al.*, “Gas to liquids: A technology for natural gas industrialization in bolivia,” *Journal of Natural Gas Science and Engineering*, vol. 2, no. 5, pp. 222–228, 2010.
- [17] T. J. Remans, G. Jenzer, and A. Hoek, “Gas-to-liquids,” *Handbook of Heterogeneous Catalysis: Online*, pp. 2994–3010, 2008.
- [18] B. Bao, M. M. El-Halwagi, and N. O. Elbashir, “Simulation, integration, and economic analysis of gas-to-liquid processes,” *Fuel Processing Technology*, vol. 91, no. 7, pp. 703–713, 2010.
- [19] L. Dong *et al.*, “Gtl or lng: which is the best way to monetize ‘stranded’ natural gas?” *Petroleum Science*, vol. 5, no. 4, pp. 388–394, 2008.
- [20] A. Steynberg, “Introduction to fischer-tropsch technology,” in *Studies in surface science and catalysis*. Elsevier, 2004, vol. 152, pp. 1–63.
- [21] K. Aasberg-Petersen *et al.*, “Synthesis gas production for ft synthesis,” in *Studies in surface science and catalysis*. Elsevier, 2004, vol. 152, pp. 258–405.
- [22] D. Wood and S. Mokhatab, “Gas monetization technologies remain tantalizingly on the brink,” *World oil*, vol. 229, no. 1, pp. 103–108, 2008.
- [23] J. Na *et al.*, “Optimal design and operation of fischer-tropsch microchannel reactor for pilot-scale compact gas-to-liquid process,” *Chemical Engineering and Processing-Process Intensification*, vol. 128, pp. 63–76, 2018.

- [24] J. A. Velasco *et al.*, “Synthesis gas production for gtl applications: Thermodynamic equilibrium approach and potential for carbon formation in a catalytic partial oxidation pre-reformer,” *Journal of Natural Gas Science and Engineering*, vol. 20, pp. 175–183, 2014.
- [25] E. F. Sousa-Aguiar, F. B. Noronha, and A. Faro Jr, “The main catalytic challenges in gtl (gas-to-liquids) processes,” *Catalysis Science & Technology*, vol. 1, no. 5, pp. 698–713, 2011.
- [26] J. R. Rostrup-Nielsen, “Natural gas: fuel or feedstock?” in *Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges, and Opportunities*. Springer, 2005, pp. 3–24.
- [27] —, “Steam reforming,” *Handbook of Heterogeneous Catalysis: Online*, pp. 2882–2905, 2008.
- [28] A. C. Vosloo, “Fischer–tropsch: a futuristic view,” *Fuel processing technology*, vol. 71, no. 1-3, pp. 149–155, 2001.
- [29] B. Albrecht, “Reactor modeling and process analysis for partial oxidation of natural gas,” *SMR*, vol. 750, no. 900, pp. 15–40, 2004.
- [30] L. Basini, “Issues in h<sub>2</sub> and synthesis gas technologies for refinery, gtl and small and distributed industrial needs,” *Catalysis Today*, vol. 106, no. 1-4, pp. 34–40, 2005.
- [31] J. R. Rostrup-Nielsen, J. Sehested, and J. K. Nørskov, “Hydrogen and synthesis gas by steam-and c<sub>02</sub> reforming,” *Advances in Catalysis*, vol. 47, pp. 65–139, 2002.
- [32] K. Aasberg-Petersen *et al.*, “Technologies for large-scale gas conversion,” *Applied Catalysis A: General*, vol. 221, no. 1-2, pp. 379–387, 2001.
- [33] K. J. Gabriel *et al.*, “Gas-to-liquid (gtl) technology: Targets for process design and water-energy nexus,” *Current Opinion in Chemical Engineering*, vol. 5, pp. 49–54, 2014.
- [34] R. J. Kee, C. Karakaya, and H. Zhu, “Process intensification in the catalytic conversion of natural gas to fuels and chemicals,” *Proceedings of the Combustion Institute*, vol. 36, no. 1, pp. 51–76, 2017.
- [35] D. Wilhelm *et al.*, “Syngas production for gas-to-liquids applications: technologies, issues and outlook,” *Fuel processing technology*, vol. 71, no. 1-3, pp. 139–148, 2001.

- [36] S. Bharadwaj and L. Schmidt, "Catalytic partial oxidation of natural gas to syngas," *Fuel processing technology*, vol. 42, no. 2-3, pp. 109–127, 1995.
- [37] M. Peymani, S. M. Alavi, and M. Rezaei, "Preparation of highly active and stable nanostructured ni/ceo<sub>2</sub> catalysts for syngas production by partial oxidation of methane," *International Journal of Hydrogen Energy*, vol. 41, no. 15, pp. 6316–6325, 2016.
- [38] M. Khajenoori, M. Rezaei, and B. Nematollahi, "Preparation of noble metal nanocatalysts and their applications in catalytic partial oxidation of methane," *Journal of Industrial and Engineering Chemistry*, vol. 19, no. 3, pp. 981–986, 2013.
- [39] H. Arandiyani *et al.*, "Methane reforming to syngas over lanixfe<sub>1-x</sub>o<sub>3</sub> ( $0 \leq x \leq 1$ ) mixed-oxide perovskites in the presence of co<sub>2</sub> and o<sub>2</sub>," *Journal of Industrial and Engineering Chemistry*, vol. 18, no. 6, pp. 2103–2114, 2012.
- [40] C. Neagoe *et al.*, "Pt on fecralloy catalyses methane partial oxidation to syngas at high pressure," *Catalysis Today*, vol. 270, pp. 43–50, 2016.
- [41] Z. Ma *et al.*, "Partial oxidation of methane to syngas over pt/rh/mgo catalyst supported on fecralloy woven fibre," *The Canadian Journal of Chemical Engineering*, vol. 94, no. 4, pp. 642–649, 2016.
- [42] M. Hegarty, A. O'Connor, and J. Ross, "Syngas production from natural gas using zro<sub>2</sub>-supported metals," *Catalysis Today*, vol. 42, no. 3, pp. 225–232, 1998.
- [43] A. M. O'Connor and J. R. Ross, "The effect of o<sub>2</sub> addition on the carbon dioxide reforming of methane over pt/zro<sub>2</sub> catalysts," *Catalysis Today*, vol. 46, no. 2-3, pp. 203–210, 1998.
- [44] L. Mattos *et al.*, "Partial oxidation and co<sub>2</sub> reforming of methane on pt/al<sub>2</sub>o<sub>3</sub>, pt/zro<sub>2</sub>, and pt/ce–zro<sub>2</sub> catalysts," *Fuel Processing Technology*, vol. 83, no. 1-3, pp. 147–161, 2003.
- [45] F. B. Passos *et al.*, "Partial oxidation of methane to synthesis gas on pt/cexzr<sub>1-x</sub>o<sub>2</sub> catalysts: the effect of the support reducibility and of the metal dispersion on the stability of the catalysts," *Catalysis Today*, vol. 101, no. 1, pp. 23–30, 2005.
- [46] M. E. Dry, "The fischer–tropsch (ft) synthesis processes," *Handbook of Heterogeneous Catalysis: Online*, 2008.

- [47] B. H. Davis, "Fischer- tropsch synthesis: Comparison of performances of iron and cobalt catalysts," *Industrial & Engineering Chemistry Research*, vol. 46, no. 26, pp. 8938–8945, 2007.
- [48] C. Cao *et al.*, "Intensified fischer–tropsch synthesis process with microchannel catalytic reactors," *Catalysis Today*, vol. 140, no. 3-4, pp. 149–156, 2009.
- [49] M. E. Dry, "Practical and theoretical aspects of the catalytic fischer-tropsch process," *Applied Catalysis A: General*, vol. 138, no. 2, pp. 319–344, 1996.
- [50] S. Sie and R. Krishna, "Fundamentals and selection of advanced fischer–tropsch reactors," *Applied Catalysis A: General*, vol. 186, no. 1-2, pp. 55–70, 1999.
- [51] B. H. Davis, "Overview of reactors for liquid phase fischer–tropsch synthesis," *Catalysis Today*, vol. 71, no. 3-4, pp. 249–300, 2002.
- [52] D. J. Duvenhage and T. Shingles, "Synthol reactor technology development," *Catalysis Today*, vol. 71, no. 3-4, pp. 301–305, 2002.
- [53] A. N. Pour *et al.*, "Kinetics study of co hydrogenation on a precipitated iron catalyst," *Journal of Industrial and Engineering Chemistry*, vol. 18, no. 2, pp. 597–603, 2012.
- [54] S.-H. Kang *et al.*, "Catalytic performance on iron-based fischer–tropsch catalyst in fixed-bed and bubbling fluidized-bed reactor," *Applied Catalysis B: Environmental*, vol. 103, no. 1-2, pp. 169–180, 2011.
- [55] F. A. Fernandes and E. M. Sousa, "Fischer-tropsch synthesis product grade optimization in a fluidized bed reactor," *AIChE journal*, vol. 52, no. 8, pp. 2844–2850, 2006.
- [56] W. Chen *et al.*, "Recent advances in the investigation of nanoeffects of fischer-tropsch catalysts," *Catalysis Today*, vol. 311, pp. 8–22, 2018.
- [57] B. I. Kamara and J. Coetzee, "Overview of high-temperature fischer- tropsch gasoline and diesel quality," *Energy & Fuels*, vol. 23, no. 4, pp. 2242–2247, 2009.
- [58] E. Iglesia, S. C. Reyes, and R. J. Madon, "Transport-enhanced  $\alpha$ -olefin readsorption pathways in ru-catalyzed hydrocarbon synthesis," *Journal of Catalysis*, vol. 129, no. 1, pp. 238–256, 1991.
- [59] A. E. Abusrafa *et al.*, "Experimental verification of 2-dimensional computational fluid dynamics modeling of supercritical fluids fischer tropsch reactor bed," *Catalysis Today*, 2019.

- [60] S. Abelló and D. Montané, “Exploring iron-based multifunctional catalysts for fischer–tropsch synthesis: A review,” *ChemSusChem*, vol. 4, no. 11, pp. 1538–1556, 2011.
- [61] J. Chang *et al.*, “Kinetic modeling of fischer–tropsch synthesis over fe–cu–k–sio<sub>2</sub> catalyst in slurry phase reactor,” *Chemical Engineering Science*, vol. 62, no. 18-20, pp. 4983–4991, 2007.
- [62] G. A. Huff Jr and C. N. Satterfield, “Evidence for two chain growth probabilities on iron catalysts in the fischer–tropsch synthesis,” *Journal of Catalysis*, vol. 85, no. 2, pp. 370–379, 1984.
- [63] R. Madon and W. Taylor, “Fischer–tropsch synthesis on a precipitated iron catalyst,” *Journal of Catalysis*, vol. 69, no. 1, pp. 32–43, 1981.
- [64] W. Zimmerman, D. Bukur, and S. Ledakowicz, “Kinetic model of fischer–tropsch synthesis selectivity in the slurry phase,” *Chemical engineering science*, vol. 47, no. 9-11, pp. 2707–2712, 1992.
- [65] L. Nowicki, S. Ledakowicz, and D. B. Bukur, “Hydrocarbon selectivity model for the slurry phase fischer–tropsch synthesis on precipitated iron catalysts,” *Chemical engineering science*, vol. 56, no. 3, pp. 1175–1180, 2001.
- [66] H. Schulz and M. Claeys, “Kinetic modelling of fischer–tropsch product distributions,” *Applied Catalysis A: General*, vol. 186, no. 1-2, pp. 91–107, 1999.
- [67] G. P. van der Laan and A. A. Beenackers, “Hydrocarbon selectivity model for the gas-solid fischer–tropsch synthesis on precipitated iron catalysts,” *Industrial & engineering chemistry research*, vol. 38, no. 4, pp. 1277–1290, 1999.
- [68] J. Patzlaff *et al.*, “Studies on product distributions of iron and cobalt catalyzed fischer–tropsch synthesis,” *Applied Catalysis A: General*, vol. 186, no. 1-2, pp. 109–119, 1999.
- [69] —, “Interpretation and kinetic modeling of product distributions of cobalt catalyzed fischer–tropsch synthesis,” *Catalysis Today*, vol. 71, no. 3-4, pp. 381–394, 2002.
- [70] M. E. Dry, “Fischer–tropsch reactions and the environment,” *Applied Catalysis A: General*, vol. 189, no. 2, pp. 185–190, 1999.
- [71] D. Selvatico, A. Lanzini, and M. Santarelli, “Low temperature fischer–tropsch fuels from syngas: Kinetic modeling and process simulation of different plant configurations,” *Fuel*, vol. 186, pp. 544–560, 2016.

- [72] A. Razmjooie, H. Atashi, and F. Shahraki, "Analysis of the effective operating factors of fischer-tropsch synthesis; investigation of modeling and experimental data," *Journal of Natural Gas Science and Engineering*, vol. 40, pp. 72–78, 2017.
- [73] M. E. Dry, "The fischer-tropsch process: 1950–2000," *Catalysis today*, vol. 71, no. 3-4, pp. 227–241, 2002.
- [74] V. R. Ahón *et al.*, "Kinetic rates of the fischer tropsch synthesis on a co/nb2o5 catalyst," *Journal of natural gas chemistry*, vol. 15, no. 4, pp. 307–312, 2006.
- [75] A. N. Pour *et al.*, "Kinetics studies of nano-structured iron catalyst in fischer-tropsch synthesis," *Journal of Natural Gas Chemistry*, vol. 19, no. 4, pp. 441–445, 2010.
- [76] ———, "Deactivation studies of nano-structured iron catalyst in fischer-tropsch synthesis," *Journal of Natural Gas Chemistry*, vol. 19, no. 3, pp. 333–340, 2010.
- [77] D. B. Bukur, X. Lang, and L. Nowicki, "Comparative study of an iron fischer- tropsch catalyst performance in stirred tank slurry and fixed-bed reactors," *Industrial & Engineering Chemistry Research*, vol. 44, no. 16, pp. 6038–6044, 2005.
- [78] S.-H. Kang *et al.*, "Zsm-5 supported iron catalysts for fischer-tropsch production of light olefin," *Fuel Processing Technology*, vol. 91, no. 4, pp. 399–403, 2010.
- [79] A. Steynberg *et al.*, "High temperature fischer-tropsch synthesis in commercial practice," *Applied Catalysis A: General*, vol. 186, no. 1-2, pp. 41–54, 1999.
- [80] J.-S. Kim *et al.*, "Promotion of co 2 hydrogénation to hydrocarbons in three-phase catalytic (fe-cu-k-al) slurry reactors," *Korean Journal of Chemical Engineering*, vol. 20, no. 5, pp. 967–972, 2003.
- [81] Y. Kang *et al.*, "Particle flow behavior in three-phase fluidized beds," *Korean Journal of Chemical Engineering*, vol. 16, no. 6, pp. 784–788, 1999.
- [82] D. Glasser *et al.*, "Recent advances in understanding the fischer-tropsch synthesis (fts) reaction," *Current Opinion in Chemical Engineering*, vol. 1, no. 3, pp. 296–302, 2012.
- [83] M. E. Dry, "High quality diesel via the fischer-tropsch process—a review," *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, vol. 77, no. 1, pp. 43–50, 2002.
- [84] J. Xu, Y. Yang, and Y.-W. Li, "Fischer-tropsch synthesis process development: steps from fundamentals to industrial practices," *Current Opinion in Chemical Engineering*, vol. 2, no. 3, pp. 354–362, 2013.

- [85] V. Rao *et al.*, “Iron-based catalysts for slurry-phase fischer-tropsch process: Technology review,” *Fuel processing technology*, vol. 30, no. 1, pp. 83–107, 1992.
- [86] B. Jager and R. Espinoza, “Advances in low temperature fischer-tropsch synthesis,” in *Fuel and Energy Abstracts*, vol. 5, no. 36, 1995, p. 331.
- [87] T. Fu and Z. Li, “Review of recent development in co-based catalysts supported on carbon materials for fischer–tropsch synthesis,” *Chemical Engineering Science*, vol. 135, pp. 3–20, 2015.
- [88] C. I. Méndez and J. Ancheyta, “Kinetic models for fischer-tropsch synthesis for the production of clean fuels,” *Catalysis Today*, vol. 353, pp. 3–16, 2020.
- [89] M. E. Dry, “Advances in fishcher-tropsch chemistry,” *Industrial & Engineering Chemistry Product Research and Development*, vol. 15, no. 4, pp. 282–286, 1976.
- [90] E. S. Lox and G. F. Froment, “Kinetics of the fischer-tropsch reaction on a precipitated promoted iron catalyst. 2. kinetic modeling,” *Industrial & engineering chemistry research*, vol. 32, no. 1, pp. 71–82, 1993.
- [91] A. Jess, R. Popp, and K. Hedden, “Fischer–tropsch-synthesis with nitrogen-rich syngas: fundamentals and reactor design aspects,” *Applied Catalysis A: General*, vol. 186, no. 1-2, pp. 321–342, 1999.
- [92] J. Yang *et al.*, “Detailed kinetics of fischer- tropsch synthesis on an industrial fe- mn catalyst,” *Industrial & engineering chemistry research*, vol. 42, no. 21, pp. 5066–5090, 2003.
- [93] M. Rahmati, M. Mehdi, and M. Bargah-Soleimani, “Rate equations for the fischer-tropsch reaction on a promoted iron catalyst,” *The Canadian Journal of Chemical Engineering*, vol. 79, no. 5, pp. 800–804, 2001.
- [94] M. A. Marvast *et al.*, “Fischer-tropsch synthesis: Modeling and performance study for fe-hzsm5 bifunctional catalyst,” *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, vol. 28, no. 1, pp. 78–86, 2005.
- [95] G. P. Van der Laan and A. A. Beenackers, “Intrinsic kinetics of the gas–solid fischer–tropsch and water gas shift reactions over a precipitated iron catalyst,” *Applied Catalysis A: General*, vol. 193, no. 1-2, pp. 39–53, 2000.

- [96] F. A. Fernandes, “Polymerization kinetics of fischer-tropsch reaction on iron based catalysts and product grade optimization,” *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, vol. 28, no. 8, pp. 930–938, 2005.
- [97] P. Van Berge and R. Everson, “Cobalt as an alternative fischer-tropsch catalyst to iron for the production of middle distillates,” in *Studies in Surface Science and Catalysis*. Elsevier, 1997, vol. 107, pp. 207–212.
- [98] Y.-N. Wang *et al.*, “Kinetics modelling of fischer–tropsch synthesis over an industrial fe–cu–k catalyst,” *Fuel*, vol. 82, no. 2, pp. 195–213, 2003.
- [99] D. Kunii and O. Levenspiel, *Fluidization engineering*. Butterworth-Heinemann, 1991.
- [100] M. Menéndez *et al.*, “Experimental methods in chemical engineering: Reactors—fluidized beds,” *The Canadian Journal of Chemical Engineering*, vol. 97, no. 9, pp. 2383–2394, 2019.
- [101] A. Bérard, B. Blais, and G. S. Patience, “Residence time distribution in fluidized beds: diffusion, dispersion, and adsorption,” *Advanced Powder Technology*, vol. 32, no. 5, pp. 1677–1687, 2021.
- [102] G. S. Patience, *Experimental methods and instrumentation for chemical engineers*. Elsevier, 2017.
- [103] S. Fogler, *Elements of chemical reaction engineering, Fifth edit.* Prentice Hall International Series, 2016.
- [104] E. Georget *et al.*, “Residence time distributions in a modular micro reaction system,” *Journal of Food Engineering*, vol. 116, no. 4, pp. 910–919, 2013.
- [105] K. Abou Hweij and F. Azizi, “Hydrodynamics and residence time distribution of liquid flow in tubular reactors equipped with screen-type static mixers,” *Chemical engineering journal*, vol. 279, pp. 948–963, 2015.
- [106] L. Hua, J. Wang, and J. Li, “Cfd simulation of solids residence time distribution in a cfb riser,” *Chemical Engineering Science*, vol. 117, pp. 264–282, 2014.
- [107] M. J. Lorences *et al.*, “Fluid bed gas rtd: Effect of fines and internals,” *Powder technology*, vol. 168, no. 1, pp. 1–9, 2006.

- [108] O. Levenspiel and W. Smith, "Notes on the diffusion-type model for the longitudinal mixing of fluids in flow," *Chemical Engineering Science*, vol. 6, no. 4-5, pp. 227–235, 1957.
- [109] J. C. Gregory S. Patience, *Circulating fluidized beds: hydrodynamics and reactor modelling*. Ecole Polytechnique de Montreal, 1990.
- [110] S. Karimipour *et al.*, "Evaluation of heat transfer coefficient in gas–solid fluidized beds using cluster-based approach," *Powder technology*, vol. 172, no. 1, pp. 19–26, 2007.
- [111] J. Ngoh and E. W. C. Lim, "Effects of particle size and bubbling behavior on heat transfer in gas fluidized beds," *Applied Thermal Engineering*, vol. 105, pp. 225–242, 2016.
- [112] S. W. Kim and S. D. Kim, "Heat transfer characteristics in a pressurized fluidized bed of fine particles with immersed horizontal tube bundle," *International Journal of Heat and Mass Transfer*, vol. 64, pp. 269–277, 2013.
- [113] N. Masoumifard *et al.*, "Investigation of heat transfer between a horizontal tube and gas–solid fluidized bed," *International Journal of Heat and Fluid Flow*, vol. 29, no. 5, pp. 1504–1511, 2008.
- [114] T. White, A. Mathur, and S. Saxena, "Effect of vertical boiler tube diameter on heat transfer coefficient in gas-fluidized beds," *Chem. Eng. J. (Lausanne); (Switzerland)*, vol. 32, no. 1, 1986.
- [115] J. Doherty *et al.*, "Heat transfer from immersed horizontal tubes of different diameter in a gas-fluidized bed," *Energy*, vol. 11, no. 8, pp. 773–783, 1986.
- [116] L. Cheng *et al.*, "Heat transfer in circulating fluidized bed and its modeling," American Society of Mechanical Engineers, New York, NY (United States), Tech. Rep., 1995.
- [117] R. Sundaresan and A. K. Kolar, "Core heat transfer studies in a circulating fluidized bed," *Powder technology*, vol. 124, no. 1-2, pp. 138–151, 2002.
- [118] H. Taofeeq and M. Al-Dahhan, "Heat transfer and hydrodynamics in a gas-solid fluidized bed with vertical immersed internals," *International Journal of Heat and Mass Transfer*, vol. 122, pp. 229–251, 2018.
- [119] A. Y. Looi, Q.-M. Mao, and M. Rhodes, "Experimental study of pressurized gas-fluidized bed heat transfer," *International journal of heat and mass transfer*, vol. 45, no. 2, pp. 255–265, 2002.

- [120] D. Pence, D. Beasley, and R. Figliola, "Heat transfer and surface renewal dynamics in gas-fluidized beds," 1994.
- [121] A. Blaszczyk, M. Pogorzelec, and T. Shimizu, "Heat transfer characteristics in a large-scale bubbling fluidized bed with immersed horizontal tube bundles," *Energy*, vol. 162, pp. 10–19, 2018.
- [122] S. Rasouli, M. R. Golriz, and A. Hamidi, "Effect of annular fins on heat transfer of a horizontal immersed tube in bubbling fluidized beds," *Powder technology*, vol. 154, no. 1, pp. 9–13, 2005.
- [123] H. Taofeeq *et al.*, "Investigation of the effect of vertical immersed tube diameter on heat transfer in a gas-solid fluidized bed," *International Journal of Thermal Sciences*, vol. 135, pp. 546–558, 2019.
- [124] A. Stefanova *et al.*, "Heat transfer from immersed vertical tube in a fluidized bed of group a particles near the transition to the turbulent fluidization flow regime," *International Journal of Heat and Mass Transfer*, vol. 51, no. 7-8, pp. 2020–2028, 2008.
- [125] M. Leva and M. Grummer, "A correlation of solids turnovers in fluidized systems," *Chem. Eng. Prog.*, vol. 48, no. 6, pp. 307–313, 1952.
- [126] H. Vreedenberg, "Heat transfer between a fluidized bed and a horizontal tube," *Chemical engineering science*, vol. 9, no. 1, pp. 52–60, 1958.
- [127] B. Andeen and L. Glicksman, "Heat transfer to horizontal tubes in shallow fluidized beds," *ASME paper*, vol. 76, 1976.
- [128] V. Borodulya *et al.*, "Heat transfer between a surface and a fluidized bed: consideration of pressure and temperature effects," *International journal of heat and mass transfer*, vol. 34, no. 1, pp. 47–53, 1991.
- [129] O. Molerus, A. Burschka, and S. Dietz, "Particle migration at solid surfaces and heat transfer in bubbling fluidized beds—ii. prediction of heat transfer in bubbling fluidized beds," *Chemical Engineering Science*, vol. 50, no. 5, pp. 879–885, 1995.
- [130] J. Grace and D. Harrison, "The effect of internal baffles in fluidized beds: a guide to design," in *Inst. Chem. Eng. Symp. Ser.*, vol. 27, 1968, pp. 93–100.

- [131] S. Ramamoorthy and N. Subramanian, "Axial solids mixing and bubble characteristics in gas-fluidized beds with vertical internals," *The Chemical Engineering Journal*, vol. 22, no. 3, pp. 237–242, 1981.
- [132] M. Rudisuli *et al.*, "Radial bubble distribution in a fluidized bed with vertical tubes," *Industrial & engineering chemistry research*, vol. 51, no. 42, pp. 13 815–13 824, 2012.
- [133] M. Arabpour *et al.*, "Evaluation of maximum gasoline production of fischer–tropsch synthesis reactions in gtl technology: A discretized approach," *Journal of Natural Gas Science and Engineering*, vol. 9, pp. 209–219, 2012.
- [134] N. Park *et al.*, "Modeling of a pilot-scale fixed-bed reactor for iron-based fischer–tropsch synthesis: Two-dimensional approach for optimal tube diameter," *Fuel*, vol. 122, pp. 229–235, 2014.
- [135] A. Steynberg *et al.*, "Fischer-tropsch reactors," *Studies in surface science and catalysis*, vol. 152, pp. 64–195, 2004.
- [136] L. Dancuart, R. De Haan, and A. De Klerk, "Processing of primary fischer-tropsch products," in *Studies in Surface Science and Catalysis*. Elsevier, 2004, vol. 152, pp. 482–532.
- [137] A. de Klerk, "Fischer–tropsch refining: technology selection to match molecules," *Green Chemistry*, vol. 10, no. 12, pp. 1249–1279, 2008.
- [138] W. Pu *et al.*, "Inherent safety concept based proactive risk reduction strategies: A review," *Journal of Loss Prevention in the Process Industries*, p. 105133, 2023.
- [139] F. Khan, S. Rathnayaka, and S. Ahmed, "Methods and models in process safety and risk management: Past, present and future," *Process safety and environmental protection*, vol. 98, pp. 116–147, 2015.
- [140] F. J. Pawolocki, "Layer of protection analysis as auxiliary technique in process safety incident investigations," *Process Safety Progress*, vol. 40, pp. S13–S23, 2021.
- [141] M. T. Amin, F. Khan, and P. Amyotte, "A bibliometric review of process safety and risk analysis," *Process Safety and Environmental Protection*, vol. 126, pp. 366–381, 2019.
- [142] B. J. Seligmann *et al.*, "A blended hazard identification methodology to support process diagnosis," *Journal of Loss Prevention in the Process Industries*, vol. 25, no. 4, pp. 746–759, 2012.

- [143] K. Basak, "Process safety," in *Integration and Optimization of Unit Operations*. Elsevier, 2022, pp. 293–306.
- [144] E. A. Khan and S. R. Syeda, "Chemical substitution in processes for inherently safer design: pros and cons," *Pure and Applied Chemistry*, vol. 94, no. 7, pp. 889–899, 2022.
- [145] I. Cameron *et al.*, "Process hazard analysis, hazard identification and scenario definition: Are the conventional tools sufficient, or should and can we do much better?" *Process Safety and Environmental Protection*, vol. 110, pp. 53–70, 2017.
- [146] R. Perne, "Model-based control system for exothermic chemical reactions," *IFAC Proceedings Volumes*, vol. 23, no. 8, pp. 187–189, 1990.
- [147] J. Diaz-Salgado *et al.*, "Interlaced estimator-control design for continuous exothermic reactors with non-monotonic kinetics," *IFAC Proceedings Volumes*, vol. 40, no. 5, pp. 41–46, 2007.
- [148] I. Nájera, J. Álvarez, and R. Baratti, "Feedforward output-feedback control for a class of exothermic tubular reactors," *IFAC-PapersOnLine*, vol. 48, no. 8, pp. 1075–1080, 2015.
- [149] K. F. Jensen and W. H. Ray, "The bifurcation behavior of tubular reactors," *Chemical Engineering Science*, vol. 37, no. 2, pp. 199–222, 1982.
- [150] R. Caetano *et al.*, "Modeling and control of an exothermal reaction," *Chemical Engineering Journal*, vol. 238, pp. 93–99, 2014.
- [151] G. Karer, I. Škrjanc, and B. Zupančič, "Self-adaptive predictive functional control of the temperature in an exothermic batch reactor," *Chemical Engineering and Processing: Process Intensification*, vol. 47, no. 12, pp. 2379–2385, 2008.
- [152] A. Kummer, T. Varga, and L. Nagy, "Semi-batch reactor control with nmpc avoiding thermal runaway," *Computers & Chemical Engineering*, vol. 134, p. 106694, 2020.
- [153] J. Alvarez-Ramirez, J. Alvarez, and A. Morales, "An adaptive cascade control for a class of chemical reactors," *International Journal of Adaptive Control and Signal Processing*, vol. 16, no. 10, pp. 681–701, 2002.
- [154] W. L. Luyben, *Process modeling, simulation and control for chemical engineers*. McGraw-Hill Higher Education, 1989.

- [155] J. Diaz-Salgado *et al.*, “Feedforward output-feedback control for continuous exothermic reactors with isotonic kinetics,” *Journal of Process Control*, vol. 22, no. 1, pp. 303–320, 2012.
- [156] D. E. Seborg *et al.*, *Process dynamics and control*. John Wiley & Sons, 2010.
- [157] R. De, S. Bhartiya, and Y. Shastri, “Parameter estimation and optimal control of a batch transesterification reactor: An experimental study,” *Chemical Engineering Research and Design*, 2020.
- [158] M. Shamsuzzoha and S. Skogestad, “The setpoint overshoot method: A simple and fast closed-loop approach for pid tuning,” *Journal of Process control*, vol. 20, no. 10, pp. 1220–1234, 2010.
- [159] D. E. Rivera, M. Morari, and S. Skogestad, “Internal model control: Pid controller design,” *Industrial & engineering chemistry process design and development*, vol. 25, no. 1, pp. 252–265, 1986.
- [160] S. Skogestad, “Simple analytic rules for model reduction and pid controller tuning,” *Journal of process control*, vol. 13, no. 4, pp. 291–309, 2003.
- [161] J. G. Ziegler, N. B. Nichols *et al.*, “Optimum settings for automatic controllers,” *trans. ASME*, vol. 64, no. 11, 1942.
- [162] B. D. Tyreus and W. L. Luyben, “Tuning pi controllers for integrator/dead time processes,” *Industrial & Engineering Chemistry Research*, vol. 31, no. 11, pp. 2625–2628, 1992.
- [163] B. W. Bequette, *Process control: modeling, design, and simulation*. Prentice Hall Professional, 2003.
- [164] G. C. Goodwin, S. F. Graebe, and M. E. Salgado, *Control System Design*. Prentice Hall, 2000.
- [165] D. C. Boffito and D. Fernandez Rivas, “Process intensification connects scales and disciplines towards sustainability,” *The Canadian Journal of Chemical Engineering*, vol. 98, no. 12, pp. 2489–2506, 2020.
- [166] J. Janošovský, J. Labovský, and L. Jelemensky, “Automated model-based hazop study in process hazard analysis,” *Chemical Engineering Transactions*, vol. 48, pp. 505–510, 2016.

- [167] A. López-Molina *et al.*, “A novel approach to identify hazards in non-conventional/intensified biofuels production processes,” *Chemical Engineering and Processing-Process Intensification*, vol. 157, p. 108139, 2020.
- [168] F. Crawley and B. Tyler, *Hazard Identification Methods*. IChemE, 2003.
- [169] Z. Labovská *et al.*, “Model-based hazard identification in multiphase chemical reactors,” *Journal of Loss Prevention in the Process Industries*, vol. 29, pp. 155–162, 2014.
- [170] P. Mocellin *et al.*, “Experimental methods in chemical engineering: Hazard and operability analysis—HAZOP,” *The Canadian Journal of Chemical Engineering*, 2022.
- [171] J. Dunj   *et al.*, “Hazard and operability (hazop) analysis. a literature review,” *Journal of hazardous materials*, vol. 173, no. 1-3, pp. 19–32, 2010.
- [172] J. Taylor, “Automated hazop revisited,” *Process Safety and Environmental Protection*, vol. 111, pp. 635–651, 2017.
- [173] P. Baybutt, “A critique of the hazard and operability (hazop) study,” *Journal of Loss Prevention in the Process Industries*, vol. 33, pp. 52–58, 2015.
- [174] D. Ego and R. MacGregor, “Improve your facility’s pha methodology: engage, motivate and challenge your process safety team,” *Hydrocarbon Processing*, vol. 83, no. 4, pp. 81–87, 2004.
- [175] R. J. MacGregor, “Assess hazards with process flow failure modes analysis,” *Chemical Engineering Progress*, vol. 109, no. 3, pp. 48–56, 2013.
- [176] R. MacGregor, “Results matter: Three case studies comparing and contrasting pffm and hazop pha reviews,” *Journal of Loss Prevention in the Process Industries*, vol. 49, pp. 266–279, 2017.
- [177] B. M. Ayyub, *Risk analysis in engineering and economics*. Chapman and Hall/CRC, 2003.
- [178] P. Marhavilas, “Risk estimation in the greek constructions’ worksites by using a quantitative assessment technique and statistical information of occupational accidents,” *Journal of Engineering Science and Technology Review*, vol. 2, no. 1, pp. 51–55, 2009.
- [179] P. K. Marhavilas and D. Koulouriotis, “A risk-estimation methodological framework using quantitative assessment techniques and real accidents’ data: Application in an aluminum extrusion industry,” *Journal of Loss Prevention in the Process Industries*, vol. 21, no. 6, pp. 596–603, 2008.

- [180] F. Henselwood and G. Phillips, "A matrix-based risk assessment approach for addressing linear hazards such as pipelines," *Journal of loss prevention in the process industries*, vol. 19, no. 5, pp. 433–441, 2006.
- [181] J. M. Woodruff, "Consequence and likelihood in risk estimation: A matter of balance in uk health and safety risk assessment practice," *Safety Science*, vol. 43, no. 5-6, pp. 345–353, 2005.
- [182] K. T. Kosmowski, "Functional safety concept for hazardous systems and new challenges," *Journal of Loss Prevention in the Process Industries*, vol. 19, no. 2-3, pp. 298–305, 2006.
- [183] M. M. Van der Voort *et al.*, "A quantitative risk assessment tool for the external safety of industrial plants with a dust explosion hazard," *Journal of Loss Prevention in the Process Industries*, vol. 20, no. 4-6, pp. 375–386, 2007.
- [184] V. Cozzani, G. Antonioni, and G. Spadoni, "Quantitative assessment of domino scenarios by a GIS-based software tool," *Journal of Loss Prevention in the process industries*, vol. 19, no. 5, pp. 463–477, 2006.
- [185] P. Trucco and M. Cavallin, "A quantitative approach to clinical risk assessment: the crea method," *Safety science*, vol. 44, no. 6, pp. 491–513, 2006.
- [186] E. R. Vaidogas, "First step towards preventing losses due to mechanical damage from abnormal actions: Knowledge-based forecasting the actions," *Journal of Loss Prevention in the Process Industries*, vol. 19, no. 5, pp. 375–385, 2006.
- [187] S. Suddle and P. Waarts, *The safety of risk or the risk of safety?* AA Balkema Publishers; Swets & Zeitlinger, 2003.
- [188] S. Suddle, "The weighted risk analysis," *Safety Science*, vol. 47, no. 5, pp. 668–679, 2009.
- [189] P.-K. Marhavilas, D. Koulouriotis, and V. Gemeni, "Risk analysis and assessment methodologies in the work sites: On a review, classification and comparative study of the scientific literature of the period 2000–2009," *Journal of Loss Prevention in the Process Industries*, vol. 24, no. 5, pp. 477–523, 2011.
- [190] A. C. Torres-Echeverria, "On the use of LOPA and risk graphs for sil determination," *Journal of Loss Prevention in the Process Industries*, vol. 41, pp. 333–343, 2016.

- [191] W. Gulland, “Methods of determining safety integrity level (SIL) requirements-pros and cons,” in *Practical Elements of Safety: Proceedings of the Twelfth Safety-critical Systems Symposium, Birmingham, UK, 17–19 February 2004*. Springer, 2004, pp. 105–122.
- [192] C. De Salis, *Using Risk Graphs for SIL Assessment*. IChemE, 2011.
- [193] Z. Ma *et al.*, “Thermodynamically unconstrained forced concentration cycling of methane catalytic partial oxidation over CeO<sub>2</sub> fccr alloy catalysts,” *Chemical Engineering Journal*, vol. 380, p. 122470, 2020.
- [194] G. Pauletto *et al.*, “Ni/CeO<sub>2</sub> promoted ru and pt supported on fccr gauze for cycling methane catalytic partial oxidation—CPOX,” *Applied Catalysis B: Environmental*, vol. 286, p. 119849, 2021.
- [195] L. Huang *et al.*, “Assessment of flammability and explosion risks of natural gas-air mixtures at high pressure and high temperature,” *Fuel*, vol. 247, pp. 47–56, 2019.
- [196] G. Cui *et al.*, “Experimental study and theoretical calculation of flammability limits of methane/air mixture at elevated temperatures and pressures,” *Journal of Loss Prevention in the Process Industries*, vol. 41, pp. 252–258, 2016.
- [197] S. Haugwitz and P. Hagander, “Challenges in start-up control of a heat exchange reactor with exothermic reactions; a hybrid approach,” *IFAC Proceedings Volumes*, vol. 39, no. 5, pp. 185–190, 2006.
- [198] S. Mokhatab *et al.*, *Handbook of Liquefied Natural Gas*. Gulf Professional Publishing, 2013.
- [199] S. Jordan, H. Mitterhofer, and L. Jørgensen, “The interdiscursive appeal of risk matrices: Collective symbols, flexibility normalism and the interplay of ‘risk’ and ‘uncertainty’,” *Accounting, Organizations and Society*, vol. 67, pp. 34–55, 2018.
- [200] J. S. Arendt and D. K. Lorenzo, *Evaluating Process Safety in the Chemical Industry: A User’s Guide to Quantitative Risk Analysis*. John Wiley & Sons, 2010, vol. 3.
- [201] M. Najafi *et al.*, “Value of the lost load with consideration of the failure probability,” *Ain Shams Engineering Journal*, vol. 12, no. 1, pp. 659–663, 2021.
- [202] R. Billinton and R. N. Allan, *Reliability Evaluation of Engineering Systems*. Springer, 1992.

- [203] C. for Chemical Process Safety (CCPS), *Guidelines for Risk Based Process Safety*. John Wiley & Sons, 2010.
- [204] A. S. Markowski and M. S. Mannan, “Fuzzy risk matrix,” *Journal of Hazardous Materials*, vol. 159, no. 1, pp. 152–157, 2008.
- [205] R. Green *et al.*, *Perry’s Chemical Engineers’ Handbook, Eighth Edition*. McGraw-Hill Education, 2008, no. v. 8, pt. 2008.
- [206] A. I. of Chemical Engineers. Center for Chemical Process Safety, *Guidelines for Hazard Evaluation Procedures*. American Institute of Chemical Engineers, 1985.
- [207] N. Boonthum, U. Mulalee, and T. Srinophakun, “A systematic formulation for HAZOP analysis based on structural model,” *Reliability Engineering & System Safety*, vol. 121, pp. 152–163, 2014.
- [208] K. Sano, Y. Koshiba, and H. Ohtani, “Risk assessment and risk reduction of an acrylonitrile production plant,” *Journal of Loss Prevention in the Process Industries*, vol. 63, p. 104015, 2020.
- [209] IOGP, *Risk assessment data directory—Process release frequencies*. London: The International Association of Oil & Gas Producers, 2019.
- [210] R. API, “581 risk-based inspection technology,” *Second Edition*, 2008.
- [211] R. Benintendi, *Process safety calculations*. Elsevier, 2021.
- [212] D. Macdonald, *Practical hazops, trips and alarms*. Elsevier, 2004.
- [213] G. S. Patience and D. C. Boffito, “Distributed production: Scale-up vs experience,” *Journal of Advanced Manufacturing and Processing*, vol. 2, no. 2, p. e10039, 2020.
- [214] M. H. Rafiq *et al.*, “Experimental studies and modeling of a fixed bed reactor for Fischer–Tropsch synthesis using biosyngas,” *Fuel Processing Technology*, vol. 92, no. 5, pp. 893–907, 2011.
- [215] B. Kaskes *et al.*, “Numerical optimization of a structured tubular reactor for Fischer–Tropsch synthesis,” *Chemical Engineering Journal*, vol. 283, pp. 1465–1483, 2016.
- [216] S.-H. Kwack *et al.*, “Reaction modeling on the phosphorous-treated Ru/Co/Zr/SiO<sub>2</sub> Fischer–Tropsch catalyst with the estimation of kinetic parameters and hydrocarbon distribution,” *Fuel*, vol. 90, no. 4, pp. 1383–1394, 2011.

- [217] C. I. Méndez, J. Ancheyta, and F. Trejo, "Importance of proper hydrodynamics modelling in fixed-bed reactors: Fischer–Tropsch synthesis study case," *The Canadian Journal of Chemical Engineering*, vol. 97, no. 10, pp. 2685–2698, 2019.
- [218] D. F. Rivas *et al.*, "Process intensification education contributes to sustainable development goals. part 1," *Education for Chemical Engineers*, vol. 32, pp. 15–24, 2020.
- [219] K. V. K. Boodhoo *et al.*, "Bioprocess intensification: A route to efficient and sustainable biocatalytic transformations for the future," *Chemical Engineering and Processing - Process Intensification*, vol. 172, p. 108793, 2022.
- [220] E. S. Langer and R. A. Rader, "Continuous bioprocessing and perfusion: wider adoption coming as bioprocessing matures," *Bioprocess Journal*, vol. 13, no. 1, pp. 43–49, 2014.
- [221] B. Anne and K. Bommineni, "Dynamic Analysis of a CSTR using Aspen Dynamics," in *International Conference on Chemical, Environmental and Biological Sciences, Malaysia*, 2012.
- [222] C. I. Méndez and J. Ancheyta, "Modeling and control of a Fischer-Tropsch synthesis fixed-bed reactor with a novel mechanistic kinetic approach," *Chemical Engineering Journal*, vol. 390, p. 124489, 2020.
- [223] E. Pahija *et al.*, "Perspectives on the process intensification of CO<sub>2</sub> capture and utilization," *Chemical Engineering and Processing-Process Intensification*, vol. 176, p. 108958, 2022.
- [224] A. C. Dimian, C. S. Bildea, and A. A. Kiss, *Integrated Design and Simulation of Chemical Processes*. Elsevier, 2014.
- [225] W. L. Luyben, *Distillation Design and Control Using Aspen Simulation*. John Wiley & Sons, 2013.
- [226] S. A. Taqvi *et al.*, "Rigorous dynamic modelling and identification of distillation column using Aspen Plus," in *2017 IEEE 8th Control and System Graduate Research Colloquium (ICSGRC)*. IEEE, 2017, pp. 262–267.
- [227] W. L. Luyben, *Chemical reactor design and control*. John Wiley & Sons, 2007.
- [228] M. Rahimpour and H. Elekaei, "Optimization of a novel combination of fixed and fluidized-bed hydrogen-permselective membrane reactors for Fischer–Tropsch synthesis in GTL technology," *Chemical Engineering Journal*, vol. 152, no. 2-3, pp. 543–555, 2009.

- [229] H. Schulz, "Short history and present trends of Fischer–Tropsch synthesis," *Applied Catalysis A: General*, vol. 186, no. 1-2, pp. 3–12, 1999.
- [230] F. G. Botes, B. van Dyk, and C. McGregor, "The development of a macro kinetic model for a commercial Co/Pt/Al<sub>2</sub>O<sub>3</sub> Fischer–Tropsch catalyst," *Industrial & Engineering Chemistry Research*, vol. 48, no. 23, pp. 10 439–10 447, 2009.
- [231] Y. H. Kim *et al.*, "A simulation study on gas-to-liquid (natural gas to fischer–tropsch synthetic fuel) process optimization," *Chemical Engineering Journal*, vol. 155, no. 1-2, pp. 427–432, 2009.
- [232] W. H. Zimmerman and D. B. Bukur, "Reaction kinetics over iron catalysts used for the Fischer-Tropsch synthesis," *The Canadian Journal of Chemical Engineering*, vol. 68, no. 2, pp. 292–301, 1990.
- [233] A. Rafiee and M. Hillestad, "Staging of the Fischer–Tropsch reactor with an iron based catalyst," *Computers & Chemical Engineering*, vol. 39, pp. 75–83, 2012.
- [234] E. S. Lox and G. F. Froment, "Kinetics of the Fischer-Tropsch reaction on a precipitated promoted iron catalyst. 2. Kinetic modeling," *Industrial & Engineering Chemistry Research*, vol. 32, no. 1, pp. 71–82, 1993.
- [235] —, "Kinetics of the Fischer-Tropsch reaction on a precipitated promoted iron catalyst. 1. Experimental procedure and results," *Industrial & Engineering Chemistry Research*, vol. 32, no. 1, pp. 61–70, 1993.
- [236] N. Mostoufi, H. Cui, and J. Chaouki, "A comparison of two-and single-phase models for fluidized-bed reactors," *Industrial & Engineering Chemistry Research*, vol. 40, no. 23, pp. 5526–5532, 2001.
- [237] H. Cui, N. Mostoufi, and J. Chaouki, "Characterization of dynamic gas–solid distribution in fluidized beds," *Chemical Engineering Journal*, vol. 79, no. 2, pp. 133–143, 2000.
- [238] Y. Zhang and Q. Wei, "CPFD simulation of bed-to-wall heat transfer in a gas-solids bubbling fluidized bed with an immersed vertical tube," *Chemical Engineering and Processing: Process Intensification*, vol. 116, pp. 17–28, 2017.
- [239] Y. A. Cengel, S. Klein, and W. Beckman, *Heat Transfer: A Practical Approach*. WBC McGraw-Hill Boston, 1998, vol. 141.

- [240] API Standard 661, *Petroleum, Petrochemical, and Natural Gas Industries—Air-cooled Heat Exchangers*, 7th ed. American Petroleum Institute Washington DC (USA), 2013.
- [241] A. C. Dimian, C. S. Bildea, and A. A. Kiss, “Chapter 20 - equipment selection and design,” in *Integrated Design and Simulation of Chemical Processes*, ser. Computer Aided Chemical Engineering, A. C. Dimian, C. S. Bildea, and A. A. Kiss, Eds. Elsevier, 2014, vol. 35, pp. 757–788. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/B9780444627001000206>
- [242] M. Alizadeh *et al.*, “Modeling of fluidized bed reactor of ethylene polymerization,” *Chemical Engineering Journal*, vol. 97, no. 1, pp. 27–35, 2004.
- [243] M. B. Nikoo and N. Mahinpey, “Simulation of biomass gasification in fluidized bed reactor using ASPEN PLUS,” *Biomass and bioenergy*, vol. 32, no. 12, pp. 1245–1254, 2008.
- [244] R. Jafari, R. Sotudeh-Gharebagh, and N. Mostoufi, “Modular simulation of fluidized bed reactors,” *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, vol. 27, no. 2, pp. 123–129, 2004.
- [245] M. M. El-Halwagi and M. A. El-Rifai, “Mathematical modeling of catalytic fluidized-bed reactors—i. the multistage three-phase model,” *Chemical engineering science*, vol. 43, no. 9, pp. 2477–2486, 1988.
- [246] A. Ranjan, U. Mehta, and S. Saxena, “A comprehensive review of modified internal model control (imc) structures and their filters for unstable processes,” *Annual Reviews in Control*, 2023.
- [247] W. A. Poe and S. Mokhatab, *Modeling, control, and optimization of natural gas processing plants*. gulf professional publishing, 2016.
- [248] G. Pauletto *et al.*, “Short contact time CH<sub>4</sub> partial oxidation over Ni based catalyst at 1.5 MPa,” *Chemical Engineering Journal*, vol. 414, p. 128831, 2021.
- [249] A. Al-Douri, D. Sengupta, and M. M. El-Halwagi, “Shale gas monetization—a review of downstream processing to chemicals and fuels,” *Journal of Natural Gas Science and Engineering*, vol. 45, pp. 436–455, 2017.
- [250] S. D. Kim and Y. Kang, “Heat and mass transfer in three-phase fluidized-bed reactors—an overview,” *Chemical Engineering Science*, vol. 52, no. 21-22, pp. 3639–3660, 1997.

- [251] Z. W. Hasan *et al.*, “Experimental investigation on the impact of tube bundle designs on heat transfer coefficient in gas-solid fluidized bed reactor for Fischer-Tropsch synthesis,” *International Communications in Heat and Mass Transfer*, vol. 136, p. 106169, 2022.
- [252] F. Jiang *et al.*, “Heat-transfer performance and pressure drop in a gas-solid circulating fluidized bed spiral-plate heat exchanger,” *Applied Thermal Engineering*, vol. 171, p. 115091, 2020.
- [253] X. Wang and H. Si, “Novel concept of fluidized bed reactor design for highly efficient internal heat transfer,” *Industrial & Engineering Chemistry Research*, vol. 55, no. 34, pp. 9276–9283, 2016.
- [254] Y. Huang *et al.*, “Bed-to-tube heat transfer characteristics with an immersed horizontal tube in the pressurized fluidized bed at high temperature,” *International Communications in Heat and Mass Transfer*, vol. 124, p. 105270, 2021.
- [255] Y. Bai, J. Qi, and H. Si, “Analytical study on the heat-transfer characteristics of a fluidized bed reactor heated by multi-stage resistance,” *Chemical Engineering and Processing-Process Intensification*, vol. 164, p. 108395, 2021.
- [256] M. Doble, “Perry’s chemical engineers’ handbook,” *McGraw-Hil, New York, US*, 2007.
- [257] C. H. Bartholomew and R. J. Farrauto, *Fundamentals of industrial catalytic processes*. John Wiley & Sons, 2011.
- [258] V. Gnielinski, “New equations for heat and mass transfer in turbulent pipe and channel flow,” *International chemical engineering*, vol. 16, no. 2, pp. 359–367, 1976.
- [259] Y. A. Cengel, *Heat Transfer: A Practical Approach*. New York: WBC McGraw-Hill, 2002.
- [260] S. E. Haaland, *Simple and explicit formulas for the friction factor in turbulent pipe flow*. The American Society of Mechanical Engineers (ASME), 1983.
- [261] R. Verma and S. Saxena, “Heat transfer from an immersed vertical tube to a gas fluidized bed,” *Energy*, vol. 8, no. 12, pp. 909–925, 1983.
- [262] J. Klassen, P. Gishler, and A. Baerg, “Heat transfer in a fluidized solids bed,” *Canadian Journal of Research*, vol. 28, no. 8, pp. 287–307, 1950.
- [263] C. A. Smith and A. B. Corripio, *Principles and practices of automatic process control*. John wiley & sons, 2005.

- [264] D. E. Seborg *et al.*, *Process dynamics and control*. John Wiley & Sons, 2016.
- [265] X. Zhu *et al.*, “Study of radial heat transfer in a tubular fischer- tropsch synthesis reactor,” *Industrial & engineering chemistry research*, vol. 49, no. 21, pp. 10 682–10 688, 2010.
- [266] J. Zhang *et al.*, “Enhanced stability of a fused iron catalyst under realistic Fischer–Tropsch synthesis conditions: insights into the role of iron phases ( $\chi$ -Fe<sub>5</sub>C<sub>2</sub>,  $\theta$ -Fe<sub>3</sub>C and  $\alpha$ -Fe),” *Catalysis Science & Technology*, vol. 12, no. 13, pp. 4217–4227, 2022.
- [267] H.-S. Song *et al.*, “Operating strategies for fischer-tropsch reactors: A model-directed study,” *Korean Journal of Chemical Engineering*, vol. 21, pp. 308–317, 2004.

## APPENDIX A NOMENCLATURE FOR P&ID

### Equipment and instruments

- C : Compressor
- P : Pump
- M : Motor
- E : Heat exchanger / intercooler
- RC : Reactor
- PI : Pressure transducer
- PDI : Pressure differential transducer
- PG : Pressure gauge
- TI : Temperature transmitter of FT
- FI : Flow meter/gauge
- FIS : Flow indicator switch
- AI : Gas analyzer / detector
- R : Temperature transmitter of CPOX
- FE : Fire eye
- PE : Rupture disc
- PCV : Pressure regulator
- PSV : Pressure safety valve
- PV : Back pressure regulator
- MFC : Mass flow controller module
- FC : Flow controller

- TV : Temperature control valve
- S : Solenoid valve
- LEL : Lower explosion limit
- ESD : Emergency shut down
- PB : Push button
- H : High
- HH : High High

### **Pipeline**

- FHA : Filtered high pressure air
- PR : Process gas
- A : Air
- NG: Natural gas
- PA : Plant air
- CW : Cold water
- HW : Hot water
- V : Vent
- CS : Carbon steel
- N : No protection
- P : Personnel protection

### **Instrumentation symbols for P&ID**



PLC interlock



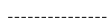
Local indicator / measurement



Transmitter / PLC interface



Pneumatic signal



Electronic signal

## APPENDIX B    NOMENCLATURE

- $A$ —heat transfer area of the coil,  $\text{m}^2$
- $Ar$ —Archimedes number, dimensionless
- $C_p$ —heat capacity,  $\text{kJ kg}^{-1} \text{K}^{-1}$
- $d_p$ —catalyst diameter,  $\text{m}$
- $D_C$ —coil diameter,  $\text{m}$
- $e$ —deviation of temperature variable from set point,  $^{\circ}\text{C}$
- $g$ —gravity,  $\text{m s}^{-2}$
- $G(s)_P$ —system transfer function for powerlaw mechanism
- $G(s)_L$ —system transfer function for LHHW mechanism
- $h$ —convective heat coefficient,  $\text{W m}^{-2} \text{K}^{-1}$
- $k_i$ —powerlaw pre-exponent factor of the rate constant,  $\text{mol/g/Pa}^{m+n}$
- $K_i$ —LHHW rate constant,  $\text{mol g}^{-1} \text{Pa}^{-1}$
- $k_i^0$ —LHHW pre-exponent of the rate constant,  $\text{mol g}^{-1} \text{Pa}^{-1}$
- $K_P$ —equilibrium constant rate of water gas shift
- $K$ —process gain
- $K_c$ —proportional constant of the PI controller
- $E_{a,i}$ —powerlaw activation energy,  $\text{kJ mol}^{-1}$
- $E_i$ —LHHW activation energy,  $\text{kJ mol}^{-1}$
- $F$ —flow rate,  $\text{mol h}^{-1}$
- $GHSV$ —gas hourly space velocity,  $\text{h}^{-1}$
- $\dot{m}$ —mass flow rate,  $\text{kg h}^{-1}$
- $P$ —pressure  $\text{kPa}$
- $P_i$ —partial pressure of component  $i$ ,  $\text{Pa}$
- $r_i$ —reaction rate,  $\text{mol g}^{-1} \text{s}^{-1}$
- $R_f$ —fouling resistance of the cooling side,  $\text{m}^2 \text{K W}^{-1}$

$Re$ —Reynolds number, dimensionless

$Nu$ —Nusselt number, dimensionless

$Pr$ —Prandtl number, dimensionless

$Q$ —Heat duty, W

$s$ —Laplace variable

$T$ —temperature, K

$t$ —time, min

$\tilde{t}$ —specified time in open-loop response, min

$u_0$ —superficial gas velocity,  $\text{m s}^{-1}$

$u_{\text{mf}}$ —minimum fluidization velocity,  $\text{m s}^{-1}$

$U$ —overall heat transfer coefficient,  $\text{W m}^{-2} \text{K}^{-1}$

$R$ —gas constant,  $8.314 \text{ J mol}^{-1} \text{K}^{-1}$

### **Greek Letters**

$\alpha$ —chain growth probability

$\gamma_{\text{FT}}$ —olefin to paraffin distribution ratio

$\delta$ —bubble phase fraction

$\theta$ —impulse dimensionless time

$\Delta T_{\text{lm}}$ —log mean temperature difference, K

$\varepsilon$ —void fraction, dimensionless

$\mu$ —viscosity,  $\text{kg m}^{-1} \text{s}^{-1}$

$\rho_{\text{g}}$ —gas density,  $\text{kg m}^{-3}$

$\rho_{\text{p}}$ —catalyst density,  $\text{kg m}^{-3}$

$\tau$ —time constant, min

$\tau_I$ —Integral time constant, min

$\varphi$ —time delay, min

$\eta$ —pulse injection length, dimensionless

### **Indices**

$b$ —bubble, bed

$c$ —cooling

$e$ —emulsion phase

$f$ —feed

$g$ —gas

$i$ —experiment number

$j$ —carbon number

$mf$ —minimum fluidization

$s$ —solid particles

$ss$ —steady state

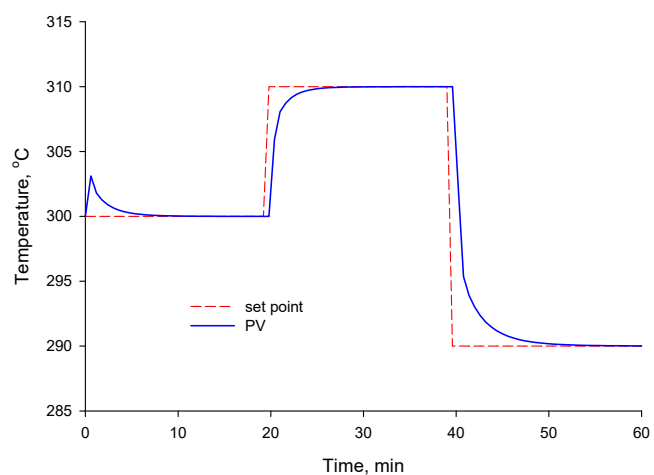
$t$ —total

$\infty$ —final value

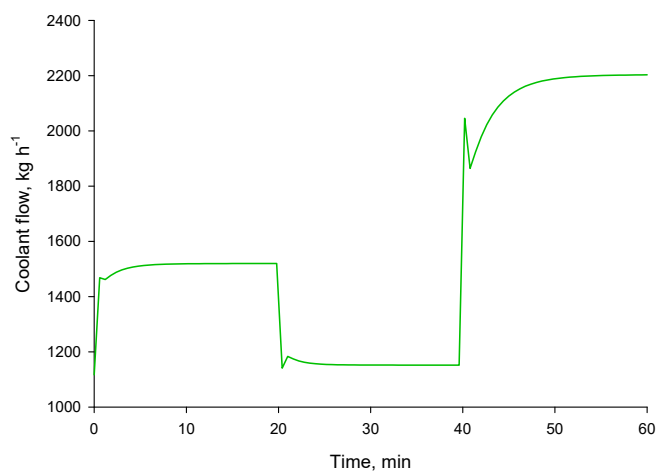
## APPENDIX C SUPPORTING DATA

### **Controller robustness for overestimating the ‘ $U$ ’**

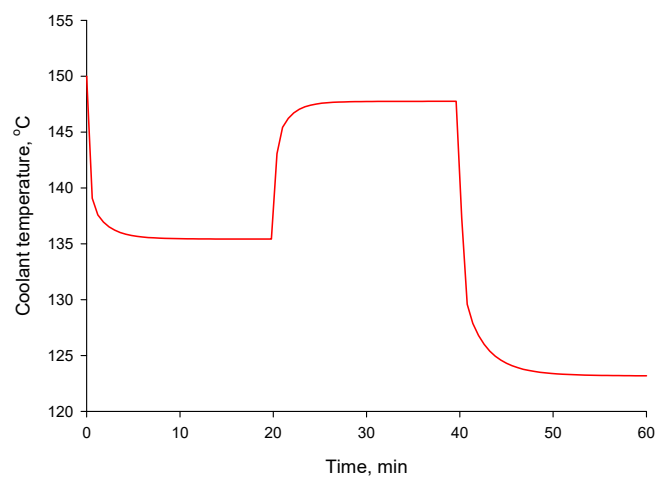
To ensure the robustness of the PI controller 4, we made a supplementary test in terms of overestimating the overall heat transfer coefficient. We tested the controller performance with changing the set point of the bed temperature when the actual  $U$  was 10% less than the estimated value in table 4.7 (Fig. C.1).



(a)



(b)



(c)

Figure (C.1) Closed loop response of the process against step change in set temperature for uncertainty of overall heat transfer coefficient, -10% increase in  $UA$ : (a) process temperature and set point value, (b) coolant flow rate, and (c) coolant temperature.

As expected, when the heat transfer coefficient decreases, the outlet temperature of the coolant drops and the corresponding approach temperature gets higher accordingly. We notice that if the  $U$  is considered less than 90% of its maximum, then to restore the temperature on the set point 290 °C, the controller completely opens the control valve resulting in reaching the upper limit of the cooling flow rate, 2200 kg h<sup>-1</sup> which consequently make offset even though the controller operates properly, because Aspen dynamics assumes that the control valve is 50% open at steady state conditions which is usually the normal criteria. In order to overcome this problem, considering the higher coolant flow rates is recommended.