

Numerical and Experimental Investigations of Thermally Coupled Catalytic Hydrogen Combustion - Reverse Water Gas Shift Reactor for CO₂ Conversion to Synthesis Gas

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

From technological, societal, and political perspectives, the optimization of energy utilization, reduction of CO₂ emissions, and mitigation of global environmental challenges have emerged as paramount concerns. In this study, a thermally coupled reactor that utilizes catalytic H₂ combustion (CHC) as an energy source to drive reverse water gas shift (RWGS) was designed. The lab-scale reactor with a shell-and-tube configuration was experimentally tested utilizing the inner (tube) compartment for CHC over Ni/Al₂O₃ and outer (shell) compartment for RWGS over Mo₂C/Al₂O₃. A maximum H₂ conversion of 88% for CHC was achieved, while RWGS compartment achieved 58% CO₂ conversion, with complete selectivity towards CO. The reactor was successfully operated for extended periods of time, with approximate 40 on/off cycles, totaling 400 h. It's also analyzed numerically using a two-dimensional pseudo-homogeneous model. Both experimental and numerical results demonstrated the feasibility of the reactor concept and emphasized the importance of thermal management. Further investigations were conducted to examine the effects of reactor geometric parameters, specifically the length-to-diameter and diameter-to-diameter ratios, as well as operating conditions such as space velocities and feed temperatures, providing insights into the reactor's thermal behavior and the interplay between key parameters and reactor performance. Consequently, these findings serve as a basis for future design optimizations for enhanced efficiency and performance.

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Dedication

I dedicate this thesis to

My father, Sun Kuisong.

And my mother, Tang Xiuxiang.

I could not have done this without them.

Table of Contents

Examining Committee Membership	ii
Author's Declaration	iii
Acknowledgements	v
Dedication	vi
List of Figures.....	x
List of Tables.....	xiii
Nomenclature	xiv
Chapter 1 Introduction.....	1
1.1 Background	1
1.2 Project objective.....	9
1.3 Thesis layout.....	10
Chapter 2 Literature review	12
2.1 Reverse water gas shift catalysis.....	12
2.1.1 Noble metal catalysts	12
2.1.2 Cu-based catalysts.....	15
2.1.3 Transition metal carbides catalysts	16
2.2 Reactor design	18
2.2.1 Experimental design	18
2.2.2 Reverse water gas shift reactor models and simulation studies.....	21
2.2.3 Thermally coupled reactor.....	26
Chapter 3 Lab-scale proof-of-concept reactor	29
3.1 Methodology	29
3.1.1 Conceptual design	29
3.1.2 Flow system setup	31
3.1.3 Reactor assembly	32
3.1.4 Reactor ignition.....	34
3.1.5 Reactor performance evaluation	35
3.2 Results and discussion	37
3.2.1 Catalytic performance evaluation	37

3.2.2	Reactor ignition	39
3.2.3	Effect of catalytic H ₂ combustion on the reactor performance	41
3.2.4	Near-stoichiometric catalytic H ₂ combustion feed	49
3.2.5	Reactor stability	51
Chapter 4 Modeling of thermally coupled reactor		54
4.1	Methodology	54
4.1.1	Reaction kinetics	54
4.1.2	Reactor configuration and dimensions	58
4.1.3	Reactor formulations	60
4.1.4	Transport parameters.....	65
4.1.5	Reactor performance	68
4.1.6	Numerical modelling.....	69
4.2	Results and discussion	70
4.2.1	Dynamic analysis and general performance.....	71
4.2.2	Effects of reactor geometric parameters (L/R _{RWGS} and R _{CHC} /R _{RWGS})..	84
4.2.3	Effects of space velocity of exothermic/endothermic streams.....	90
4.2.4	Effects of feed temperature of exothermic/endothermic streams.....	96
4.2.5	Analysis of reactor performance with respect to operating parameters 101	
4.2.6	Model validation.....	106
Chapter 5 Conclusions.....		108
5.1	Lab scale reactor	108
5.2	Reactor modeling	110
Bibliography		112
Appendix A Analytical instruments.....		118
Appendix B Reactor configurations		120
Appendix C Carbon balance derivation		123
Appendix D Explosion pressure and rate of pressure rise		124
Appendix E Supplementary experimental results		126
Appendix F Mass and heat transfer criteria.....		132
Appendix G Thermophysical properties.....		133

Appendix H Dimensionless numbers	135
Appendix I Dimensional model.....	137
Appendix J Parameter estimation and MATLAB scripts	139
Appendix K Non-distributed flow CHC-RWGS reactor MATLAB scripts and 2D CHC-RWGS reactor COMSOL model.....	149

List of Figures

Figure 1. Global risks ranked by severity over the long term (10 years) [1].	2
Figure 2. Breakdown of Canada's emission by GHG in 2021 [6].	3
Figure 3. Breakdown of Canada's emission by source in 2021 [6].	3
Figure 4. Reaction pathways of producing synthetic fuels and chemicals from CO ₂ [13].	5
Figure 5. Syngas derivatives with reference to their composition (* H ₂ /CO molar ratio) [21].	6
Figure 6. Electricity generation in Canada (2019) [28].	8
Figure 7. Configurations (a), picture and schematic diagram (b) of Zeolite membrane reactor for RWGS [68].	19
Figure 8. Schematic of setup and membrane reactor with ceramic-carbonate dual-phase membrane coupling of CO ₂ separation with RWGS [69].	20
Figure 9. Schematic diagram of the helium-heated RWGS reactor [72].	23
Figure 10. Schematic diagram of the RWGS membrane reactor [73].	25
Figure 11. Schematic diagram of the fixed-bed adsorptive reactor (a); the moving-bed adsorptive reactor (b).	26
Figure 12. A conceptual diagram for the coupled catalytic H ₂ combustion – reverse water gas shift system.	30
Figure 13. Flow system for reactor tests. Abbreviations: ADC – analog-to-digital converter, BPR – back pressure regulator, FM – flow meter, GC – gas chromatograph, HJ – heating jacket, IR – infrared analyzer, MFC – mass flow controller, OWV – one-way valve, PC – personal computer, PI – pressure indicator, PRV – pressure relief valve, PT – pressure transducer, RH – relative humidity sensor.	32
Figure 14. Reactor diagram showing locations of thermocouples (a) and pictures of the assembled reactor and reactor covered with the insulation layer and connected to the flow system (b).	34
Figure 15. Isothermal reaction tests for Ni/Al ₂ O ₃ (a) and Mo ₂ C/Al ₂ O ₃ (b,c) catalysts, showing H ₂ and O ₂ conversion vs. temperature (a), CO ₂ conversion and CO selectivity vs. temperature (b), and stability at 600 °C (c). Parameters: P = 1 bar, Q _f = 100/900 ml/min for H ₂ /air (a); P = 3 bar, H ₂ :CO ₂ = 3, GHSV = 60,000 ml/(g h) (b, c), T = 600 °C (c).	38
Figure 16. Typical profiles of the reactor ignition, showing transient temperatures in the catalytic bed (a), O ₂ and H ₂ conversion (b), reactor wall temperatures (c), and spatial temperature profiles for different points in time (d). Parameters: Q _{f,exo} = 230/400 ccm air/H ₂ , Q _{f,endo} = 2000 ml/min N ₂ , (after preheating).	41
Figure 17. The effect of the feed composition and flow rate in the catalytic H ₂ combustion compartment on the reactor temperature profiles. Parameters: air and H ₂ flow rates in the exothermic compartment are specified in the upper panel; Q _{f,endo} = 2000 mL/min N ₂ for t < 8.6 h, followed by a stepwise decrease to 600 mL/min N ₂ , with a step of 200 mL/min each 0.5 h.	44

Figure 18. The effect of heat generation in the catalytic H ₂ combustion compartment. Parameters: $Q_{f,endo} = 100/300$ mL/min CO ₂ /H ₂ , air and H ₂ flow rates in the exothermic compartment are specified in (b).	47
Figure 19. The effect of feed flow (CHC compartment) on the reactor temperatures and performance. Parameters: $Q_{f,endo} = 100/300$ ml/min CO ₂ /H ₂ , air and H ₂ flow rates are specified in (a).....	49
Figure 20. Reactor testing with near-stoichiometric catalytic H ₂ combustion feed. Parameters: $Q_{f,endo} = 100/300$ ccm CO ₂ /H ₂ , air and H ₂ flow rates are specified in (c).....	51
Figure 21. Reactor stability test. Parameters: $Q_{f,exo} = 230/400$ ml/min air/H ₂ , $Q_{f,endo} = 100/300$ ml/min CO ₂ /H ₂	53
Figure 22. Performance comparison between the simulation and experimental results in terms of CO ₂ and CO mole fraction over the range of temperatures (a) and space velocities (b). Parameters: $P = 3$ bar, GHSV = 60,000 mL/(g h) (a); $T = 600$ °C (b).	57
Figure 23. Performance comparison between the simulation and experimental results in terms of H ₂ and O ₂ mole fraction over the range of temperatures. Parameters: $P = 1$ bar, GHSV = 200,000 mL/(g h), H ₂ :air = 1:9	58
Figure 24. Schematic diagram of the thermally coupled reactor (a, b, c), and the locations of the cutline to visualize along the line (d).....	59
Figure 25. Typical profiles of the reactor ignition, introducing RWGS feed stream at $\tau = 2000$ and stabilization, showing transient temperatures in the catalytic bed (a), CO ₂ , H ₂ and O ₂ conversions (b) for three different points in time. Parameters: $y_{H_2}(CHC) = 0.20$, $P_{endo} = 5$ bar, $P_{exo} = 6$ bar, GHSV _{RWGS} = 500 L/(kg h), GHSV _{CHC} = 2000 L/(kg h), $T_f = 400$ °C, $T_0 = 300$ °C.	73
Figure 26. Typical profiles of the reactor ignition, introducing RWGS and stabilization, showing transient mole fractions in the RWGS compartment (a), and CHC compartment (b) for three different points in time. Parameters: $y_{H_2}(CHC) = 0.20$, $P_{endo} = 5$ bar, $P_{exo} = 6$ bar, GHSV _{RWGS} = 500 L/(kg h), GHSV _{CHC} = 2000 L/(kg h), $T_f = 400$ °C, $T_0 = 300$ °C. .	74
Figure 27. Dynamic reactor temperature profiles, introducing RWGS at $\tau = 2000$. Parameters: $y_{H_2}(CHC) = 0.08$, $P_{endo} = 4$ bar, $P_{exo} = 5$ bar, GHSV _{CHC} = 3,500 L/(kg h), GHSV _{RWGS} = 750 L/(kg h), $T_f = 400$ °C, $T_0 = 350$ °C.	76
Figure 28. Dynamic profiles of CO ₂ conversion in the RWGS compartment, introducing RWGS at $\tau = 2000$. Parameters: $y_{H_2}(CHC) = 0.08$, $P_{endo} = 4$ bar, $P_{exo} = 5$ bar, GHSV _{CHC} = 3,500 L/(kg h), GHSV _{RWGS} = 750 L/(kg h), $T_f = 400$ °C, $T_0 = 350$ °C.....	78
Figure 29. Dynamic profiles of H ₂ conversion in the CHC compartment, introducing RWGS at $\tau = 2000$. Parameters: $y_{H_2}(CHC) = 0.08$, $P_{endo} = 4$ bar, $P_{exo} = 5$ bar, GHSV _{CHC} = 3,500 L/(kg h), GHSV _{RWGS} = 750 L/(kg h), $T_f = 400$ °C, $T_0 = 350$ °C.....	79
Figure 30. Representative 3D steady state temperature (a), and conversion profiles (b and c). Parameters: $y_{H_2}(CHC) = 0.07$, $P_{endo} = P_{exo} = 5$ bar, GHSV _{RWGS} = 20 L/(kg h), GHSV _{CHC} = 100 L/(kg h), $T_f = T_0 = 300$ °C.	81
Figure 31. Representative 3D steady state mole fraction profiles in the RWGS	

compartment. Parameters: $y_{H_2(CHC)} = 0.07$, $P_{endo} = P_{exo} = 5$ bar, $GHSV_{RWGS} = 20$ L/(kg h), $GHSV_{CHC} = 100$ L/(kg h), $T_f = T_0 = 300$ °C.....	82
Figure 32. Representative steady state temperature (a), and conversion profiles(b) for three different points in radial direction. Parameters: $y_{H_2(CHC)} = 0.07$, $P_{endo} = P_{exo} = 5$ bar, $GHSV_{RWGS} = 20$ L/(kg h), $GHSV_{CHC} = 100$ L/(kg h), $T_f = T_0 = 300$ °C.	84
Figure 33. The effect of L/R_{RWGS} on the reactor performance and temperatures. Parameters: $y_{H_2(CHC)} = 0.14$, $P_{endo} = 1$ bar, $P_{exo} = 5$ bar, $GHSV_{CHC} = 7,000$ L/(kg h), $GHSV_{RWGS} = 10,000$ L/(kg h), $T_f = 430$ °C, $T_0 = 350$ °C.....	86
Figure 34. The effect of R_{CHC}/R_{RWGS} (R_1/R_2) on the reactor performance and temperatures. Parameters: $y_{H_2(CHC)} = 0.08$, $P_{endo} = 4$ bar, $P_{exo} = 5$ bar, $GHSV_{CHC} = 5,000$ L/(kg h), $GHSV_{RWGS} = 1,500$ L/(kg h), $T_f = 400$ °C, $T_0 = 350$ °C.....	89
Figure 35. The effect of space velocity in the CHC compartment on the reactor performance and temperatures. Parameters: $y_{H_2(CHC)} = 0.14$, $P_{endo} = 4$ bar, $P_{exo} = 5$ bar, $GHSV_{RWGS} = 1,500$ L/(kg h), $T_f = 400$ °C, $T_0 = 350$ °C.....	92
Figure 36. The effect of space velocity in the RWGS compartment on the reactor performance and temperatures. Parameters: $y_{H_2(CHC)} = 0.14$, $P_{endo} = 1$ bar, $P_{exo} = 5$ bar, $GHSV_{CHC} = 10,000$ L/(kg h), $T_f = 450$ °C, $T_0 = 350$ °C. $GHSV_{RWGS}$, L/(kg h), 1: 8,000; 2: 10,000; 3: 12,500; 4: 15,000; 5: 20,000; 6: 100,000.....	95
Figure 37. The effect of feed temperature in the CHC compartment on the reactor performance and temperatures. Parameters: $y_{H_2(CHC)} = 0.14$, $P_{endo} = 1$ bar, $P_{exo} = 5$ bar, $GHSV_{CHC} = 5,000$ L/(kg h), $GHSV_{RWGS} = 5,000$ L/(kg h), $T_{f,RWGS} = 400$ °C, $T_0 = 350$ °C. 1 - 6: 600 – 350 °C with a step of 50 °C.	98
Figure 38. The effect of feed temperature in the RWGS compartment on the reactor performance and temperatures. Parameters: $y_{H_2(CHC)} = 0.14$, $P_{endo} = 4$ bar, $P_{exo} = 5$ bar, $GHSV_{CHC} = 5,000$ L/(kg h), $GHSV_{RWGS} = 2,500$ L/(kg h), $T_{f,CHC} = 450$ °C, $T_0 = 350$ °C.	100
Figure 39. The effect of GHSVs on reactor maximum temperature (T_{max}), outlet temperature (T_{out}), and outlet conversions. Parameters: $y_{H_2(CHC)} = 0.14$, $P_{exo} = 5$ bar, $T_0 = 350$ °C. $GHSV_{RWGS} = 1,500$ L/(kg h), $P_{endo} = 4$ bar, $T_f = 400$ °C (a, b); $GHSV_{CHC} = 10,000$ L/(kg h), $P_{endo} = 1$ bar, $T_f = 450$ °C (c, d).....	102
Figure 40. The effect of feed temperatures on reactor maximum temperature (T_{max}), outlet temperature (T_{out}), and outlet conversions. Parameters: $y_{H_2(CHC)} = 0.14$, $P_{exo} = 5$ bar, $GHSV_{CHC} = 5,000$ L/(kg h), $T_0 = 350$ °C. $GHSV_{RWGS} = 1,500$ L/(kg h), $P_{endo} = 1$ bar, $T_{f,RWGS} = 450$ °C (a, b); $GHSV_{RWGS} = 2,500$ L/(kg h), $P_{endo} = 4$ bar, $T_{f,CHC} = 450$ °C (c, d).	105
Figure 41. Experimentally obtained and simulated reactor inlet, outlet and wall temperatures plotted versus dimensionless reactor length with single parameter fitting U_{WL} (a); $10*U_{WL}$ (b); $10*U_{WL}$ (c). Parameters: $y_{H_2(CHC)} = 0.37$, $P_{endo} = 1$ bar, $P_{exo} = 5$ bar, $T_0 = 400$ °C. $GHSV_{CHC} = 19,000$ L/(kg h), $T_{f,CHC} = 430$ °C, $GHSV_{RWGS} = 4,000$ L/(kg h), $T_{f,RWGS} = 400$ °C.....	107

List of Tables

Table 1. The estimated kinetic parameters of reverse water gas shift reaction.	56
Table 2. The estimated kinetic parameters of catalytic H ₂ combustion reaction.	57
Table 3. Reactor dimensions.	60
Table 4. Model formulation.	62
Table 5. Dimensionless variables, parameters and functions.	63
Table 6. Initial and boundary conditions.	64
Table 7. Effective thermal conductivity and diffusion coefficient.	67
Table 8. Mass and heat transfer criteria.	68
Table 9. Operating conditions.	71
Table 10. Simulated and experimentally obtained reactor performance.	106

Nomenclature

A^k	external surface area of reactor compartment k
A_j	pre-exponential of the rate coefficient of reaction j
B_i	pre-exponential of the adsorption enthalpy of species i
C_i	molar concentration of species i, mol/m ³
C_{Pg}	gas heat capacity, kJ/(mol K)
C_{Ps}	solid heat capacity, kJ/(kg K)
D_{ae}	effectivity axial diffusion coefficient, m ² /s.
D_{re}	effectivity radial diffusion coefficient, m ² /s.
D_e	effectivity diffusion coefficient, m ² /s.
D_m	diffusion coefficient, m ² /s.
d_p	particle diameter
d_w	reactor wall thickness, m
E_{aj}	activation energy for reaction j, kJ/mol
f_1	CO ₂ conversion to CO
f_2	CO ₂ conversion to CH ₄
f_j	dimensionless function of reaction j
F	molar flow rate, mol/s
$F_{C,f}$	feed molar flow rate of all carbon-containing species, mol/min
$F_{C,out}$	total outlet molar flow rate of carbon-containing species, mol/min
$F_{CH_4,out}$	outlet molar flow rate of CH ₄ , mol/min
$F_{CO,out}$	outlet molar flow rate of CO, mol/min
F_{CO_2}	CO ₂ molar flow rate, mol/min
$F_{CO_2,f}$	feed molar flow rate of CO ₂ , mol/min
$F_{H_2,f}$	feed molar flow rate of H ₂ , mol/min
F_{syngas}	syngas molar flow rate, mol/year
$F_{t,out}$	total outlet molar flow rate, mol/min
h	heat transfer coefficient, kJ/(m ² s K)

k_{ae}	effective axial thermal conductivity, kJ/(m s K)
k_{re}	effective radial thermal conductivity, kJ/(m s K)
k_e	effective thermal conductivity, kJ/(m s K)
k_c	mass transfer coefficient, m/s
k_{ins}	thermal conductivity of insulation layer, kJ/(m s K)
k_j	rate coefficient of reaction j
K_i	adsorption coefficient of specie i
$K_{eq,j}$	equilibrium constant of reaction j
L	reactor length, m
P_i	partial pressure of species i, bar
P_{input}	total power required, kW
P_t	reactor total pressure, bar
Q_f	volumetric feed flow rate
R	reactor radius, m
R_g	gas constant
R_j	rate of reaction j, mol/(kg s)
R_p	particle radius, m
R'_{obs}	observed reaction rate, mol/(kg s)
S	L/R ratio
S_{CO}	CO selectivity
t	time, s
T	temperature, K
T_a	ambient temperature, K
T_{feed}	feed temperature, °C
T_{in}	inlet temperature, °C
T_{out}	outlet temperature, °C
T_{hj}	heating jacket temperature, °C
T_w	wall temperature, °C
U_w	overall heat transfer coefficient, J/(m ² K s)

V^k	volume of a compartment k, m ³
v	fluid velocity, m/s
W_c	catalyst weight, kg
X_{CO_2}	CO ₂ conversion
y_i	mole fraction of species i
z	reactor length coordinate, m

Greek letters

α	H ₂ /CO ₂ ratio
α_{RWGS}	H ₂ /CO ₂ ratio in RWGS feed gas
α_{syngas}	H ₂ /CO ₂ ratio in syngas
α_i	stoichiometric coefficient of species i
$\Delta G_f(H_2O)$	standard Gibbs free energy of formation of water
ΔH_i	adsorption enthalpy of species i, kJ/mol
ΔH_j	reaction enthalpy of reaction j, kJ/mol
ε	catalyst bed porosity
η_e	electrolyzer efficiency
η_{HO}	hydrogen oxidation conversion and heat loss
η_p	process efficiency
θ	dimensionless temperature
λ_g	gas thermal conductivity, kJ/(m s K)
λ_s	solid thermal conductivity, kJ/(m s K)
λ_w	wall thermal conductivity, kJ/(m s K)
μ	viscosity, kg/(m s)
ρ_g	gas molar density, mol/m
ρ_s	solid density, kg/m ³
$\rho(C_p)_{eff}$	effective heat capacity, kJ/(m ³ K)
τ_s	tortuosity of the catalyst bed
τ	dimensionless time

Subscripts

<i>CHC</i>	catalytic hydrogen combustion
<i>eff</i>	effective
<i>endo</i>	endothermic
<i>exo</i>	exothermic
<i>f</i>	feed
<i>g</i>	gas
<i>HE</i>	heat exchange
<i>HL</i>	heat loss
<i>ins</i>	insulation
<i>s</i>	solid
<i>RWGS</i>	reverse water gas shift

Abbreviations

<i>ADC</i>	analog-to-digital converter
<i>BPR</i>	back pressure regulator
<i>CB</i>	carbon balance
<i>CCS</i>	carbon capture and storage/sequestration
<i>CCU</i>	carbon capture and utilization
<i>CHC</i>	catalytic hydrogen combustion
<i>FM</i>	flow meter
<i>GC</i>	gas chromatograph
<i>GHG</i>	greenhouse gas
<i>GRPS</i>	Global Risks Perceptions Survey
<i>GHSV</i>	gas hourly space velocity
<i>HJ</i>	heating jacket
<i>HO</i>	hydrogen oxidation
<i>IR</i>	infrared analyzer

<i>MDR</i>	methane dry reforming
<i>MFC</i>	mass flow controller
<i>MS</i>	methanol synthesis
<i>MSR</i>	methane steam reforming
<i>OWV</i>	one-way valve
<i>PC</i>	personal computer
<i>PI</i>	pressure indicator
<i>PRV</i>	pressure relief valve
<i>PT</i>	pressure transducer
<i>RH</i>	relative humidity sensor
<i>RME</i>	reverse microemulsion
<i>RWGS</i>	reverse water gas shift
<i>TMC</i>	transition metal carbides
<i>WEF</i>	World Economic Forum

Chapter 1 Introduction

1.1 Background

In early 2023, the World Economic Forum (WEF) released the Global Risks Perceptions Survey (GRPS), a comprehensive document that aggregated insights from more than 1,200 global risk experts, policymakers, and industry leaders. As depicted in Figure 1, the report ranked the ten most significant global risks for the next decade based on their degree of severity. Climate change, which threatens human existence, occupied the top four positions among the ten risks. Additionally, the sixth and tenth rankings issued a resounding warning to the entire human population that the environmental crisis can no longer be ignored [1]. The current environmental challenges represented by global climate change are primarily considered to arise from CO₂ emissions from the combustion of fossil fuels [2]. Despite the rapid growth of alternative and renewable energy sources, fossil fuels will remain the main source of energy for the coming decades [3]. With the increase in the world population, the corresponding demand for energy supply is expected to increase significantly [4]. In 2022, global CO₂ emissions from energy consumption and industrial processes grew by 0.9%, equivalent to 321 million tons (Mt), causing emissions to reach a new all-time high of 36.8 gigatons (Gt) [5]. The threat it poses upon the environment has led to increased efforts to reduce or minimize CO₂ atmospheric emissions.

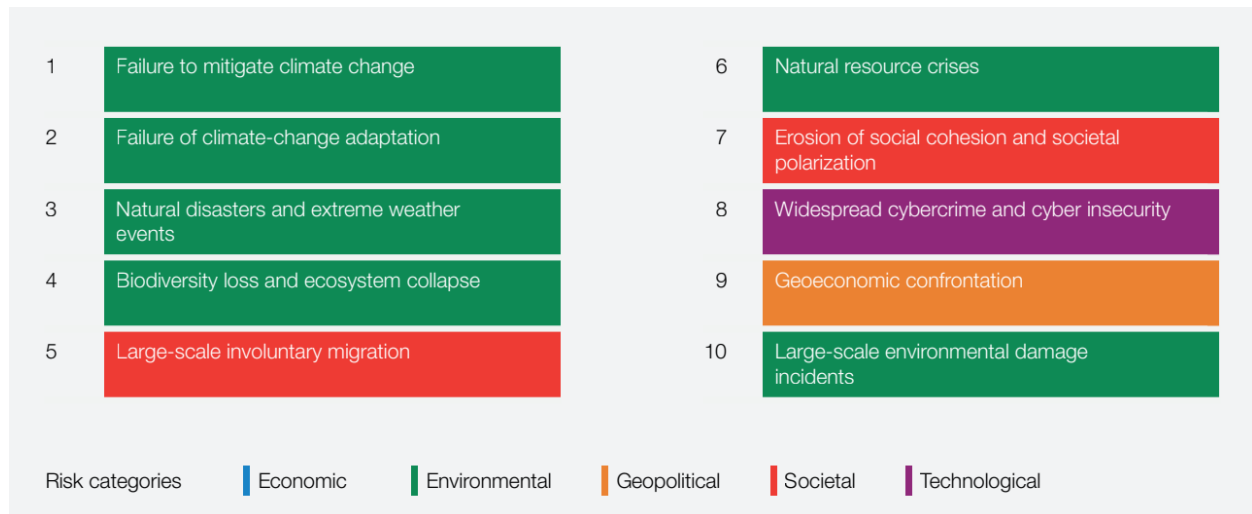


Figure 1. Global risks ranked by severity over the long term (10 years) [1].

Canada's emissions profile is similar to that of most industrialized countries, in that CO₂ is the largest contributor to total emissions, accounting for 80% of total emissions in 2021 as shown in Figure 2 [6]. The majority of the CO₂ emissions in Canada result from the combustion of fossil fuels. The energy - stationary combustion and transport emitted 45% and 28% of Canada's total GHG emissions separately while the waste and industrial processes emitted approximately 10.8% of Canada's total GHG emissions as illustrated in Figure 3 [6]. Efficient, economical and sustainable utilization of CO₂ waste as an important carbon resource is still a major challenge. Among the most widely used approaches to reduce CO₂ emissions is carbon capture and storage (CCS), also known as carbon capture and sequestration. CCS is a technology of capturing CO₂ emissions usually produced from large contributor sources, transporting the CO₂ captured to a storage site, and depositing and securely storing the CO₂ emissions [7]. Compared with other sources, such as energy - transport sources, it's feasible to capture CO₂ emissions from energy -

stationary combustion, waste and industrial processes sources.

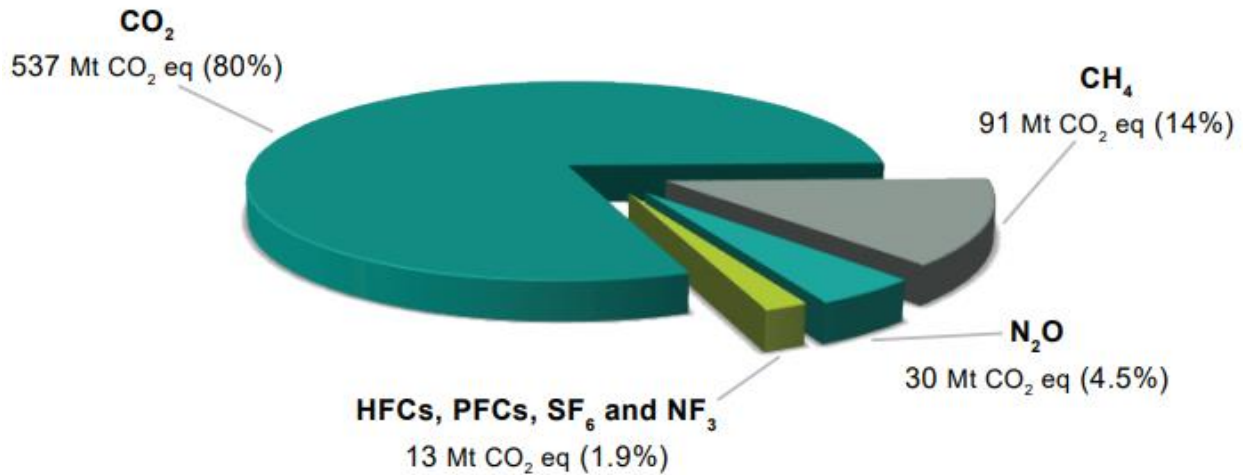


Figure 2. Breakdown of Canada's emission by GHG in 2021 [6].

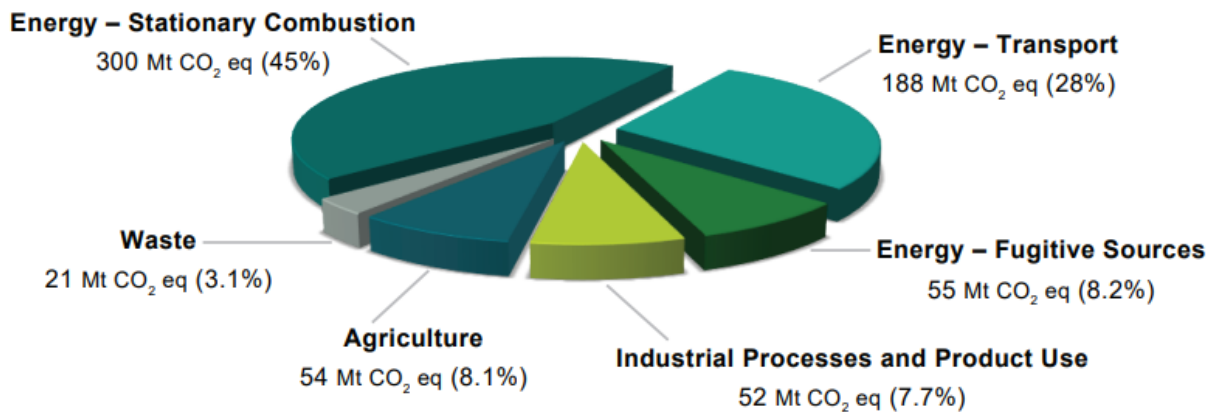


Figure 3. Breakdown of Canada's emission by source in 2021 [6].

Further deployment of CCS has been hampered by a variety of factors, including high costs, need for further technological progress, limited resources and a lack of strong regulatory signals [3]. Alternatively, CO₂ capture and utilization (CCU) has received tremendous attention as it is

regarded as an important and achievable technology to diminish anthropogenic carbon emissions. CO₂ capture is considered as an economical and feasible method to restrain carbon emission from industrial point sources [4]. Subsequent utilization of captured CO₂ into useful chemicals provides a solution to CO₂ emission control and enables CO₂ recycling into the chemical industry's production chain [8]. Additionally, the hydrogenation of captured CO₂ via renewable H₂ generation is of particular interest as this approach allows for the integration of renewable energy into the industry, which is of vital importance for mitigating global warming [9-11].

Optimizing the CO₂ conversion rate and minimizing the energy consumption are the primary challenges in developing novel CCU technologies [12]. The utilization of CO₂ for the synthesis of value-added chemicals has been investigated through various pathways, including electrochemical, thermocatalytic, photochemical, and biological approaches [13]. The implementation of CO₂ reduction pathways via photo and electrochemical methods has significant potential, but it is restrained by the low solubility of CO₂ in water and transport limitations [13-15]. The high costs involved in cultivating and maintaining biomass growth systems prevent the implementation of large-scale biofuel production [13]. Among these various utilization approaches, the thermocatalytic conversion of CO₂ is considered a viable approach due to its technical feasibility, considering its similarity to some well-established industrial processes [13, 16]. In addition, thermocatalytic conversion of CO₂ offers the benefits of fast reaction rates and high conversion efficiencies allowing for compact, high throughput operation. Various thermocatalytic routes allow for conversion of CO₂ into synthetic fuels and chemicals which are of large demand, as illustrated

in Figure 4 [13, 17]. Among them is syngas (synthesis gas), which is a mixture comprising of primarily H_2 and CO , and very often some CO_2 as well.

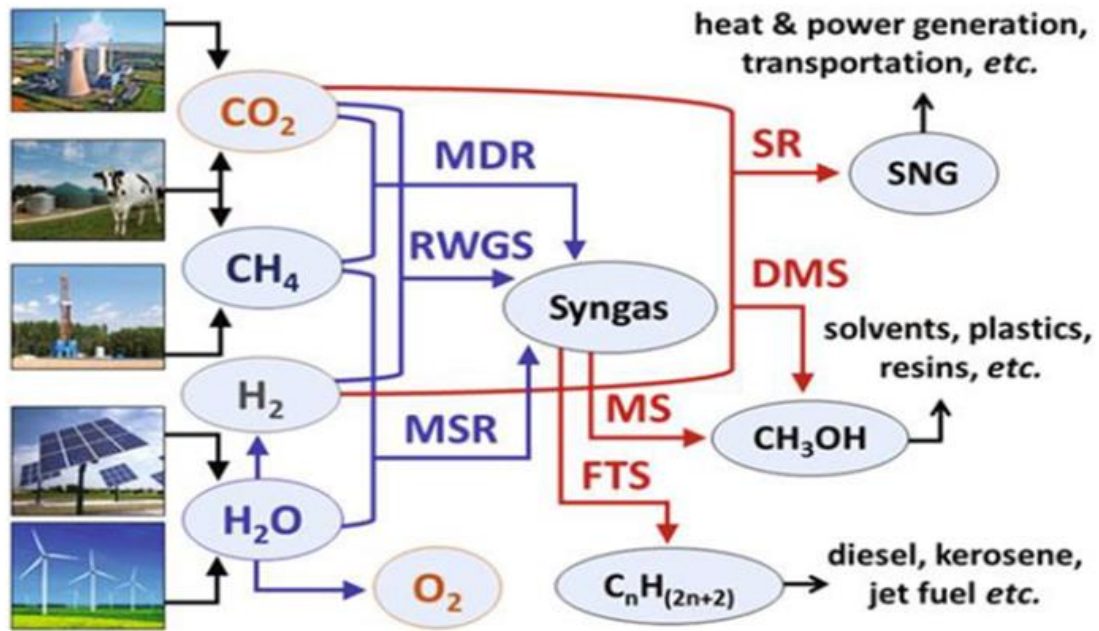
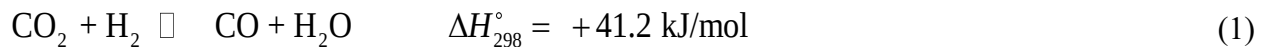


Figure 4. Reaction pathways of producing synthetic fuels and chemicals from CO_2 [13].

Syngas is commonly generated via methane steam reforming (MSR) [18] and gasification [19] but could be potentially produced by methane dry reforming (MDR) [20]. Reverse water gas shift (RWGS), Eq. (1), is another promising avenue for syngas generation.



There are multiple pathways for converting syngas into fuels and chemicals, depending on the syngas H_2/CO and operating conditions, as depicted in Figure 5 [21]. Syngas could be further converted into ethanol, methanol via methanol synthesis (MS). In addition, syngas could be used

to produce hydrogen and used for power generation. Notably, conversion of CO_2 to CO by RWGS followed by CO conversion to fuels with the Fischer-Tropsch process, which is well established and well characterized in current industry to produce chemicals and synthetic fuels from syngas ($\text{CO}+\text{H}_2$), had the highest current and estimated potential efficiency when CO_2 is captured from a flue gas or from the atmosphere [17, 22, 23]. RWGS is also of great interest to be used in space exploration due to high (95%) atmospheric CO_2 concentration on Mars and availability of H_2 as a by-product of oxygen generation [24, 25].

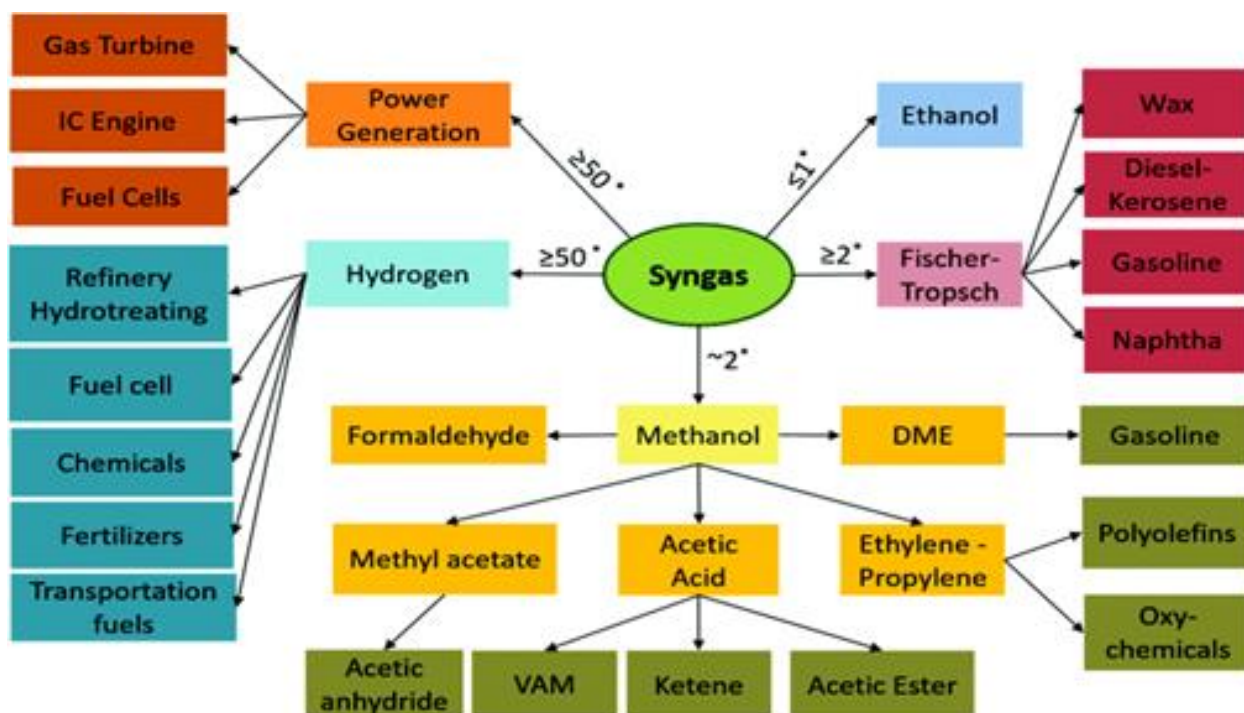
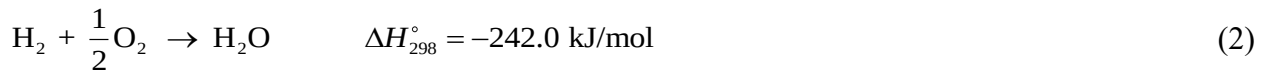


Figure 5. Syngas derivatives with reference to their composition (* H_2/CO molar ratio) [21].

To conduct the thermocatalytic hydrogenation reaction, it is necessary to produce H_2 . H_2 has been proposed as one of the most desirable and efficient energy carriers, which has the potential

to replace fossil fuels and significantly decrease greenhouse gas emissions [26, 27]. In comparison to conventional hydrogen-air combustion, catalytic hydrogen combustion (CHC), Eq. (2) achieves greater safety and efficiency as well as lower NO_x emissions. CHC is a total oxidation reaction that involves a heterogeneous catalyst, and it is highly suitable for flame avoidance. Only water vapor is produced from the reactor, which is accompanied by the release of a large amount of energy that can be utilized as a source of heat (to drive endothermic reactions).



The source of hydrogen can be versatile and cheaper sources can help reduce the overall production cost from CO₂ hydrogenation. Water electrolysis powered by renewable (or low-carbon footprint) sources can be a sustainable solution for H₂ production. Gasification of biomass is another potential solution to hydrogen source. The total electricity generation in Canada in 2019 is 632 TWh, and ~66% are from renewable sources which could be potentially utilized, Figure 6 [28]. In this approach, H₂ is first separated from H₂O using renewable or low-carbon footprint electricity and then used for CO₂ hydrogenation and catalytic H₂ combustion, creating a sustainable pathway for the generation of renewable synthetic fuels from CO₂. Importantly, intermittent renewable energy (wind and solar) can be stored as chemical energy using such processes. Ultimately, an artificial carbon cycle could be created by the large scale thermocatalytic conversion of CO₂ in combination with the utilization of renewable H₂, recycling the emitted CO₂ in energy distribution systems, while reducing the consumption of unsustainable (fossil) energy [29]. However, both reactor design and catalyst selection for such pathway still faces significant

technological challenges.

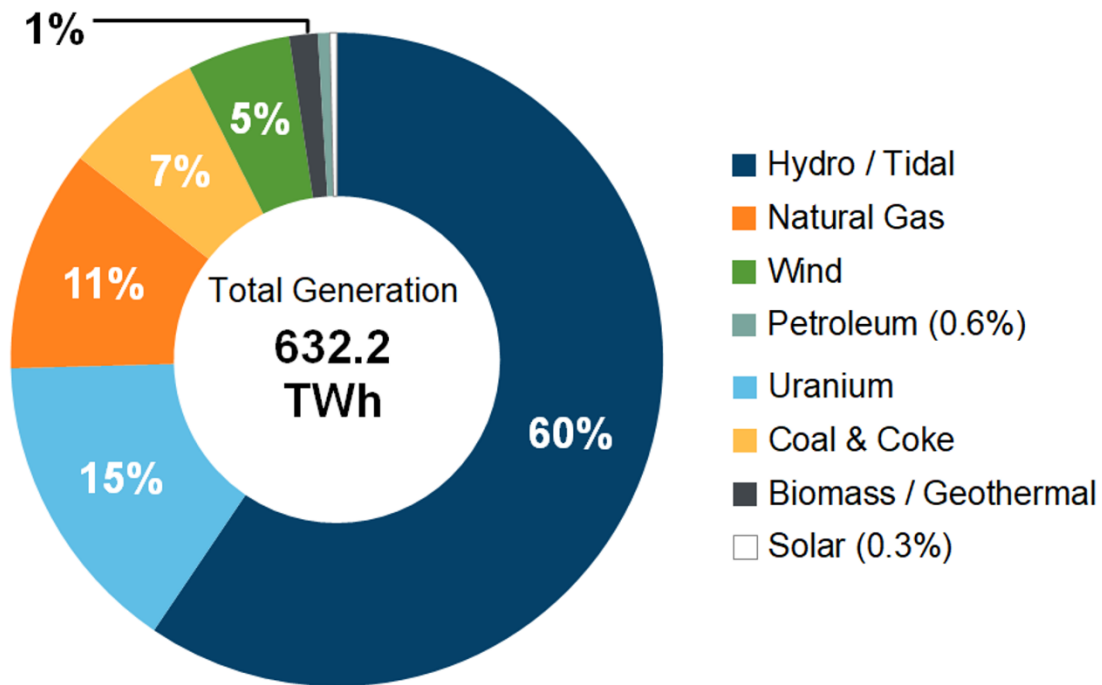


Figure 6. Electricity generation in Canada (2019) [28].

Multifunctional reactors, play the principal role in process integration, could achieve the goals of reducing energy and material consumption and mitigating environmental emissions by combining multiple processes [30, 31]. It also substantially reduces the size of equipment, leading to significant capital cost savings and improved intrinsic safety [32]. Multifunctional reactors which couple exothermic with endothermic reactions is proposed as a significant improvement in reactor performance and energy integration by optimizing the utilization of energy and materials [31]. One of the reactions is considered as heat source (exothermic reaction) for another reaction (endothermic reaction), as the endothermic reaction requires effective heat supply to the reaction

zone. Recuperative coupled reactors have received significant attention in literature [33-35]. These reactors operate by conducting two reactions simultaneously with a separating wall. Typically, recuperative coupled reactors consist of two vertical concentric tubes, with the exothermic reaction occurring on the inner tube side and the endothermic reaction on the outer tube side.

1.2 Project objective

Currently, there is a lack of literature on RWGS reactors, in particular experimental studies. The present study aims to address this research gap and fill this void in the literature related to the RWGS reactors by conducting both experimental and numerical investigations on a thermally coupled RWGS reactor. Through this research, our aim is to provide valuable insights into RWGS reactors and thermally coupled reactors, thereby providing a foundation for future research and practical applications.

The principal objective of this project is to construct, test and model a proof-of-concept lab-scale thermally coupled reactor that utilizes CHC as an energy source to drive RWGS for synthesis gas production from CO₂. The experimental studies focus on ignition tests and feasibility assessments while also investigating the effects of operating conditions on thermal behavior and reactor performance. Additionally, a reliable mathematical model is developed. The effects of geometric parameters and operating conditions are investigated numerically.

The specific research objectives are:

1. Constructing the lab-scale proof-of-concept thermally coupled CHC – RWGS reactor. Investigating the ignition, importance of CHC reaction, effect of operating conditions on reactor performance. Verifying the long-term stability.
2. Developing a reliable 2D pseudo-homogeneous model with suitable kinetic models.
3. Investigating the reactor's thermal behaviors and the interplay between key parameters and reactor performance.

1.3 Thesis layout

This thesis consists of one provisional patent and two research papers. The provisional patent and first manuscript proposed the process for renewable syngas production from captured CO₂ and designed the thermally coupled reactor. The feasibility, ignition test and effect of CHC reaction were investigated. The effects of operating conditions on reactor performance and long-term stability were also examined. The second manuscript focused on the numerical study of the thermally coupled reactor. A reliable mathematical model was built and the operating patterns of the reactor were studied under different configurations and operating conditions.

Chapter 2 briefly reviews literature on RWGS catalysts, experimental and numerical RWGS reactors and thermally coupled reactors. Chapter 3 presents the experimental methodology and results on lab-scale proof-of-concept thermally coupled CHC-RWGS reactor. As mentioned above,

this chapter is based on results from the provisional patent and first manuscript. Chapter 4 presents the kinetic models and a 2D pseudo-homogeneous model based on the prototype. It presents dynamic behaviors and steady-state thermal distribution and reactor performance with varying geometric parameters and operating conditions. Chapter 5 includes a summary of the results, conclusions, recommendations, and future work of this research.

Chapter 2 Literature review

2.1 Reverse water gas shift catalysis

Representative RWGS catalysts consist of isolated and dispersed nanoparticles supported on a metal-oxide to maximize the interfacial area between the metal and the support. Two reaction pathways have been proposed for CO generation through RWGS reaction. One is the formate decomposition mechanism in which CO₂ is first hydrogenated into formate [22], followed by cleavage of the C=O bond. Therefore, metal nanoparticles supported on metal-oxides are promising materials since dispersed metal catalytic sites dissociate hydrogen relatively easily [36]. Then the reactive atomic hydrogen are spread out onto the support and hydrogenate CO₂ that is adsorbed on the oxides [37]. The other widely accepted pathway is the redox mechanism, which is discussed in detail in section 2.1.2 when Cu-based catalysts are reviewed. The RWGS studies of supported metal catalysts mainly composed of noble metals (Pt and Rh) immobilized on various supports and Cu-based catalysts. Furthermore, a wide variety of metals have attracted attention and have been found to exhibit high activity. A comprehensive review is conducted below; details of the activity and selectivity with reaction conditions of these catalysts are reviewed.

2.1.1 Noble metal catalysts

Some noble metals supported on various supports such as Al₂O₃, ZrO₂, TiO₂, and CeO₂ have been found possessing excellent activity and superior resistance against sintering and coking. Pt-based catalysts are generally popular because of their high hydrogenation activity. Porosoff et al.

found that Pt–Ni bimetallic catalyst exhibited greater activity but also generated greatest amount of CH₄ while Pt–Co bimetallic catalyst showed higher CO production than their parent metals [38].

Chen et al. investigated the catalytic performance over different loading of Pt/TiO₂ catalysts. 0.1 wt.% Pt/TiO₂ achieved around 1% CO₂ conversion at 250 °C and 14% CO₂ conversion at 400 °C, with almost complete selectivity to CO under a 50 ml/min feed gas flow with CO₂:H₂:N₂ = 45:45:10. By contrast, 1 wt.% Pt/TiO₂ achieved around 2.5% CO₂ conversion at 250 °C with 100% selectivity to CO and 20% CO₂ conversion with 95% selectivity to CO at 400 °C under a 50 ml/min feed gas flow with CO₂:H₂:N₂ = 45:45:10. The study pointed that the active sites for the CO production were identified as Pt-Ov-Ti³⁺ species formed at the interface between Pt and reducible TiO₂ support and product selectivity of CO₂ hydrogenation was controlled by the Pt particle size anchored on the TiO₂ support and reaction condition, such as the reaction temperature and space velocity [39].

In the study of Liang et al., 2 wt.% Pt supported on mullite achieved 23% CO₂ conversion at 550 °C under the flow of CO₂:H₂:N₂ with a molar ratio of 45:45:10 (50 mL/min total flow rate) while the selectivity to CO decreasing at higher temperatures. The addition of potassium on Pt/mullite significantly enhanced the CO₂ conversion and hindered the formation of CH₄. Under the same condition, K-Pt/mullite achieved 30% conversion of CO₂ with almost complete CO selectivity over the 300-550 °C temperature range, which could be ascribed to a different reaction pathway. The introduction of K weakened the interaction between CO and Pt and facilitated the formation of formate intermediate species [40].

Kim et al. indicated that 1 wt.% Pt/Al₂O₃ reached 42% CO₂ conversion at 600 °C under a 100 ml/min feed gas flow with CO₂:H₂:N₂ = 21:30:49 [41].

Rh supported catalysts have also been studied in the hydrogenation of CO₂ to methanol, methane while RWGS process participates as the intermediate step. For Rh deposited on various supports (TiO₂, ZrO₂, Nb₂O₅ and MgO), the combined methanol and methane selectivity could reach more than 80% at low temperature range and 1/1 feed ratios of CO₂/H₂ [42]. Gogate et al. conducted a comparative study on Rh, Rh-Fe and Fe supported on TiO₂ to investigate the promoting effect of Fe. All tests in this study were evaluated under the same reaction conditions: 20 ml/min feed gas flow with CO₂:H₂ = 1:1, temperature = 270 °C and pressure = 20 bar. 2 wt.% Rh/TiO₂, 2.5 wt.% Fe/TiO₂ and 2% Rh-2.5% Fe/TiO₂ showed 7.9%, 2.7% and 9.2% CO₂ conversion with 14.5%, 73.0% and 28.4% CO selectivity respectively [43]. Since the product being relatively diverse, some research groups are also interested in how to achieve high RWGS selectivity through modifying the surface properties of Rh nanoparticles. Matsubu et al. demonstrate that at low temperature of 200 °C and low H₂/CO₂ feed ratios, the selectivity of CO/CH₄ over Rh supported on TiO₂ increased at low Rh loadings. When Rh is deposited in small loadings, it is dispersed on the support surface, forming isolated Rh sites where CO₂ conversion to CO is preferred. In contrast, Rh forms NPs at large loadings, which facilitates CO₂ hydrogenation to CH₄. Similarly, high availability of H atoms would also favor CH₄ formation [44]. Kusama et al. studied Rh-based catalysts on SiO₂ for CO₂ hydrogenation at high pressure up to 50 bar. 1 wt.% Rh/SiO₂ achieved 0.52% CO₂ conversion at 200 °C and 50 bar under a 100 ml/min feed gas flow with CO₂:H₂ = 1:3 [45].

Although platinum-based catalysts are active and selective towards RWGS, the cost

associated with noble metal catalysts due to the relatively high loadings (usually 1-5 wt.%) is prohibitively high, which is unattractive for large scale conversion of CO₂.

2.1.2 Cu-based catalysts

The other widely accepted pathway for CO formation from RWGS is redox mechanism, where over Cu-based catalysts, CO₂ oxidizes Cu⁰ to generate CO and Cu⁺ while H₂ reduces Cu⁺ to form H₂O [46]. Further evidence for this mechanism is provided by FTIR spectroscopy studies over Cu/ZnO catalyst which indicate CO₂ dissociates to CO [47], but formate has also been detected over CuO [48]. One advantage of using Cu for RWGS reaction is that little or no methane is formed as a side product [49-51]. The other advantage is Cu has been shown to perform RWGS at low temperatures. Cu-based catalysts have been commercially utilized for low temperature water gas shift (WGS). Considering the reversibility of the reaction, Cu-based catalysts have been considered exhibiting promising catalytic performance.

Zhang et al. investigated the catalytic activity and stability of different Cu loading on β -Mo₂C and pointed 1 wt.% Cu/ β -Mo₂C exhibited the greatest performance over the catalysts tested. The CO₂ conversion of 1 wt.% Cu/ β -Mo₂C at 300 °C was around 6% with 96.5% selectivity towards CO under the reaction condition: GHSV = 300,000 mL/(g h), atmospheric pressure and CO₂:H₂ =1:2. As temperature increased to 600 °C, the CO₂ conversion increased to 38% with almost complete selectivity to CO (99.2%) [52]. In another study conducted by Zhuang et al., for 40 wt.% Cu/ZnO/Al₂O₃ catalyst, 30% CO₂ conversion with complete selectivity to CO was

achieved at 500°C under the reaction condition: GHSV = 90,000 mL/ (g h), $H_2:CO_2 = 4$, pressure = 3 bar. By contrast, 0.5 wt.% Ru-promoted 40 wt.% Cu/ZnO/Al₂O₃ reached 46% CO₂ conversion with complete CO selectivity under the same reaction conditions [53]. However, regarding catalyst stability, Cu-oxide catalysts have a tendency to deactivate dramatically in RWG reaction, because of the aggregation of supported copper particles at high temperature [52, 53].

2.1.3 Transition metal carbides catalysts

Transition metal carbides (TMCs) have attracted vast interest due to their appealing properties such as good electrical and thermal conductivity, high chemical stability and thermal stability. With the rapid development of nanotechnology, more and more novel transition metal carbides structures have been prepared and investigated in catalyzing CO₂ hydrogenation.

Rodriguez' group and Chen's group have investigated deep into this kind of promising material with consideration in catalyzing CO₂ reduction reactions [17, 54-57]. The high activity of TMCs compared with their parent metals originates from a modification of the electronic properties from the addition of carbon [56], which in turn affects the binding energy and the reactivity of adsorbates [58]. Looking into the surface reaction chemistry of RWGS over TMCs, Mo₂C is particularly interesting for CO₂ hydrogenation because of dual functionality for H₂ dissociation and C=O bond scission. The studies showed that CO₂ binds to Mo₂C in a bent configuration and one of the C=O bonds can spontaneously break [57, 59], leaving adsorbed CO and O on the catalyst surface. The adsorbed CO can desorb, but the adsorbed O, in the form of an

oxycarbide ($\text{Mo}_2\text{C-O}$), must be removed by H_2 . Regarding catalytic performance, the performance of the Mo_2C catalyst prepared by carburizing in C_2H_4 at 700 K in the RWGS reaction was found to be superior to Pt and Pd in terms of both conversion and selectivity [57].

In another study conducted by Gao et al., Mo_2C nanowires synthesized via calcining the ammonium heptamolybdate/aniline co-precipitate provided CO_2 conversion greater than 60% at 600 °C and GHSV of 36,000 ml/(g h). The catalyst presented 100% selectivity to CO at $\text{H}_2:\text{CO}_2$ molar ratio of 4. The selectivity to CO production was maintained for 20 h at 873 K at a space velocity of 240,000 ml/(g h) and $\text{H}_2:\text{CO}_2$ molar ratio of 1, although the conversion dropped to 28% [60].

Liu et al. showed that polycrystalline $\alpha\text{-Mo}_2\text{C}$ is a highly efficient catalyst towards RWGS. It gives about 16% CO_2 conversion at 400 °C and CO selectivity of >99% [61]. Xu et al. investigated the catalytic performance of Mo_2C at low temperature (200 °C) and high pressure (20 bar), the CO_2 conversion reached 6% with only 39% CO selectivity under the feed $\text{H}_2:\text{CO}_2$ ratio = 5:1 [62].

TMCs are low-cost and behave similarly to precious metal catalysts, which is particularly important for large-scale processes that would be required to substantially reduce CO_2 emissions.

2.2 Reactor design

Currently, there is a lack of literature on RWGS reactors, in particular experimental studies. Typical reactor designs for thermocatalytic conversion of CO₂ include fluidized and fixed beds, which were mainly employed so far for CO₂ methanation reactions [63-66]. Methanation is a different type of thermocatalytic hydrogenation that is, unlike RWGS, is exothermic in nature. Fluidized bed reactors have been proven to offer high mass transfer efficiency, favorable hydrodynamic characteristics [63], less carbon deposition, and better tolerance for poisonous compounds [64, 65]. However, fluidized beds are limited to a narrow range of operating conditions dictated by fluidization velocity and generally have higher capital cost [64]. Another significant drawback is the attrition and entrainment of the catalyst due to high mechanical stress between the catalyst particles and reactor wall [66, 67]. Experimental and simulation studies on the RWGS reactors and thermally coupled reactors are reviewed.

2.2.1 Experimental design

Only two literature sources directly relevant to the experimental RWGS reactor were discovered, one potential design is membrane-based reactors, as recently suggested [68, 69]. These studies investigated two configurations: H₂O removal coupled with CO₂ utilization [68], and CO₂ separation coupled with CO₂ utilization [69]. Sakai et al. reported three configurations (a conventional plug-flow reactor without membrane, and two types of RWGS membrane reactors using ZSM-5 membranes) as shown in Figure 7a. The temperature was controlled in the range of

240-335 °C. The yield of CO was almost the same as the equilibrium conversion (case 1). A membrane reactor (case 2) exhibited a CO yield 2-3% above that of case 1, which verified the effectiveness. The yields of CO in case 3 was further increased to 7% above the equilibrium conversion. Note that the ZSM-5 membrane reported showed H₂O selectivity for both H₂O/H₂ and H₂O/CO₂ mixture, with 2.99×10^{-7} and 3.64×10^{-7} mol/(m² s pa), respectively.

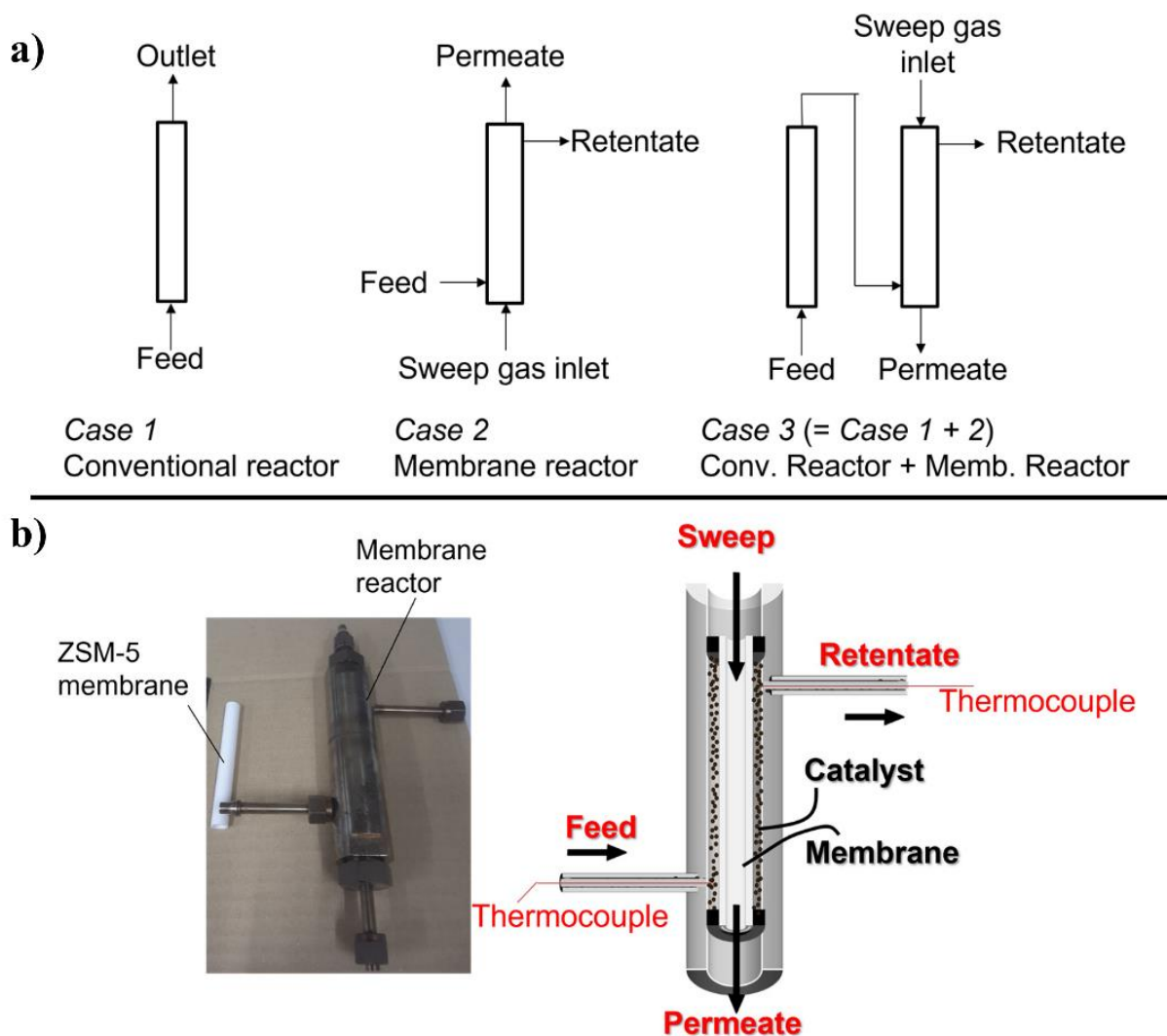


Figure 7. Configurations (a), picture and schematic diagram (b) of Zeolite membrane reactor for RWGS [68].

Chen et al. investigated that CO₂ can be simultaneously separated and catalytically activated using a ceramic-carbonate dual-phase membrane comprised of the ceramic oxygen-ion conductor and molten carbonate phases, with an additional catalytic bed as indicated in Figure 8 [69]. The membrane reactor yielded CO₂ flux of 4.25 ml/(min cm²) which is 4 times higher than a single CO₂ separation process. A CO₂ conversion of 56.8% and CO production rate of 2.41 ml/(min cm²) were achieved at 750 °C. The membrane can simultaneously realize physical separation and chemical reaction in one integrated system. One drawback in operation of ceramic membrane reactors for CO₂ separation is limited membrane permeability. Generally speaking, high capital costs, membrane stability, and membrane-to-module sealing at high temperatures are other technical issues associated with membrane reactors [70].

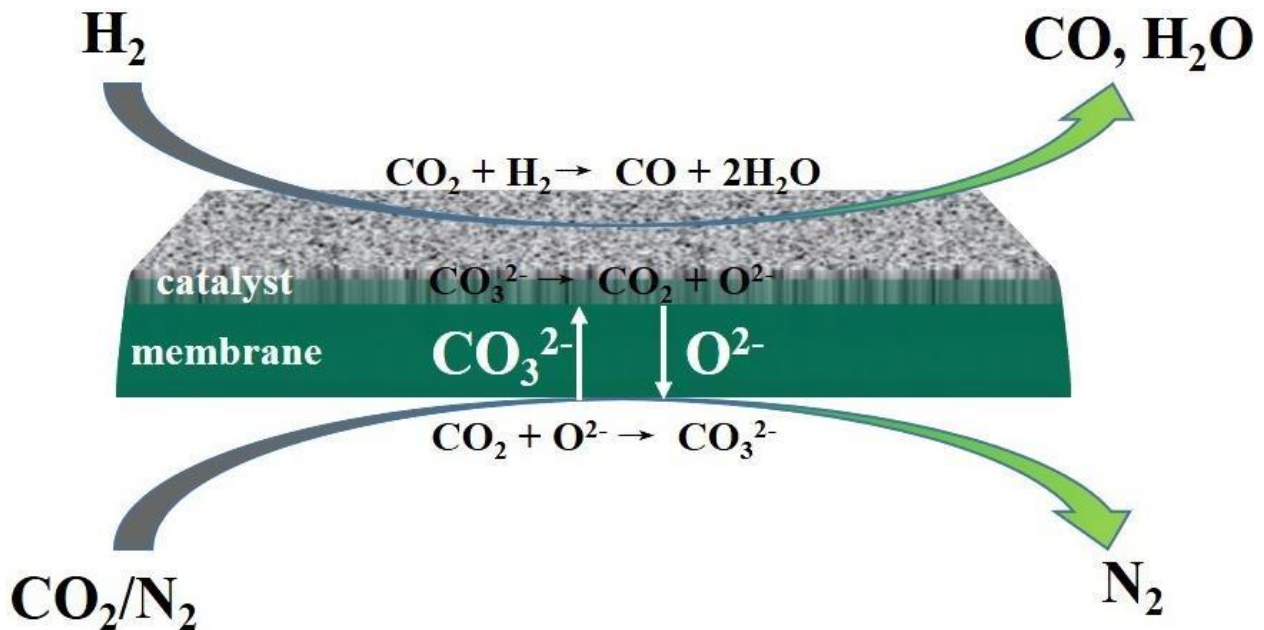


Figure 8. Schematic of setup and membrane reactor with ceramic-carbonate dual-phase membrane coupling of CO₂ separation with RWGS [69].

2.2.2 Reverse water gas shift reactor models and simulation studies

Ghodoosi et al. studied the RWGS reaction in a fixed-bed reactor using two-dimensional pseudo-homogeneous reactor model under steady-state conditions, with one of the objectives to investigate the effect of space velocity, feed composition and feed gas temperature [71]. The study showed that the CO_2 conversion decreased with increasing space velocity which is due to the shortened residence time of reactants, meanwhile, with increasing space velocity, the temperature drop in the reactor increases. Under the conditions of high space velocity, the conversion was relatively low, but a large inlet gas flux and a large amount of raw materials resulted in much greater reaction heat consumption and a great temperature drop. Besides, the study demonstrated that the increase in H_2/CO_2 leads to an increase in CO_2 conversion and this rise in conversion before $\text{H}_2/\text{CO}_2 = 1$ has a steep slope and after that the slope becomes gentler. Also, the study illustrated that at high feed temperatures, the temperature drops in the reactor increased because with increasing feed temperature, the rate of the reaction increased, and more heat was consumed since the RWGS reaction is an endothermic reaction. Furthermore, the temperature and concentration profiles inside the reactor were predicted. The concentration of CO_2 was reduced along the axial direction because of the consumption of in the reaction. In the initial section of the bed, the decrease in CO_2 concentration was relatively high because of a high reaction rate, but the profile became smoother upon consumption of reactants and a decrease in the reaction rate along the bed. The concentration change in the radial direction of the bed was very small which could be explained by no radial velocity existed and the mass dispersion coefficient in the radial direction

was very small. The maximum temperature drop was about 10 °C along the axial and radial directions since the heat was obtained from the contents of the reactor (gases and catalyst bed) and there was not a sufficient heat transfer rate from the wall into the reactor. Nevertheless, the implementation of a conventional furnace-heated reactor with compact dimensions (length = 10 mm) is not a viable solution for effectively utilizing captured CO₂ and achieving the objective of emission reduction by introducing the renewable energy and recycling the emitted CO₂.

Zhang et al. investigated thermodynamic performance of helium-heated reverse water gas shift (RWGS) reactor and examined the influence of the effective parameters on reactor performance. A comprehensive two-dimensional pseudo-homogeneous mathematical model was established to represent the reactor. The helium heated RWGS reactor consisted of two concentric tubes as shown in Figure 9. The high temperature hot gaseous helium flowed through an annular heating section, which could be both parallel and counter compared to the feed gases, to provide heat to the endothermic RWGS reaction in the inner tube [72]. The study revealed more uniform axial distributions of the temperature difference between hot gaseous helium and outer wall, the temperature difference between inner wall and outer wall and the heat flux were observed in the counter-flow reactor, compared to the parallel-flow reactor. In addition, the outlet mean conversion rate and outlet helium temperature of the counter-flow reactor were slightly higher than those for the parallel-flow reactor. Furthermore, the effects of inlet helium temperature, inlet helium molar flow rate, inlet RWGS temperature, inlet RWGS pressure and total molar flow rate on the profile of radial temperature difference and mean conversion rate along the tube were examined.

Increasing the inlet helium temperature and inlet molar flow rate of helium, the resulting larger temperature difference led to higher heat supplies, which was the main reason for the increase of the mean conversion rate. Besides, raising the inlet temperature of feed gases was an effective measure to reduce radial temperature difference and improve outlet conversion rate simultaneously. The temperature difference and mean conversion rate increased with the increment of the inlet pressure, but the resulting response of changing pressure was not significant compared with other decision variables. An increase in inlet total molar flow rate decreased both the temperature difference and mean conversion rate since the residence time of feed gas mixture decreased. However, the reactor was designed for the operating conditions under a helium feed temperature of 1000 °C and a RWGS feed temperature of 600 °C, wherein the mean CO₂ conversion at the reactor outlet was limited to less than 50%. From the perspective of energy conversion, design optimization needs to be emphasized.

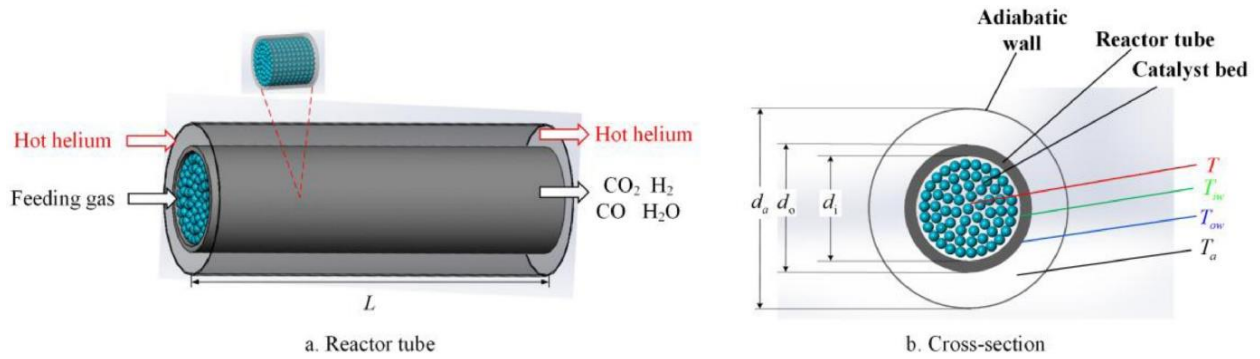


Figure 9. Schematic diagram of the helium-heated RWGS reactor [72].

Samimi et al. investigated and compared two different reactors (RWGS reactor and RWGS membrane reactor) for indirect CO₂ conversion process to produce methanol via RWGS reaction.

When a water permselective membrane was applied in the RWGS reactor, the produced water during the RWGS reaction is separated by the membrane; therefore, the free of water product no longer needed a separator before the methanol synthesis. In addition to water removal, a higher CO_2 conversion and CO yield and subsequently a more proper synthesis gas composition were obtained. As demonstrated in Figure 10, the reactor walls were coated by the membrane. H_2O penetrates through the membrane layer during the reaction. A sweep gas (N_2) flows in the permeation side to carry the permeated H_2O [73]. The study firstly investigated the RWGS reactor (RWGS-R): the minimum inlet temperature was around $227\text{ }^\circ\text{C}$ to begin the RWGS reaction, and the effect of inlet pressure was much lower, the inlet pressure greater than 10 bar had no remarkable influence on the reactor performance. In contrast to the RWGS-R, the CO_2 conversion was strongly dependent on the inlet pressure and it increased as the pressure increased for RWGS membrane reactor (RWGS-MR). This is because by increasing the pressure differences between the reaction and permeation sides, the driving force for water separation also increased. In addition, the study compared RWGS-R and RWGS-MR. In RWGS-R, the conversion of CO_2 increased along the reactor length and followed a constant trend after reaching equilibrium. In RWGS-MR, by removing water during the reaction, the higher conversions were achieved since thermodynamic equilibrium was shifted towards more CO_2 and H_2 consumption. Furthermore, H_2O mole fraction in the RWGS-R increased and then followed a monotonous profile. In the RWGS-MR, H_2O mole fraction first rose up to a certain point at the beginning of the reaction and then diminished along the rest of the reactor. The water permeation rate through the membrane was higher than the water

production rate of the RWGS reaction from the peak point to the end of the reactor. However, the impracticability for membrane reactors used for high throughout thermocatalytic CO_2 conversion were mentioned in the above section.

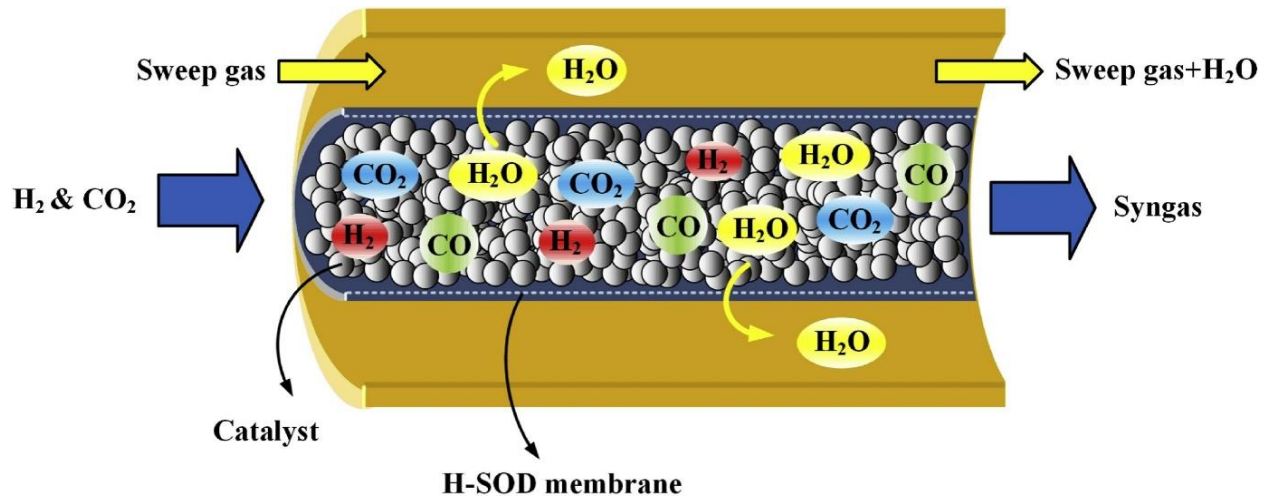


Figure 10. Schematic diagram of the RWGS membrane reactor [73].

Parra et al. proposed a fixed-bed adsorptive reactor and a moving-bed adsorptive reactor to circumvent the unfavorable equilibrium of RWGS reaction at low temperatures, by adsorbing the water vapor formed [74, 75]. A fixed-bed adsorptive reactor (Figure 11a) consisted of a fixed bed containing a certain fraction of catalyst and a complementing fraction of adsorbent. In order to overcome the limit of design operational flexibility, a moving-bed adsorptive reactor was proposed as shown in Figure 11b. The reactor shown was in counter-current configuration where the feed gas enters the reactor from the bottom and encounters a downward, continuous flow of solids, which are fed through the top of the reactor. The reactor also could be operated co-currently. The CO_2 conversion reached at the outlet of the reactor was considerably higher than the equilibrium

at 250 °C for both reactor configurations, showing the improvement due to the adsorptive functionality. The study also compared the counter-current moving-bed adsorptive reactor with co-current one. The performance of the counter-current reactor was improved in comparison to the co-current case, due to greater driving force. Moreover, the study demonstrated that the performance of counter-current reactors could be improved from the economical perspective by lowering solid velocity, increasing the reactor length and reducing the gas velocity. As previously mentioned, the fluidized bed reactor has several drawbacks.

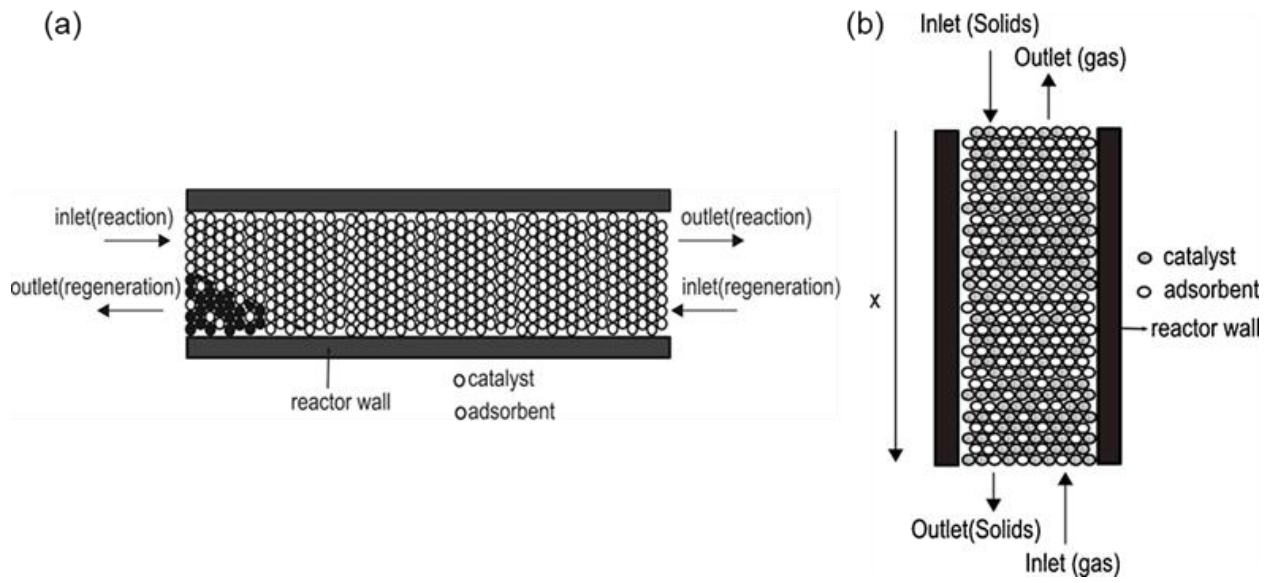


Figure 11. Schematic diagram of the fixed-bed adsorptive reactor (a); the moving-bed adsorptive reactor (b).

2.2.3 Thermally coupled reactor

RWGS process needs high temperatures to yield a favorable equilibrium (500-700 °C to achieve 50-70% CO₂ conversion), which implies high energy demand. To minimize environmental

pollution, capital and operating expenses and enhance the efficiency and productivity, combining processes within the scope of the reactors represents a feasible option. One possible solution is coupling an exothermic reaction with the endothermic process of interest, which can result in a significant improvement in reactor performance and more efficient energy integration [30]. In such configuration, the endothermic reaction is driven by the heat generated by the exothermic reaction. Significant attention has been paid to recuperative thermally coupled reactors in the literature due to their advantages of reduced equipment size and improved energy utilization. A typical thermally coupled reactor consists of two concentric tubes, with the inner (tube) compartment utilized for an exothermic reaction and the outer (shell) compartment used for an endothermic reaction (shell-and-tube reactor) [32].

Farniaei et al. utilized tri-reforming process (CO_2 reforming, steam reforming and oxidation of methane) as an energy source for driving highly endothermic process of methane dry reforming process in a multi-tubular recuperative thermally coupled reactor [76]. 184 two concentric tubes had been considered for the reactor configuration in which tri- and dry reforming processes occur in outer and inner tube sides of the reactor respectively. By the concept of thermally coupled reactor, the generated heat from TR process can be transferred to dry reforming reaction and thus both processes proceed simultaneously. The study pointed that tri-reforming process was supplied for providing necessary heat of endothermic dry reforming process plus production of two types of syngas by different quality in a multi-tubular thermally coupled reactor (TCTDR). At the entrance of TR side, all oxygen is rapidly consumed by COM reaction and CO_2 is produced at first but then

CO₂ mole fraction is decreased because of consuming by reforming reactions. Moreover, the comparison between tri- and dry reforming reactor and tri- and steam reforming reactor (TCTDR), which tri-reforming process is coupled with steam reforming process were discussed. Results identified that CH₄ conversion at the output of dry reforming (DR) side of TCTDR reached to 63% that is very higher than steam reforming (SR) side of TCTSR reactor with 26%. Also, syngas quality of DR side in TCTDR is lower than SR side of TCTSR (0.958 vs. 9.19).

Yin et al. carried out a preliminary study of the thermally coupling of the catalytic combustion of methane with the CO₂ reforming and RWGS reaction using a tubular jacket reactor packed with metallic monolith catalysts [77]. The heat coupling of the exothermic and endothermic reactions had been realized on the laboratory scale over a wide range of experimental conditions. Moreover, the study evaluated the efficiency of utilization of the reaction heat evolved in the exothermic reaction. In order to retain high conversions of methane and CO₂ in the methane reforming reaction and to produce large amounts of hydrogen, the flow rates of reactant mixtures through the inner and annular catalyst beds should be matched. The reactor was placed in an electric furnace. When the temperature of the electric furnace was 815 °C and the GHSVs of inner tube and outer tube were 382 h⁻¹ and 40 h⁻¹, the conversions of CH₄ and CO₂ were 93.6% and 91.7% and molar ratio of H₂ to CO was close to unity. The heat efficiency reached 81.9% and stability tests showed that neither catalyst underwent deactivation during 150 h on stream.

Chapter 3 Lab-scale proof-of-concept reactor

3.1 Methodology

3.1.1 Conceptual design

The syngas produced from RWGS reaction could be used as a fuel or converted into industrial chemicals or liquid fuels. Hydrogen, as a reactant for RWGS, could also be catalytically oxidized as the energy sources for RWGS with low emissions, high energy efficiency and density. The integrated process of syngas production through the thermally coupled CHC/RWGS reactor is conceptually shown in Figure 12. The hydrogen necessary for both reactions can be procured through the electrolysis of water utilizing renewable energy sources or surplus electricity generated with a minimal carbon footprint. The mixture of air and the oxygen produced by the electrolyzer is compressed into the exothermic compartment of the reactor. Carbon dioxide could be captured from flue gas produced by power plants, cement plants, and other industrial facilities. After purification to remove impurities such as sulfur dioxide, particulate matter, CO₂ is fed to the RWGS compartment of the reactor. Syngas is derived from the reactor outlet following water condensation (recirculated to the electrolyzer for reuse) and additional production enhancements (removal of unreacted CO₂) that may be necessary.

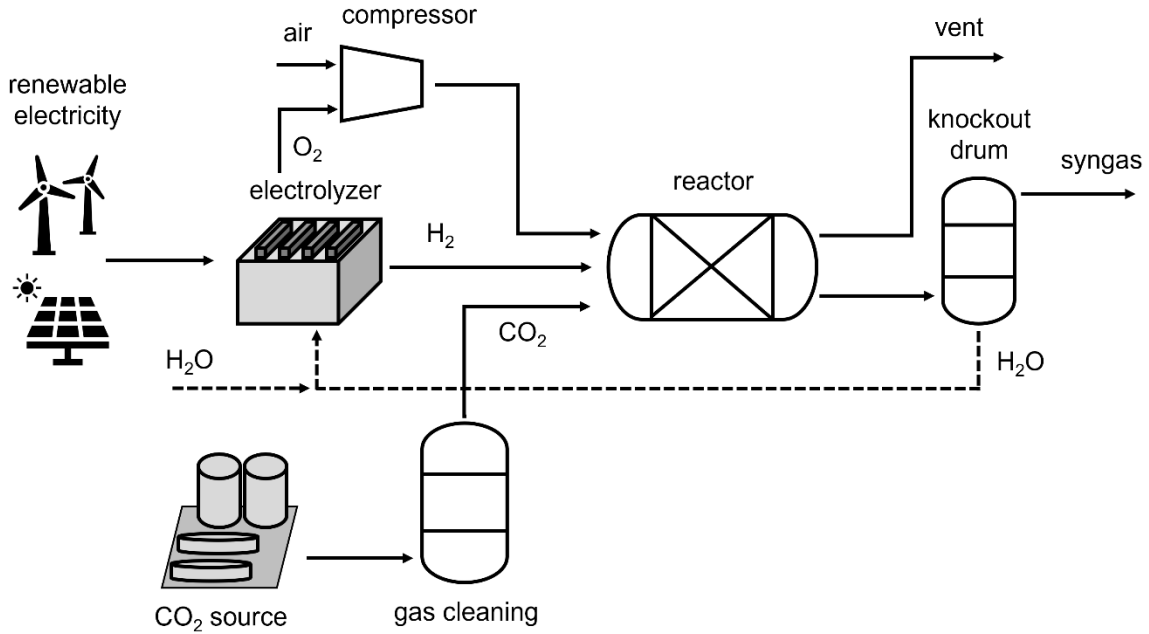


Figure 12. A conceptual diagram for the coupled catalytic H₂ combustion – reverse water gas shift system.

The energetic feasibility of this approach has been assessed. Ideally (complete heat transfer without heat losses), 0.17 mole H₂ would be consumed per 1 mole CO₂ converted:

$$\frac{\text{CO}_2 \text{ reduced}}{\text{H}_2 \text{ combusted}} = \frac{\Delta H_{RWGS}}{\Delta H_{CHC}} = 0.17 \quad (3)$$

Assuming 75% electrolysis efficiency, a maximum chemical efficiency of RWGS of 80% and a maximum CHC conversion of 90%, process efficiency could reach 68%, Eq. (4), however this number does not account for any heat recuperation and additional improvements on electrolyzer efficiency, which has been already considered as acceptable for utilization of renewable or excess electricity.

$$\eta_p = \frac{\text{HHV}_{\text{syngas}} \times F_{\text{syngas}}}{P_{\text{input}}} \quad (4)$$

$$F_{\text{syngas}} = F_{\text{CO}_2} \times X_{\text{CO}_2} \times (1 + \alpha_{\text{syngas}}) \quad (5)$$

$$P_{\text{input}} = \left(F_{\text{CO}_2} \times \left(\alpha_{\text{RWGS}} + \left(\frac{\Delta H_{\text{RWGS}}}{\Delta H_{\text{HO}}} \right) \times \frac{1}{\eta_{\text{HO}}} \right) \right) \times \Delta G_f^\circ (\text{H}_2\text{O}) \times \frac{1}{\eta_e} \quad (6)$$

3.1.2 Flow system setup

The flow system used in reactor tests is shown in Figure 13. Reactor inlet and outlet were connected to the flow system. N₂, CO₂, H₂ and Air were controlled by the mass flow controllers. The back-pressure regulators were used to adjust the reactor pressure. Water was removed from the outlet stream using the mist trap (SMC Corporation, AFM40-N02-Z-A) installed before the back-pressure regulator and a silica gel column (Agilent Technologies, 5182-9411, the original adsorbent was replaced with orange silica gel, Fisher Scientific) for the Endo compartment. The mass flow controllers and back pressure regulator were computer-controlled using LabVIEW, with the flow rates, pressure, temperature, and outlet gas concentrations being continuously monitored and recorded using analog-to-digital converters.

Concentrations of CO and CO₂ in the outlet stream of the Endo compartment were measured on a dry basis (after the removal of water and moisture) with an IR analyzer (IR-208, Infrared Industries, Inc., USA) continuously monitored using an analog-to-digital converter (NI 9215, National Instruments) and LabVIEW (National Instruments). Concentrations of H₂, O₂ and N₂ in

the outlet stream of the Exo compartment were measured with a gas chromatograph (Micro GC FUSION® gas analyzer, Inficon).

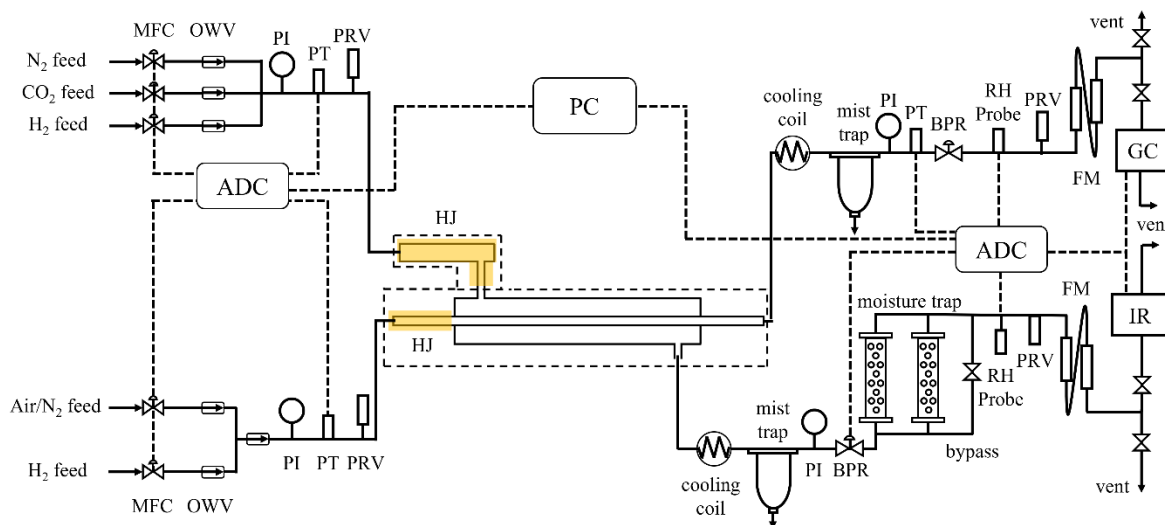


Figure 13. Flow system for reactor tests. Abbreviations: ADC – analog-to-digital converter, BPR – back pressure regulator, FM – flow meter, GC – gas chromatograph, HJ – heating jacket, IR – infrared analyzer, MFC – mass flow controller, OWV – one-way valve, PC – personal computer, PI – pressure indicator, PRV – pressure relief valve, PT – pressure transducer, RH – relative humidity sensor.

3.1.3 Reactor assembly

The reactor was made from an 8" long ½" OD stainless steel tube, with a piece of ¼" OD tube placed inside, Figure 14. Reducing tees (Swagelok) were used to seal the space between the tubes. 1.3g of commercial Ni/Al₂O₃ catalyst (12 wt. % Ni, BASF, supplied by Research Catalysts, Inc. USA) and 5.9g Mo₂C/Al₂O₃ (RME) catalyst were sieved to ca. 0.275-0.425 mm and loaded inside the Exo and Endo compartment via the port on the reducing tee separately. The stainless-

steel mesh and quartz wool were placed to prevent the catalyst bed from moving. Two heating jackets (300W, Omega Engineering) controlled by a dedicated temperature controller (CN7200, Omega Engineering) were wrapped around the inlet to warm up reactor to ignition temperature. Multiple thermocouples were used to monitor the temperature of the reactor. Two thermocouples (K type, 1/16", Omega Engineering, Inc.) connected to the temperature controller were placed inside the heating jackets to monitor the temperature of heating jacket (T_{hj}). Quartz wool was wrapped around the reactor body and reflective aluminum foil was put on the top of the insulation layer to prevent reaction going to extinction due to heat loss to environment. The thermocouples (1/8", Omega Engineering, Inc.) were placed inside the reactor for both compartments to measure the reactor inlet (T_{in}) and outlet (T_{out}) temperatures. A thermocouple (1/8", Omega Engineering, Inc.) was placed before the reactor inlet (the Endo compartment) to measure the feed temperature (T_{feed}). Five thermocouples (J type, 1/16", Omega Engineering, Inc.) were placed on the reactor wall to monitor the temperature distribution along the reactor (T_{w1} , T_{w2} , T_{w3} , T_{w4} , and T_{w5}).

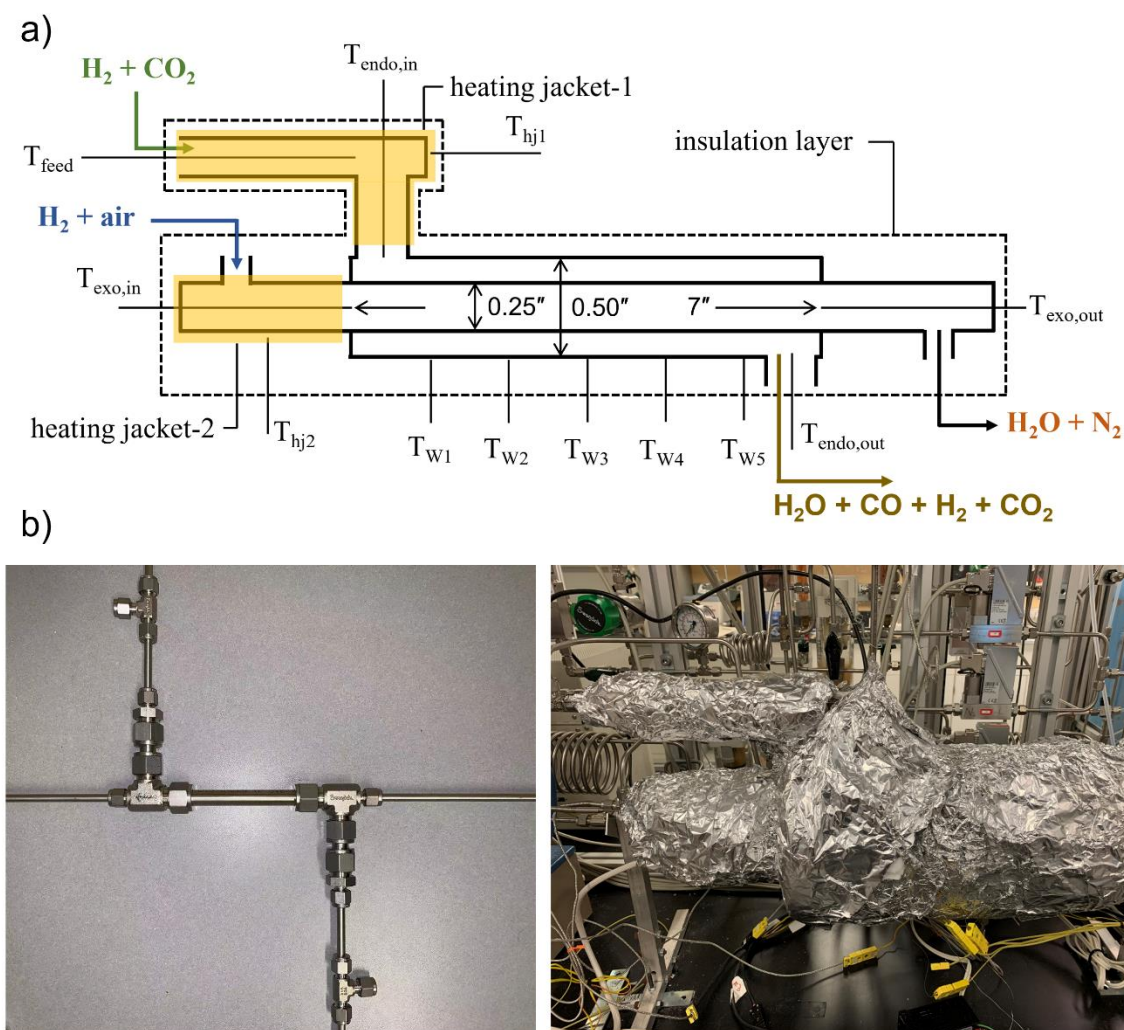


Figure 14. Reactor diagram showing locations of thermocouples (a) and pictures of the assembled reactor and reactor covered with the insulation layer and connected to the flow system (b).

3.1.4 Reactor ignition

The reactor is first initiated with external heating jackets. The reactor ignition has the following steps: warming up the reactor under the conditions of $T_{hj1} = 525\text{ }^{\circ}\text{C}$, $T_{hj2} = 450\text{ }^{\circ}\text{C}$, $Q_{f,exo/endo} = 500/2000\text{ ml/min N}_2$ and reducing the catalyst, starting the reaction and switching to

desired operating conditions. For the results reported in the Figure 18, the T_{hj1} was gradually decreased from 525 °C to 430 °C. The catalytic bed in the Exo compartment had to be heated up to around 320-340 °C to initiate the catalytic H_2 combustion reaction first. The N_2 flow with 10% H_2 preheated by the heating jacket was used to heat up the reactor to the ignition temperature and reduce the Ni catalyst. Once the ignition temperature was reached, the N_2/H_2 mixture was replaced by the Air/ H_2 mixture to start the combustion reaction and obvious rising of the reactor temperature was observed immediately. After the temperature achieved a steady state which indicated the completion of the ignition, the reactor was then ready for testing.

3.1.5 Reactor performance evaluation

Reactor performance was evaluated in terms of H_2 and O_2 conversions within the CHC compartment, the conversion of CO_2 and the selectivity toward CO within the RWGS compartment, as well as the overall stability. In all experiments conducted, pressure of 5 bar was maintained for the Exo compartment and pressure of 1 bar was kept for the Endo compartment. Gas hourly space velocity (GHSV) is calculated as follows (Q_f is the total volumetric feed flow rate at atmospheric pressure and room temperature and W_c is the catalyst weight):

$$GHSV = \frac{Q_f}{W_c} \quad (7)$$

Feed composition parameter α is defined as $H_2:CO_2$ ratio, Eq. (8):

$$\alpha = \frac{F_{H_2,f}}{F_{CO_2,f}} \quad (8)$$

CO₂ conversion to CO and CH₄ are defined as f_1 and f_2 respectively:

$$f_1 = \frac{F_{CO,out}}{F_{CO_2,f}} = \frac{y_{CO}}{(y_{CO} + y_{CO_2} + y_{CH_4})} \quad (9)$$

$$f_2 = \frac{F_{CH_4,out}}{F_{CO_2,f}} = \frac{y_{CH_4}}{(y_{CO} + y_{CO_2} + y_{CH_4})} \quad (10)$$

Total CO₂ conversion and CO selectivity are then obtained as follows:

$$X_{CO_2} = f_1 + f_2 \quad (11)$$

$$S_{CO} = \frac{f_1}{f_1 + f_2} \quad (12)$$

H₂ and O₂ conversions are defined as X_{H_2} and X_{O_2} (assuming no change in total volumetric flow rate):

$$X_{H_2} = \frac{(y_{f,H_2} - y_{H_2})^{CHC}}{y_{f,H_2}^{CHC}} \quad (13)$$

$$X_{O_2} = \frac{(y_{f,O_2} - y_{O_2})^{CHC}}{y_{f,O_2}^{CHC}} \quad (14)$$

Carbon balance, defined as the ratio of the rate of carbon exiting the reactor and the rate of carbon fed to the reactor (a detailed derivation is attached in Appendix), was computed using the following equation:

$$CB = \frac{F_{C,out}}{F_{C,f}} = (y_{CO_2} + y_{CO} + y_{CH_4})(1 + \alpha - f_1 - 4f_2) \quad (15)$$

Carbon balance (CB) was continuously monitored and recorded in all experiments (using

LabVIEW). Deviations did not exceed 5% in all experiments.

3.2 Results and discussion

3.2.1 Catalytic performance evaluation

Kinetic reactors were used for isothermal reaction tests. In each experiment, a fresh catalyst was first reduced at 300 °C under a flow of H₂ (200 ml min⁻¹) for 1 h. The reaction mixture was introduced after reduction and the temperature was increased stepwise. At each step, the reaction was conducted for 2 h to ensure that a steady state was attained. Ni/Al₂O₃ catalyst performance in terms of H₂ and O₂ conversion as a function of temperature is shown in Figure 15a. The H₂ and O₂ conversions generally increased with the reaction temperature, no obvious reaction was observed between 300 °C to 400 °C, while mild reaction was detected starting at 425 °C. Under the particular conditions of this test, the optimal temperature range is above 575 °C, where the conversion increased sharply and reached over 84% at temperatures of 600 °C.

Figure 15b compares the CO₂ conversion obtained from Mo₂C/Al₂O₃ catalyst and equilibrium calculated. As expected, conversion increased linearly with temperature and near equilibrium conversions were achieved for temperatures higher than 500 °C. Complete formation selectivity to CO is achieved over the entire temperature range. The stability test for Mo₂C/Al₂O₃ is shown in Figure 15c. Both conversion and selectivity remain stable. The following characterization results [78] were also consistent with the stability test, indicating that the catalyst exhibits good stability with no obvious coking and deactivation process. After verifying the

catalytic performances, the catalysts were loaded to the thermally coupled CHC/RWGS reactor for the subsequent reactor tests.

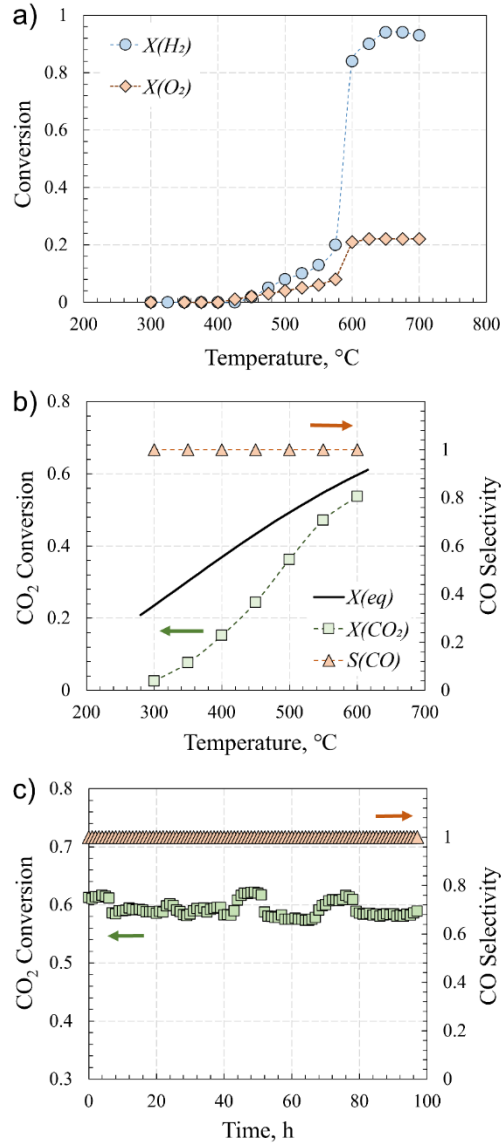


Figure 15. Isothermal reaction tests for Ni/Al₂O₃ (a) and Mo₂C/Al₂O₃ (b,c) catalysts, showing H₂ and O₂ conversion vs. temperature (a), CO₂ conversion and CO selectivity vs. temperature (b), and stability at 600 °C (c). Parameters: P = 1 bar, Q_f = 100/900 ml/min for H₂/air (a); P = 3 bar, H₂:CO₂ = 3, GHSV = 60,000 ml/(g h) (b, c), T = 600 °C (c).

3.2.2 Reactor ignition

The dynamic behavior of reactor ignition was analyzed first. Figure 16a,b,c show the evolution of the temperatures at different locations (inlet, outlet and wall) and the conversion of H_2 and O_2 within the exothermic compartment. Spatial temperature profiles at three distinct time points is present in Figure 16d. During first 3 h, the reactor was heated, and the Ni/Al_2O_3 catalyst was reduced using oven-preheated 20% H_2/N_2 mixture at 1.5 h. After 2 h, the temperatures stabilized, but addition an hour was given for sufficient catalyst reduction. Ignition takes place immediately after changing the reduction mixture to the reaction mixture at approximate 3 h, as evident from the sharp rise of the reactor temperatures and the hotter Exo compartment. Complete O_2 conversion and 20% H_2 conversion were achieved as shown in Figure 16b, also corroborating the ignition process. Figure 16a indicates all inlet and outlet temperatures increased simultaneously, while the Exo compartment inlet temperature jump is much more notable increasing from 320 °C to 560 °C. However, the other inlet and outlet temperatures increased by only around 100 °C. The observed phenomenon clearly demonstrated that the heat generated by the CHC reaction was transferred to the RWGS compartment through the wall. Another noteworthy piece of information that can be gleaned from Figure 16c is that the slope of the wall temperatures at the entrance of the reactor is clearly steeper than those downstream regions following ignition. This discrepancy could be attributed to the presence of supplementary heat generation from exothermic CHC reaction. In alternative phrasing, it is probable that the ignition occurred in close proximity to the reactor inlet. Figure 16c, d demonstrate that after ignition, the temperature of T_{W3} displayed a trend

of gradually catching up with and eventually surpassing T_{W2} slightly, which illustrates a small hot region may be formed at this area. A consistent O_2 and H_2 conversion within the CHC compartment was achieved throughout the entire ignition test. Approximately one hour following the ignition, the temperature of the reactor inlet exhibited a trend of stabilization. A stabilization in the overall temperature of the reactor was observed after two hours.

The experimental findings further revealed a notable radial temperature difference between the CHC and RWGS compartment at the inlet ($\Delta T = 90\text{ }^{\circ}\text{C}$) compared with the outlet ($\Delta T = 31\text{ }^{\circ}\text{C}$). This phenomenon could be attributed to the rapid and violent CHC reaction occurring at the entrance of the reactor which generated a significant amount of heat. The heat was further transferred to the RWGS compartment and its surroundings.

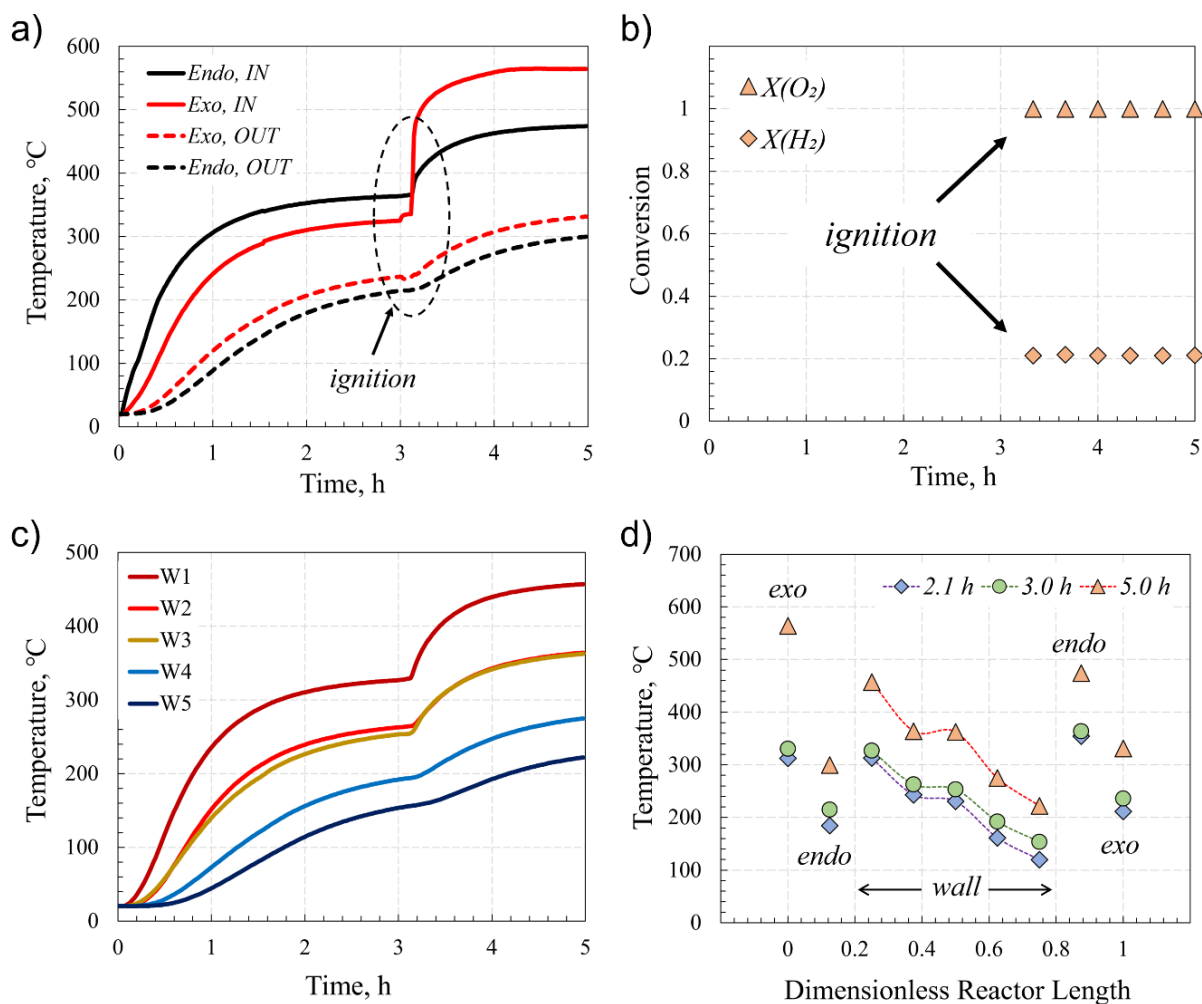


Figure 16. Typical profiles of the reactor ignition, showing transient temperatures in the catalytic bed (a), O_2 and H_2 conversion (b), reactor wall temperatures (c), and spatial temperature profiles for different points in time (d). Parameters: $Q_{f,exo} = 230/400$ ccm air/ H_2 , $Q_{f,endo} = 2000$ ml/min N_2 , (after preheating).

3.2.3 Effect of catalytic H_2 combustion on the reactor performance

The effect of catalytic H_2 combustion on the reactor temperature only (introducing N_2 in the Endo compartment instead of RWGS reaction gas) was investigated. The effect of the Endo feed

flow rate was also discussed briefly. Figure 17a depicts the composition and flow rate of the feed stream, along with the conversion profiles of H_2 and O_2 within the CHC compartment. Temporal evolution of the temperatures (inlet, outlet, and wall) is illustrated in Figure 17b,c. An important observation from Figure 17c is the outstanding and abrupt temperature rise in T_{W3} , which became notably higher than T_{W2} immediately after ignition. This phenomenon could be attributed to the formation of a hot spot in the vicinity of T_{W3} , which provides further support for the conclusion drawn in section 3.2 of this study.

After ignition and stabilization, the ratio of air: H_2 in the CHC feed stream gradually increased from 0.6 to 1.4. As shown in Figure 17a, the H_2 conversion showed a gradual climb, starting from 24% and reaching 58% as this ratio increased. In Figure 17a,b, an interplay between the reactor temperature and the feed composition within the CHC compartment was illustrated. It's evident that the overall reactor temperature increased as more hydrogen was converted. A positive effect was highlighted that the increased consumption of hydrogen in catalytic H_2 combustion resulted in an enhanced release of heat, owing to the nature of the exothermic reaction. Consequently, the elevated temperature promoted a higher conversion of H_2 , driving it towards complete conversion.

The effect of flow rate in the RWGS compartment was further investigated. As $Q_{f,endo}$ decreased from 2000 mL/min to 600 mL/min, the temperatures of the forepart of the reactor, including the inlet, T_{W1} and T_{W2} , augmented. In contrast, the temperatures in the remaining sections of the reactor dropped. The observed temperature increase in the front part of the reactor

can be attributed to the fact that less heat generated by the CHC reaction was taken away with a reduced convective heat transport due to lower flow rate in the RWGS compartment. It allowed for more heat to accumulate in the forepart, leading to temperature augmentation. Conversely, lessening the flow rate in the RWGS compartment resulted in less heat being transported to the latter part of the reactor. This included both heat from the external heating jacket and heat generated by the CHC reaction. With $Q_{f,endo} = 600 \text{ mL/min}$, the ratio of air/H₂ was finally increased to 1.6, resulting in maximum inlet temperatures of 690 °C and 580 °C in the CHC and RWGS compartment, respectively. In contrast, the outlet temperatures remained stable at 330 °C and 290 °C. A significant axial temperature difference was observed with a variation of 360 °C in the CHC compartment and 290 °C in the RWGS compartment. These findings underscored the significance of effective insulation at the laboratory scale. The principal finding from this experiment is that the inlet temperature could be increased to around 700 °C and 600 °C in the Exo and Endo compartments, respectively, along with a 68% H₂ conversion and complete O₂ conversion.

From the perspective of radial temperature distribution, there was a gradual increase in the temperature gap between the Exo and Endo inlets, from 60 °C ($t = 4 \text{ h}$) to 160 °C ($t = 8 \text{ h}$) when $Q_{f,endo} = 2000 \text{ mL/min}$. As $Q_{f,endo}$ decreased gradually to 600 mL/min, the temperature difference stabilized at approximately 100 °C. However, there was little change in the temperature difference between the outlets, which remained constant at around 40 °C throughout the entire test.

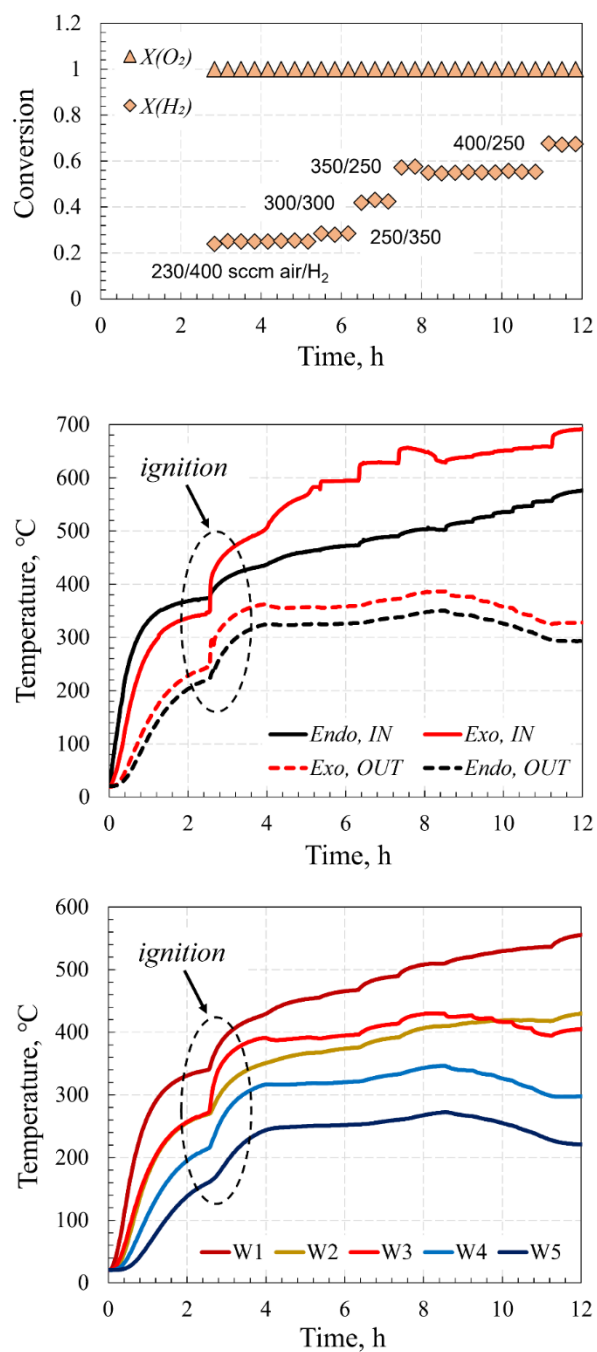


Figure 17. The effect of the feed composition and flow rate in the catalytic H₂ combustion compartment on the reactor temperature profiles. Parameters: air and H₂ flow rates in the exothermic compartment are specified in the upper panel; $Q_{f,endo} = 2000$ mL/min N₂ for $t < 8.6$ h, followed by a stepwise decrease to 600 mL/min N₂, with a step of 200 mL/min each 0.5 h.

Figure 18 demonstrates the impact of catalytic H_2 combustion on both the reactor temperature and CO_2 conversion. Upon ignition, the flow rate within the CHC compartment was switched to 500/500 mL/min air/ H_2 . The ratio of air to H_2 was raised from 1.0 to 1.4 by gradually increasing the air flow rate by 50 ml/min every hour, while maintaining a constant H_2 flow rate. Before introducing RWGS reaction gas, the reactor stabilized with an inlet temperature of 600 °C, outlet temperature of 560 °C, and 60% H_2 conversion in the CHC compartment. Heat transfer resulted in an inlet temperature of 430 °C and outlet temperature of 370 °C on the endothermic side. After switching to 100/300 mL/min CO_2/H_2 from 2000 mL/min N_2 , the overall reactor temperature decreased as expected. The temperature at the inlet and outlet in the CHC and RWGS compartments, respectively, decreased by 50 °C and 30 °C. This could be attributed to the combined effects of heat consumption by the RWGS process as well as decreased heat input the external heating element due to the reduced flow rate. Figure 18c shows an apparent decrease in T_{w3} compared to other wall temperatures. A hypothesis is that the hot spot formed near this location was eliminated due to the combined effects mentioned above.

After one-hour stabilization, there was a 60% H_2 conversion in the CHC compartment and 44% CO_2 conversion in the RWGS compartment. Subsequently, the H_2 in the CHC feed stream was stopped. A significant reduction in both the reactor temperature and CO_2 conversion was observed. The temperature at the reactor inlet experienced a decline, reaching a value of 360 °C, and the outlet temperature underwent a reduction to 250°C. As a result, the CO_2 conversion

dropped to 18%. It can be inferred that the CHC reaction is critical to the thermally coupled reactor, increasing the reactor temperature and promoting the endothermic reaction.

It's evident that the radial inlet temperature distribution was slightly narrowed, with the CHC compartment temperature consistently higher than the RWGS compartment temperature, as anticipated. This phenomenon supports the hypothesis proposed earlier that the enhanced convective heat transport caused the downstream propagation of the hot spot, where the severe CHC reaction occurred, due to the increased flow rate. These findings are further corroborated by the wall temperatures recorded in Figure 18c.

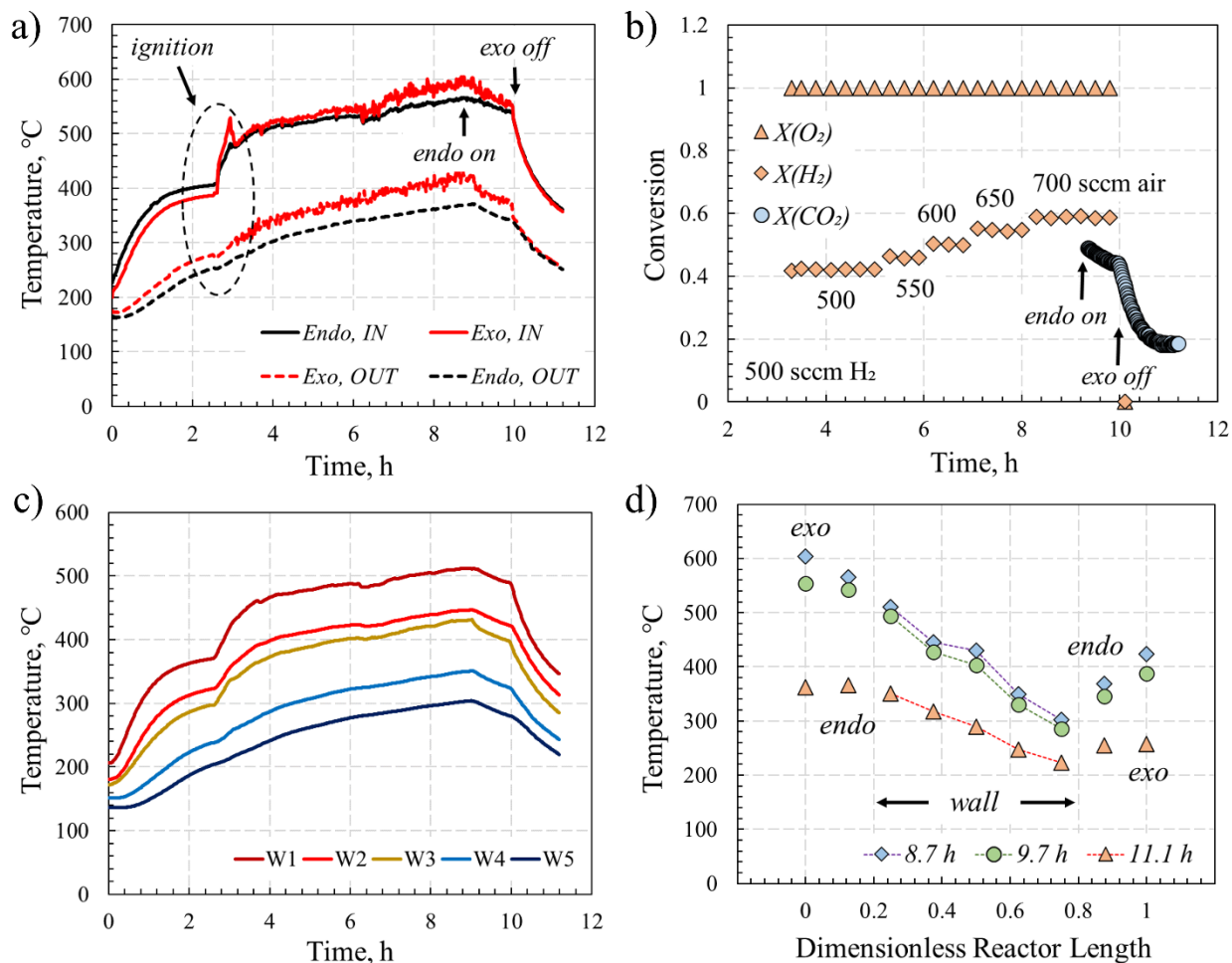


Figure 18. The effect of heat generation in the catalytic H_2 combustion compartment. Parameters: $Q_{f,endo} = 100/300$ mL/min CO_2/H_2 , air and H_2 flow rates in the exothermic compartment are specified in (b).

The Air/ H_2 flow rates and H_2 consumption rate are indicated in Figure 19a. A re-ignition test was conducted at $t = 7.2$ h, which demonstrated that the reactor operation is capable of being reignited. Following re-ignition and stabilization, the RWGS feed stream was introduced and the exothermic flow rate was adjusted to 240/150 mL/min air/ H_2 , with a ratio of air: $H_2 = 1.5$. The CHC inlet temperature stabilized at 600 °C with a H_2 conversion of 69% and full conversion of

O₂, while the inlet temperature in the RWGS compartment achieved 560 °C with 52% CO₂ conversion and complete CO selectivity. Subsequently, the feed flow rate was further adjusted in a series of discrete steps to 240/120 mL/min air/H₂, with a stoichiometric air:H₂ ratio of 2.0. The H₂ conversion experienced a notable increase from 69% to 88%. However, the CO₂ conversion slightly decreased to from 52% to 49%. Upon the introduction of a stoichiometric CHC feed stream, a trend of decline in inlet temperature was observed. After approximately 40 minutes of operation, the consumption rate of H₂ in the CHC compartment dropped significantly, followed by a sudden drop in inlet temperature. The temperatures within the reactor remained relatively stable until the final breakpoint, despite a slight downward trend. There was a slight decrease in the conversion of CO₂ from 52% to 49%, in accordance with the temperature decrease.

One hypothesis for the marked decrease in the conversion of H₂ and O₂, as well as the rate of H₂ consumption in the CHC compartment is that a gas explosion occurred with violence. The range of H₂ mole fraction that exhibits violence in gas explosion is 20-60%, especially in the range of stoichiometric composition. At lower temperatures, the explosion (both explosion rate, dp/dt , and the ratio of explosion pressure to initial pressure) becomes more pronounced [79]. During the final stages of this experiment ($t > 11h$), the inlet temperature in the CHC compartment clearly began to decrease, eventually reaching 500 °C, at which point there was an abrupt drop. One plausible explanation is that when the temperature lowers and the mole fraction of H₂ (33.3%) is within the range of maximum explosion potential, the reaction may become less stable and more prone to perturbation. Subsequently, extinction happened as observed. This observation reinforces

the conclusions drawn. These findings emphasize the significance of maintaining high reactor temperatures in order to preserve the operation of high conversion of CHC reaction.

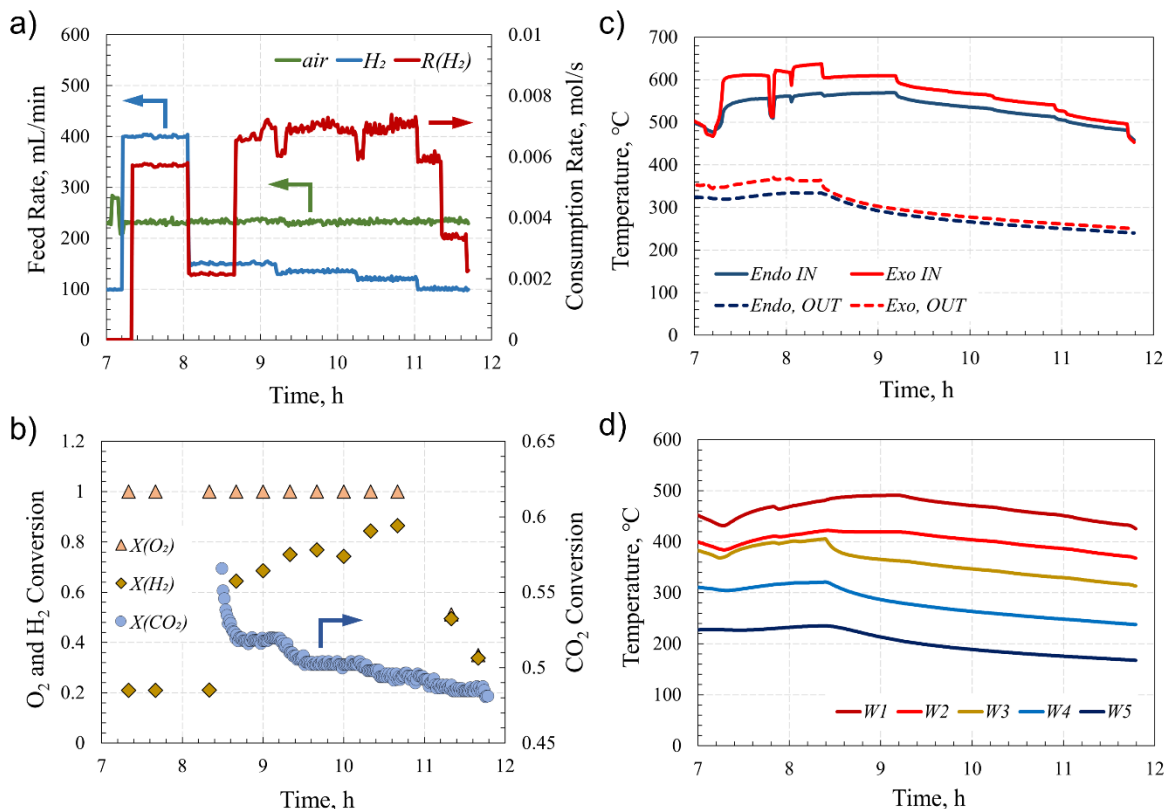


Figure 19. The effect of feed flow (CHC compartment) on the reactor temperatures and performance. Parameters: $Q_{f,endo} = 100/300$ ml/min CO_2/H_2 , air and H_2 flow rates are specified in (a).

3.2.4 Near-stoichiometric catalytic H_2 combustion feed

A near-stoichiometric CHC feed (air: $H_2 = 1.7$) and RWGS feed stream was introduced after the ignition and stabilization. Figure 20 illustrates an important observation that a strong correlation existed between the inlet temperatures and the CO_2 conversion detected. Despite the

severe drop in outlet temperature (approximate 160 °C), there was negligible impact on performance in the RWGS compartment. These findings suggest that the outlet CO₂ conversion was highly dependent on inlet temperatures, rather than the outlet temperatures. This conclusion aligns with the findings presented earlier, which indicate that the CHC took place in the front section of the reactor, and the RWGS reaction also occurred in this area due to the efficient heat transfer between the two compartments. Moreover, it can be deduced that the reactor performance remained robust to substantial changes in axial reactor temperature distribution within the CHC and RWGS compartments. This is evident by the fact that reactor operation continued smoothly despite variations between 500 °C and 450 °C in the aforementioned compartments.

The experimental results indicated that the reactor could achieve a 72% H₂ conversion and complete O₂ conversion while preserving inlet temperatures above 600 °C for both compartments. These conditions were within the optimal temperature range for both reactions to take place. Moreover, a consistent CO₂ conversion of 45-50%, along with complete CO selectivity throughout the experiments.

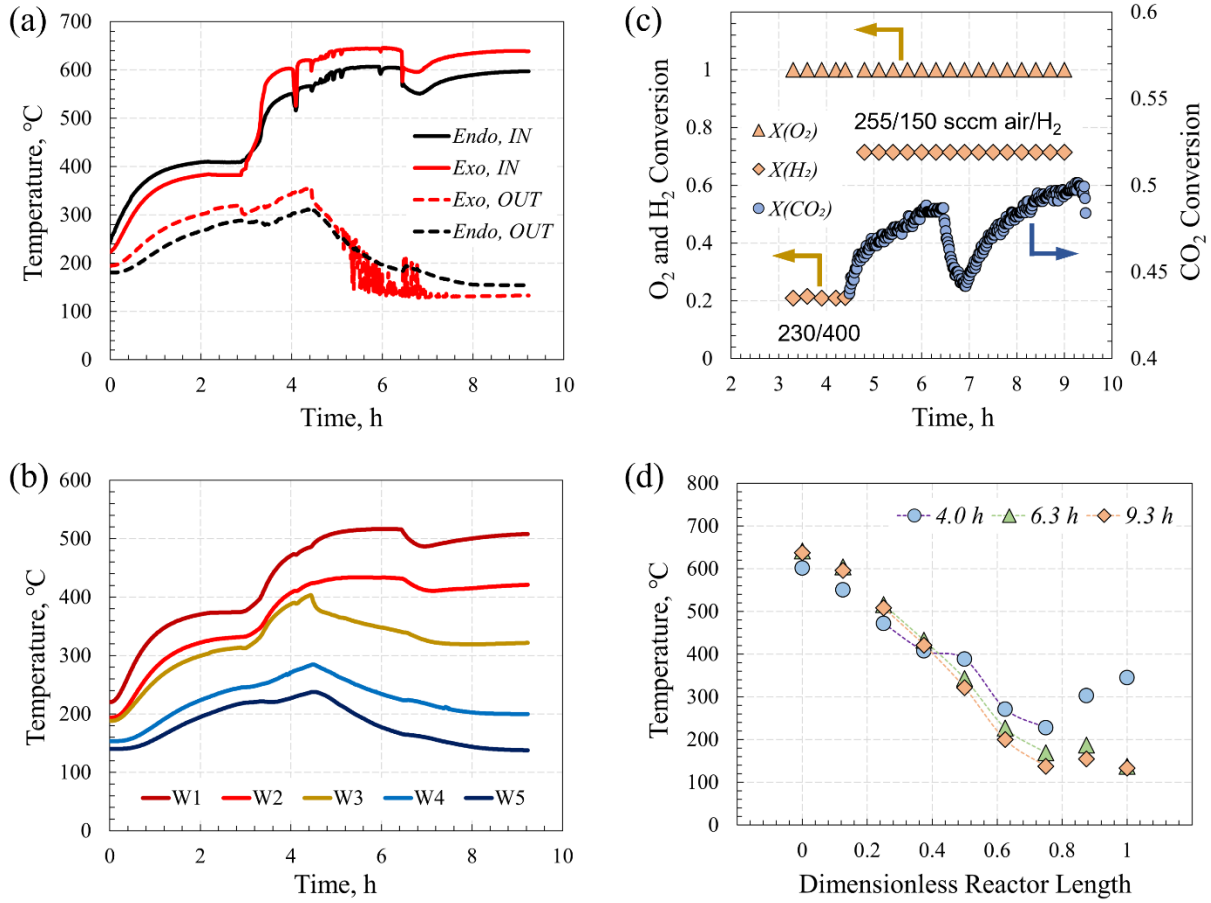


Figure 20. Reactor testing with near-stoichiometric catalytic H₂ combustion feed. Parameters: $Q_{f,endo} = 100/300$ ccm CO₂/H₂, air and H₂ flow rates are specified in (c).

3.2.5 Reactor stability

The stability of the catalyst is a crucial factor that should be taken into account in laboratory research studies when evaluating catalytic performance. It is of particular importance to investigate the catalyst stability in a reactor that has spatial distribution, both radial and axial temperature gradients. From a practical perspective, the stability of the reactor is of paramount importance as instability will lead to significant increases in the maintenance and operating costs (e.g., regenerating or replacing catalyst, monitoring, and controlling).

Figure 21 illustrates the results of the reactor performance stability test. After initial ignition and thermal stabilization, the RWGS reaction gas was introduced into the reactor. A CO_2 conversion of 42% was achieved with 100% generation selectivity to CO throughout the duration of the experiment. The stability of the reactor temperatures was observed to be consistent, as depicted in Figure 21b, c. Both inlet temperatures stabilized at ca. 420 °C ultimately, with significantly lower outlet temperatures of 141 °C for the Exo and 116 °C for the Endo. It was observed that there was a substantial difference of approximate 300 °C in axial temperature and a minor variation in the radial temperature difference at the outlet, which was attributed to the appearance of both CHC and RWGS reactions in the front region of the reactor, in addition to the considerable heat loss through the reactor wall. The wall temperatures, T_{W1} - T_{W5} , stabilized at 396 °C, 337 °C, 269 °C, 154 °C and 136 °C, respectively, indicating significant heat losses through the wall. It's important to note that no performance decline was observed during the test.

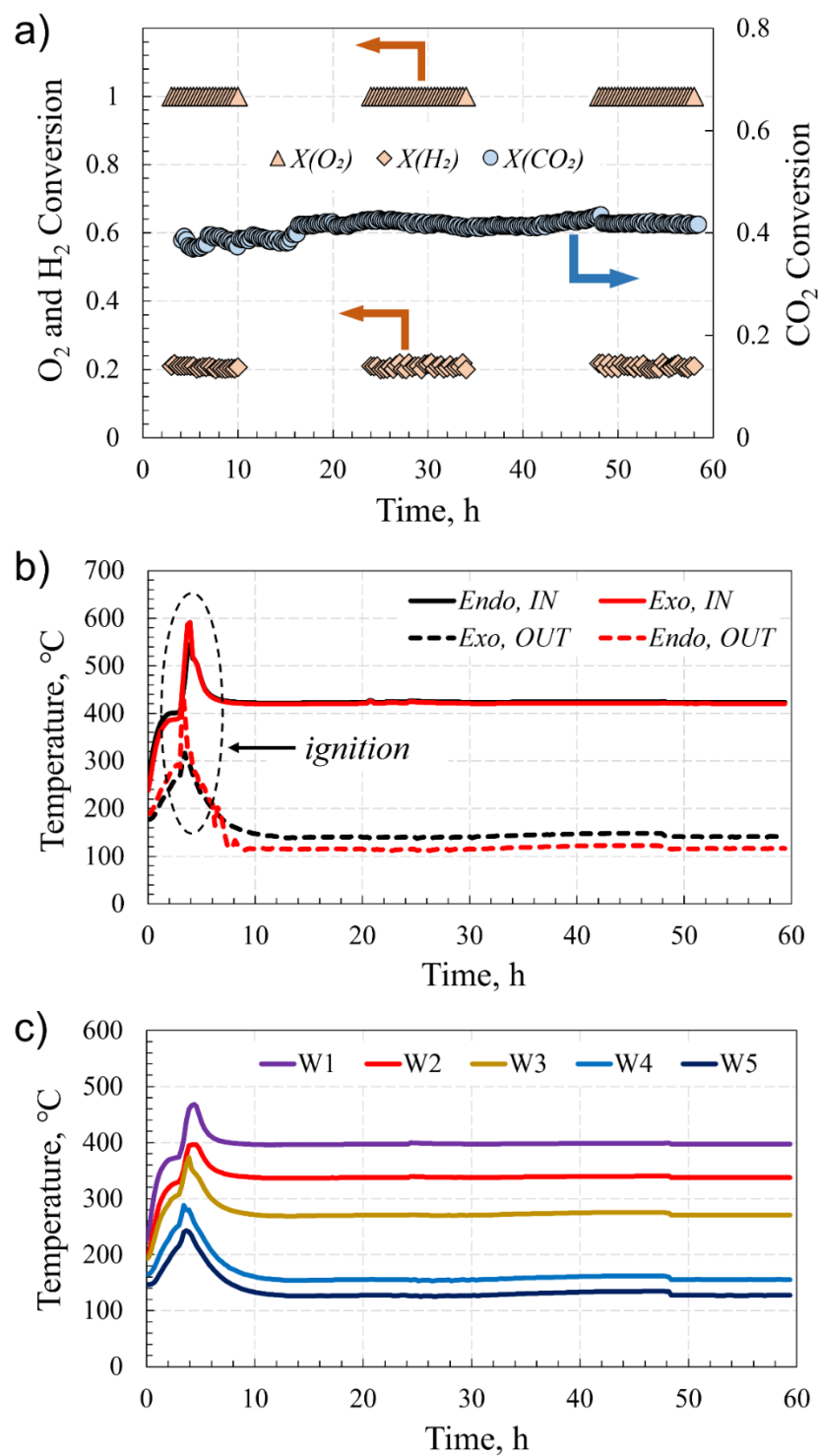


Figure 21. Reactor stability test. Parameters: $Q_{f,exo} = 230/400$ ml/min air/ H_2 , $Q_{f,endo} = 100/300$ ml/min CO_2/H_2 .

Chapter 4 Modeling of thermally coupled reactor

4.1 Methodology

4.1.1 Reaction kinetics

To predict the rates of the reactions and then optimize the design and predict the behavior of the reactor under different conditions, the kinetic models are developed for RWGS over a $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ synthesized by RME method and catalytic hydrogen combustion over $\text{Ni}/\text{Al}_2\text{O}_3$. An intrinsic rate equation for RWGS can be written using the Langmuir-Hinshelwood–Hougen-Watson (LHHW) approach. Assuming no CH_4 formation (as it was observed indeed for the $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst), a simple RWGS mechanism is suggested (L stands for an active site):



Following the Langmuir-Hinshelwood formalism (all reactions, including the surface reaction, can be represented by elementary reversible reactions), and assuming that the rate limiting step is CO_2 dissociation, a suitable kinetic equation, Eq. (17) was determined.

$$R = k_{RWGS} \left(P_{\text{CO}_2} - \frac{P_{\text{CO}} P_{\text{H}_2\text{O}}}{K_{RWGS} P_{\text{H}_2}} \right) \frac{1}{\text{DEN}^2}\tag{17}$$

$$DEN = 1 + K_{CO}P_{CO} + \frac{K_{H_2O}P_{H_2O}}{P_{H_2}}$$

in which k_{RWGS} is the rate constant, which according to the Arrhenius equation is given by Eq. (18), K_{RWGS} is the equilibrium constant which for the RWGS reaction is given by Eq. (19) [80], K_{CO} and K_{H_2O} are the adsorption coefficient of CO and H₂O, which are related to the temperature through Eq. (20):

$$k_{RWGS} = A_{RWGS} \exp\left(-\frac{E_a}{R_g T}\right) \quad (18)$$

$$K_{RWGS} = 56.60 \exp\left(-\frac{36.58}{R_g T}\right) \quad (19)$$

$$K_i = B_i \exp\left(-\frac{\Delta H_i}{R_g T}\right) \quad (20)$$

Parameter estimation was done using the minimization of the sum of weighted residual squares of the CO₂ and CO concentrations by means of the Trust-Region Reflective Algorithm [81]. Experimental values were measured by the IR analyzer. Simulated mole fractions were obtained by integrating a set of ordinary differential equations (4th Runge-Kutta) representing time evolution of all species participating in the RWGS reaction,

$$\varepsilon \frac{dC_i}{dt} = -\frac{\varepsilon Q_f (C_i - C_{if})}{V_r} + (1 - \varepsilon) \rho_{cat} \alpha_i R_{RWGS} \quad (21)$$

C_i is molar concentration for species i , ε is void fraction, Q_f is volumetric flow rate, V_r is reactor volume, ρ_{cat} is catalyst density, and α_i is stoichiometric coefficient. Initial guesses for

adsorption constants were adopted from Xu and Froment [82], and the initial guesses for the activation energy and the reaction rate constant were obtained experimentally. An MSE-based model selection criterion was employed to determine which parameters should be estimated and which should be left at their initial guesses to obtain the best fitting non-linear multivariate model [81]. This analysis revealed that all six parameters are estimable from the available data. The associated parameter estimation results are shown in Table 1, based on the data shown in Figure 22. The suggested rate expression with the estimated parameters listed in Table 1 was found to fit the experimental data well, predicting quite accurately the experimentally measured mole fractions of CO₂ and CO over a variety of operating conditions, as it is shown in Figure 22 (error bars show standard deviation between three separate data sets obtained with different catalyst batches).

Table 1. The estimated kinetic parameters of reverse water gas shift reaction.

	A_{RWGS}	E_a	B_{CO}	ΔH_{CO}	B_{H_2O}	ΔH_{H_2O}
value	1.54×10^7	72.73	6.47×10^{-3}	-60.31	3.15×10^6	77.82
unit	mol/(kg bar s)	kJ/mol	1/bar	kJ/mol	-	kJ/mol

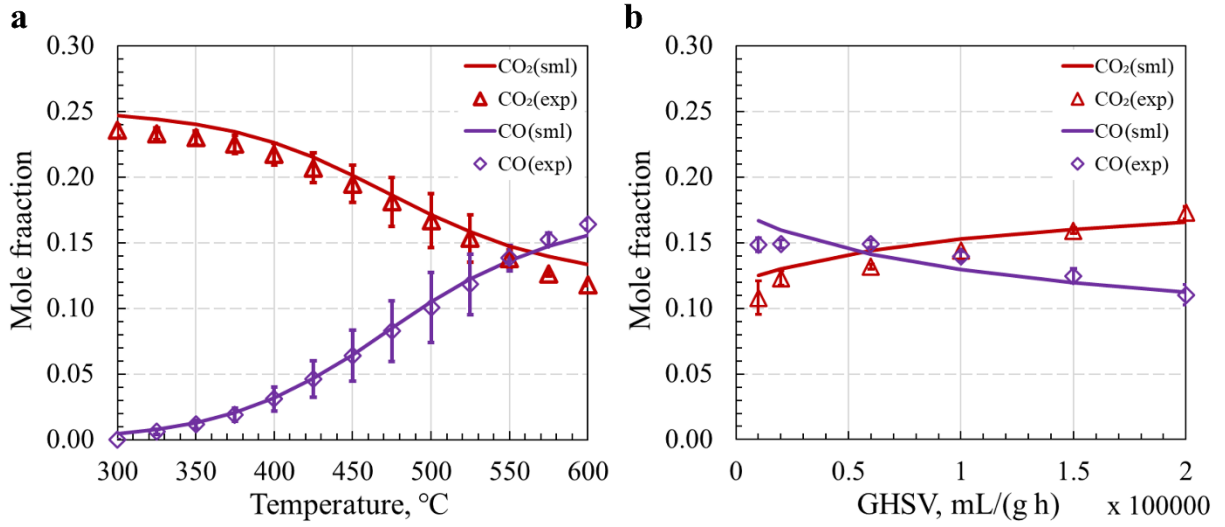


Figure 22. Performance comparison between the simulation and experimental results in terms of CO₂ and CO mole fraction over the range of temperatures (a) and space velocities (b). Parameters: P = 3 bar, GHSV = 60,000 mL/(g h) (a); T = 600 °C (b).

For the catalytic hydrogen combustion reaction over commercial Ni catalyst (12 wt% Ni/Al₂O₃, BASF, supplied by Research Catalysts, Inc. USA), the pre-exponent and activation energy were obtained experimentally as shown in Table. 2. Assuming the kinetics is 1st-order in oxygen and 2nd-order in hydrogen, a reaction rate expression, Eq. (22) was determined and was found to fit the experimental data well with the parameters estimated as shown in Figure 23.

$$R_{Ox} = A_{Ox} \exp\left(-\frac{E_a}{R_g T}\right) \rho_g^3 y_{H_2}^2 y_{O_2} \quad (22)$$

Table 2. The estimated kinetic parameters of catalytic H₂ combustion reaction.

	A _{CHC}	E _a
value	78.56	93.07
unit	m ⁹ /(kg mol ² s)	kJ/mol

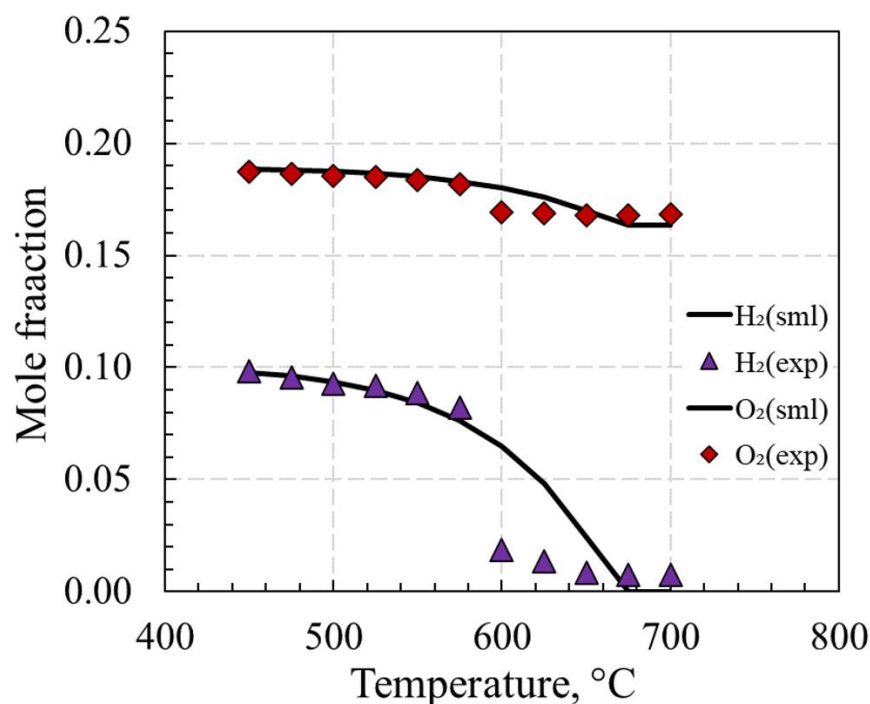


Figure 23. Performance comparison between the simulation and experimental results in terms of H₂ and O₂ mole fraction over the range of temperatures. Parameters: P = 1 bar, GHSV = 200,000 mL/(g h), H₂:air = 1:9

4.1.2 Reactor configuration and dimensions

A schematic representation of the suggested thermal coupled reactor is shown in Figure 24. The reactor in a concentric tube configuration comprised of two compartments: catalytic hydrogen combustion takes place on the commercial Ni catalyst in the exothermic side and reverse water gas shift process takes place on the Mo₂C/Al₂O₃ catalyst in the endothermic side which are separated by solid tube wall. RWGS is supposed to take place on the shell side whereas the CHC is considered to provide the heat in the tube side. The whole reactor is simulated to be covered

with an insulation layer. A two-dimensional pseudo-homogeneous model has been developed in order to determine the concentration and temperature distributions inside the reactor. Only the half reactor needs to be utilized, due to symmetrical conditions at the centerline of the channels. Thus, three different domains could be identified: CHC compartment (Exo compartment), RWGS compartment (Endo compartment), and insulation layer. Notice the locations of the cutline, Figure. 24d, are applied to all the simulations results.

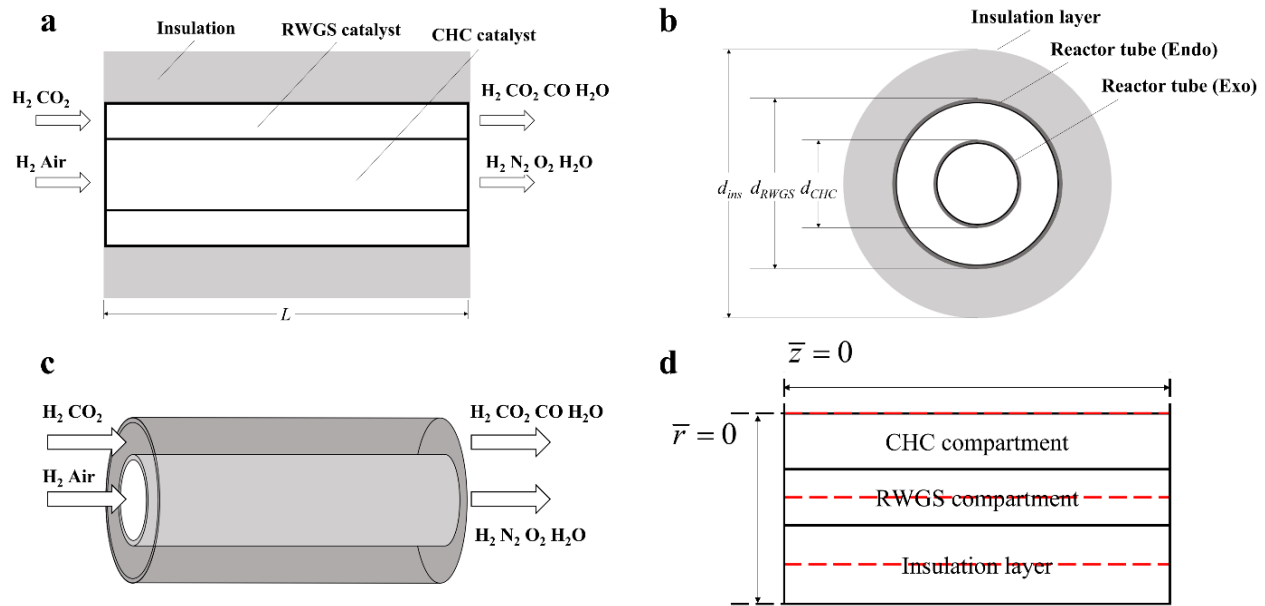


Figure 24. Schematic diagram of the thermally coupled reactor (a, b, c), and the locations of the cutline to visualize along the line (d).

The reactor dimensions (based on the experimentally investigated reactor) used in the simulation are listed in Table. 3. It's assumed that material of solid phase is stainless steel from Swagelok (all related parameters are taken from Swagelok tubing data sheet).

Table 3. Reactor dimensions.

Parameters	Symbol	Value	Units
CHC compartment radius	R_{CHC}	0.00318– 0.25	m
CHC compartment wall thickness	$d_{w,CHC}$	0.0009 – 0.005	m
RWGS compartment radius	R_{RWGS}	0.00635 – 0.5	m
RWGS compartment wall thickness	$d_{w,RWGS}$	0.00124 – 0.005	m
insulation layer thickness	d_{iw}	0.07 – 0.5	m
reactor length	L	0.2 - 10	m
void fraction (CHC & RWGS)	ε	0.5	
spherical catalyst pellet diameter	d_p	0.003 – 0.005	m

4.1.3 Reactor formulations

A two-dimensional pseudo-homogeneous model was used to simulate the reactor. The fundamental principle governing the procedures for establishing a reactor model is to present the actual reactor under the conditions of necessary assumptions and simplifications. This principle facilitates the convergence of the simulation to a reliable result in an efficient and steady manner. Consequently, the following assumptions are considered for both sides of the reactor:

- The gas mixture is an ideal gas in both compartments.
- The transport mechanisms considered are convection for axial direction while conduction and diffusion occur in both directions.
- Bed porosity in axial and radial directions is constant.
- Plug flow is employed in both compartments.

- The pressure drop along the channels is neglected.
- Catalyst deactivation is neglected.
- Diffusive mass flux and conductive heat flux at reactor outlet are assumed to be zero.

In order to facilitate the numerical procedures, the equations were derived and then transformed into their dimensionless forms as shown in Table. 4. Component mass balances for the CHC compartment and RWGS compartments are given by Eqs. (23), (24) ($i \equiv \text{H}_2, \text{O}_2, \text{H}_2\text{O}$ for CHC and $i \equiv \text{CO}_2, \text{H}_2, \text{CO}, \text{H}_2\text{O}$ for RWGS). Energy balances in the CHC, RWGS and insulation compartments are described by Eqs. (25-27), respectively.

Table 4. Model formulation.

Mass balances in the CHC compartment

$$\frac{\partial y_i^{CHC}}{\partial \tau} = \left(\frac{S^2}{Pe_{rm}} \right)^{CHC} \left(\frac{\partial^2 y_i}{\partial \bar{r}^2} + \frac{1}{\bar{r}} \frac{\partial y_i}{\partial \bar{r}} \right)^{CHC} + \left(\frac{1}{Pe_{zm}} \right)^{CHC} \frac{\partial^2 y_i^{CHC}}{\partial \bar{z}^2} - \frac{\partial y_i^{CHC}}{\partial \bar{z}} + Da_{CHC} \alpha_i f_{CHC} \quad (23)$$

Mass balances in the RWGS compartment

$$\begin{aligned} \frac{\partial y_i^{RWGS}}{\partial \tau} = & \left(\frac{S^2}{Pe_{rm}} \right)^{RWGS} \left(\frac{\partial^2 y_i}{\partial \bar{r}^2} + \frac{1}{\bar{r}} \frac{\partial y_i}{\partial \bar{r}} \right)^{RWGS} + \left(\frac{1}{Pe_{zm}} \right)^{RWGS} \frac{\partial^2 y_i^{RWGS}}{\partial \bar{z}^2} - \frac{\partial y_i^{RWGS}}{\partial \bar{z}} \\ & + Da_{RWGS} \alpha_i f_{RWGS} \end{aligned} \quad (24)$$

Energy balances in the CHC compartment

$$\begin{aligned} \sigma^{CHC} \frac{\partial \theta^{CHC}}{\partial \tau} = & \left(\frac{S^2}{Pe_{rh}} \right)^{CHC} \left(\frac{\partial^2 \theta}{\partial \bar{r}^2} + \frac{1}{\bar{r}} \frac{\partial \theta}{\partial \bar{r}} \right)^{CHC} + \left(\frac{1}{Pe_{zh}} \right)^{CHC} \frac{\partial^2 \theta^{CHC}}{\partial \bar{z}^2} - \frac{\partial \theta^{CHC}}{\partial \bar{z}} \\ & + \beta_{CHC} Da_{CHC} f_{CHC} \end{aligned} \quad (25)$$

Energy balances in the RWGS compartment

$$\begin{aligned} \sigma^{RWGS} \frac{\partial \theta^{RWGS}}{\partial \tau} = & \left(\frac{S^2}{Pe_{rh}} \right)^{RWGS} \left(\frac{\partial^2 \theta}{\partial \bar{r}^2} + \frac{1}{\bar{r}} \frac{\partial \theta}{\partial \bar{r}} \right)^{RWGS} + \left(\frac{1}{Pe_{zh}} \right)^{RWGS} \frac{\partial^2 \theta^{RWGS}}{\partial \bar{z}^2} - \frac{\partial \theta^{RWGS}}{\partial \bar{z}} \\ & + \beta_{RWGS} Da_{RWGS} f_{RWGS} \end{aligned} \quad (26)$$

Energy balances in the insulation layer

$$S^2 k_i \frac{1}{\bar{r}} \left(\frac{\partial \theta_i}{\partial \bar{r}} + \bar{r} \frac{\partial^2 \theta_i}{\partial \bar{r}^2} \right) + k_i \frac{\partial^2 \theta_i}{\partial \bar{z}^2} = 0 \quad (27)$$

The dimensionless variables, parameters and functions are defined in Table 5. The initial and boundary conditions are listed in Eqs (38 - 48) in Table 6.

Table 5. Dimensionless variables, parameters and functions.

Dimensionless variables	
$\tau = \frac{t}{L / v_g}$	$\bar{z} = \frac{z}{L}$
$\bar{r} = \frac{r}{R}$	$\theta = \frac{T}{T_{ad}}$
Dimensionless parameters	
$S^2 = \frac{L^2}{R^2}$	$\sigma = \frac{\varepsilon \rho_g C_{pg} + (1 - \varepsilon) \rho_s C_{ps}}{\varepsilon \rho_g C_{pg}}$
$\beta_{Ox} = \frac{-\Delta H_{Ox}}{T_{ad} C_{pg}}$	$\beta_{RWGS} = \frac{-\Delta H_{RWGS}}{T_{ad} C_{pg}}$
$Pe_{zm} = \frac{\varepsilon v_g L}{D_{ae}}$	$Pe_{rm} = \frac{\varepsilon v_g L}{D_{re}}$
$Pe_{zh} = \frac{\varepsilon v_g L \rho_g C_{pg}}{k_{ae}}$	$Pe_{rh} = \frac{\varepsilon v_g L \rho_g C_{pg}}{k_{re}}$
$Da_{Ox} = \frac{W_{cat}^{Ox} \cdot A_{Ox} \cdot \rho_{gf}^2}{Q_f^{Ox}}$	$Da_{RWGS} = \frac{W_{cat}^{RWGS} \cdot A_{RWGS} \cdot P_t}{Q_f^{RWGS} \rho_{gf}}$
$Bi_{RWGS} = \frac{U_{w,HL} \cdot R^{RWGS}}{k_{re}^{RWGS}}$	$Bi_{Ox} = \frac{U_{w,HE} \cdot R^{Ox}}{k_{re}^{Ox}}$
Dimensionless functions	
$f_{RWGS} = \exp\left(-\frac{\gamma_{RWGS,ad}}{\theta^{RWGS}}\right) \left(y_{CO_2} - \frac{y_{CO} y_{H_2O}}{K_{RWGS} y_{H_2}}\right) \frac{1}{DEN^2}$	
$f_{Ox} = \exp\left(-\frac{\gamma_{Ox,ad}}{\theta^{Ox}}\right) y_{H_2}^2 y_{O_2}$	

Table 6. Initial and boundary conditions.

Initial conditions		
$\tau = 0:$	$y_i^k = y_{i0}^k, \theta^k = \theta_0^k$	(38)
Boundary conditions		
radial		
$\bar{r} = 0, 0 \leq \bar{z} \leq 1:$	$\frac{\partial \theta^{Ox}}{\partial \bar{r}} = 0, \frac{\partial y_i^{Ox}}{\partial \bar{r}} = 0$	(39)
$\bar{r} = \bar{r}^{Ox}, 0 \leq \bar{z} \leq 1:$	$\frac{\partial \theta^{Ox}}{\partial \bar{r}} = -Bi_{Ox} (\theta^{Ox} - \theta^{RWGS}), \frac{\partial y_i^{Ox}}{\partial \bar{r}} = 0$	(40)
$\bar{r} = \bar{r}^{RWGS}, 0 \leq \bar{z} \leq 1:$	$\frac{\partial \theta^{RWGS}}{\partial \bar{r}} = -Bi_{RWGS} (\theta^{RWGS} - \theta_a), \frac{\partial y_i^{RWGS}}{\partial \bar{r}} = 0$	(41)
$\bar{r} = \bar{r}^{ins}, 0 \leq z \leq L:$	$\frac{\partial \theta^{ins}}{\partial \bar{r}} = -Bi_{HL} (\theta_{ins} - \theta_a)$	(42)
axial		
$\bar{z} = 0, 0 \leq \bar{r}^{Ox} \leq 1$	$-\left(\frac{1}{Pe_{zm}}\right)^{Ox} \frac{\partial y_i^{Ox}}{\partial \bar{z}} = (y_{if}^{Ox} - y_i^{Ox})$	(43)
	$-\left(\frac{1}{Pe_{zh}}\right)^{Ox} \frac{\partial \theta^{Ox}}{\partial \bar{z}} = (\theta_f^{Ox} - \theta^{Ox})$	(44)
$\bar{z} = 0, \frac{R^{Ox}}{R^{RWGS}} \leq \bar{r}^{RWGS} \leq 1$	$-\left(\frac{1}{Pe_{zm}}\right)^{RWGS} \frac{\partial y_i^{RWGS}}{\partial \bar{z}} = (y_{if}^{RWGS} - y_i^{RWGS})$	(45)
	$-\left(\frac{1}{Pe_{zh}}\right)^{RWGS} \frac{\partial \theta^{RWGS}}{\partial \bar{z}} = (\theta_f^{RWGS} - \theta^{RWGS})$	(46)
$\bar{z} = 1, 0 \leq \bar{r}^{Ox} \leq 1$	$\frac{\partial y_i^{Ox}}{\partial \bar{z}} = 0, \frac{\partial \theta^{Ox}}{\partial \bar{z}} = 0$	(46)
$\bar{z} = 1, \frac{R^{Ox}}{R^{RWGS}} \leq \bar{r}^{RWGS} \leq 1$	$\frac{\partial y_i^{RWGS}}{\partial \bar{z}} = 0, \frac{\partial \theta^{RWGS}}{\partial \bar{z}} = 0$	(48)

4.1.4 Transport parameters

a. Overall heat transfer coefficient

Wall heat transfer coefficients for heat exchange between the RWGS compartment and Ox compartment, Eq. (49), and heat loss to the environment, Eq. (50), were calculated by resistances in series. These parameters account for the contribution of the effective wall heat transfer coefficient for each compartment (h_w), wall thermal conductivity (λ_w), insulation layer (λ_{iw}) and natural convection from the external reactor surface (h_{nc}).

$$U_{w,HE} = \left(\frac{1}{h_w^{RWGS}} + \frac{d_w^{Ox}}{h_w^{Ox}} + \frac{1}{h_w^{Ox}} \right)^{-1} \quad (49)$$

$$U_{w,HL} = \left(\frac{1}{h_w^{RWGS}} + \frac{d_w^{RWGS}}{\lambda_w^{RWGS}} + \frac{d_{iw}}{\lambda_{iw}} + \frac{1}{h_{nc}} \right)^{-1} \quad (50)$$

The effective wall heat transfer coefficient for the reaction compartment was estimated using the following correlation [83, 84]:

$$Nu_{w,HE} = \frac{h_w d_p}{k_g} = 0.23 Re_p + 27.9 \quad (51)$$

The values for the insulation layer (quartz wool) conductivity (λ_{iw}) and natural convection (h_{nc}) were adopted from the literature [85, 86]. These contributions were dominant in Eq. (50) and the wall heat loss coefficient was nearly constant in all simulations: $U_{w,HL} = 0.03 \text{ kW}/(\text{m}^2 \text{ K})$.

b. Effective thermal conductivity and diffusion coefficient

In a two-dimensional model that considers both axial and radial dispersion, the transport of heat is facilitated through the utilization of both convection and thermal dispersion. Numerous studies, both theoretical and experimental, have been conducted to estimation of the effective thermal conductivity in a packed bed [87, 88]. Correlations for predicting the axial or the radial thermal conductivity are primarily represented in a linear form with respect to particle-based Reynold or Peclet number are shown in Table. 7. The value for the radial effective heat conductivity and axial effective heat coefficient could be well described by the correlations, Eqs. (52), (53) [89, 90]. The effective axial and the radial dispersion coefficients were calculated using a typical correlation adopted from literature, Eqs. (54), (55) [91, 92].

Table 7. Effective thermal conductivity and diffusion coefficient.

Effective heat coefficient

axial

$$k_{ea} = k_g \left(4 + \frac{\text{Re}_p \text{Pr}}{2} \right) \quad (52)$$

radial

$$k_{er} = k_g \left(4 + \frac{\text{Re}_p \text{Pr}}{7 \left[2 - (1 - 2d_p / d_R)^2 \right]} \right) \quad (53)$$

Effective diffusion coefficient

axial

$$D_e = \varepsilon \left(\frac{D_m}{\tau_{bed}} \right), \text{ for } \text{Re} < 1 \quad D_e = \varepsilon \left(\frac{D_m}{\tau_{bed}} + 0.1d_p v_g \right), \text{ for } \text{Re} > 5 \quad (54)$$

radial

$$D_e = \varepsilon \left(\frac{D_m}{\tau_{bed}} \right), \text{ for } \text{Re} < 1 \quad D_e = \varepsilon \left(\frac{D_m}{\tau_{bed}} + 0.5d_p v_g \right), \text{ for } \text{Re} > 5 \quad (55)$$

correlations

$$\text{Re}_p = \frac{v_g \rho_g d_p}{\mu_g} \quad \text{Pr} = \frac{\mu_g C_{pg}}{\lambda_g} \quad D_m = D_0 \left(\frac{T}{T_0} \right)^\alpha \left(\frac{P_0}{P} \right) \quad \tau_{bed} = \frac{1}{\sqrt{\varepsilon_{bed}}} \quad (56)$$

c. Transport limitation

In the study of heterogeneously catalyzed reactions, it is important to determine whether the investigation is on catalytic kinetics or the interplay between kinetics and transport phenomena. This distinction is fundamental to the interpretation of the results and to the development of meaningful conclusions and insights into the reaction mechanism. The absence of interphase and intraparticle mass and heat transfer limitations was confirmed by calculating corresponding criteria in Table 8 [92, 93]. Interphase mass and heat transfer coefficients (k_c and h) were calculated using

the following correlations [94]. More details are listed in Appendix E Mass and heat transfer criteria.

Table 8. Mass and heat transfer criteria.

Mears criterion for interphase mass transfer	$\frac{R'_{obs}\rho_b R_p}{k_c C_{CO_2,b}} \leq 0.15$	(57)		
Mears criterion for interphase heat transfer	$\frac{ \Delta H_{Rx} R'_{obs}\rho_b R_p}{hT} \leq \frac{0.15TR_g}{E_a}$	(58)		
Weisz-Prater criterion for internal diffusion	$\frac{R'_{obs}\rho_b R_p^2}{D_m C_{CO_2,s}} \leq 1$	(59)		
Isothermal pellet criterion	$\frac{ \Delta H_{Rx} R'_{obs}\rho_b R_p^2}{\lambda_s T_s} \leq \frac{0.75T_s R_g}{E_a}$	(60)		
correlations				
	$Sh = \frac{k_c d_p}{D_m} = 2 + 0.6 Re^{\frac{1}{2}} Sc^{\frac{1}{3}}$	$Nu_p = \frac{h d_p}{\lambda_g} = 2 + 0.6 Re^{\frac{1}{2}} Pr^{\frac{1}{3}}$	$Sc = \frac{\mu_g}{\rho_g D_m}$	(61)

4.1.5 Reactor performance

Reactor performance was evaluated in terms of H₂ and O₂ conversions within the CHC compartment, the conversion of CO₂ and the selectivity toward CO within the RWGS compartment, as well as the overall stability. Gas hourly space velocity (GHSV) is calculated as follows (Q_f is the total volumetric feed flow rate at atmospheric pressure and room temperature and W_c is the catalyst weight):

$$GHSV = \frac{Q_f}{W_c} \quad (62)$$

Feed composition parameter α in the RWGS compartment is defined as H₂:CO₂ ratio, Eq. (63):

$$\alpha = \frac{F_{H_2, f}}{F_{CO_2, f}} \quad (63)$$

CO₂ conversion to CO is defined as X_{CO_2} :

$$X_{CO_2} = \frac{F_{CO, out}}{F_{CO_2, f}} = \frac{y_{CO}}{(y_{CO} + y_{CO_2})} \quad (64)$$

H₂ and O₂ conversions are defined as X_{H_2} and X_{O_2} :

$$X_{H_2} = \frac{(y_{f, H_2} - y_{H_2})^{CHC}}{y_{f, H_2}^{CHC}} \quad (65)$$

$$X_{O_2} = \frac{(y_{f, O_2} - y_{O_2})^{CHC}}{y_{f, O_2}^{CHC}} \quad (66)$$

In the Eqs. (64-66), y_i stand for mole fractions.

4.1.6 Numerical modelling

The two-dimensional numerical simulations in this study are performed using COMSOL Multiphysics 5.5, a simulation platform that provides fully coupled multiphysics and single-physics modeling capabilities. The time-dependent models are by default solved with an adaptive timestepping scheme, which the software will automatically adjust the timestep size to maintain the desired relative tolerance. 10 dimensionless equations, ten initial conditions, 35 boundary

conditions, 128 constant parameters, and 41 variable-dependent parameters are defined and implemented as referred to in the Appendix K COMSOL model. The mesh element parameters are customized as the following: 0.008 maximum element size, 0.00005 minimum element size, 1.1 maximum element growth rate, 0.2 curvature factor and 1.0 resolution of narrow regions. Time interval for simulation is the step entry method of range(0,5,10,000), which ranges from 0 to 10,000 with a step of 5. Regarding the type of solver, operation node is selected as a time-dependent solver and attribute node is fully-coupled in this study.

4.2 Results and discussion

In the CHC compartment, where hydrogen and air are initially fed, the heat produced by their reaction is continuously transferred to the endothermic compartment through the wall. After reaching a steady state within the entire reactor, the RWGS feed stream is introduced into the RWGS compartment. Table 9 lists all simulation operating conditions.

Table 9. Operating conditions.

Parameters	Symbol	Value	Units
RWGS feed composition	$H_2:CO_2$	3:1	
fuel concentration (feed H_2 mole fraction in CHC)	y_{H_2}	0.07 – 0.20	
gas hourly space velocity (CHC)	$GHSV_{CHC}$	100 – 100,000	L/(kg h)
gas hourly space velocity (RWGS)	$GHSV_{RWGS}$	20 – 100,000	L/(kg h)
feed pressure (CHC)	P_{exo}	5 - 6	bar
feed pressure (RWGS)	P_{endo}	1 - 5	bar
feed temperature (CHC)	$T_{f,CHC}$	300 - 600	°C
feed temperature (RWGS)	$T_{f,RWGS}$	300 - 600	°C
initial temperature (CHC & RWGS)	T_0	300 - 350	°C
ambient temperature	T_a	50	°C

4.2.1 Dynamic analysis and general performance

The dynamic behavior of a typical reactor start-up process is analyzed first. Figures 25 and 26 present the evolution of the temperature, conversions and mole fractions in both compartments at three locations ($z/L = 0.1, 0.5$ and 0.9) along the cutlines defined in Figure 24d. At the beginning, pure nitrogen was fed to the endothermic side to achieve a steady state with a higher temperature. Figure 25a appeals that the ignition causes rapid formation of a hot spot at the front, which propagates downstream due to the complete combustion and axial heat transfer. The simultaneous temperature increase in the CHC, RWGS, and insulation side confirms the efficient transfer between compartments inside the reactor. The drop in temperature in both the CHC and RWGS compartments along the axial direction is primarily a result of heat loss.

After changing from pure N_2 to the RWGS feed stream at $\tau = 2000$, the reactor temperature drops because of heat consumption by the RWGS process, which is confirmed by the instant CO_2 conversion in the RWGS compartment. The temperature difference between the CHC and RWGS compartments decreases as the flow progresses through the reactor. This difference is further reduced after introducing the feed stream, illustrating how heat from the exothermic side is absorbed by the RWGS reaction. Prior to RWGS introduction, a temperature difference of approximately $100\text{ }^{\circ}C$ is observed between the two compartments at the reactor entrance. This difference decreases to approximately $50\text{ }^{\circ}C$ upon introducing the feed stream. Complete consumption of H_2 occurs at the reactor front, causing the temperature to decrease across the remainder of the reactor due to the comparative heat utilization by RWGS and heat loss. A minor temperature difference was observed between the two compartments in the middle of the reactor, and at the reactor exit, the temperature difference was negligible.

The simulations demonstrate the feasibility of the novel reactor concept. The results also emphasize the importance of thermal management, suggesting that the CHC feed supply should be sufficient to sustain the RWGS process temperature as well as compensate for heat losses. Furthermore, the results show that the steady state is reached within $\tau = 1000$ after ignition and $\tau = 2000$ after introducing the RWGS feed stream. These heat equilibration times were consistent across all the simulation results.

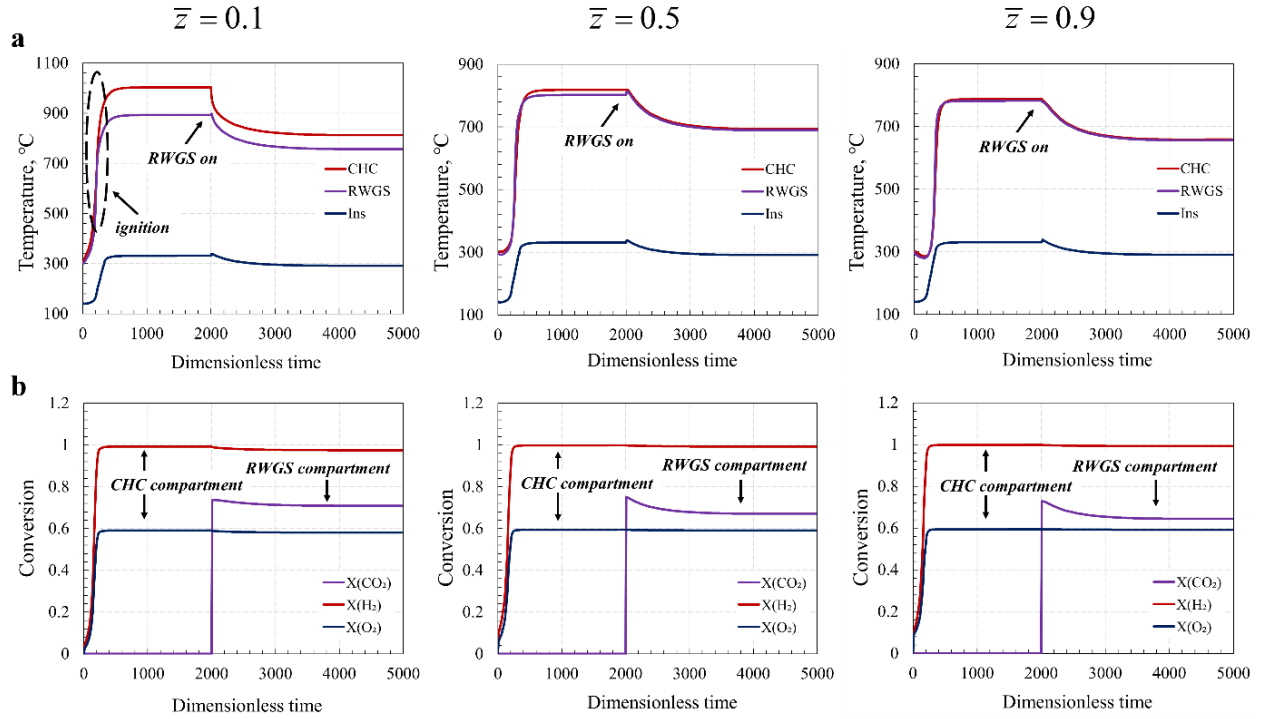


Figure 25. Typical profiles of the reactor ignition, introducing RWGS feed stream at $\tau = 2000$ and stabilization, showing transient temperatures in the catalytic bed (a), CO_2 , H_2 and O_2 conversions (b) for three different points in time. Parameters: $y_{\text{H}_2}(\text{CHC}) = 0.20$, $P_{\text{endo}} = 5$ bar, $P_{\text{exo}} = 6$ bar, $\text{GHSV}_{\text{RWGS}} = 500$ L/(kg h), $\text{GHSV}_{\text{CHC}} = 2000$ L/(kg h), $T_f = 400$ °C, $T_0 = 300$ °C.

Figure 26 shows the evolution of the mole fractions in both exothermic and endothermic compartments. Figure 26a indicates that pure N_2 was provided in the RWGS compartment until $\tau = 2000$. After switching to RWGS feed gas, CO_2 was instantaneously converted to CO , as the reactor had already reached the optimal temperature range due to the CHC reaction. Figure 26b shows the fast consumption of H_2 upon introducing the CHC reaction gas to the reactor. Complete utilization of H_2 occurred at the entrance of the reactor.

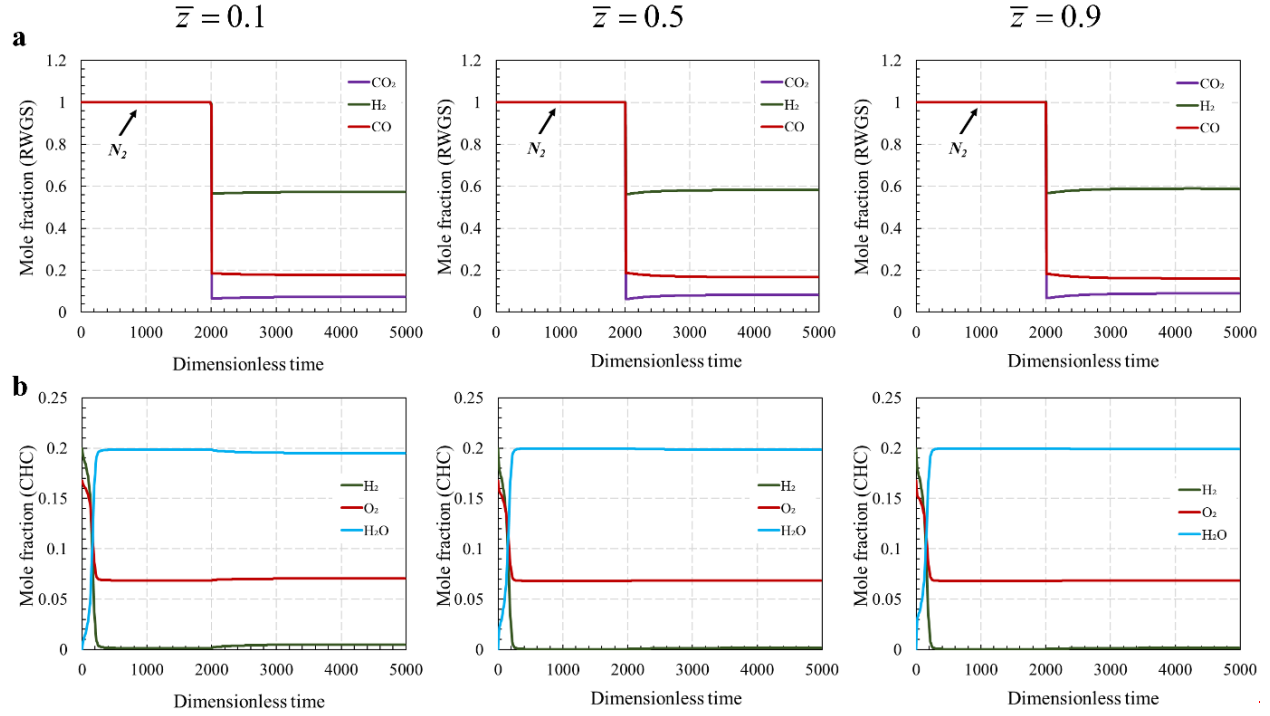


Figure 26. Typical profiles of the reactor ignition, introducing RWGS and stabilization, showing transient mole fractions in the RWGS compartment (a), and CHC compartment (b) for three different points in time. Parameters: $y_{H_2}(CHC) = 0.20$, $P_{\text{endo}} = 5$ bar, $P_{\text{exo}} = 6$ bar, $GHSV_{RWGS} = 500$ L/(kg h), $GHSV_{CHC} = 2000$ L/(kg h), $T_f = 400$ °C, $T_0 = 300$ °C.

The dynamic reactor temperature and performance are further illustrated as scenes of 3D animation in Figures 27-29. Temperatures and conversions can be interpreted using the colored scale included in each figure. Figure 27 displays the spatiotemporal evolution of the entire reactor temperature. At $\tau = 0$, both compartments maintained the initial temperature, T_0 , and a uniformly decreasing distribution was visible in the radial direction up to the outer layer of the insulation compartment. After introducing H_2 /air mixture into the CHC compartment and stabilizing until $\tau = 1950$, a hot spot was detected at $z/L = 0.2$. The CHC compartment witnesses a 100 °C temperature distribution downstream while a relatively small difference (~ 20 °C) was observed in the RWGS

compartment. Additionally, a clear radial temperature differences appeared across the entire reactor from the tube compartment to the insulation layer due to heat loss through heat conduction from the exothermic compartment to the surroundings. Within a brief period ($\tau = 100$) after introducing the RWGS feed stream, an obvious heat consumption was noticed due to the onset of the endothermic reaction at the hot spot area ($z/L = 0.2$) which is already favorable for RWGS process. The emergence of the hotspot comes because H_2 combustion is faster than the endothermic reaction, resulting in heat generation exceeding heat consumption, and both streams become heated up. The temperature rise accelerates the RWGS reaction rate, which leads to an increase in heat consumption, causing the temperature to drop ultimately. The convective mass and heat transport due to the axial velocity in the RWGS compartment compels the wave-shaped spatial temperature distribution to shift towards the top (towards the reactor exit). Consequently, the heat wave is forced to propagate downstream, and the reactor obtains a steady-state, as visible from the clips of $\tau = 2100$ to 5000. Another phenomenon is affirmed wherein consuming all the H_2 in conjunction with thorough heat released by the CHC at the front end generates a noticeable decrease in temperature throughout the rest of the reactor. Ultimately, a triangle-type heat area is formed at the location of $z/L = 0.3$, and the reactor temperature reduced as anticipated compared to the steady-state achieved before introducing RWGS. The temperatures in both compartments are nearly uniform closer to the outlet.

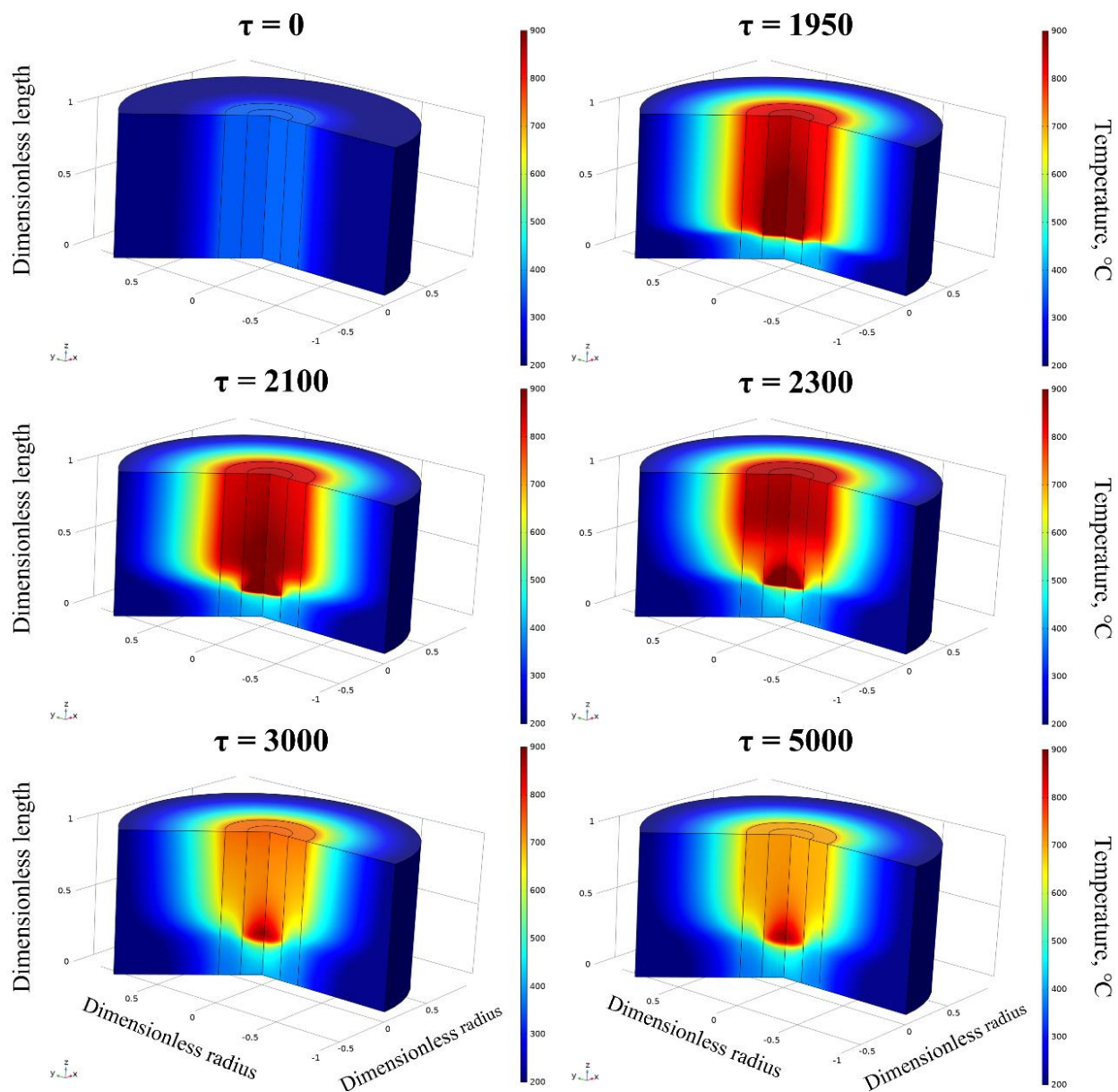


Figure 27. Dynamic reactor temperature profiles, introducing RWGS at $\tau = 2000$. Parameters: $y_{H_2(CHC)} = 0.08$, $P_{\text{endo}} = 4$ bar, $P_{\text{exo}} = 5$ bar, $GHSV_{CHC} = 3,500$ L/(kg h), $GHSV_{RWGS} = 750$ L/(kg h), $T_f = 400$ °C, $T_0 = 350$ °C.

The dynamic CO_2 conversion in the RWGS compartment and H_2 conversion in the CHC compartment are shown in Figures 28 and 29. Before $\tau = 2000$, no CO_2 conversion is observed as

the RWGS feed is yet to be introduced. Upon contact between the RWGS stream and the hot spot, a significant conversion occurs due to the advantageous temperature. The distribution of CO₂ conversion portrays a similar pattern to the temperature distribution both radially and axially, as it largely depends on the temperature of the RWGS compartment. At the same axial position, the conversion is greater in the proximity of the CHC wall than that in proximity to the insulation wall.

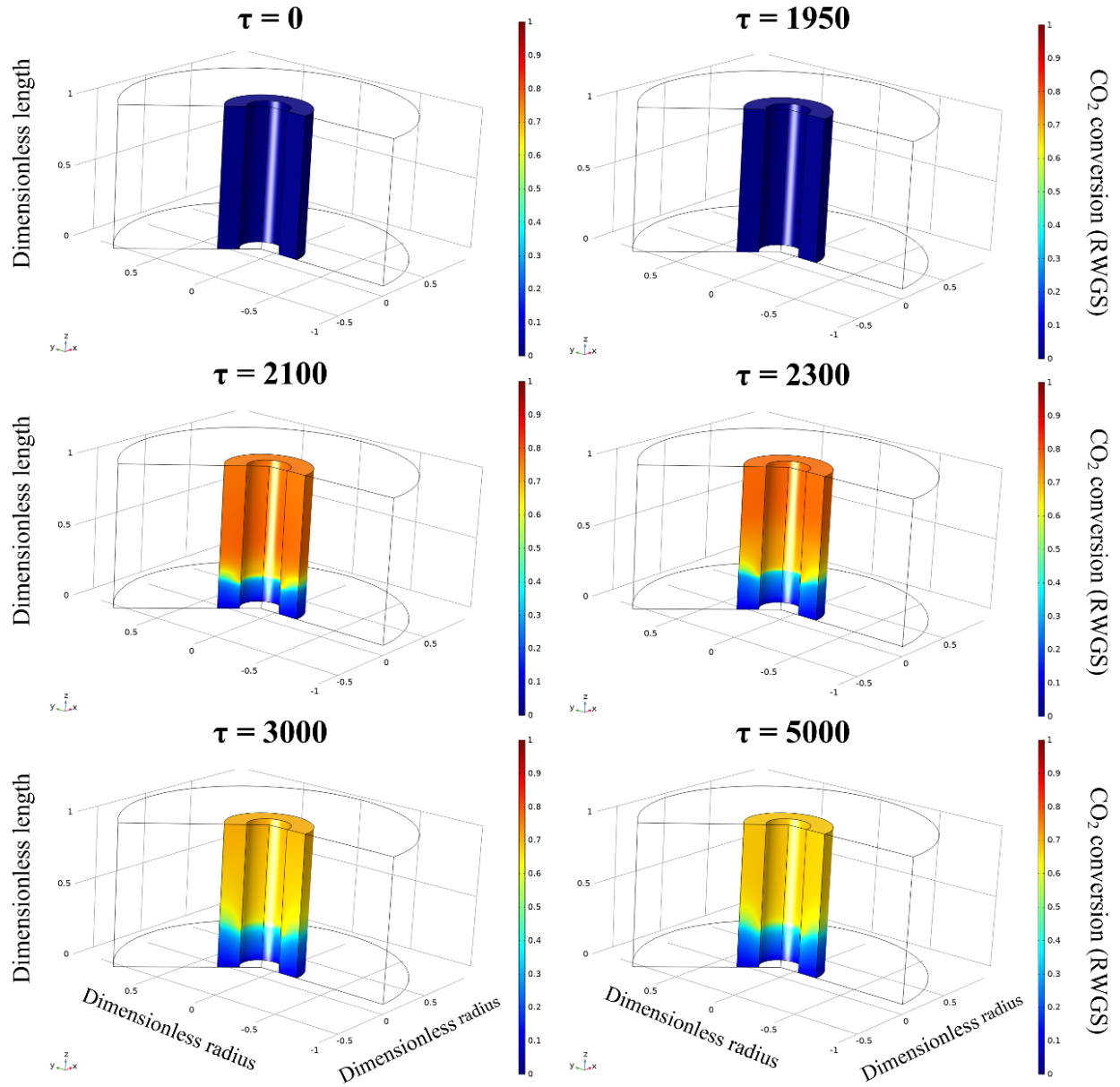


Figure 28. Dynamic profiles of CO₂ conversion in the RWGS compartment, introducing RWGS at $\tau = 2000$. Parameters: $y_{H_2(CHC)} = 0.08$, $P_{\text{endo}} = 4$ bar, $P_{\text{exo}} = 5$ bar, $GHSV_{CHC} = 3,500$ L/(kg h), $GHSV_{RWGS} = 750$ L/(kg h), $T_f = 400$ °C, $T_0 = 350$ °C.

Figure 29 presents the H₂ conversion in CHC compartment. Complete conversion of H₂ occurs at the location of the hot spot. Upon the introduction of RWGS, at steady state, the location

of full conversion shifts downstream coordinately following the movement of the hot spot.

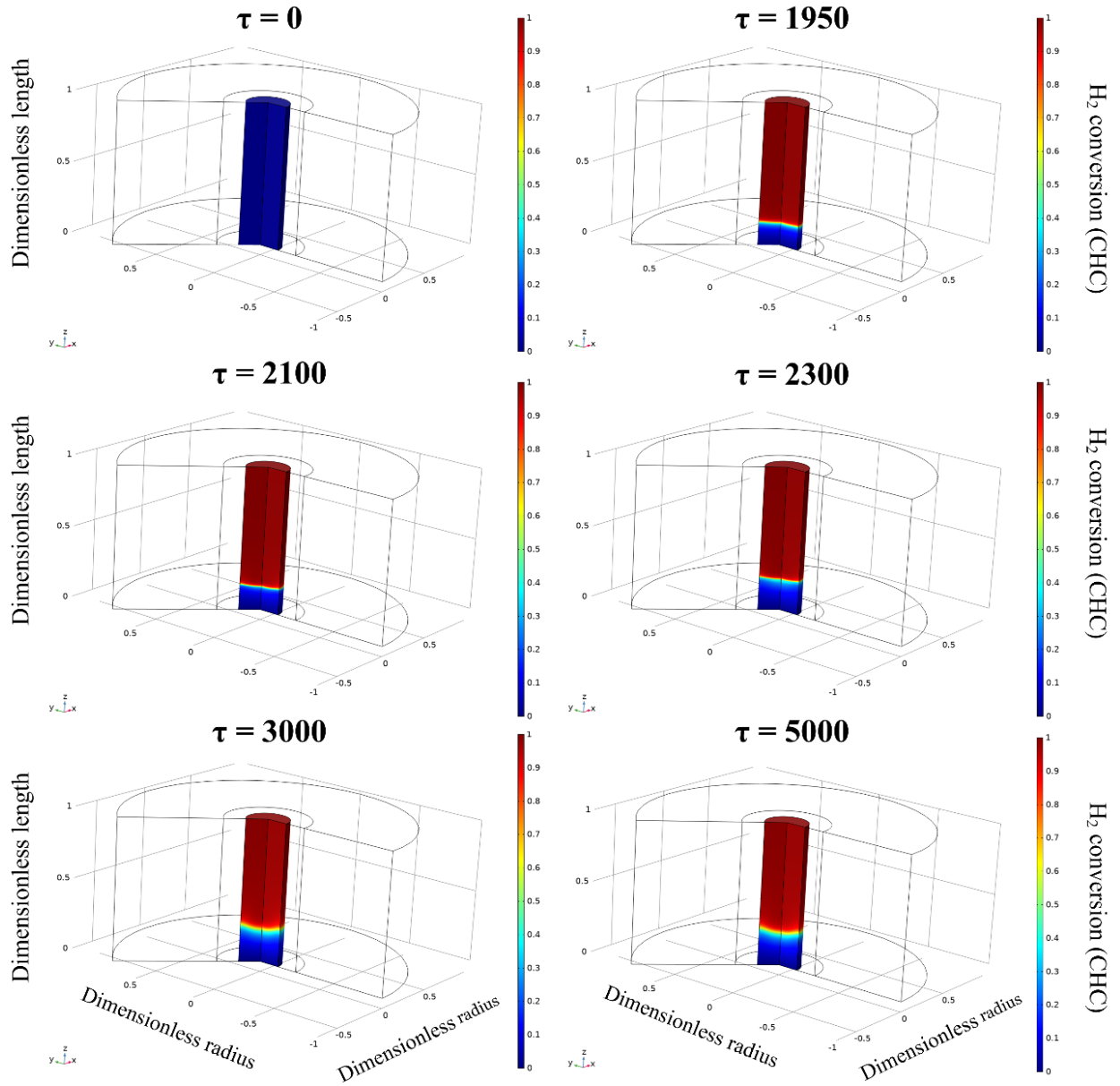


Figure 29. Dynamic profiles of H_2 conversion in the CHC compartment, introducing RWGS at $\tau = 2000$. Parameters: $y_{H_2}(CHC) = 0.08$, $P_{\text{endo}} = 4$ bar, $P_{\text{exo}} = 5$ bar, $GHSV_{CHC} = 3,500$ L/(kg h), $GHSV_{RWGS} = 750$ L/(kg h), $T_f = 400$ °C, $T_0 = 350$ °C.

Following dynamic analysis, a simulation was conducted on a reactor with larger diameters

with a low GHSV, and 3D steady-state temperature, conversion and RWGS mole fraction profiles are illustrated in Figures 30 and 31. Both the axial and radial temperature profiles in the CHC compartment, RWGS compartment and insulation layer are displayed in Figure 30a. The low gas velocity on the combustion side does not delay the combustion reaction either in terms of time or space, and the RWGS reaction proceeds at the entrance of the reactor as well. The RWGS process and heat loss, which cool the compartment temperature, cause more heat to be transferred from the exothermic CHC side due to the larger temperature gradients. The spatial distribution of CO_2 conversion portrays a similar trend to the temperature distribution in both radial and axial dimensions due to its substantial dependence on the temperature within the RWGS compartment. Unlike RWGS reaction, catalytic H_2 combustion proceeds quickly. The utilization of H_2 is much more abrupt and attains complete conversion at the reactor inlet.

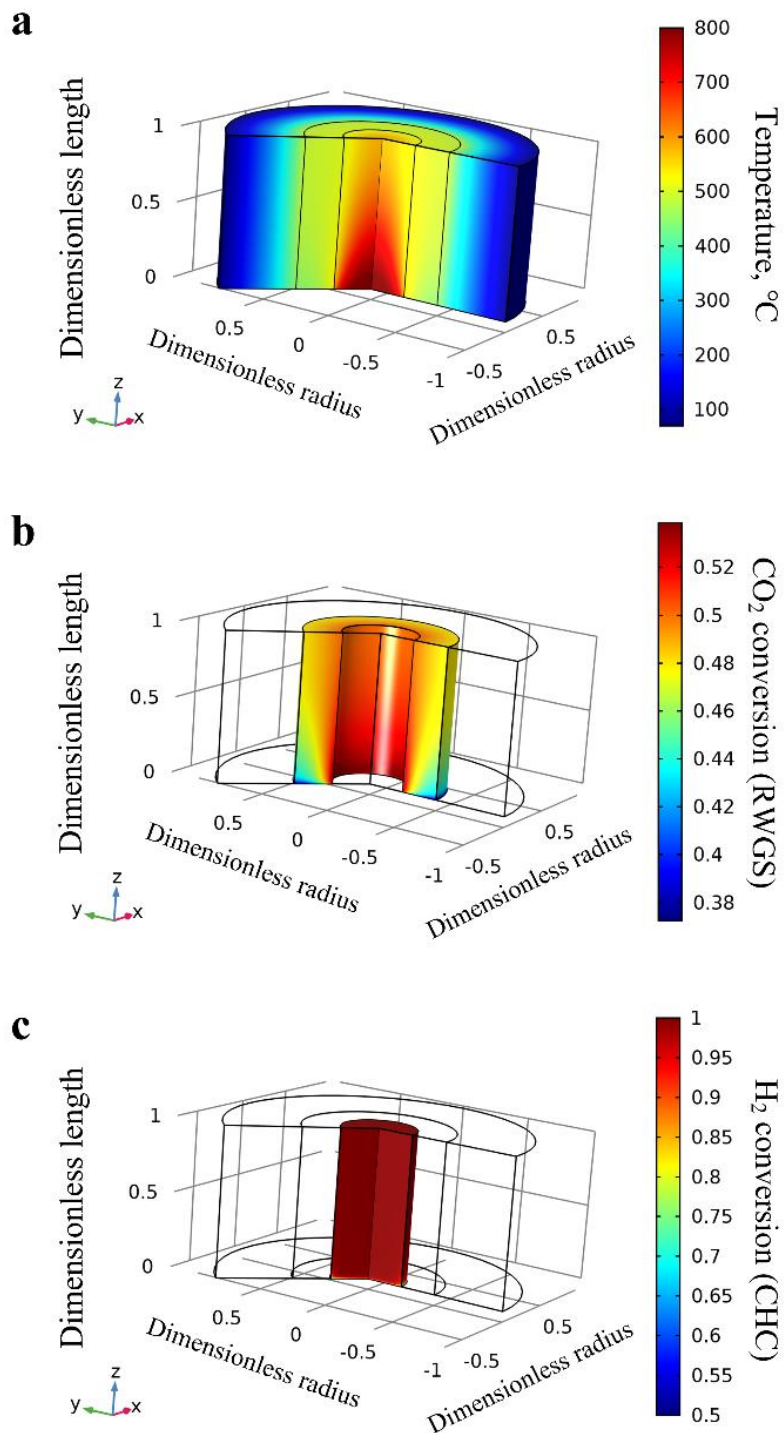


Figure 30. Representative 3D steady state temperature (a), and conversion profiles (b and c). Parameters: $y_{H_2(CHC)} = 0.07$, $P_{\text{endo}} = P_{\text{exo}} = 5$ bar, $GHSV_{RWGS} = 20$ L/(kg h), $GHSV_{CHC} = 100$ L/(kg h), $T_f = T_0 = 300$ °C.

Figure 31 indicates the mole fraction of all species involved, showcasing the 3D steady state distribution within the RWGS compartment. Owing to the equimolar nature of all species involved in the RWGS reaction, observed trends remain identical except for the processes of consumption and generation. A noteworthy observation is the comparatively uniform distribution of axial concentration close to the CHC compartment, in contrast to the region adjacent to the insulation layer. Similarly, in the radial direction, mass distribution exhibits greater variability at the reactor inlet than at the outlet.

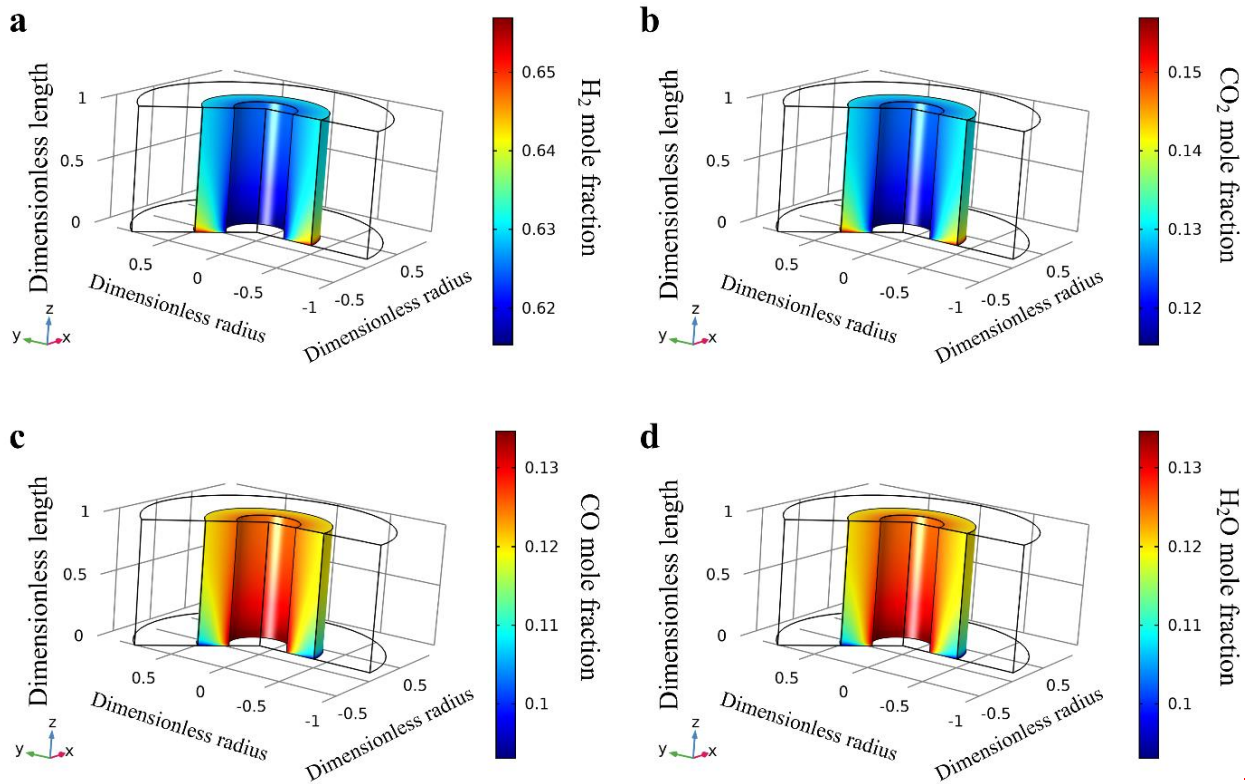


Figure 31. Representative 3D steady state mole fraction profiles in the RWGS compartment. Parameters: $y_{H_2(CHC)} = 0.07$, $P_{\text{endo}} = P_{\text{exo}} = 5$ bar, $GHSV_{RWGS} = 20$ L/(kg h), $GHSV_{CHC} = 100$ L/(kg h), $T_f = T_0 = 300$ °C.

Figure 32 offers channel-specific temperature and conversion profiles for three distinct locations ($z/L = 0.1, 0.5$, and 0.9) to perform a comprehensive analysis of the reactor's thermal behavior in the radial direction. It's noticeable that significant radial temperature differences (over $200\text{ }^{\circ}\text{C}$) occur at the entrance of the reactor, while the difference dropped to $100\text{ }^{\circ}\text{C}$ at the exit of the reactor. The above behavior is attributable to the fact that heat conduction is insufficiently efficient in transporting the large amount of heat generated by the combustion axially downstream the reactor. Under conditions of low velocities, an accumulation of heat occurs primarily at the front section of the reactor, leading to the emergence of elevated temperatures within the combustion compartment. Simultaneously, a significant temperature drop is observed in the radial direction, attributable to the presence of substantial temperature gradients. The outcomes of the simulations underscore the critical influence of flow rates in both compartments on the overall performance of the reactor.

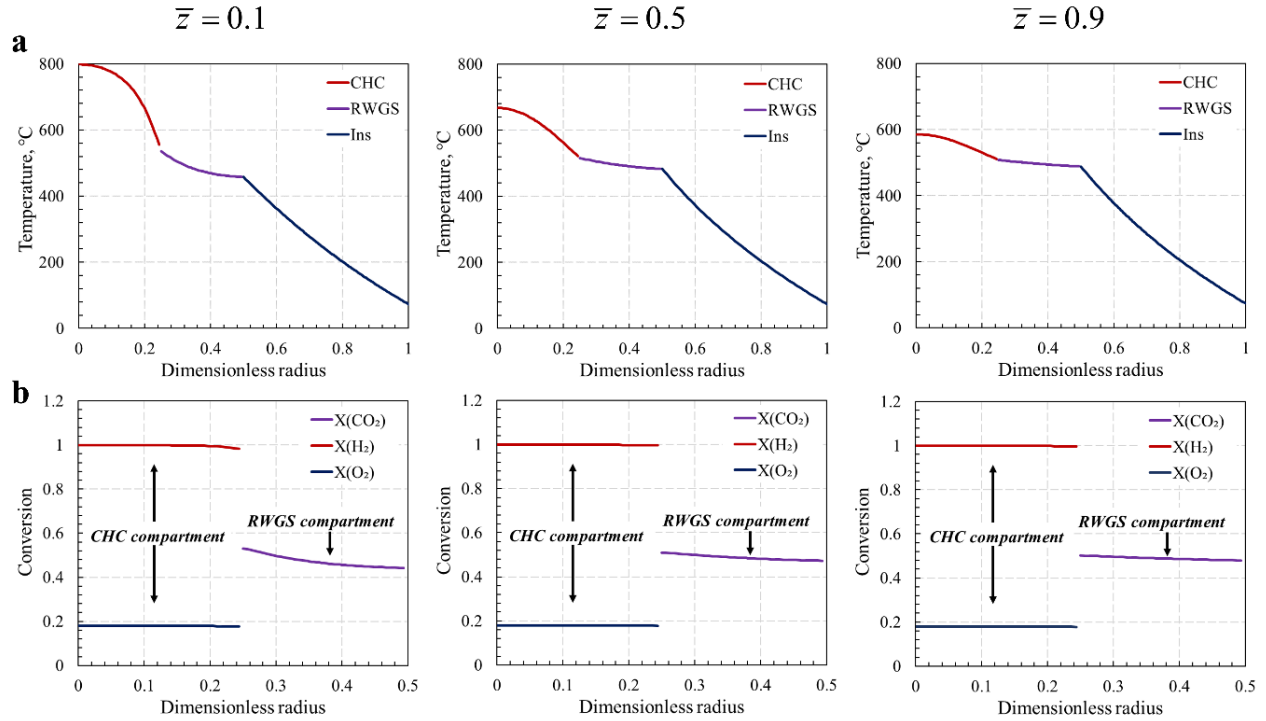


Figure 32. Representative steady state temperature (a), and conversion profiles(b) for three different points in radial direction. Parameters: $y_{H_2}(CHC) = 0.07$, $P_{endo} = P_{exo} = 5$ bar, $GHSV_{RWGS} = 20$ L/(kg h), $GHSV_{CHC} = 100$ L/(kg h), $T_f = T_0 = 300$ °C.

4.2.2 Effects of reactor geometric parameters (L/R_{RWGS} and R_{CHC}/R_{RWGS})

Initially, an examination of the influence of geometric parameters on various aspects of the reactor performance is conducted. Figs. 33 and 34 showcase temperature and conversion profiles along the reactor under steady state conditions, considering varying geometric parameters configurations. It aims to elucidate the intricate interplay between design choices and reactor performance. This analysis can ultimately inform and guide future reactor design endeavors, aiding in the optimization of geometric parameters for enhanced performance and efficiency.

Figure 33 illustrates the temperature and conversion profiles of the reactor as the ratio of

L/R_{RWGS} is increased, while the R_{RWGS} remains constant. The simulations all show almost identical behaviors for L/R_{RWGS} ratios between 30 and 80. At the reactor's onset, rapid combustion of H_2 occurs in coincidence with an abrupt exothermic temperature increase. The beginning of the reactor experiences the most significant heat transfer due to the high temperature gradient between the CHC and RWGS compartments, outstandingly increasing the endothermic side's temperatures from feed temperature to a maximum temperature of approximate 800 °C. After reaching the maximum value, the reaction rate of the RWGS process increases, leading to a decrease in the reactor's temperature. This leads to an approximate temperature endpoint of 530 °C, which occurs through a combination of increased RWGS reaction rate and heat loss.

Increasing L/R_{RWGS} above a threshold of 90 significantly reduce the maximum temperature the reactor could achieve from approximate 960 °C to 650 °C. Moreover, reactor operation changes to a more gradual pattern for both compartments in terms of temperature and conversion rate. The location of T_{max} shifts from the reactor's immediate entrance to its midsection, while H_2 conversion in the CHC compartment and CO_2 conversion in the RWGS conversion increase more gradually. A plausible reason is that the increase in convective transport is due to higher velocities. Additionally, the reactor's outlet temperature and outlet CO_2 conversion increase from 530 °C to 580 °C and from 53% to 58% respectively. However, further increasing the ratio up to 150 does not crucially change the pattern, keeping the same outlet temperatures and outlet conversions for both compartments. As a result, the maximum temperature undergoes a further 20 °C decrease, and the hot spot propagates further towards the end of the reactor, where z/L is approximate 0.7.

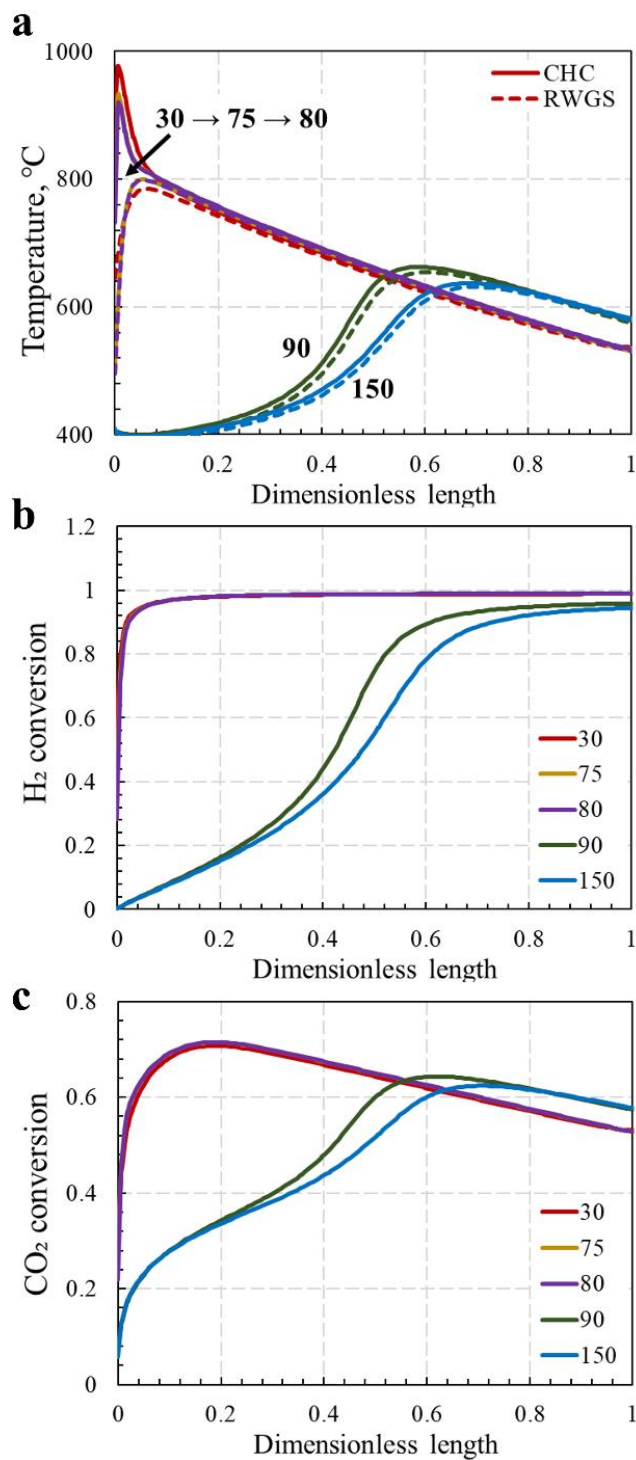


Figure 33. The effect of L/R_{RWGS} on the reactor performance and temperatures. Parameters: $y_{H_2}(CHC) = 0.14$, $P_{endo} = 1$ bar, $P_{exo} = 5$ bar, $GHSV_{CHC} = 7,000$ L/(kg h), $GHSV_{RWGS} = 10,000$ L/(kg h), $T_f = 430$ °C, $T_0 = 350$ °C.

The effect of R_{CHC} to R_{RWGS} ratio (R_1/R_2) was investigated by fixing the R_{RWGS} value and adjusting the R_{CHC} value. Figure 34a presents the reactor temperature profiles on the exothermic and endothermic sides of the reactor. Increasing R_1/R_2 from 0.4 to 0.8 leads to a rise in reactor temperature arising from the increase in the ratio of CHC to RWGS compartment volumes, resulting in more heat generated and less heat consumed. With R_1/R_2 equal to 0.5, 0.65, and 0.8, the CHC compartment observes nearly complete H_2 conversion, the outlet temperature is at 650 °C, 750°C and 900°C, respectively; with CO_2 conversion of 63%, 72% and 78% CO_2 correspondingly. In addition, the exothermic side experienced an abrupt temperature rise at the locations of $z/L = 0.3, 0.4, \text{ and } 0.5$, whereas the RWGS compartment temperature increases smoothly concerning the reactor's length. The distance between the ignition point and the RWGS compartment temperature increase location expands as the R_1/R_2 ratio increases. A reduction of the surface area-to-volume ratio of the CHC chamber that allows for less contact points with the RWGS compartment and inhibits heat transfer elucidates this circumstance. As a result, the amount of heat generated and maintained on the exothermic side is significantly greater than the amount of heat transferred and consumed on the endothermic side at the reactor's front section. The ensuing heat transfers spread along the reactor and balance the heat generated on the exothermic side with the amount of heat consumed on the endothermic side and heat loss, narrowing the temperature difference between the compartments. This produces a uniform temperature throughout the reactor eventually.

With a specific scenario of $R_1/R_2 = 0.4$, the volume of the RWGS compartment is overly large compared to that of CHC compartment. The evident cooling effect of the RWGS prevents

the CHC compartment from reaching approximate 600 °C, the temperature required for nearly complete H₂ combustion under the designated operating conditions. The temperatures of both compartments increase monotonously from the feed temperatures to reach values of 530 °C and 460 °C, respectively. The conversion profiles also exhibit near-linear increments, resulting in an outlet conversion of 66% for H₂ and 43% for CO₂.

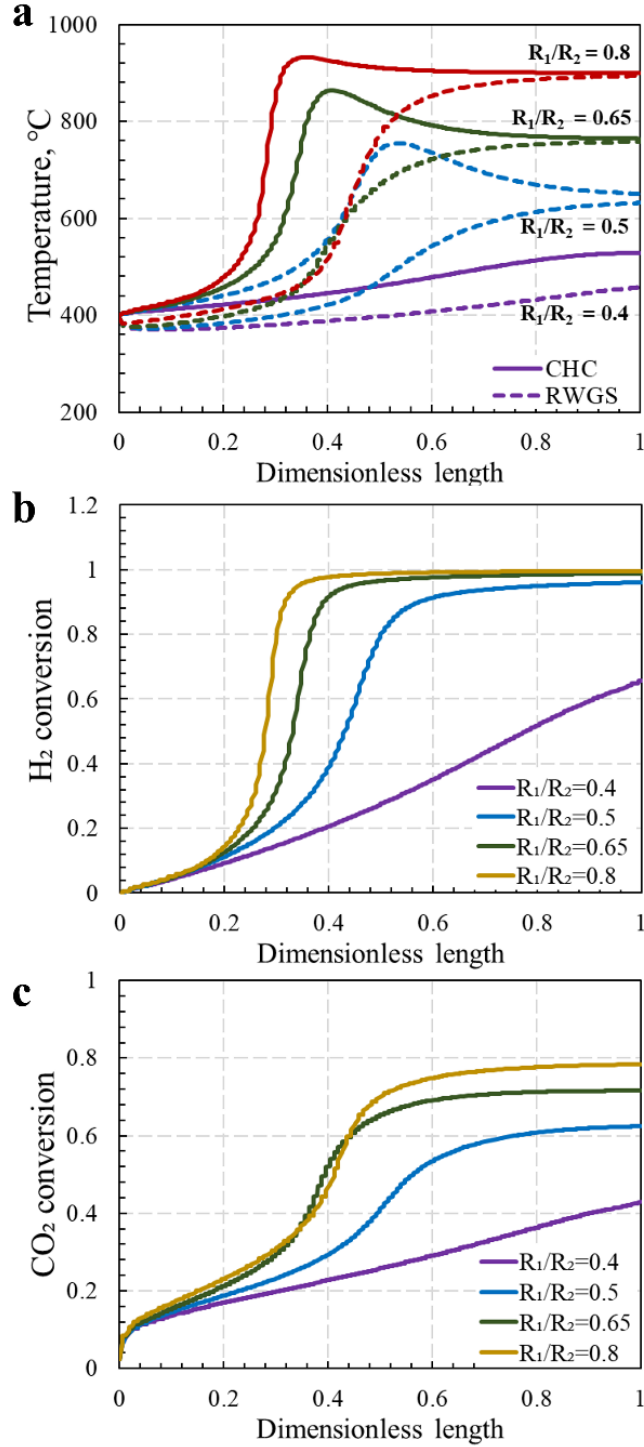


Figure 34. The effect of $R_{\text{CHC}}/R_{\text{RWGS}}$ (R_1/R_2) on the reactor performance and temperatures. Parameters: $y_{\text{H}_2}(\text{CHC}) = 0.08$, $P_{\text{endo}} = 4$ bar, $P_{\text{exo}} = 5$ bar, $\text{GHSV}_{\text{CHC}} = 5,000$ L/(kg h), $\text{GHSV}_{\text{RWGS}} = 1,500$ L/(kg h), $T_f = 400$ °C, $T_0 = 350$ °C.

4.2.3 Effects of space velocity of exothermic/endothermic streams

The effects of space velocities in the CHC and RWGS compartments are investigated. The simulations aim to elucidate the effect on reactor behavior by systematically varying the space velocities in one compartment while keeping the other constant. The temperature profiles offer valuable insights into the thermal distribution within the reactor, highlighting variations and gradients. Similarly, the conversion profiles provide a comprehensive understanding of the extent to which reactants are transformed as they progress through the reactor. Figures 35 and 36 depict the temperature and conversion profiles along the reactor at the steady state.

Figure 35 presents a comparison of compartment temperatures and conversions along the reactor for different CHC flow rates as indicated in the figure. With simulated conditions ranging from 1,000 to 10,000 L/(kg h), an increase in CHC flow rate causes the hot spot to propagate upstream and leads to higher temperatures due to increased heat generation. Specifically, in the instance where $GSHV_{CHC} = 1,000$ L/(kg h), the reactor achieved ignition with a complete H_2 conversion, but the introduction of RWGS results in a temperature drop below 400 °C, decreased H_2 conversion and diminished heat generation due to the exothermic reaction. This manifested in a decline of H_2 conversion to 36% as shown in Figure 35b, while the unfavorable conditions in the RWGS compartment resulted in an 18% CO_2 conversion as demonstrated in Figure 35c. Upon increasing to 5,000 L/(kg h), both compartment temperatures increased significantly to 622 °C with an 84% H_2 conversion in the CHC compartment and 62% CO_2 conversion in the RWGS compartment. For 7,000 and 10,000 L/(kg h), the operating pattern is similar, with temperatures

increasing to a maximum of 950 °C and 815 °C, respectively, at the rear part of the reactor, then decreasing by 20 °C along the reactor's length. The conversion profiles illustrate sigmoid-like curves, with almost complete H₂ conversion and 80% and 74% CO₂ conversion achieved independently at the end of the reactor separately.

Elevating the GHSV_{CHC} to 100,000 L/(kg h) results in the emergence of nearly linear temperature distribution within the reactor, with temperatures slightly surpassing that of the feed temperature. It was observed that even before introducing RWGS stream, the reactor could not be ignited at such high velocity, and eventually, a 4% H₂ conversion was achieved in the CHC compartment at the steady state. The strengthening of convective heat transport due to the higher velocity becomes the dominant factor, leading to an enhanced rate of heat outflow.

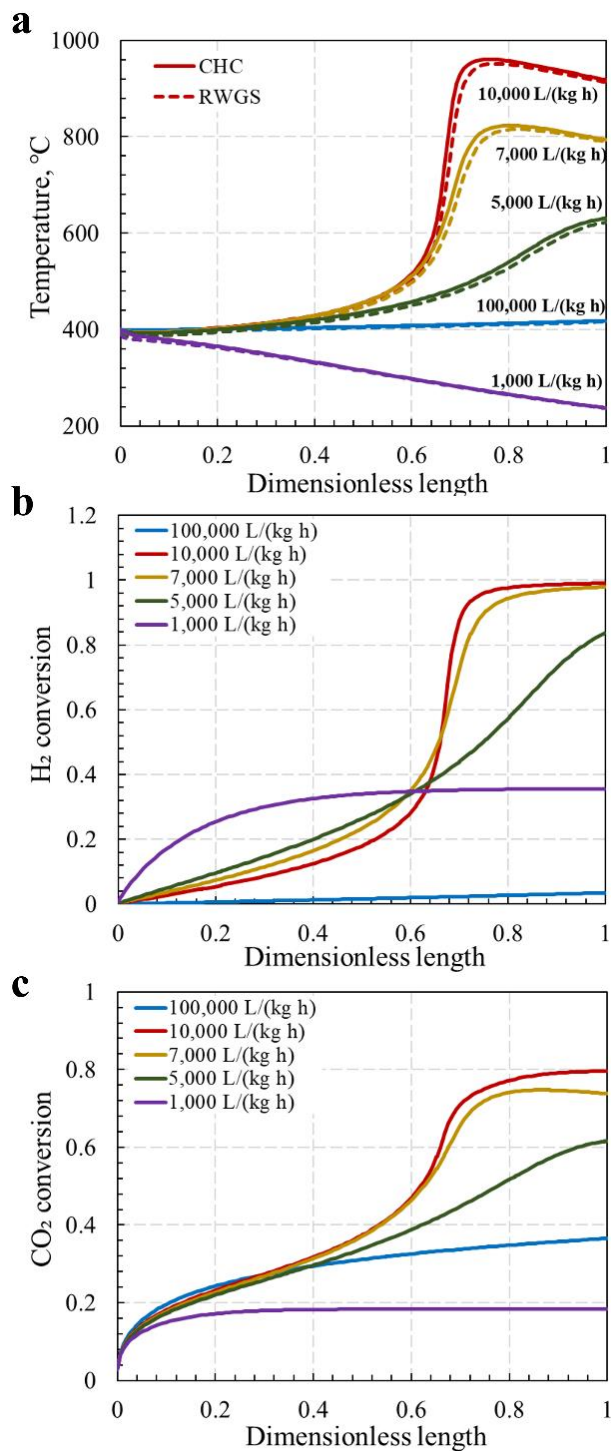


Figure 35. The effect of space velocity in the CHC compartment on the reactor performance and temperatures. Parameters: $y_{H_2}(CHC) = 0.14$, $P_{\text{endo}} = 4$ bar, $P_{\text{exo}} = 5$ bar, $GHSV_{RWGS} = 1,500$ L/(kg h), $T_f = 400$ °C, $T_0 = 350$ °C.

In Figure 36, a comparative analysis of temperatures and performance across the longitudinal axis for different $GHSV_{RWGS}$ cases is presented, as indicated in the caption. Increasing the endothermic flow rate from 8,000 to 100,000 L/(kg h) reduces the reactor temperature and moves the hot spot downstream, ultimately extinguished the reactor due to the combined effect of increased heat consumption by RWGS and enhanced convective heat transport.

The temperature profiles in the $GHSV_{RWGS}$ range of 8,000 – 15,000 L/(kg h) demonstrate a similar trend, with maximum temperatures occurring in both compartments simultaneously after H_2 combustion, followed by gradual temperature decrease along the reactor. Increasing the axial gas velocity in the RWGS channel causes the hot spot to migrate toward the reactor outlet, along with a general decrease in the reactor temperature at the steady state. Since the conversion profiles are heavily influenced by the temperature profiles, an increase in $GHSV_{RWGS}$ shifts the point of steep H_2 conversion in the CHC compartment and CO_2 conversion in the RWGS compartment downstream. An interesting phenomenon observed is that while the difference in temperature (approximate 260 °C for T_{max} and 120 °C for T_{out}) for different $GHSV_{RWGS}$ was substantial, no significant deviation is noticed in H_2 and CO_2 conversions. A mere 5% deduction in H_2 conversion, from 100% to 95%, and 6% deduction in CO_2 conversion from 76% to 70% are recorded. Further raising the $GHSV_{RWGS}$ to 20,000 L/(kg h) significantly decreases reactor performance because convective transport in the RWGS compartment becomes the key factor influencing the reactor. The reactor temperature increases from the feed temperature to a maximum of 550 °C at the end directly, with corresponding H_2 and CO_2 conversions of 58% and 54%, respectively. Raising

GHSV_{RWGS} to the threshold of 100,000 L/(kg h) results in a monotonic decrease in the reactor temperature from feed temperature to 390 °C at steady state. The cooling effect exhibits excessive strength owing to the escalated heat consumption induced by the RWGS process. Before introducing RWGS reaction, the reactor could be ignited, with a maximum temperature of approximately 700 °C and complete H₂ conversion in the CHC compartment. However, after introducing RWGS feed stream, a significant amount of heat is consumed by the endothermic reaction. As a result, the reactor reaches a steady state at a lower temperature with 20% H₂ conversion and 27% CO₂ conversion, respectively.

Another noteworthy observation is that despite the evident decrease in axial temperatures from 990 °C to 850°C and 920°C to 820°C for low GHSV_{RWGS} values of 8,000 and 10,000 L/(kg h), no detectable trend of declining CO₂ conversion was observed, remaining at 76% and 75%, respectively.

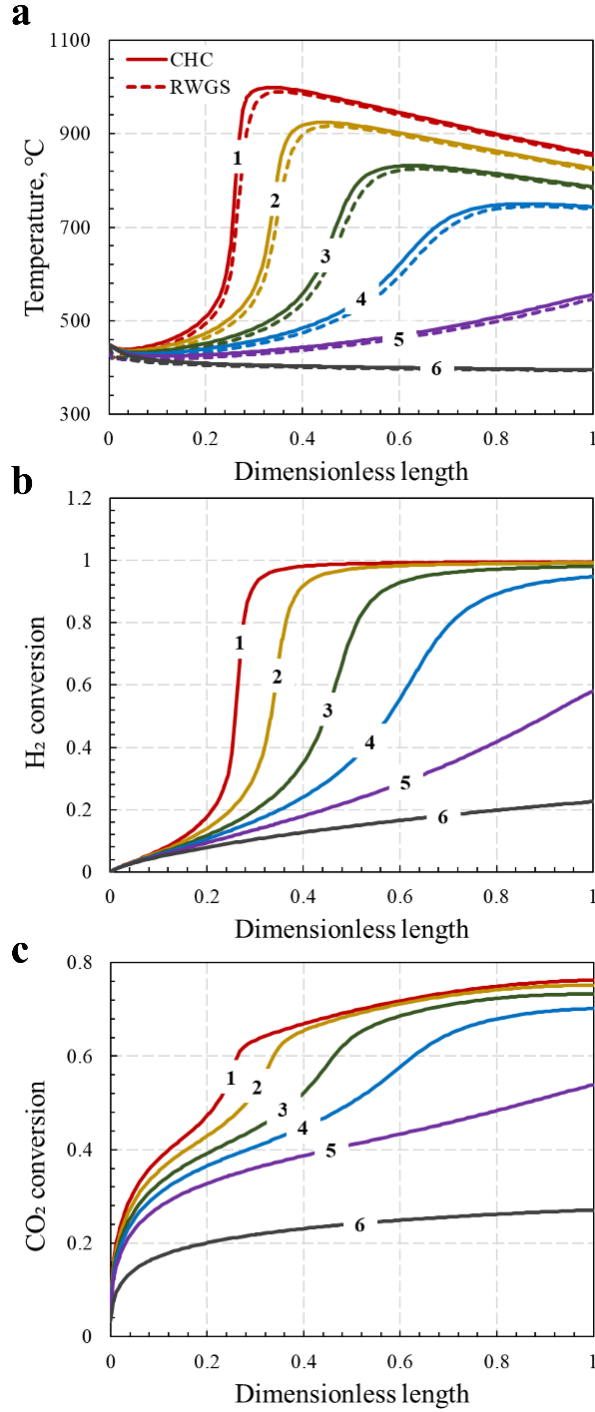


Figure 36. The effect of space velocity in the RWGS compartment on the reactor performance and temperatures. Parameters: $y_{H_2}(CHC) = 0.14$, $P_{endo} = 1$ bar, $P_{exo} = 5$ bar, $GHSV_{CHC} = 10,000$ L/(kg h), $T_f = 450$ °C, $T_0 = 350$ °C. $GHSV_{RWGS}$, L/(kg h), **1**: 8,000; **2**: 10,000; **3**: 12,500; **4**: 15,000; **5**: 20,000; **6**: 100,000.

4.2.4 Effects of feed temperature of exothermic/endermthermic streams

The investigation focuses on examining the effects of feed temperatures on both sides of the reactor. It is noteworthy that the feed temperatures are augmented through the utilization of external heaters. The section places particular emphasis on the reduction of excessive heat input, aiming to minimize unnecessary thermal energy contributions.

The effect of the CHC feed temperature on the reactor is investigated over a range of 350 – 600 °C. Figure 37 shows the temperature and conversion values for both compartments. In the case of $T_f = 600$ °C, the catalytic combustion occurs immediately and violently, resulting in the rapid and complete conversion of H_2 and the release of a large amount of heat, causing a sudden increase in temperature on the exothermic side in a short reactor distance. Immediately subsequent to the intensified heat transfer due to this significant temperature difference between two compartments, the endothermic side is affected, and the RWGS process is activated rapidly, reaching as high as 74% conversion of CO_2 . In the remaining simulations, the temperature difference between the two compartments is uniform, and heat transfer occurs smoothly. As the temperature of the CHC feed increases from 450 °C to 600 °C, both CHC and RWGS side temperature profiles peak and then gradually decline as a result of increased endothermic heat consumption and heat loss. Additionally, the peak temperature increases, but the exit temperature and CO_2 conversion decrease. In all cases, the H_2 conversion of the catalytic combustion reaction is complete. The decrease in temperature on the exothermic side could be attributed to the elevated feed temperature, which leads to amplified heat transfer and subsequent augmentation of the RWGS reaction rate as well as heat

dissipation. When the $T_{f,CHC}$ is reduced to 400 °C, the reactor performance decreases significantly. The reactor temperature increases directly from the feed temperature at the entrance to 455 °C at the end, with conversion achieved for both H_2 and CO_2 . A further decrease to 350 °C results in a steady decline in the reactor temperature from feed temperature to 293 °C at steady state, leading to decreased H_2 and CO_2 conversions of 11% and 22%, respectively.

Raising $T_{f,CHC}$ does result in an elevation of the maximum reactor temperature. However, it could not lead to improvements in the reactor outlet temperatures or conversions. Conversely, rapid and complete catalytic H_2 combustion initially enhances the rate of the endothermic reaction, subsequently increasing the rate of heat removal. As a consequence, the temperature decreases, thereby limiting the rate of the RWGS reaction at the outlet.

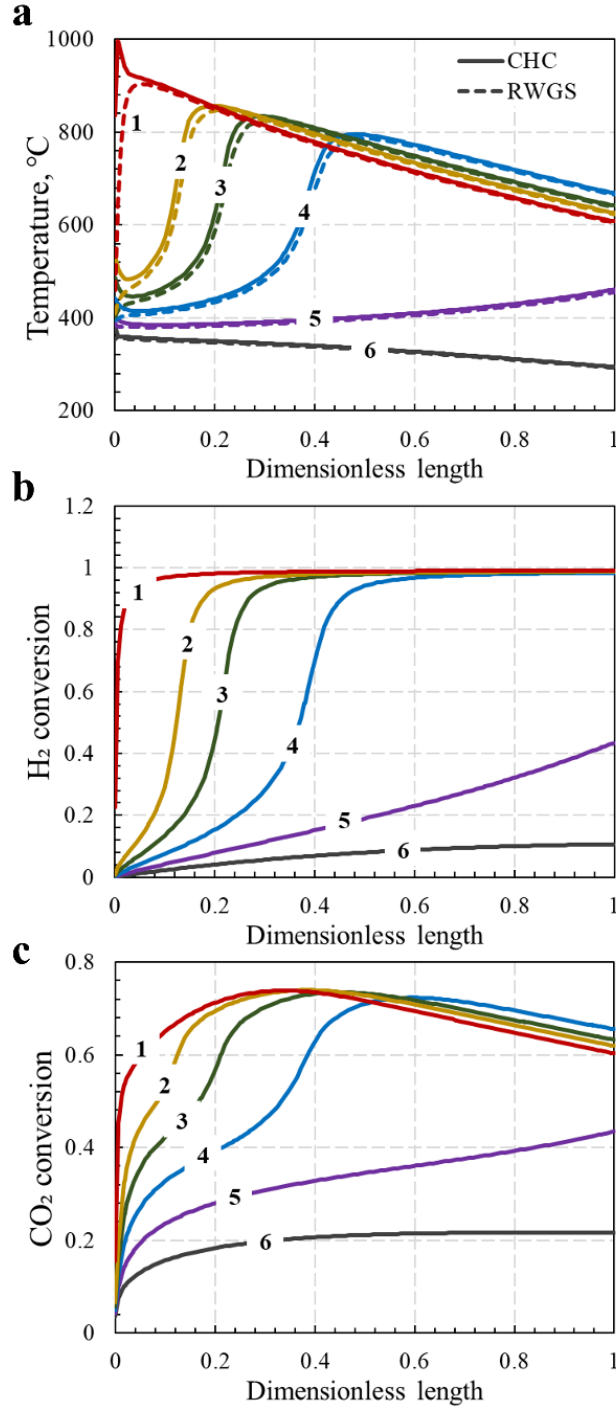


Figure 37. The effect of feed temperature in the CHC compartment on the reactor performance and temperatures. Parameters: $y_{H_2(CHC)} = 0.14$, $P_{endo} = 1$ bar, $P_{exo} = 5$ bar, $GHSV_{CHC} = 5,000$ L/(kg h), $GHSV_{RWGS} = 5,000$ L/(kg h), $T_{f,RWGS} = 400$ °C, $T_0 = 350$ °C. **1 - 6:** 600 – 350 °C with a step of 50 °C.

Figure 38 presents the impact of the feed temperature of the endothermic stream on the temperature and conversion profiles within the reactor. An increase in the feed temperature of the RWGS results in higher maximum temperature, outlet temperature, and increased conversions. This observed phenomenon can be attributed to the additional heat input to the reactor when raising the endothermic feed temperature. Furthermore, this heightened heat input aids the reactor in attaining a steady state characterized by higher temperatures prior to the introduction of the RWGS stream. . Specifically, for the case of $T_{f,RWGS}$ reaching the threshold of 600 °C, an intensified hot spot was observed at the reactor entrance. In cases where $T_{f,RWGS}$ ranged from 600 °C to 450 °C, a maximum temperature was achieved, followed by a gradual temperature decrease along the reactor. Decreasing the $T_{f,RWGS}$ from 600 °C to 450 °C results in a slight drop in the outlet temperature from 629 °C to 582 °C, and CO₂ conversion from 64% to 58%. Further reducing the feed temperature to 400 °C, the temperature profile appears as a nearly straight line slightly above the feed temperature, accompanied by a 40% H₂ conversion and 35% CO₂ conversion.

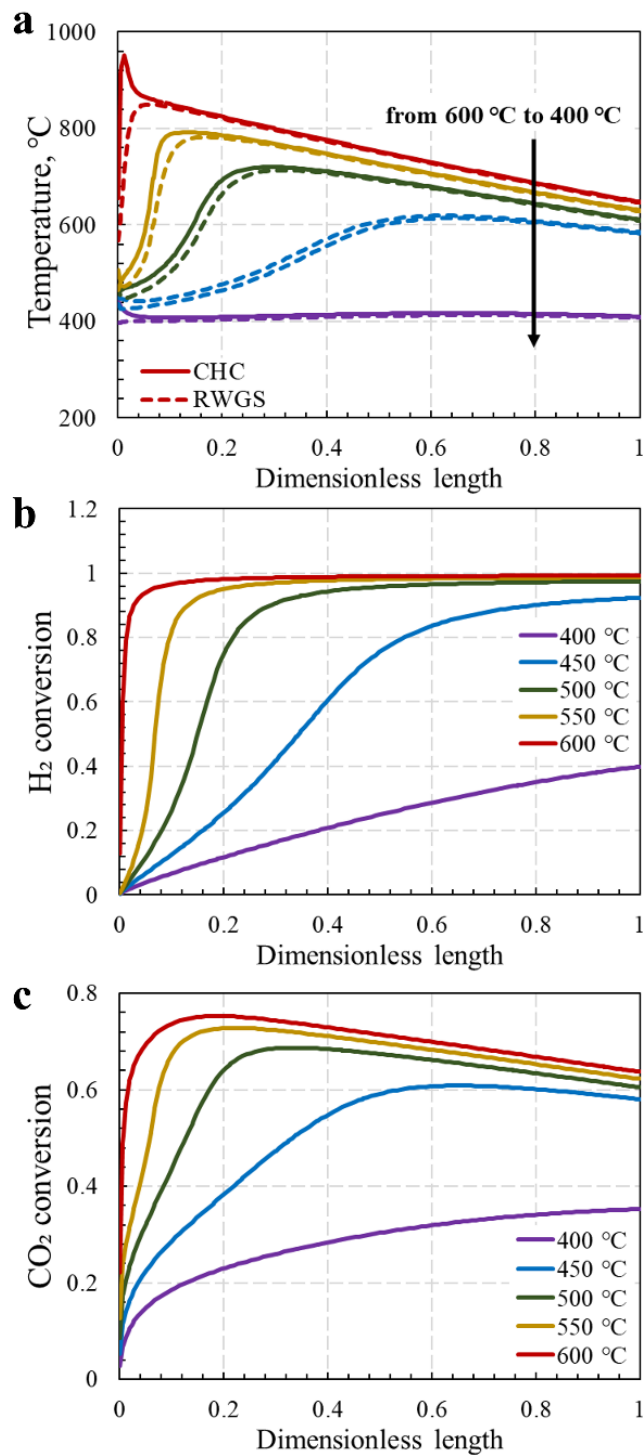


Figure 38. The effect of feed temperature in the RWGS compartment on the reactor performance and temperatures. Parameters: $y_{\text{H}_2(\text{CHC})} = 0.14$, $P_{\text{endo}} = 4$ bar, $P_{\text{exo}} = 5$ bar, $\text{GHSV}_{\text{CHC}} = 5,000$ L/(kg h), $\text{GHSV}_{\text{RWGS}} = 2,500$ L/(kg h), $T_{\text{f,CHC}} = 450$ °C, $T_0 = 350$ °C.

4.2.5 Analysis of reactor performance with respect to operating parameters

A summary of the simulation outcomes is presented, encompassing the variation of operating conditions, specifically the flow rates and feed temperatures, in both the CHC and RWGS compartments. Figures 39 and 40 provide an insightful overview of the reactor's performance in response to these key parameters.

The evolutionary trends of the maximum reactor temperature, outlet temperature, and overall performance, as influenced by the $GHSV_{CHC}$ and $GHSV_{RWGS}$, are depicted in Figure 39. Across all simulated scenarios, no substantial deviations in either max temperature or outlet temperature are observed between the CHC and RWGS compartments. Figures 39a and b elucidate that elevating the CHC flow rate up to a specific threshold result in higher values of T_{max} , T_{out} and outlet conversions. This phenomenon can be attributed to the augmented heat generation resulting from an increased quantity of reactants passing through the compartment per unit of catalyst weight and time. In the $GHSV_{CHC}$ range spanning 1,000 to 10,000 L/(kg h), T_{max} rises from 400 °C to 960 °C, H_2 conversion (CHC) escalates from 36% to 100%, and CO_2 conversion exhibits an increase from 18% to 80%. However, upon surpassing the designated threshold of $GHSV_{CHC}$, convective heat transport emerges as the predominant factor, ultimately leading to escalated heat removal and eventual extinction.

Figures 39c and d illustrate the consistent decline observed in T_{max} , T_{out} and outlet conversions as the $GHSV_{RWGS}$ increases. Within the $GHSV_{RWGS}$ range spanning from 8,000 to 100,000 L/(kg h), T_{max} exhibits a reduction from 990 °C to 449 °C, while H_2 conversion (CHC)

undergoes a decrease from 100% to 23%, and CO_2 conversion experiences a decrease from 76% to 27%. Particularly notable is the substantial temperature difference exceeding 100 °C between the maximum temperature and outlet temperature observed for the relatively low space velocities of 8,000 to 10,000 L/(kg h). This robust reactor performance, despite the axial temperature deduction, highlights the ample heat generation by the CHC compartment, which effectively supplies the enthalpy for the RWGS reaction and compensates for heat losses.

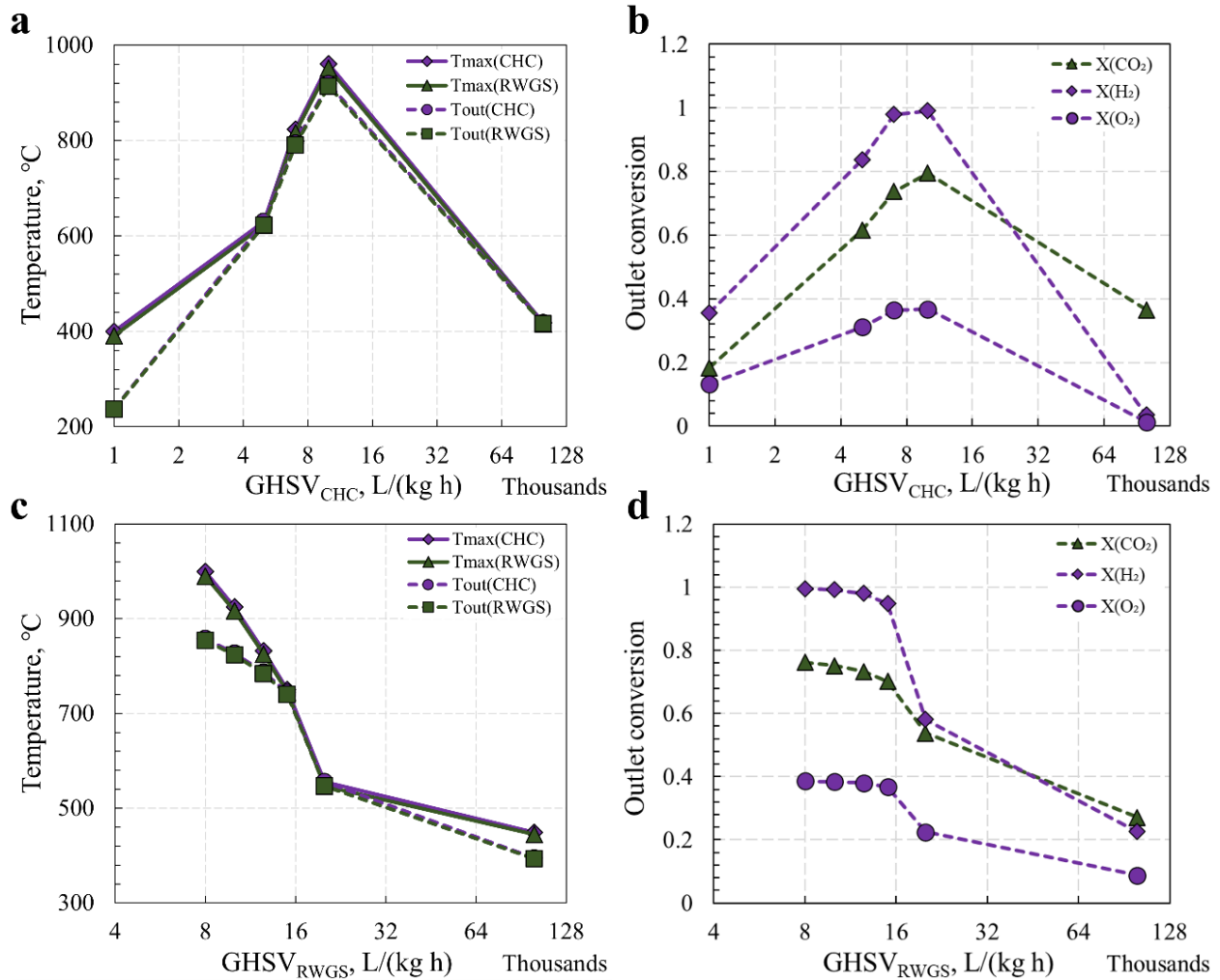


Figure 39. The effect of GHSVs on reactor maximum temperature (T_{max}), outlet temperature

(T_{out}), and outlet conversions. Parameters: $y_{H_2}(CHC) = 0.14$, $P_{exo} = 5$ bar, $T_0 = 350$ °C. $GHSV_{RWGS} = 1,500$ L/(kg h), $P_{endo} = 4$ bar, $T_f = 400$ °C (a, b); $GHSV_{CHC} = 10,000$ L/(kg h), $P_{endo} = 1$ bar, $T_f = 450$ °C (c, d).

The impact of the feed temperature in both the CHC and RWGS compartments on the maximum temperature, outlet temperature and performance are illustrated in Figure 40. Across all simulated outcomes, no significant deviations in either maximum temperature or outlet temperature are observed between the CHC and RWGS compartments, except for two instances when $T_{f,CHC}$ and $T_{f,RWGS} = 600$ °C. In these cases, a difference of 100 °C in T_{max} is observed. The underlying reason for this phenomenon is thoroughly discussed earlier. Briefly, excessively high feed temperature triggers the immediate and complete H_2 consumption in the CHC compartment, accompanied by a significant release of heat, resulting in a sudden rise in temperature. The differences between the maximum temperatures and outlet temperatures are more pronounced for $T_{f,CHC} > 400$ °C and $T_{f,RWGS} > 450$ °C.

The results depicted in Figures 40a and b demonstrate that raising the $T_{f,CHC}$ has a positive effect on the maximum temperature and conversions within the CHC compartment. A notable enhancement is observed in the reactor temperature, with an approximate increase of 400 °C in both maximum temperature and outlet temperature, along with remarkable improvements in reactor performance. Specifically, the H_2 conversion in CHC compartment increases from 11% to 98%, and CO_2 conversion increases from 22% to 66% when the feed temperature is elevated from 350 °C to 450 °C. In the $T_{f,CHC}$ range of 450 – 600 °C, nearly complete H_2 conversions are achieved

within the CHC compartment. However, an increase in $T_{f,CHC}$ results in slight decreases in the outlet temperature (from 665 °C to 606 °C) and CO₂ conversion (from 66% - 60%).

Figures 40c and d reveal a nearly linear correlation between the maximum temperatures and feed temperature in the RWGS compartment. The $T_{max}(CHC)$ increases from 441 °C to 952 °C, while $T_{max}(RWGS)$ increases from 413 °C to 850 °C as $T_{f,RWGS}$ rises from 400 °C to 600 °C. Substantial increases in the outlet temperatures are also observed, ranging from 410 °C to 585 °C, as well as notable enhancements in $XH_2(CHC)$ (from 40% to 92%) and $XCO_2(RWGS)$ (from 35% to 58%) when $T_{f,RWGS}$ is increased from 400 °C to 450 °C. Subsequently, a slight increase in the outlet temperature from 585 °C to 648 °C, as well as incremental improvements in H₂ conversion from 92% to 99%, and CO₂ conversion from 58% to 64% are observed as $T_{f,RWGS}$ is further increased up to 600 °C.

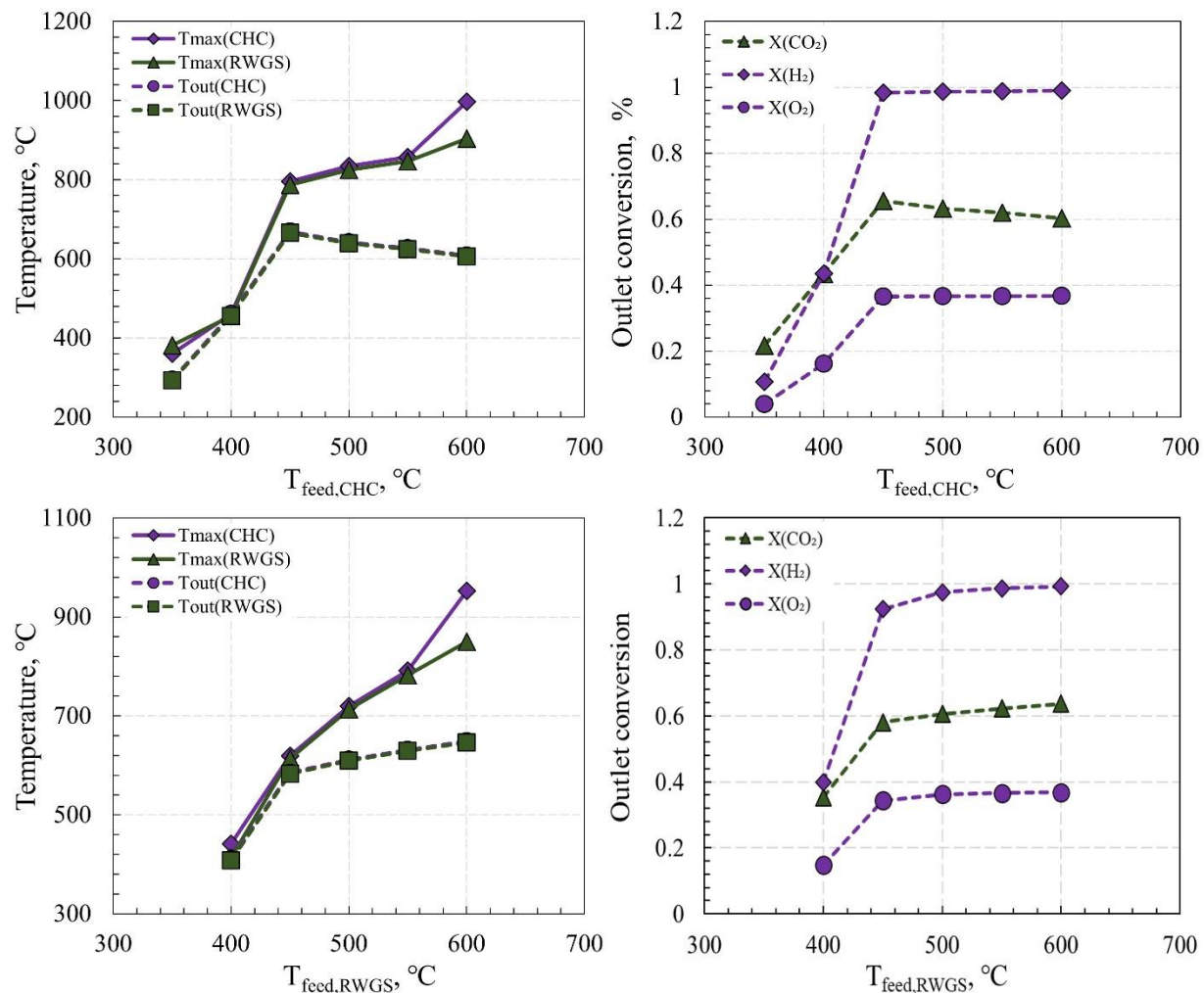


Figure 40. The effect of feed temperatures on reactor maximum temperature ($T_{\max}$), outlet temperature (T_{out}), and outlet conversions. Parameters: $y_{\text{H}_2}(\text{CHC}) = 0.14$, $P_{\text{exo}} = 5$ bar, $\text{GHSV}_{\text{CHC}} = 5,000$ L/(kg h), $T_0 = 350^\circ\text{C}$. $\text{GHSV}_{\text{RWGS}} = 1,500$ L/(kg h), $P_{\text{endo}} = 1$ bar, $T_{\text{f,RWGS}} = 450^\circ\text{C}$ (a, b); $\text{GHSV}_{\text{RWGS}} = 2,500$ L/(kg h), $P_{\text{endo}} = 4$ bar, $T_{\text{f,CHC}} = 450^\circ\text{C}$ (c, d).

4.2.6 Model validation

The model was found to predict well the experimentally measured temperature profiles and the experimental data in general. Simulated reactor performance with the single parameter (U_{WL} , overall heat loss heat transfer coefficient) fitting and experimentally measured outlet conversions are shown in Table 10, where a 6% CO_2 conversion deviation was observed in the RWGS compartment, and nearly identical H_2 and O_2 conversions were perceived in the CHC compartment.

Table 10. Simulated and experimentally obtained reactor performance.

	RWGS	CHC	
	X(CO_2)	X(H_2)	X(O_2)
experiment	50%	71%	100%
U_{HL}	56%	71%	100%
$5*U_{HL}$	56%	71%	100%
$10*U_{HL}$	56%	70%	100%

The agreement was found for the simulated and experimental measured temperature profiles as shown in Figure 41, where the inlet and outlet temperatures of both compartments and wall temperatures are plotted versus the dimensionless reactor length. For the case of $10*U_{HL}$, the simulation describes the experimental measured temperatures very appropriately, except for the unrealistic high CHC inlet temperature due to numerical issues. The model with the correlations on the mass and heat transfer from the literature fit the experimental data well, except the overall heat loss heat transfer coefficient is high than expected.

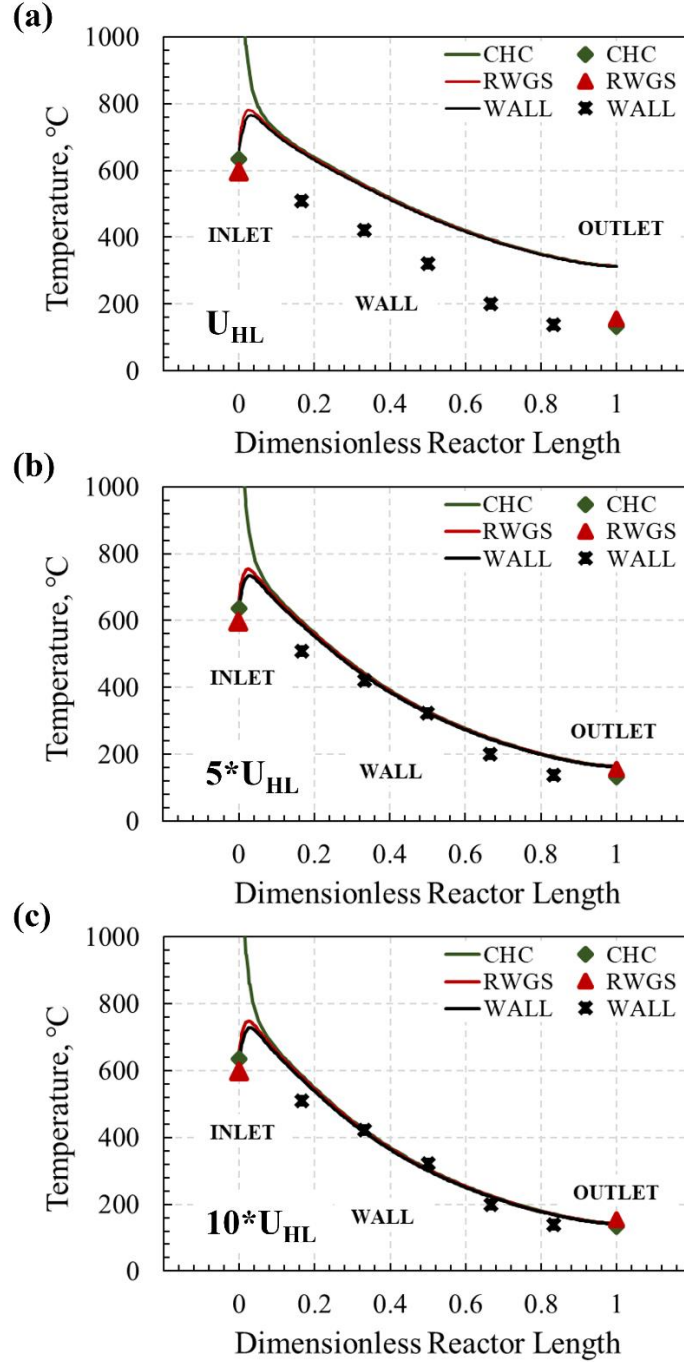


Figure 41. Experimentally obtained and simulated reactor inlet, outlet and wall temperatures plotted versus dimensionless reactor length with single parameter fitting U_{WL} (a); $10*U_{WL}$ (b); $10*U_{WL}$ (c). Parameters: $y_{H_2}(CHC) = 0.37$, $P_{endo} = 1$ bar, $P_{exo} = 5$ bar, $T_0 = 400$ °C. $GHSV_{CHC} = 19,000$ L/(kg h), $T_{f,CHC} = 430$ °C, $GHSV_{RWGS} = 4,000$ L/(kg h), $T_{f,RWGS} = 400$ °C.

Chapter 5 Conclusions

5.1 Lab scale reactor

A stainless steel thermally coupled packed bed reactor comprising two separated compartments was designed and built: the tube side for exothermic catalytic hydrogen combustion over a commercial Ni/Al₂O₃ catalyst and the shell side for endothermic reverse water gas shift over Mo₂C/Al₂O₃ catalyst. Ignition happened instantly after switching from the reduction mixture to the reaction mixture, which was proved by the abrupt increase of the temperature and conversions within the CHC compartment. The simultaneous temperature increase in the overall reactor showed the efficient heat transfer from the CHC compartment to the RWGS compartment. With the introduction of the pure N₂ rather than reaction gas in the RWGS compartment, increasing the air/H₂ ratio could significantly increase the reactor temperature up to 700 °C with a H₂ conversion of 70% and complete O₂ conversion. The existence of CHC reaction in the Exo compartment resulted in a significant increase in the reactor temperatures and CO₂ conversion, thereby demonstrating the viability of the CHC/RWGS reactor system. With the CHC reaction turned off, the temperature at the reactor inlet experienced a decline, reaching a value of 360 °C, and the outlet temperature underwent a reduction to 250 °C. As a result, the CO₂ conversion dropped from 44% to 18%. The reactor temperatures rose concurrently as more oxygen with sufficient hydrogen was introduced and reacted in the Exo compartment. The maximum H₂ conversion realized in the Exo compartment was 88%, while the CO₂ conversion was attained around 49%. Reactor performance with near-stoichiometric H₂ combustion feed and stability were

also examined. The reactor could achieve a 72% H₂ conversion and a complete O₂ conversion, while maintaining the inlet temperatures above 600 °C for both compartments. The CO₂ conversion reached in the 45-50% range with a complete CO selectivity throughout the experiments. The stability of the reactor temperatures and conversions were observed to be consistent over 60 h of continuous operation. The reactor was successfully operated for extended periods of time, with approximate 40 on/off cycles, totaling 400 h.

The results reported offer crucial understanding into the operation of laboratory-scale thermally coupled reactors. CHC and RWGS reactions occurred at the front area of the reactor were confirmed. The formation of hot spot in the middle part of the reactor was also observed. The potential method to eliminate the hot spots was also discussed. The strengthening of the convective heat transport could propagate this severe reaction region downstream due to the increase CHC flow rate. A mild radical temperature difference and significant axial temperature difference were observed. However, the reactor performance is quite robust with respect to significant variations in the reactor axial temperature distribution. In the present experimental conditions, the temperature in the inlet section of the reactor was mainly influenced by the CHC reaction, while the outlet section of the reactor was primarily affected by convective heat transport. As a result, decreasing the flow rate in the RWGS compartment led to an increase in inlet temperature due to heat accumulation and a decrease in outlet temperature due to less convection-based heat transport.

Maintaining high temperatures in the reactor is vital to preserve high conversion of CHC reaction during operating to prevent gas explosions, ensuring stable and smooth operation. These

findings underscored the significance of effective insulation and maintaining high temperature at the laboratory scale. The results of the investigation could also be used as a calibration set of data for building a reliable mathematical model, which can be further scaled up via numerical simulations. Additionally, this study provides insight into coupling exothermic with endothermic reactions in a catalytic fixed bed reactor, which could aid in optimizing the process.

5.2 Reactor modeling

In this study, a novel reactor concept for syngas production through the RWGS reaction has been investigated. The feasibility of thermally coupled catalytic hydrogen combustion-reverse water gas shift reactor is first demonstrated by numerical simulations. The dynamic behavior of a typical reactor, including the ignition, the introduction of the RWGS and stabilization is analyzed. The simulations reveal the evolution of temperature, conversions, and mole fractions along the reactor's length, offering a comprehensive understanding of the reactor's behavior. The relation between heat generation (supplied by the CHC reaction) and heat consumption (enthalpy required for the RWGS process and heat loss) is important for efficient performance of the reactor. The efficient transfer of heat between the combustion and RWGS compartments is crucial for maintaining the desired temperatures and achieving high conversions.

The simulations and analyses have provided valuable insights into the effects of geometric parameters and operating conditions in the reactor. Increasing the ratio of the reactor length to diameter to a certain threshold could change the operating pattern significantly. Increasing the ratio

of R_{CHC} to R_{RWGS} leads to a rise in reactor temperature arising from the increase in the ratio of CHC to RWGS compartment volumes, resulting in more heat generated and less heat consumed.

Overall, this study provides valuable insights into the performance and design considerations of the novel reactor concept. The findings can serve as a basis for further optimizations and advancements in hydrogen production technologies.

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Appendix A Analytical instruments

GC

The GC column type is 10 m Rt-Msieve 5A, and the method parameters are taken from the manual provided by the manufacturer as shown in Figure S1. The accuracy of the GC analyzer is provided as shown in Figure S2.

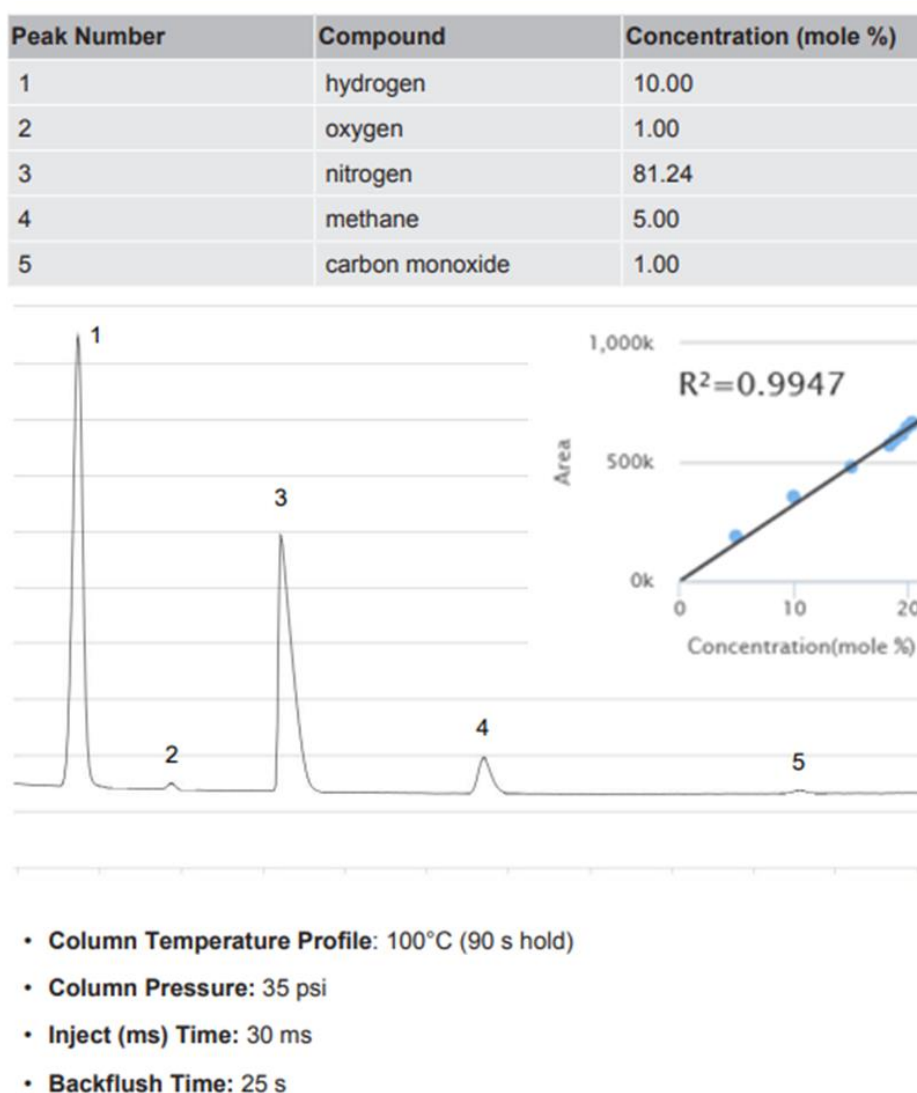


Figure S1. Method parameters from the manufacture and calibration profile.

Repeatability	Specification
Retention time	≤0.1% RSD (WCOT columns)
Peak area	≤1% RSD (≥0.1% concentration, WCOT columns)

Figure S2. Accuracy of the GC analyzer.

IR

Mist trap (AFM40-N02-Z-A, SMC Corporation) and moisture trap (5182-9411, Agilent Technologies and orange silica gel, Fisher Scientific) are installed in the flow system, and a RH sensor (HIH-4000, Honeywell) is installed as well to ensure that the stream is dry before entering the IR analyzer. The accuracy of the IR analyzer is shown in Figure S3.

Repeatability/Accuracy*: +/- 1% of Full Scale
Linearity: +/- 1% of Full Scale
Noise Level: 1% of Full Scale
Zero Drift:** +/- 1% of Full Scale /24 hr.
Span Drift:** +/- 1% of Full Scale /24 hr.

Speed of Response
Display: 90% of Reading in 1 sec (updated every 1 sec)
Output: 90% of Reading in 1 sec (updated every 1 sec)

Outputs
Digital: Data RS 232
Analog – Recorder: 0-1, 5 or 10VDC Standard; 4-20mA Optional

Power: 120/240 VAC; 50/60 Hz.
Operating Temperature: 0° - 50 ° C (32 ° - 122 ° F)
Storage Temperature: 40 ° - 75 ° C (-40 ° - 166 ° F)
Warm-up Time: 5 Minutes
Power Consumption: < 20 Watts

Physical
Cabinet: 9" X 11" X 24.6"
Display: 3.6" X 4.75" – Graphic LCD
Rack Mount: 19" Rack; 4U high

Figure S3. Accuracy of the IR analyzer.

Appendix B Reactor configurations

The kinetic reactor, Fig. S1, was made from a 3/8" to 1/4" reducing union (Swagelok), connected between a 1/4" and a 3/8" stainless steel tube, with a type K-type thermocouple (1/8", Omega Engineering, Inc.) placed in contact with the catalytic bed. Catalytic materials were crushed and sieved to 0.275-0.425 mm pellets. The catalyst was loaded into the 3/8"-1/4" union and sealed between quartz wool and mesh. The reactor was placed in a furnace (Lindberg/Blue M™ Mini-Mite™ Tube Furnaces, Thermo Fisher Scientific) to maintain isothermal operation.



Figure S4. Kinetic reactor configuration.

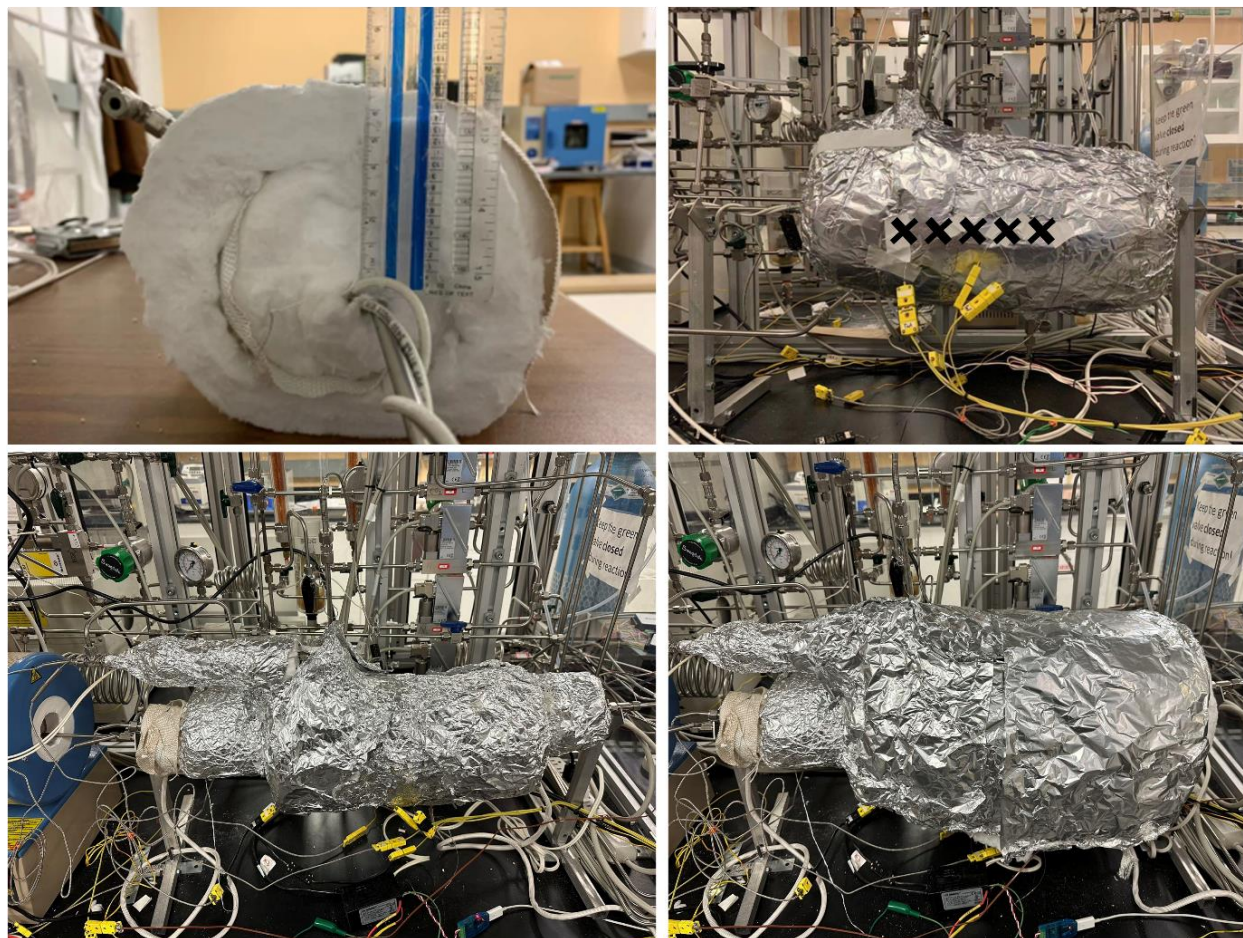


Figure S5. Thermally coupled CHC-RWGS reactor.

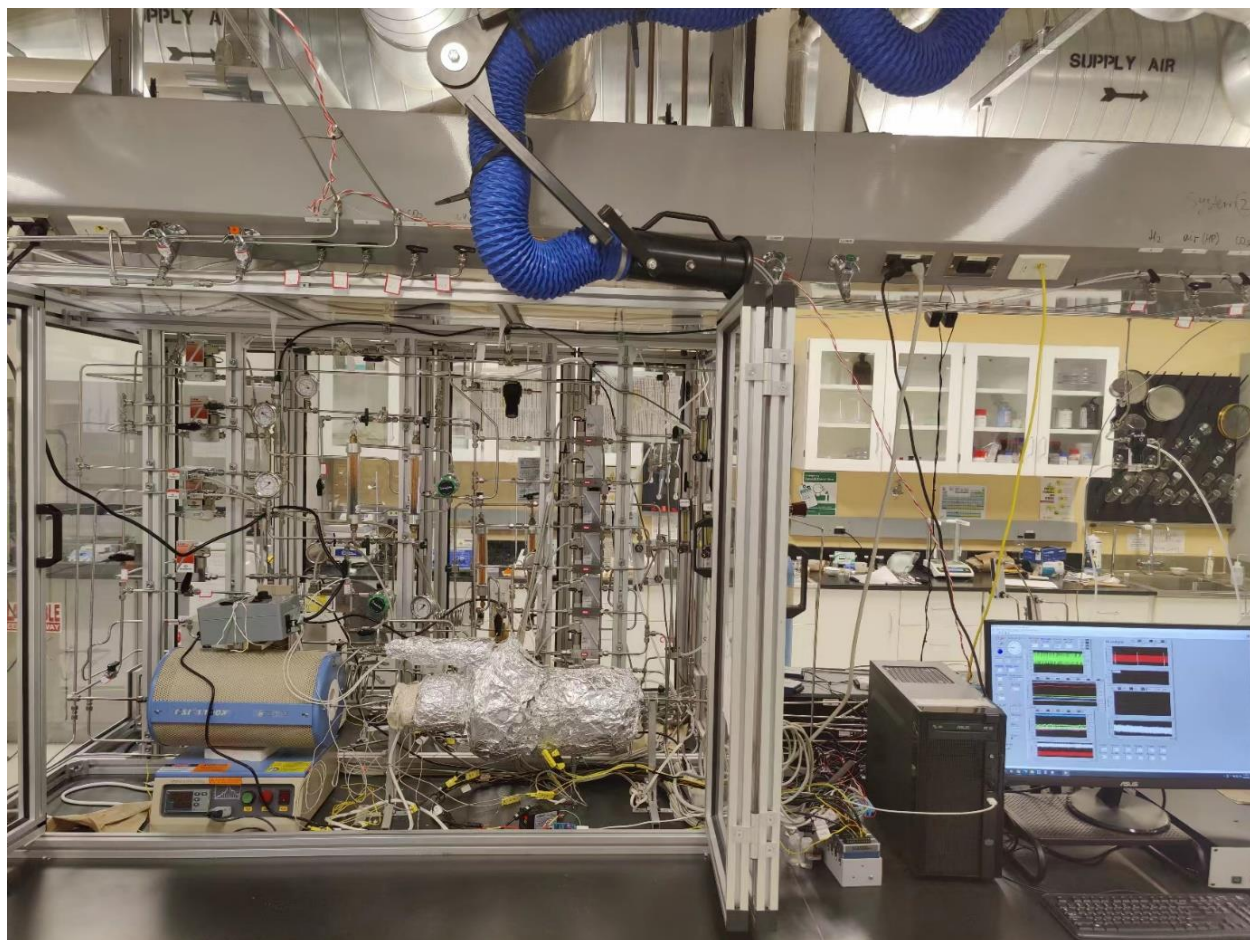


Figure S6. Flow system for reactor tests.

Appendix C Carbon balance derivation

Carbon balance, defined as the ratio of the rate of carbon exiting the reactor and the rate of carbon fed to the reactor ($F_{C,out}$ is the total outlet molar flow rate of all carbon-containing species and $F_{C,f}$ is the total feed molar flow rate of all carbon-containing species):

$$CB = \frac{F_{C,out}}{F_{C,f}} = (y_{CO_2} + y_{CO} + y_{CH_4})(1 + \alpha - f_1 - 4f_2) \quad (S1)$$

In Eq. (S1), α , f_1 , and f_2 are the $H_2:CO_2$ ratio in the feed, conversion to CO, and conversion to CH_4 , respectively, as defined in Eqs (S2-S4) below ($F_{C,out}$ is the total outlet molar flow rate of all carbon-containing species):

$$\alpha = \frac{F_{H_2,f}}{F_{CO_2,f}} \quad (S2)$$

$$f_1 = \frac{y_{CO}}{(y_{CO_2} + y_{CO} + y_{CH_4})} \equiv \frac{F_{CO,out}}{F_{C,out}} = \frac{F_{CO,out}}{F_{CO_2,f}} \quad (S3)$$

$$f_2 = \frac{y_{CH_4}}{(y_{CO_2} + y_{CO} + y_{CH_4})} \equiv \frac{F_{CH_4,out}}{F_{C,out}} = \frac{F_{CH_4,out}}{F_{CO_2,f}} \quad (S4)$$

Eq. (S4) above is obtained from the carbon balance definition, Eq. (S1), using Eq. (S6) to define the total outlet molar flow rate ($F_{CO,out}$ and $F_{CH_4,out}$ correspond to H_2 consumption):

$$CB = \frac{F_{C,out}}{F_{C,f}} = \frac{(y_{CO_2} + y_{CO} + y_{CH_4})F_{t,out}}{F_{CO_2,f}} \quad (S5)$$

$$F_{t,out} = F_{CO_2,f} + F_{H_2,f} - F_{CO,out} - 4F_{CH_4,out} \quad (S6)$$

Appendix D Explosion pressure and rate of pressure rise

The effects of hydrogen explosions inside the apparatus are interesting. Therefore, mixtures within the explosion range were prepared and the explosion pressures (p_{ex}) and the highest rates of pressure rise $(dp/dt)_{\text{ex}}$ after the ignition were determined. $(dp/dt)_{\text{ex}}$ value describes the violence of a gas explosion in a closed vessel. The explosion pressures are shown as the so-called pressure rising factors p_{ex}/p_0 . In the range of lower hydrogen concentrations, the explosion pressures and particularly the rates of pressure rise are relatively low (see Figure S7 and S8). Notably, the stoichiometric range ($y_{\text{H}_2} = 29.6\%$) is close to the maximum explosion pressure.

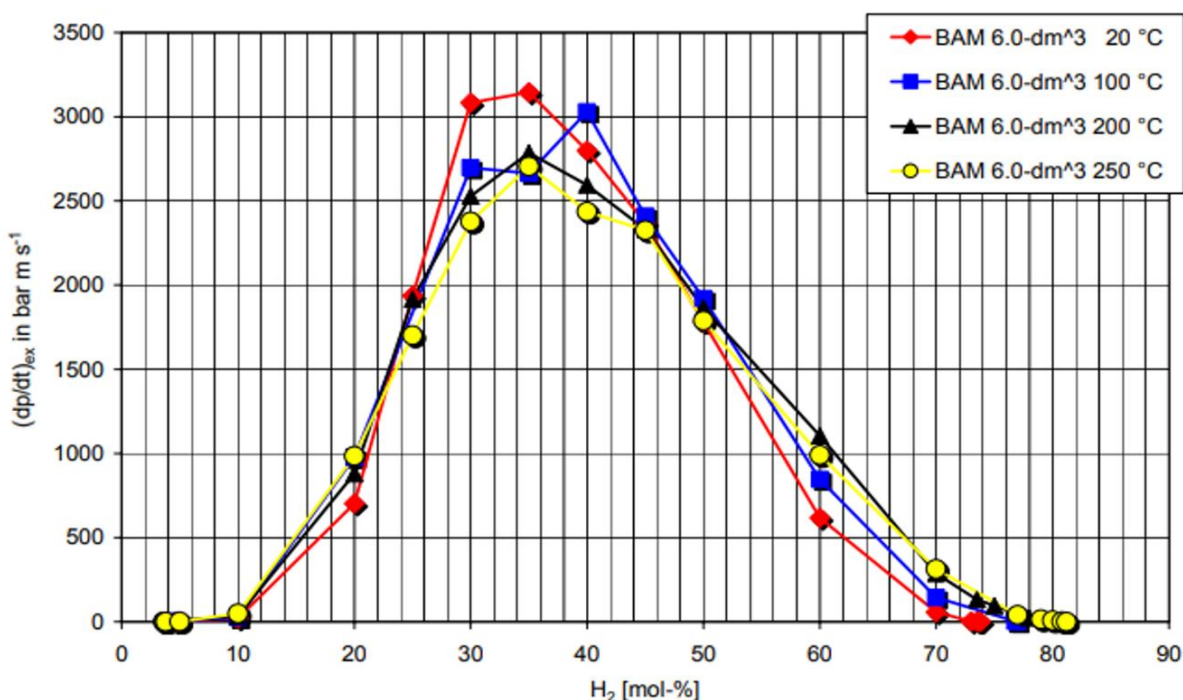


Figure S7. Rate of explosion pressure rises (K_G values) of hydrogen-air mixtures at an initial pressure of 5 bars, determined at different initial temperatures [79].

The maximum explosion pressure decreases with higher initial temperatures (see Figure S8).

According to the ideal gas law the pressure rise corresponds to the temperature increase which is smaller at higher initial temperatures.

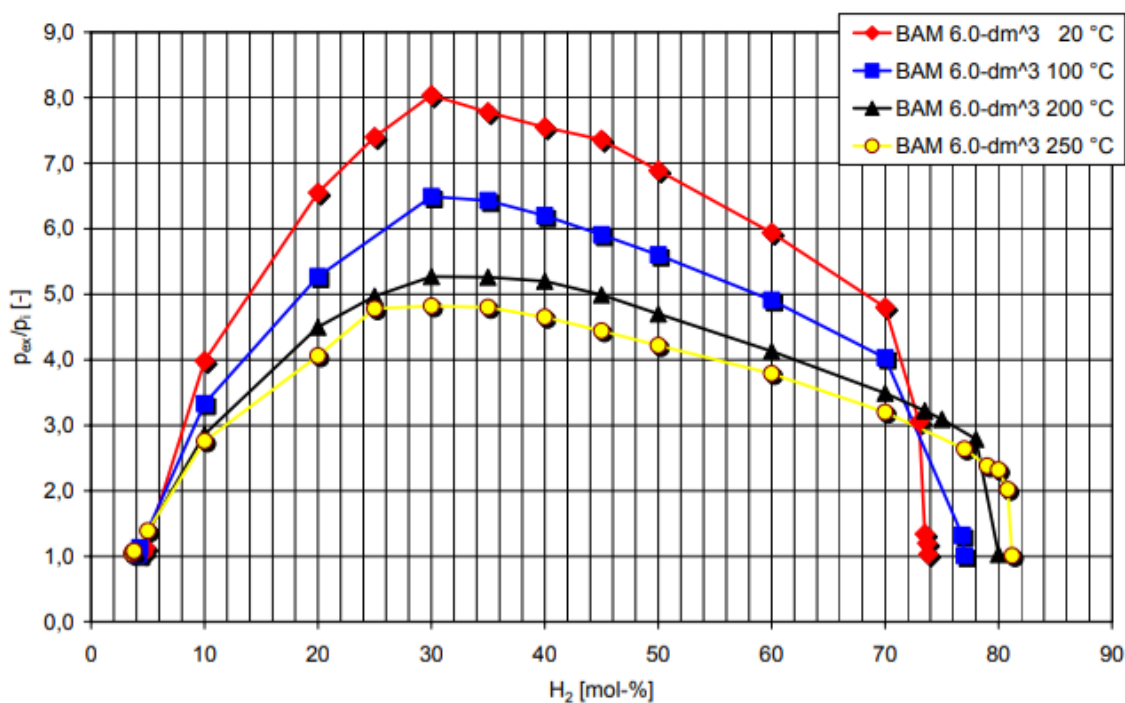


Figure S8. Explosion pressure ratios of hydrogen-air mixtures at an initial pressure of 5 bars, determined at different initial temperatures [79].

Appendix E Supplementary experimental results

a. Effects of Feed flow rate

Table S1. Flow rate. (*: extra insulation layer)

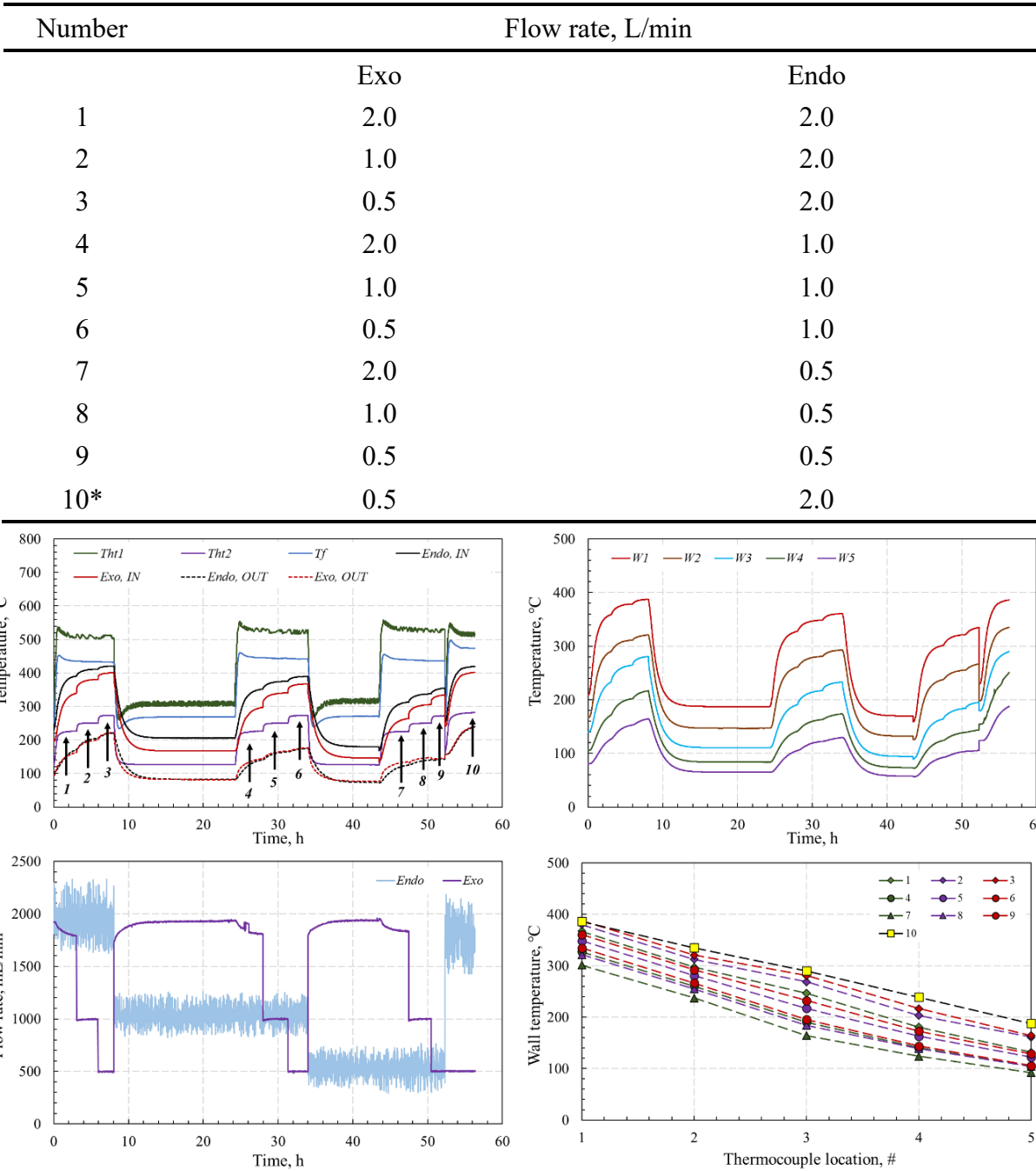


Figure S9. Effects of flow rates in the CHC and RWGS compartments.

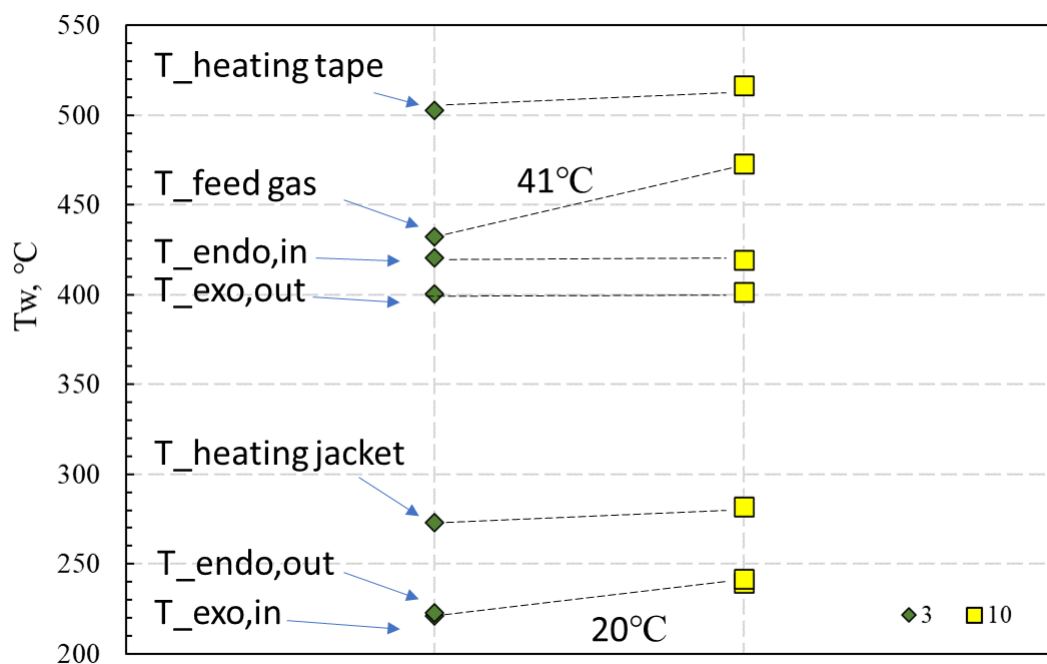


Figure S10. Temperature comparison between case 3 and case 10.

b. Operations of counter-current flow

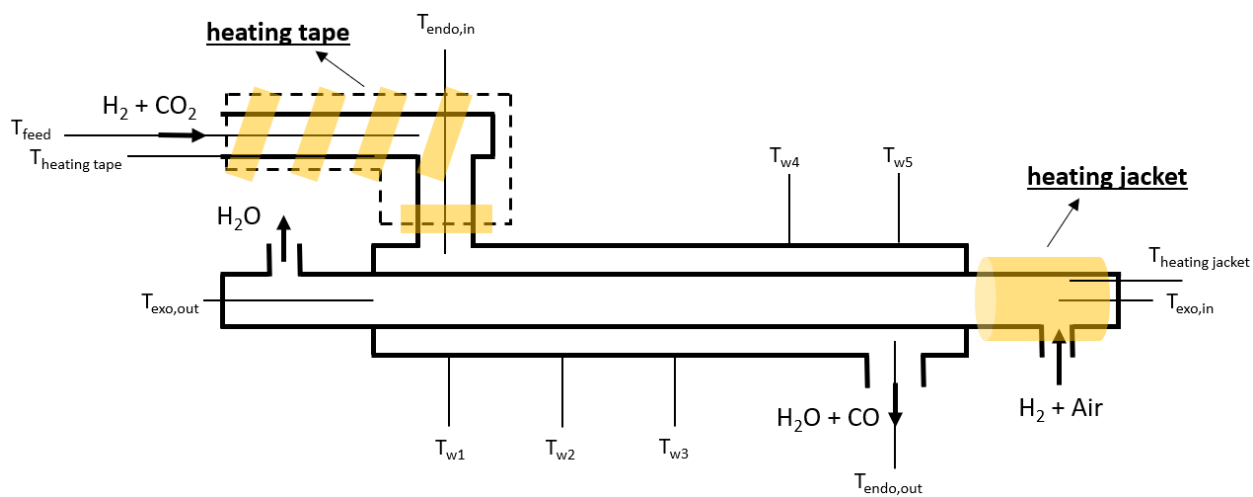


Figure S11. Reactor diagram for counter-current operation.

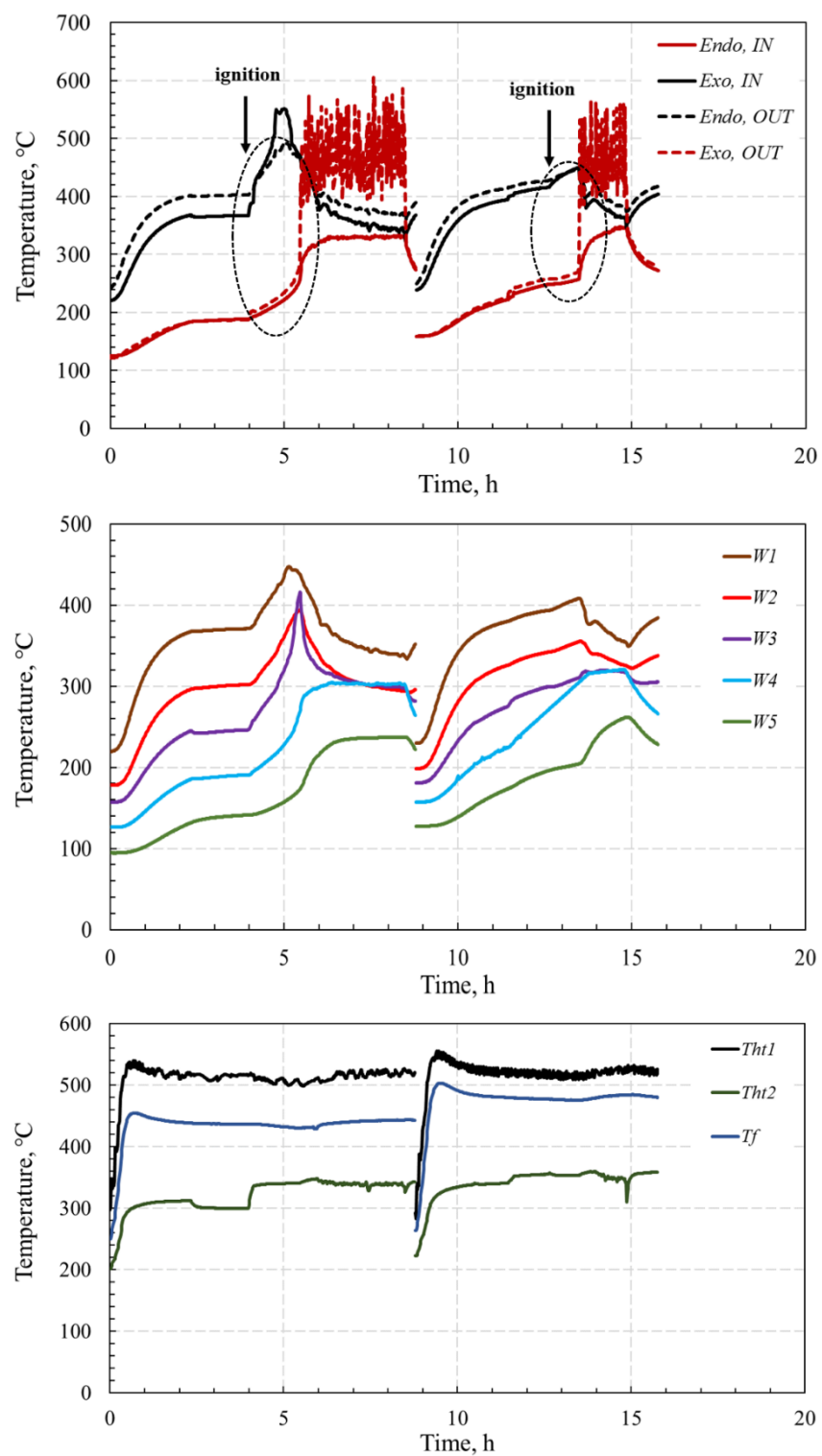


Figure S12. Temperature profiles of the operations of counter-current flow.

c. Effects of heating jacket 2

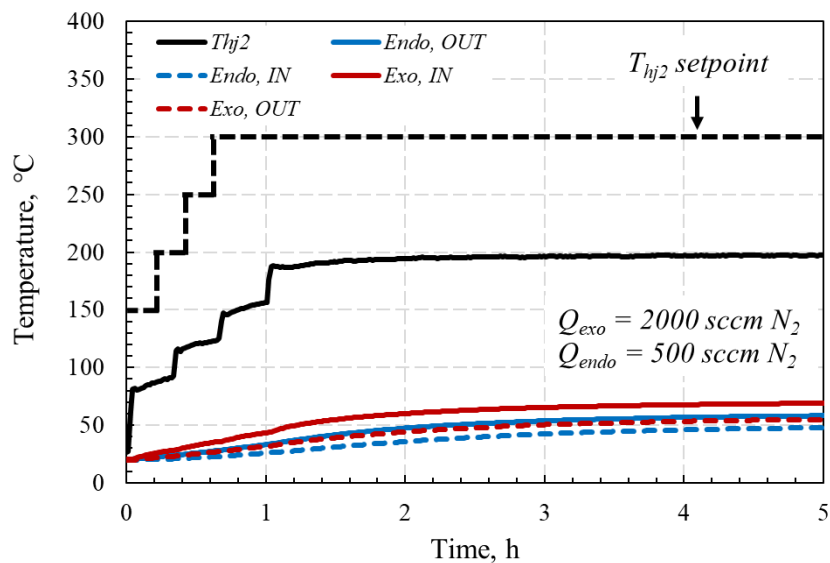


Figure S13. HJ2, Inlet, and outlet temperatures.

d. Supplementary results

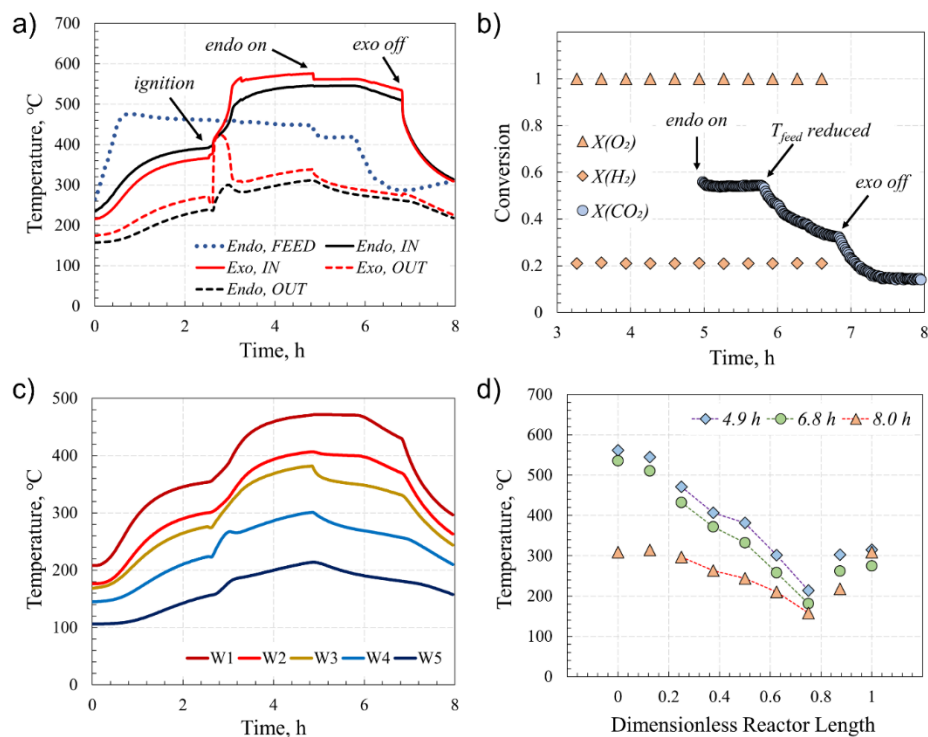


Figure S14. The effect of heat generation in the catalytic H_2 combustion compartment. Parameters:

$Q_{f,exo} = 230/400 \text{ mL/min air}/H_2$, $Q_{f,endo} = 100/300 \text{ mL/min } CO_2/H_2$.

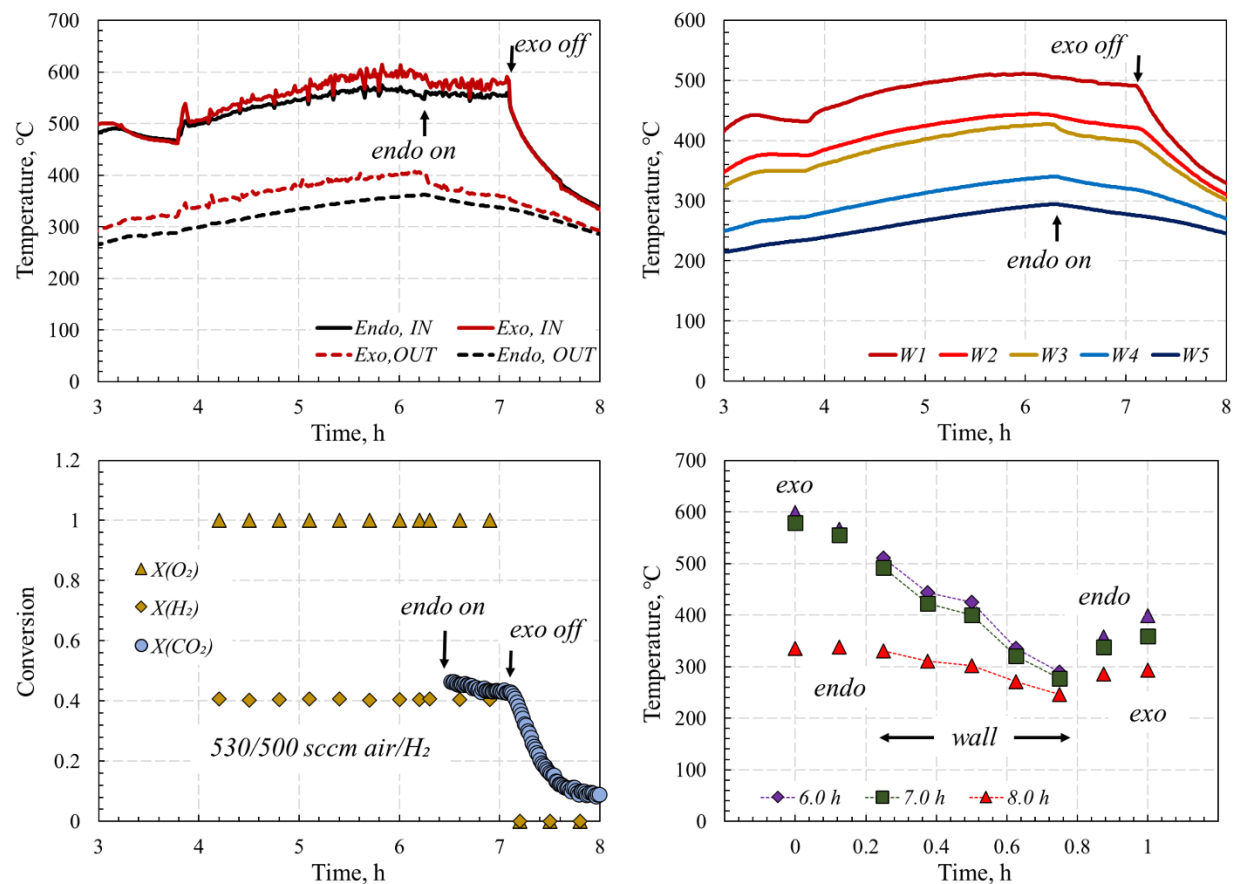


Figure S15. The effect of heat generation in the catalytic H_2 combustion compartment. Parameters: $Q_{f,endo} = 100/300$ mL/min CO_2/H_2 .

Table S2.

	Test 1	Test 2	Test3	Test4
T_{hj1} , °C	430	370	430	430
Air/ H_2 , ccm	700/500	531/550	470/475	390/400
$X(CO_2)$	(44%)	(43%)	(33%)	(33%)
CO_2/H_2 , ccm (RWGS)	100/300	100/300	100/300	100/300
$X(CO_2)$ without Exo	18%	9%	21%	21%

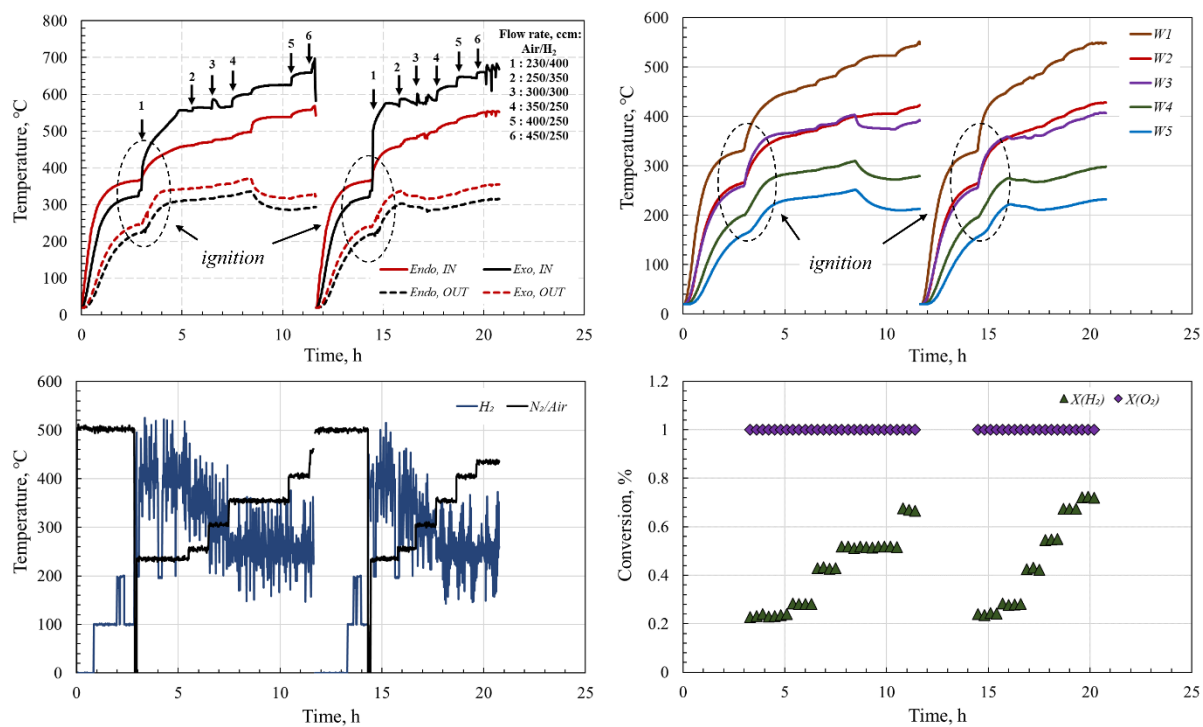


Figure S16. Effects of flow rate in the CHC compartment.

Appendix F Mass and heat transfer criteria

Calculations were conducted for low and high conversions (12-52% range) in the 400-600 °C temperature range, 1-3 bar pressure range, 1000-60000 L/(kg h) space velocity range and 275-425 μm pellet size. Constant parameters and variables are listed in Tables S4 and S4.

Table S3. List of variables.

Variable	Unit	Min	Max
X_{CO_2}		0.12	0.52
T	°C	400	600
P	bar	1	3
v_g	m/s	0.17	0.21
λ_g	kJ/(m s K)	2.95E-4	3.74E-4
dp	μm	275	425
λ_s	kJ/(m s K)	2.50	2.51
C_{pg}	kJ/(m s K)	3.48E-2	3.62E-2
μ_g	kg/(m s)	2.21E-5	2.71E-5

Table S4. Calculated minimum and maximum values for the transport limitation criteria

Criterion type	Min	Max	Criterion
Mears criterion for interphase mass transfer	4.98E-4	1.15E-3	$\square$ 0.15
Mears criterion for interphase heat transfer	1.41E-3	2.34E-3	$\square$ 0.15
Weisz-Prater criterion for internal diffusion	1.25E-3	2.8E-3	$\square$ 1.0
Isothermal pellet criterion	1.73E-7	3.64E-7	$\square$ 0.75

Appendix G Thermophysical properties

Table S5. Heat capacity constants for selected species ($C_p=AT^2+BT+C$; T in K and C_p in kJ/(mol K)). Gas mixture heat capacity $C_{pm}=\sum y_i C_{pi}$.

Species	A	B	C
gas phase			
CO ₂	-2.0E-8	5.0E-5	0.0256
H ₂	3.0E-9	-2.0E-6	0.0297
CO	1.0E-8	-7.0E-6	0.0301
H ₂ O	1.0E-8	-5.0E-6	0.0356
Air	2.0E-7	-1.0E-5	1.0
solid phase			
solid	-2.8E4	1.7E-4	1.0446

Table S6. Gas phase viscosity constants for selected species ($\mu=AT+B$; T in K and μ in kg/(m s)). Gas mixture viscosity $\mu_m=\sum y_i \mu_i$.

Species	A	B
CO ₂	4.0E-8	6.0E-6
H ₂	2.0E-8	5.0E-6
CO	4.0E-8	7.0E-6
H ₂ O	4.0E-8	-3.0E-6
Air	3.0E-8	1.0E-5

Table S7. Thermal conductivity constants for selected species ($\lambda=AT+B$; T in K and λ in kW/(m K)).

Species	A	B
gas phase		
CO ₂	8.0E-8	-4.0E-6
H ₂	5.0E-7	4.0E-5
CO	6.0E-8	8.0E-6
H ₂ O	1.0E-7	-2.0E-5
Air	6.0E-8	9.0E-6
solid phase		
solid	$34.5 \times 10^{-3} e^{[-0.0033(T-273.15)]} + 5.5 \times 10^{-3}$	

Diffusion coefficient

$$D_g = D_0 \left(\frac{T}{T_0} \right)^\alpha \left(\frac{P_0}{P} \right)$$

	Diffusion coefficient, m ² /s	α
D_0^{RWGS}	5.50e-5	1.75
D_0^{CHC}	1.81e-5	1.75

Appendix H Dimensionless numbers

Table S8. Dimensionless numbers.

Name	Expression	Physical meaning
Biot	$Bi_{RWGS} = \frac{U_{w,HL} \cdot R^{RWGS}}{k_{re}^{RWGS}}$ $Bi_{Ox} = \frac{U_{w,HE} \cdot R^{Ox}}{k_{re}^{Ox}}$	Ratio of heat advection from a surface to heat conduction inside.
Damköhler	$Da_{RWGS} = \frac{W_{cat}^{RWGS} \cdot A_{RWGS} \cdot P_t}{Q_f^{RWGS} \rho_{gf}}$ $Da_{Ox} = \frac{W_{cat}^{Ox} \cdot A_{Ox} \cdot \rho_{gf}^2}{Q_f^{Ox}}$	Ratio of reaction rate to convective mass transport rate.
Nusselt	$Nu_p = \frac{hd_p}{\lambda_g} = 2 + 0.6 Re_p^{\frac{1}{2}} Pr^{\frac{1}{3}}$ $Nu_{w,HE} = \frac{h_w d_p}{k_g} = 0.23 Re_p + 27.9$	Ratio of convective to conductive heat transfer.
Peclet (mass)	$Pe_{zm} = \frac{\varepsilon v_g L}{D_{ae}}$ $Pe_{rm} = \frac{\varepsilon v_g L}{D_{re}}$	Ratio of advective transport rate to diffusive transport rate.
Peclet (heat)	$Pe_{zh} = \frac{\varepsilon v_g L \rho_g C_{pg}}{k_{ae}}$ $Pe_{rh} = \frac{\varepsilon v_g L \rho_g C_{pg}}{k_{re}}$	Ratio of heat advection to heat conduction.

Prandtl	$\text{Pr} = \frac{\mu_g / \rho_g}{\lambda_g / (\rho_g C_{pg})} = \frac{\mu_g C_{pg}}{\lambda_g}$	Ratio of momentum diffusivity to thermal diffusivity.
Reynolds	$\text{Re}_p = \frac{v_g \rho_g d_p}{\mu_g}$	Ratio of inertia to viscosity.
Schmidt	$\text{Sc} = \frac{\mu_g}{\rho_g D_m}$	Ratio of momentum diffusivity to mass diffusivity.
Sherwood	$\text{Sh} = \frac{k_c d_p}{D_m} = 2 + 0.6 \text{Re}^{\frac{1}{2}} \text{Sc}^{\frac{1}{3}}$	Ratio of convective mass transfer rate to diffusive mass transport rate.
	$\beta_{\text{Ox}} = \frac{-\Delta H_{\text{Ox}}}{T_{ad} C_{pg}}$	
	$\beta_{\text{RWGS}} = \frac{-\Delta H_{\text{RWGS}}}{T_{ad} C_{pg}}$	
	$\sigma = \frac{\varepsilon \rho_g C_{pg} + (1 - \varepsilon) \rho_s C_{ps}}{\varepsilon \rho_g C_{pg}}$	

Appendix I Dimensional model

Table S9. Dimensional model formulation.

Mass balances in the CHC compartment

$$\begin{aligned} (\varepsilon \rho_g)^{CHC} \frac{\partial y_i^{CHC}}{\partial t} = & (\rho_g D_{re})^{CHC} \frac{\partial^2 y_i^{CHC}}{\partial r^2} + (\rho_g D_{ae})^{CHC} \frac{\partial^2 y_i^{CHC}}{\partial z^2} + \frac{1}{r} (\rho_g D_{re})^{CHC} \frac{\partial y_i^{CHC}}{\partial r} \\ & - (\varepsilon v_g \rho_g)^{CHC} \frac{\partial y_i^{CHC}}{\partial z} + (1 - \varepsilon^{CHC}) \rho_c^{CHC} \alpha_i R_j \end{aligned} \quad (S7)$$

Mass balances in the RWGS compartment

$$\begin{aligned} (\varepsilon \rho_g)^{RWGS} \frac{\partial y_i^{RWGS}}{\partial t} = & (\rho_g D_{re})^{RWGS} \frac{\partial^2 y_i^{RWGS}}{\partial r^2} + (\rho_g D_{ae})^{RWGS} \frac{\partial^2 y_i^{RWGS}}{\partial z^2} + \frac{1}{r} (\rho_g D_{re})^{RWGS} \frac{\partial y_i^{RWGS}}{\partial r} \\ & - (\varepsilon v_g \rho_g)^{RWGS} \frac{\partial y_i^{RWGS}}{\partial z} + (1 - \varepsilon^{RWGS}) \rho_c^{RWGS} \alpha_i R_j \end{aligned} \quad (S8)$$

Energy balances in the CHC compartment

$$\begin{aligned} (\rho C_p)_{eff}^{CHC} \frac{\partial T^{CHC}}{\partial t} = & k_e^{CHC} \frac{\partial^2 T^{CHC}}{\partial r^2} + k_e^{CHC} \frac{\partial^2 T^{CHC}}{\partial z^2} + \frac{k_e^{CHC}}{r} \frac{\partial T^{CHC}}{\partial r} - (\varepsilon v_g \rho_g C_{pg})^{CHC} \frac{\partial T^{CHC}}{\partial z} \\ & + (1 - \varepsilon^{CHC}) \rho_c^{CHC} (-\Delta H_j) R_j \end{aligned} \quad (S9)$$

Energy balances in the RWGS compartment

$$\begin{aligned} (\rho C_p)_{eff}^{RWGS} \frac{\partial T^{RWGS}}{\partial t} = & k_e^{RWGS} \frac{\partial^2 T^{RWGS}}{\partial r^2} + k_e^{RWGS} \frac{\partial^2 T^{RWGS}}{\partial z^2} + \frac{k_e^{RWGS}}{r} \frac{\partial T^{RWGS}}{\partial r} \\ & - (\varepsilon v_g \rho_g C_{pg})^{RWGS} \frac{\partial T^{RWGS}}{\partial z} + (1 - \varepsilon^{RWGS}) \rho_c^{RWGS} (-\Delta H_j) R_j \end{aligned} \quad (S10)$$

Energy balances in the insulation layer

$$k_i \frac{1}{r} \left(\frac{\partial T}{\partial r} + r \frac{\partial^2 T}{\partial r^2} \right) + k_i \frac{\partial^2 T}{\partial z^2} = 0 \quad (S11)$$

Table S10. Dimensional initial and boundary conditions.

Initial conditions		
$t = 0 :$	$y_i^k = y_{i0}^k, T^k = T_0^k$	(S12)
Boundary conditions		
radial		
$r = 0, 0 \leq z \leq L :$	$\frac{\partial T^{CHC}}{\partial r} = 0, \frac{\partial y_i^{CHC}}{\partial r} = 0$	(S13)
$r = R_{CHC}, 0 \leq z \leq L :$	$-k_{re}^{CHC} \frac{\partial T^{CHC}}{\partial r} = U_{w,HE} (T^{CHC} - T^{RWGS}), \frac{\partial y_i^{CHC}}{\partial r} = 0$	(S14)
$r = R_{RWGS}, 0 \leq z \leq L :$	$-k_{re}^{RWGS} \frac{\partial T^{RWGS}}{\partial r} = U_{w,HE} (T^{RWGS} - T^{ins}), \frac{\partial y_i^{RWGS}}{\partial r} = 0$	(S15)
$r = R_{ins}, 0 \leq z \leq L :$	$-k_{re}^{ins} \frac{\partial T^{ins}}{\partial r} = U_{w,HL} (T^{ins} - T_a)$	(S16)
axial		
$z = 0, 0 \leq r \leq R_{CHC}$	$-D_{ae}^{CHC} \frac{\partial y_i^{CHC}}{\partial z} = (\varepsilon v_g)^{CHC} (y_{if} - y_i)^{CHC}$	(S17)
	$-k_{ae}^{CHC} \frac{\partial T^{CHC}}{\partial z} = (\varepsilon v_g \rho_g C_{pg})^{CHC} (T_f - T)^{CHC}$	(S18)
$z = 0, R_{CHC} \leq r \leq R_{RWGS}$	$-D_{ae}^{RWGS} \frac{\partial y_i^{RWGS}}{\partial z} = (\varepsilon v_g)^{RWGS} (y_{if} - y_i)^{RWGS}$	(S19)
	$-k_{ae}^{RWGS} \frac{\partial T^{RWGS}}{\partial z} = (\varepsilon v_g \rho_g C_{pg})^{RWGS} (T_f - T)^{RWGS}$	(S20)
$z = 1, 0 \leq r \leq R_{CHC}$	$\frac{\partial y_i^{CHC}}{\partial z} = 0, \frac{\partial T^{CHC}}{\partial z} = 0$	(S21)
$z = 1, R_{CHC} \leq r \leq R_{RWGS}$	$\frac{\partial y_i^{RWGS}}{\partial z} = 0, \frac{\partial T^{RWGS}}{\partial z} = 0$	(S22)

Appendix J Parameter estimation and MATLAB scripts

1. Experimental methods for parameter estimation

RWGS

1.1 Temperature Test

For a temperature test, approximately 225 mg of pelletized catalyst was loaded into the reactor, which was then placed in the furnace. Gas hourly space velocity (GHSV) was set to approximately 60,000 mL/(g catalyst h) and the reactor outlet pressure was set to 2 bar. H₂ and CO₂ were fed in a 3:1 ratio. Temperature was set to ramp in 25 °C intervals from 600 °C to 300 °C. Each temperature was maintained for 2 hours, with 10 minutes to ramp from each temperature point to the next. Concentration data was collected using the IR analyzer.

1.2 Gas Hourly Space Velocity Test

For a gas hourly space velocity test, approximately 225 mg of pelletized catalyst was loaded into the reactor, which was then placed in the furnace. Temperature was set to 600 °C and the reactor outlet pressure was set to 2 bar. H₂ and CO₂ were fed in a 3:1 ratio.

Gas hourly space velocity (GHSV) was initially set to 10,000 mL/(g catalyst h). Once concentrations were observed to be stable for 20 minutes, GHSV was changed to 30,000 mL/(g catalyst h). Once stable for 20 minutes, GHSV was changed again. GHSVs tested were then 60,000 mL/(g catalyst h), 150,000 mL/(g catalyst h), and 200,000 mL/(g catalyst h).

1.3 Activation Energy Test

The activation energy test is similar to the temperature test. Approximately 225 mg of pelletized catalyst was loaded into the reactor, which was then placed in the furnace. Gas hourly space velocity (GHSV) was set to approximately 100,000 mL/(g catalyst h) and the reactor outlet pressure was set to 2 bar. H₂ and CO₂ were fed in a 3:1 ratio.

Temperature was set to ramp in 25 °C intervals from 425 °C to 325 °C. Each temperature was maintained for 2.5 hours, with 10 minutes to ramp from each temperature point to the next. Concentration data was collected using the IR analyzer.

The objective of the tests was to determine the catalyst performance under a variety of operating conditions. It was expected that conversion will increase with increasing temperature (due to the endothermic nature of the RWGS reaction) and decrease with increasing GHSV (due to the decrease in residence time). The activation energy test was intended to collect conversion data for conversions under 20% to be used to get an initial guess for the activation energy and reference reaction rate constant.

CHC

1.4 Temperature Test

For a temperature test, approximately 200 mg of pelletized catalyst was loaded into the reactor, which was then placed in the furnace. Gas hourly space velocity (GHSV) was set to approximately 60,000 mL/(g catalyst h) and the reactor outlet pressure was set to 1 bar. H₂ and air

were fed in a 1:9 ratio. Temperature was set to ramp in 25 °C intervals from 700 °C to 300 °C. Each temperature was maintained for half hour, with 10 minutes to ramp from each temperature point to the next. Concentration data was collected using the GC analyzer.

1.5 Activation Energy Test

The activation energy test is similar to the temperature test. Approximately 200 mg of pelletized catalyst was loaded into the reactor, which was then placed in the furnace. Gas hourly space velocity (GHSV) was set to approximately 60,000 mL/(g catalyst h) and the reactor outlet pressure was set to 1 bar. H₂ and air were fed in a 1:9 ratio.

Temperature was set to ramp in 25 °C intervals from 550 °C to 450 °C. Each temperature was maintained for 1 hour, with 10 minutes to ramp from each temperature point to the next. Concentration data was collected using the GC analyzer. The activation energy test was intended to collect conversion data for conversions under 20% to be used to get an initial guess for the activation energy and reference reaction rate constant.

2. parameter estimation

Parameter estimation was done in MATLAB by specifying initial guesses as well as upper and lower bounds for the parameters, then minimizing the residuals between the model-predicted results and the experimentally observed results. Three nested functions were used to do this. Each will be described, starting from the lowest level function and moving the highest-level function.

2.1 CSTResti Function

This is a function called on by ode45 in the SSE_CSTR function described in Section 2.2. It has time, initial mole fractions, reactor mole fractions, temperature, flowrate and pressure as inputs. Note that the parameters are declared as global variables so that if their value is changed in a superior function then the value is changed in CSTResti.

The function starts by calculating the values of the equilibrium constant, adsorption constants, and reaction rate constant given the parameter values and temperature. It then uses these, combined with the concentrations of the gases inside the reactor, to calculate the reaction rate. This reaction rate is then substituted into a CSTR balance; note that it is modelled as CSTR start-up, where concentration is a function of time. This allows the outlet concentrations for given feed conditions (temperature, GHSV, pressure) to be calculated using ode45.

2.2 SSE_CSTR Function

This function takes the initial guesses for the parameters (the only input) and turns them into global variables. The raw data from the experiments is contained in this file, as well as the inlet conditions (temperature, GHSV, feed ratio, etc.) for each test. A loop is then used to compute the predicted outlet concentrations for each set of inlet conditions (using the CSTResti function described in Section 2.1).

The residuals are then computed for both CO and CO₂ concentrations; residuals are given by the difference between the predicted and measured values divided by the pooled standard

deviation of the experimental values. The residuals are the output of the function.

2.3 SSE_lsqnonlin Function

This is the highest-level function; initial guesses for parameter values as well as upper and lower bounds are input into this function. It then calls on lsqnonlin to minimize the output of the SSE_CSTR function; this being the residuals. By minimizing the residuals, the best fit can be found.

Having now discussed what each function does independently, it can be understood how the three functions work together; SSE_lsqnonlin uses a built-in MATLAB function to minimize the residuals provided by SSE_CSTR within a set of bounds and with initial guesses guided by literature and experimental data. SSE_CSTR takes given experimental data and compares it to model-calculated data provided by CSTResti to calculate residuals that are fed to SSE_lsqnonlin. CSTResti is simply a set of ODEs to find the concentration given certain feed conditions to the reactor.

CSTResti

```

function dydt =
CSTResti(t,y,ufCO2,ufH2,ufCO,ufH2O,ufCH4,B,deltaHeq,T,P,R,Ctf,Q)
global Ea ARWGS BCO deltaHCO BH2O deltaHH2O
Ct = P/(R*T);
gamma = Ctf/Ct; %%%
uCO2 = (y(1));
uH2 = (y(2));
uCO = (y(3));
uH2O = (y(4));
uCH4 = (y(5));
%-----Kinetics and Thermodynamic Parameters-----%
%-----Reaction Constant-----%
% k = ARWGS*exp((-Ea/R)*(1/T));
%-----Equilibrium Constant-----%
Keq = B*exp(-deltaHeq/(R*T));
Keqhat = Keq; % dimensionless
%-----Adsorption Constant-----%
KCO = BCO*exp((-deltaHCO/R)*(1/T));
KH2O = BH2O*exp(-(deltaHH2O/R)*(1/T));
KCOhat = KCO*P/100; %dimensionless Pressure Unit [kpa to bar]
KH2Ohat = KH2O; %dimensionless
DEN = 1+KCOhat*gamma*uCO+KH2Ohat*uH2O/uH2;
%reaction rate
f2 = real(gamma*exp((-Ea/R)*(1/T))*(uCO2-uCO*uH2O/(uH2*Keqhat))/(DEN^2)); %%%
Keqhat?Denominator
Wc = 0.000200; %218 mg, was 603
% Ftf = Q*44.643*3600;
% Ftf = Ftf/3600;
Ftf = Q*Ctf;
Da = ARWGS*Wc*(P/100)/(Ftf); % only used when there is no methanation
dydt = zeros(5,1);
dydt(1) = ufCO2 -y(1)+ real(Da*(-f2));
dydt(2) = ufH2 -y(2) + real(Da*(-f2));
dydt(3) = ufCO -y(3)+ real(Da*(+f2));
dydt(4) = ufH2O -y(4) + real(Da*(+f2));
dydt(5) = ufCH4 -y(5) + real(Da*(0));
end

```

SSE_CSTR

```
function resids = SSE_CSTR_ALL_mod_newresults(parms)
global Ea ARWGS BCO deltaHCO BH2O deltaHH2O
deltaHeq = 36.5816; % known ref[3] pg[2]
B = 56.5995; %known ref[3] pg[2]
Ea=parms(1);
ARWGS=parms(2);
BCO=parms(3);
deltaHCO=parms(4);
BH2O = parms(5);
deltaHH2O = parms(6);
disp(Ea)
disp(ARWGS)
disp(BCO)
disp(deltaHCO)
disp(BH2O)
disp(deltaHH2O)
%Experimental Results
%Order: GHSV Tests (6 points each), Temperature Tests (13 points each)
flow = [(75/(60*1000*1000)) (150/(60*1000*1000)) (450/(60*1000*1000))
(750/(60*1000*1000)) (1125/(60*1000*1000)) (1500/(60*1000*1000)) ];
temp = [600+273.15 575+273.15 550+273.15 525+273.15 500+273.15 475+273.15
450+273.15 425+273.15 400+273.15 375+273.15 350+273.15 325+273.15
300+273.15];
CO2exp = [11.93 12.89 13.32 14.44 15.74 16.78...% 6
11.07 12.19 13.23 14.44 16.18 17.73...% 12
9.42 11.85 12.97 14.27 15.83 17.30...%18 checked
11.76 12.80 14.53 17.39 19.03 20.24 21.11 21.97 22.67 23.27 23.62 23.79
24.05...%18+13
11.76 12.54 13.58 14.62 15.83 17.30 18.69 19.81 21.11 22.06 22.75 23.10
23.27... %18+13*2
11.93 12.54 13.23 14.01 15.22 16.78 18.60 20.33 21.46 22.15 22.67 23.01
23.36]';%18+8*3
COexp = [15.41 15.26 15.16 14.34 13.12 11.90...%6
14.64 14.82 14.95 13.94 12.20 10.47... % 12
14.44 14.65 14.65 13.63 12.10 10.68... %18 checked
16.28 14.85 12.71 9.15 7.01 5.58 4.16 3.14 2.12 1.31 0.80 0.39
0.0...%18+13
```

```

    16.79 15.77 14.44 13.12 11.49 9.45 7.72 5.89 3.95 2.22 1.3 0.59
0.0 ...%18+13*2
    16.07 15.16 14.34 13.22 11.69 9.76 7.32 4.87 3.24 2.12 1.31 0.70
0.0]'; ...%18+13*3
%save('CO2exp.mat','CO2exp');
%save('COexp.mat','COexp');
%Temperature & Pressure
P = 45/0.145038; %kPa
R = 8.314e-3;
%dimensionless concentrations
ufCO2 = 0.25; %CO2
ufH2 = 0.75; %H2
ufCO = 0;
ufH2O = 0;
ufCH4 = 0;
%initial conditions
tspan = [0 10];
row = length(CO2exp);
tempcount = 1;
flowcount = 1;
yCO2PRED = zeros(row,1);
yCOPRED = zeros(row,1);
for k=1:1:row
if k <= 18
    ufCO2 = 0.25; %CO2
    ufH2 = 1-0.25; %H2
    y0 = [ufCO2 ufH2 ufCO ufH2O ufCH4];
    T = 600 + 273.15; % K
    Q = flow(flowcount);
    flowcount = flowcount+1;
    if flowcount > 6
        flowcount = 1;
    end
end
end
if k > 18 && k <= 31
    ufCO2 = 0.25; %CO2
    ufH2 = 0.75; %H2
    y0 = [ufCO2 ufH2 ufCO ufH2O ufCH4];
    T = temp(tempcount);
    Q = 220/(60*1000*1000);

```

```

    tempcount = tempcount+1;
    if tempcount > 13
        tempcount = 1;
    end
end
if k > 31
    ufCO2 = 0.25; %CO2
    ufH2 = 1-0.25; %H2
    y0 = [ufCO2 ufH2 ufCO ufH2O ufCH4];
    T = temp(tempcount);
    Q = 180/(60*1000*1000);
    tempcount = tempcount+1;
    if tempcount > 13
        tempcount = 1;
    end
end
Ctf = P/(R*T);
[t,y] = ode15s(@ (t,y)
CSTResti(t,y,ufCO2,ufH2,ufCO,ufH2O,ufCH4,B,deltaHeq,T,P,R,Ctf,Q),tspan,y0);
CO2pre = y(:,1);%(:,1) the first column of the matrix
H2pre = y(:,2);
COpre = y(:,3);
H2Opre = y(:,4);
CH4pre = y(:,5);
utpre = CO2pre+H2pre+COpre+H2Opre+CH4pre;
utdpre = utpre-H2Opre;
yCO2pre = CO2pre/utpre;
yH2pre = H2pre/utpre;
yCOpre = COpre/utpre;
yH2Opre = H2Opre/utpre;
yCH4pre = CH4pre/utpre;
ydCO2pre = CO2pre/utdpre; % dry
ydH2pre = H2pre/utdpre; % dry
ydCOpre = COpre/utdpre; % dry
ydCH4pre = CH4pre/utdpre; % dry
m = length(ydCO2pre);
yCO2PRED(k,1) = ydCO2pre(m)*100;
yCOPRED(k,1) = ydCOpre(m)*100;
end
varCO2 = 0.98414137; %0.2847005; % pooled variance

```

```

varCO = 1.449722792; %0.620211143; % pooled variance
%resids = [(CO2exp-yCO2PRED) '*(CO2exp-yCO2PRED)/varCO2 (COexp-
yCOPRED) '*(COexp-yCOPRED)/varCO]
resids = [(CO2exp-yCO2PRED)/sqrt(varCO2) ; (COexp-yCOPRED)/sqrt(varCO)]; %
%reguar residuals
% save('CO2Pred.mat','yCO2PRED');
% save('COPred.mat','yCOPRED');
% save('CO2Exp.mat','CO2exp');
% save('COExp.mat','COexp');
SSE_scaled = sum(resids.^2);
% save('SSE.mat','SSE_scaled','resids');
end

```

SSE_lsqrnonlin

```

function SSE_lsqrnonlin_mod_WTR
close all
clear
%Initial guesses for parameters and bounds may need to be changed
%parms0 = [85.50 0.09897 0.6763 -70.91 0.0042 88.68]; initial guesses for
activation energy and pre-exponential factor & adsorb constants
parms0 = [70.78 17934266.27 8.25E-05 -70.65 1.77E+05 88.68];
lb = [parms0(1)-parms0(1)*0.5 parms0(2)*0.01 parms0(3)*0.01
parms0(4)+parms0(4)*0.5 parms0(5)*0.01 parms0(6)-parms0(6)*0.5]; %lower
bounds for the solver
ub = [parms0(1)+parms0(1)*0.5 parms0(2)*100 parms0(3)*100 parms0(4)-
parms0(4)*0.5 parms0(5)*100 parms0(6)+parms0(6)*0.5]; %upper bounds for the
solver
options = optimset('Display','iter','MaxIter',1000,'TolX',1e-9,'TolFun',1e-
9); %Tolerances for the solvers
[parmshat,resnorm,residual,exitflag,output]=
lsqrnonlin('SSE_CSTR_ALL_mod_newresults',parms0,lb,ub,options); %calling the
minimization function
parmshat=parmshat'
output;
SSE = resnorm
residual
end

```

Appendix K Non-distributed flow CHC-RWGS reactor MATLAB scripts and 2D CHC-RWGS reactor COMSOL model

Non-distributed flow CHC-RWGS reactor

```

tspan = [0 500000];

%=====Feed Operating Conditions=====
%-----Feed Mole Fraction-----
yfCO2=0.25; yfH2=0.75; yfCO=0.0; yfH2O=0.0;...
    yfH2_Ox=0.2; yfO2=0.8*0.21; yfH2O_Ox=0.0;
%-----Feed & Ambient Temperature-----
Tf_RWGS=300+273.15; Tf_Ox=300+273.15; %K
Ta=(400+25)/2+273.15; %K ; room temperature
%-----Adiabatic Temperature-----
deltaH_Ox=-242.0; % kJ/mol
M_Air=29.0e-3; % kg/mol
Cpgf_Ox=yfH2_Ox*(3e-9*(Tf_Ox)^2-2e-6*(Tf_Ox)+0.0297)+... %kJ/(mol K)
    (yfO2/0.21)*(10^3*(2e-10*(Tf_Ox)^2-1e-8*(Tf_Ox)+0.001)*M_Air);
Tad=Tf_Ox+(-deltaH_Ox)/Cpgf_Ox; %K
%-----Catalyst Weight-----
Wc_RWGS=0.2/1000.0; Wc_Ox=1.0/1000.0; %g to kg
%-----Feed Pressure-----
Pt_RWGS=15.0; Pt_Ox=15.0; %bar
%=====Inital Conditions=====
%Inital Temperature; (preheat the reactor)
theta0_RWGS=(273.15+400)/Tad; theta0_Ox=(273.15+400)/Tad; %dimensionless
%Initial Mole Fraction
y0CO2=0.25; y0H2=0.75; y0CO=0.0; y0H2O=0.0;... %dimensionless
    y0H2_Ox=0.2; y0O2=0.8*0.21; y0H2O_Ox=0.0;
y0 = [y0CO2,y0H2,y0CO,y0H2O,y0H2_Ox,y0O2,y0H2O_Ox,theta0_RWGS,theta0_Ox];
%=====GHSV & FR & Molar Feed rate=====
GHSV_RWGSarray = [900.0 900.0 900.0 900.0 900.0 900.0... %mL/(g h)
    900.0 900.0 900.0 900.0 900.0 900.0...
    900.0 900.0 900.0 900.0 900.0 900.0...
    900.0 900.0 900.0 900.0];
GHSV_Oxarray = 1e4*[11. 11.5 12.0 12.5 ...
    13.00 13.5 14.00 14.5 15.0 15.5...
    16.00 16.5 17.00 17.5 18.0 19.0...
    20.0 21.0 22.0 23.0 24.0 25.0];

```

```

[m,n] = size(GHSV_RWGSarray);
flowcount = 1;
Vm = 0.024; %m3/mol; molar volume at NTP
for i=1:n
    GHSV_RWGS = GHSV_RWGSarray(flowcount);
    GHSV_Ox = GHSV_Oxarray(flowcount);
    flowcount = flowcount+1;
    if flowcount>n
        flowcount = 1;
    end
    FfCO2_RWGS = GHSV_RWGS*(Wc_RWGS*1000.0)*yfCO2...
        /(3600.0*1000.0*1000.0*Vm); % mol/s
    FfH2_Ox = GHSV_Ox*(Wc_Ox*1000.0)*yfH2_Ox/(3600.0*1000.0*1000.0*Vm);
    FR = FfH2_Ox/FfCO2_RWGS;
%=====Solver=====
    [t,y] = ode15s(@(t,y) ...
        RWGSH2oxidation(t,y,yfCO2,yfH2,yfCO,yfH2O,yfH2_Ox,yfO2,yfH2O_Ox,...
        Tf_RWGS,Tf_Ox,Ta,GHSV_RWGS,GHSV_Ox,Pt_RWGS,Pt_Ox,Wc_RWGS,Wc_Ox),...
        tspan,y0);
    [numRows,numCols]=size(y);
    % Creating Empty Arrays
%-----RWGS Reaction Performance-----%
    yCO2_RWGS = zeros(numRows,1);
    yH2_RWGS = zeros(numRows,1);
    yCO_RWGS = zeros(numRows,1);
    yH2O_RWGS = zeros(numRows,1);
    yt = zeros(numRows,1);
    ytd = zeros(numRows,1);
    ydCO2_RWGS = zeros(numRows,1);
    ydH2_RWGS = zeros(numRows,1);
    ydCO_RWGS = zeros(numRows,1);
    f1 = zeros(numRows,1);
    alpha = zeros(numRows,1);
    CB = zeros(numRows,1);
    XCO2 = zeros(numRows,1);
%-----Ox Reaction Performance-----%
    yN2_Ox = zeros(numRows,1);
    yH2_Ox = zeros(numRows,1);
    yO2_Ox = zeros(numRows,1);
    yH2O_Ox = zeros(numRows,1);

```

```

ytd_Ox = zeros(numRows,1);
ydh2_Ox = zeros(numRows,1);
ydO2_Ox = zeros(numRows,1);
XH2 = zeros(numRows,1);

%-----Compartment Temperature-----%
Temp_RWGS = zeros(numRows,1);
Temp_Ox = zeros(numRows,1);

%Populating individual dimensionless variables Arrays
for j=1:numRows
    %RWGS Reaction Performance
    yCO2_RWGS(j) = y(j,1);
    yH2_RWGS(j) = y(j,2);
    yCO_RWGS(j) = y(j,3);
    yH2O_RWGS(j) = y(j,4);
    yt(j) = yCO2_RWGS(j)+yH2_RWGS(j)+yCO_RWGS(j)+yH2O_RWGS(j);
    ytd(j) = yt(j)-yH2O_RWGS(j);
    ydCO2_RWGS(j) = yCO2_RWGS(j)/ytd(j);
    ydh2_RWGS(j) = yH2_RWGS(j)/ytd(j);
    ydCO_RWGS(j) = yCO_RWGS(j)/ytd(j);
    f1(j) = ydCO_RWGS(j)/(ydCO_RWGS(j)+ydCO2_RWGS(j));
    alpha(j) = ydh2_RWGS(1)/ydCO2_RWGS(1);
    CB(j) = (ydCO2_RWGS(j)+ydCO_RWGS(j))*(1+alpha(j)-f1(j));
    XCO2(j) = (yCO_RWGS(j))/(yCO_RWGS(j)+yCO2_RWGS(j)); % no methanation
    %Ox Reaction Performance
    yN2_Ox(j)=(yfO2/0.21)*0.79;
    yH2_Ox(j) = y(j,5);
    yO2_Ox(j) = y(j,6);
    yH2O_Ox(j) = y(j,7);
    ytd_Ox(j)=yN2_Ox(j)+yH2_Ox(j)+yO2_Ox(j);
    ydh2_Ox(j)=yH2_Ox(j)/ytd_Ox(j);
    ydO2_Ox(j)=yO2_Ox(j)/ytd_Ox(j);
    XH2(j)=(yFH2_Ox-yH2_Ox(j))/yFH2_Ox;
    %Compartment Temperature
    Temp_RWGS(j) = y(j,8);
    Temp_Ox(j) = y(j,9);
end
XCO2end(i,1) = XCO2(end);
XH2end(i,1) = XH2(end);
Temp_RWGSend(i,1) = Temp_RWGS(end);
Temp_Oxend(i,1) = Temp_Ox(end);

```

```

end
%-----Plot-----%
figure(1);
plot(Temp_RWGSend*Tad-273.15,XCO2end,'bo','linewidth',1.5);
hold on; plot((550:25:950),[5.4744e-01 5.7263e-01 5.9642e-01 6.1883e-01
6.3989e-01 6.5965e-01 6.7816e-01 6.9548e-01...
7.1167e-01 7.2680e-01 7.4092e-01 7.5410e-01 7.6640e-01 7.7789e-01...
7.8860e-01 7.9861e-01 8.0796e-01...
],'r-','linewidth',1.5);
title('CO_2 Conversion vs RWGS Compartment Temperature');
legend('simulation','Equilirbium Curve');
xlabel('Temperature, \circC');
ylabel('CO_2 Conversion');
figure(2);
plot(Temp_Oxend*Tad-273.15,XH2end,'b--o','linewidth',1.5);
title('H_2 Conversion vs Ox Compartment Temperature');
xlabel('Temperature, \circC');
ylabel('H_2 Conversion');
function dydt = RWGSH2oxidation(t,y,yfCO2,yfH2,yfCO,yfH2O,yfH2_Ox,yfO2,...
yfH2O_Ox,Tf_RWGS,Tf_Ox,Ta,GHSV_RWGS,GHSV_Ox,Pt_RWGS,Pt_Ox,Wc_RWGS,Wc_Ox)
%=====feed gas molar density=====
Pt_RWGS1=Pt_RWGS*100000.0; Pt_Ox1=Pt_Ox*100000.0; %bar to pa
R=8.314; % (m^3 Pa)/(mol K)
ro_gfRWGS=Pt_RWGS1/(R*Tf_RWGS); ro_gfOx=Pt_Ox1/(R*Tf_Ox); %mol/m^3
%=====Reactor Geometry=====
Dr_Ox=6.35e-3; Dr_RWGS=2.54e-2; L=5.0e-2; dw_Ox=8.89e-4; dw_RWGS=1.24e-3;%m
diw=5.0e-2; dp=4.0e-4; %m
epsi_Ox=0.5; epsi_RWGS=0.5; %dimensionless
Area_Ox=pi*Dr_Ox*L; Area_RWGS=pi*Dr_RWGS*L; %m^2
Vt_Ox=pi*(Dr_Ox/2)^2*L; Vt_RWGS=pi*L*((Dr_RWGS/2)^2-(Dr_Ox/2)^2); %m^3
ro_sOx=3.85e3; %kg/m^3
ro_sRWGS=3.85e3; %kg/m^3
%=====Kinetics=====
R=8.314e-3; % Gas constant,kJ/(mol K)
%-----Parameters for RWGS Equilibrium-----%
B_eq=56.5995; %dimensionless
deltaH_eq=36.5816; %kJ/mol
%-----Parameters for Reaction Rate-----%
Ea_RWGS=72.73; Ea_Ox=93.067; %kJ/mol
A_RWGS=1.53567e7; %mol/(kg bar s)

```

```

A_Ox=78.56; %m^9/(kg mol^2 s)
%-----Parameters for Adsorption Constants-----%
deltaH_CO=-60.31; %kJ/mol
deltaH_H2O=77.82; %kJ/mol
B_CO=6.468e-3; %1/bar
B_H2O=3.146e6; %dimensionless
%-----Reaction Heat-----%
deltaH_Ox=-242.0; deltaH_RWGS=41.2; %kJ/mol
%-----Thermophysical Properties-----%
% Molecular Weight
M_CO2=44e-3; M_H2=2e-3; M_CO=28e-3; M_H2O=18e-3; M_Air=29e-3; %kg/mol
% Cp heat capacity; Gas: %kJ/(mol k); Solid:%kJ/(kg K)
Cpgf_RWGS=yfCO2*(-2e-8*(Tf_RWGS)^2+5e-5*(Tf_RWGS)+0.0256)+...
    yfH2*(3e-9*(Tf_RWGS)^2-2e-6*(Tf_RWGS)+0.0297)+...
    yfCO*(1e-8*(Tf_RWGS)^2-7e-6*(Tf_RWGS)+0.0301)+...
    yfH2O*(1e-8*(Tf_RWGS)^2-5e-6*(Tf_RWGS)+0.0356); %kJ/(mol k)
Cpgf_Ox=yfH2_Ox*(3e-9*(Tf_Ox)^2-2e-6*(Tf_Ox)+0.0297)+...
    (yfO2/0.21)*(10^3*(2e-10*(Tf_Ox)^2-1e-8*(Tf_Ox)+0.001)*M_Air);
Cps_RWGS=-2.8e4*(Tf_RWGS)^(-2)+1.742e-4*(Tf_RWGS)+1.0446; %kJ/(kg K)
Cps_Ox=-2.8e4*(Tf_Ox)^(-2)+1.742e-4*(Tf_Ox)+1.0446;
% Mu Viscosity, pa s [=] kg/(m s)
miugf_RWGS=yfCO2*(4e-8*(Tf_RWGS)+6e-6)+...
    yfH2*(2e-8*(Tf_RWGS)+5e-6)+...
    yfCO*(4e-8*(Tf_RWGS)+7e-6)+...
    yfH2O*(4e-8*(Tf_RWGS)-3e-6); % pa s
miugf_Ox=yfH2_Ox*(2e-8*(Tf_Ox)+5e-6)+...
    (yfO2/0.21)*(3e-8*(Tf_Ox)+1e-5);
% Lamda Thermal Conductivity, gas solid: kW/(m K)
lamdagf_RWGS=yfCO2*(8e-8*(Tf_RWGS)-4e-6)+...
    yfH2*(5e-7*(Tf_RWGS)+4e-5)+...
    yfCO*(6e-8*(Tf_RWGS)+8e-6)+...
    yfH2O*(1e-7*(Tf_RWGS)-2e-5); % kW/(m K)
lamdagf_Ox=yfH2_Ox*(5e-7*(Tf_Ox)+4e-5)+...
    (yfO2/0.21)*(6e-8*(Tf_Ox)+9e-6);
lamdas_RWGS=5.5e-3+(34.5e-3)*exp(-0.0033*(Tf_RWGS-273)); % kW/(m K)
lamdas_Ox=5.5e-3+(34.5e-3)*exp(-0.0033*(Tf_Ox-273));
lamda_w=0.0146+1.27e-5*(Tf_Ox-273);
%-----Adiabatic Temperature-----%
Tad=Tf_Ox+(-deltaH_Ox)/Cpgf_Ox; %K
theta_a=Ta/Tad;

```

```

thetaf_Ox=Tf_Ox/Tad;
thetaf_RWGS=Tf_RWGS/Tad;
%=====Feed volumetric Flow Rate=====
Qf_RWGS = ((GHSV_RWGS*Wc_RWGS*1000.0)/(3600*1000*1000))*... % m3/s
    ((Tf_RWGS)/293.15)*(101325.0/(Pt_RWGS*100000.0));
Qf_Ox = ((GHSV_Ox*Wc_Ox*1000.0)/(3600*1000*1000))*...
    ((Tf_Ox)/293.15)*(101325.0/(Pt_Ox*100000.0));
%-----Wall heat transfer coefficients (U)-----
SVf_RWGS=Qf_RWGS/((1-epsi_RWGS)*Vt_RWGS); %l/s
SVf_Ox=Qf_Ox/((1-epsi_Ox)*Vt_Ox); %l/s
vgf_RWGS=L*SVf_RWGS/epsi_RWGS; %m/s
vgf_Ox=L*SVf_Ox/epsi_Ox; %m/s
Mgf_RWGS=yfCO2*M_CO2+yfH2*M_H2+yfCO*M_CO+yfH2O*M_H2O; %kg/mol
Mgf_Ox=yfH2_Ox*M_H2+(yfO2/0.21)*M_Air;
ro_gmfRWGS=ro_gfRWGS*Mgf_RWGS; %kg/m^3
ro_gmfOx=ro_gfOx*Mgf_Ox;
Re_RWGS=vgf_RWGS*ro_gmfRWGS*dp/miugf_RWGS;
Re_Ox=vgf_Ox*ro_gmfOx*dp/miugf_Ox;
Nu_RWGS=24.0+0.34*(Re_RWGS)^0.77;
Nu_Ox=24.0+0.34*(Re_Ox)^0.77;
hw_RWGS=lamdagf_RWGS*Nu_RWGS/dp;
hw_Ox=lamdagf_Ox*Nu_Ox/dp;
Uw_HE=1/(1/hw_RWGS+1/hw_Ox+dw_Ox/lamda_w); %kW/(m^2 K)
%Uw_HE=0.08;
Uw_HL=30e-3; % kW/(m^2 K)
%-----Dimensionless Parameters-----
gamma_RWGSad=Ea_RWGS/(R*Tad);
gamma_Oxad=Ea_Ox/(R*Tad);
deltaH_COad=deltaH_CO/(R*Tad);
deltaH_H2Oad=deltaH_H2O/(R*Tad);
deltaH_eqad=deltaH_eq/(R*Tad);
Da_RWGS=Wc_RWGS*A_RWGS*Pt_RWGS/(ro_gfRWGS*Qf_RWGS); % dimensionless
%disp(Da_RWGS)
Da_Ox=Wc_Ox*A_Ox*(ro_gfOx)^2/(Qf_Ox); % dimensionless
sigma_Ox=(epsi_Ox*ro_gfOx*Cpgf_Ox+...
    (1-epsi_Ox)*ro_sOx*Cps_Ox)/(ro_gfOx*Cpgf_Ox);
sigma_RWGS=(epsi_RWGS*ro_gfRWGS*Cpgf_RWGS+...
    (1-epsi_RWGS)*ro_sRWGS*Cps_RWGS)/(ro_gfRWGS*Cpgf_RWGS);
beta_Ox=(-deltaH_Ox/(Tad*Cpgf_Ox));
beta_RWGS=(-deltaH_RWGS/(Tad*Cpgf_RWGS));

```

```

Str1=(Uw_HE*Area_Ox)/(Qf_Ox*ro_gfOx*Cpgf_Ox);
Str1_RWGS=(Uw_HE*Area_Ox)/(Qf_RWGS*ro_gfRWGS*Cpgf_RWGS);
Str2=(Uw_HL*Area_RWGS)/(Qf_RWGS*ro_gfRWGS*Cpgf_RWGS);
%-----Dimensionless variables-----%
yCO2_RWGS=(y(1));
yH2_RWGS=(y(2));
yCO_RWGS=(y(3));
yH2O_RWGS=(y(4));
yH2_Ox=(y(5));
yO2_Ox=(y(6));
yAir_Ox=yO2_Ox/0.21;
yH2O_Ox=(y(7));
theta_RWGS=(y(8));
theta_Ox=(y(9));
%-----Dimensionless Functions-----%
Keq=B_eq*exp(-deltaH_eqad/theta_RWGS); % dimensionless
Keqhat=Keq;
KCO=B_CO*exp(-deltaH_COad/theta_RWGS); % 1/bar
KCOhat=KCO*Pt_RWGS;
KH2O=B_H2O*exp(-deltaH_H2Oad/theta_RWGS); % dimensionless
KH2Ohat=KH2O;
DEN=real(1+KCOhat*yCO_RWGS+KH2Ohat*yH2O_RWGS/yH2_RWGS);
f_RWGS=real(exp(-gamma_RWGSad/theta_RWGS)*...
    (yCO2_RWGS-(yCO_RWGS*yH2O_RWGS/(yH2_RWGS*Keqhat)))/(DEN^2));
f_Ox=real(exp(-gamma_Oxad/theta_Ox)*(yH2_Ox)^2*yO2_Ox);
dydt = zeros(9,1);
%RWGS compartment mole fraction
dydt(1) = -(y(1)-yfCO2)+real(Da_RWGS*(-f_RWGS)); %yCO2
dydt(2) = -(y(2)-yfH2)+real(Da_RWGS*(-f_RWGS)); %yH2
dydt(3) = -(y(3)-yfCO)+real(Da_RWGS*(f_RWGS)); %yCO
dydt(4) = -(y(4)-yfH2O)+real(Da_RWGS*(f_RWGS)); %H2O
%Ox compartment mole fraction
dydt(5) = -(y(5)-yfH2_Ox)+real(Da_Ox*(-f_Ox)); %yH2
dydt(6) = -(y(6)-yfO2)+real(Da_Ox*(-0.5*(f_Ox))); %yO2
dydt(7) = -(y(7)-yfH2O_Ox)+real(Da_Ox*(f_Ox)); %yH2O
%RWGS compartment Temperature
dydt(8) = (epsi_RWGS/sigma_RWGS)*(-(y(8)-thetaf_RWGS)+...
    real(beta_RWGS*Da_RWGS*f_RWGS))+...
    Str1_RWGS*(y(9)-y(8))-Str2*(y(8)-theta_a)); %theta_RWGS
%Ox compartment Temperature

```

```

dydt(9) = (epsi_Ox/sigma_Ox)*(-(y(9)-thetaf_Ox)+...
    real(beta_Ox*Da_Ox*f_Ox)-...
    Str1*(y(9)-y(8))); %theta_Ox
end

```

COMSOL Model formulation

Show equation assuming:

Study 1, Time Dependent

$$e_a \frac{\partial^2 y_1}{\partial t^2} + d_a \frac{\partial y_1}{\partial t} + \nabla \cdot (-c \nabla y_1 - \alpha y_1 + \gamma) + \beta \cdot \nabla y_1 + a y_1 = f$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

Diffusion Coefficient

$(S_i^2 / \text{Perm_Ox})$	0
c	$(1 / \text{Pezm_Ox})$
Diagonal	

Absorption Coefficient

a 0

Source Term

f $-\text{Da_Ox} * f_{\text{Ox}} * (y_1 > 0)$

Mass Coefficient

e_a 0

Damping or Mass Coefficient

d_a 1

Conservative Flux Convection Coefficient

α	0	r
	0	z

Convection Coefficient

β	$-(1/r) * (S_i^2 / \text{Perm_Ox})$	r
	1	z

Conservative Flux Source

γ	0	r
	0	z

Show equation assuming:

Study 1, Time Dependent

$$e_a \frac{\partial^2 y_2}{\partial t^2} + d_a \frac{\partial y_2}{\partial t} + \nabla \cdot (-c \nabla y_2 - \alpha y_2 + \gamma) + \beta \cdot \nabla y_2 + a y_2 = f$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Diffusion Coefficient

$(S_i^2 / \text{Perm_Ox})$	0
c	(1 / Pezm_Ox)
Diagonal	

▼ Absorption Coefficient

a 0

▼ Source Term

f -Da_Ox*f_Ox/2

▼ Mass Coefficient

e_a 0

▼ Damping or Mass Coefficient

d_a 1

▼ Conservative Flux Convection Coefficient

α	0	r
	0	z

▼ Convection Coefficient

β	-(1/r)*(S_i^2 / Perm_Ox)	r
	1	z

▼ Conservative Flux Source

γ	0	r
	0	z

Show equation assuming:

Study 1, Time Dependent

$$e_a \frac{\partial^2 y_3}{\partial t^2} + d_a \frac{\partial y_3}{\partial t} + \nabla \cdot (-c \nabla y_3 - \alpha y_3 + \gamma) + \beta \cdot \nabla y_3 + a y_3 = f$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

Diffusion Coefficient

$(S_i^2 / \text{Perm_Ox})$	0
c	(1/Perm_Ox)
Diagonal	

Absorption Coefficient

a 0

Source Term

f Da_Ox*f_Ox

Mass Coefficient

e_a 0

Damping or Mass Coefficient

d_a 1

Conservative Flux Convection Coefficient

α	0	r
	0	z

Convection Coefficient

β	$-(1/r) * (S_i^2 / \text{Perm_Ox})$	r
	1	z

Conservative Flux Source

γ	0	r
	0	z

Show equation assuming:

Study 1, Time Dependent

$$e_a \frac{\partial^2 y_4}{\partial t^2} + d_a \frac{\partial y_4}{\partial t} + \nabla \cdot (-c \nabla y_4 - \alpha y_4 + \gamma) + \beta \cdot \nabla y_4 + a y_4 = f$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Diffusion Coefficient

$(S_i^2 / \text{Perm_RWGS})$	0
c	(1 / Pezm_RWGS)
Diagonal	

▼ Absorption Coefficient

a 0

▼ Source Term

f if(t < 2000, 0, -Da_RWGS * f_RWGS)

▼ Mass Coefficient

e_a 0

▼ Damping or Mass Coefficient

d_a 1

▼ Conservative Flux Convection Coefficient

α	0	r
	0	z

▼ Convection Coefficient

β	$-(1/r) * (S_i^2 / \text{Perm_RWGS})$	r
	1	z

▼ Conservative Flux Source

γ	0	r
	0	z

Show equation assuming:

Study 1, Time Dependent

$$e_a \frac{\partial^2 y_5}{\partial t^2} + d_a \frac{\partial y_5}{\partial t} + \nabla \cdot (-c \nabla y_5 - \alpha y_5 + \gamma) + \beta \cdot \nabla y_5 + a y_5 = f$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

Diffusion Coefficient

$(S_i^2 / \text{Perm_RWGS})$	0
c	(1/Perm_RWGS)
Diagonal	

Absorption Coefficient

a	0
---	---

Source Term

f	if(t<2000,0,-Da_RWGS*f_RWGS)
---	------------------------------

Mass Coefficient

e_a	0
-------	---

Damping or Mass Coefficient

d_a	1
-------	---

Conservative Flux Convection Coefficient

α	0	r
	0	z

Convection Coefficient

β	-(1/r)*(S_i^2/Perm_RWGS)	r
	1	z

Conservative Flux Source

γ	0	r
	0	z

Show equation assuming:

Study 1, Time Dependent

$$e_a \frac{\partial^2 y_6}{\partial t^2} + d_a \frac{\partial y_6}{\partial t} + \nabla \cdot (-c \nabla y_6 - \alpha y_6 + \gamma) + \beta \cdot \nabla y_6 + a y_6 = f$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Diffusion Coefficient

$(S_i^2 / \text{Perm_RWGS})$	0
c	$(1 / \text{Pezm_RWGS})$
Diagonal	

▼ Absorption Coefficient

a	0
-----	---

▼ Source Term

f	$\text{if}(t < 2000, 0, \text{Da_RWGS} * f_RWGS)$
-----	---

▼ Mass Coefficient

e_a	0
-------	---

▼ Damping or Mass Coefficient

d_a	1
-------	---

▼ Conservative Flux Convection Coefficient

α	0	r
	0	z

▼ Convection Coefficient

β	$-(1/r) * (S_i^2 / \text{Perm_RWGS})$	r
	1	z

▼ Conservative Flux Source

γ	0	r
	0	z

Show equation assuming:

Study 1, Time Dependent

$$e_a \frac{\partial^2 y}{\partial t^2} + d_a \frac{\partial y}{\partial t} + \nabla \cdot (-c \nabla y - \alpha y + \gamma) + \beta \cdot \nabla y + a y = f$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

Diffusion Coefficient

$(S_i^2 / \text{Perm_RWGS})$	0
c	(1 / Pezm_RWGS)
Diagonal	

Absorption Coefficient

a 0

Source Term

f if(t < 2000, 0, Da_RWGS * f_RWGS)

Mass Coefficient

e_a 0

Damping or Mass Coefficient

d_a 1

Conservative Flux Convection Coefficient

α	0	r
	0	z

Convection Coefficient

β	$-(1/r) * (S_i^2 / \text{Perm_RWGS})$	r
	1	z

Conservative Flux Source

γ	0	r
	0	z

Show equation assuming:

Study 1, Time Dependent

$$e_a \frac{\partial^2 \theta_{Ox}}{\partial t^2} + d_a \frac{\partial \theta_{Ox}}{\partial t} + \nabla \cdot (-c \nabla \theta_{Ox} - \alpha \theta_{Ox} + \gamma) + \beta \cdot \nabla \theta_{Ox} + a \theta_{Ox} = f$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

Diffusion Coefficient

$(S_i^2 / \text{Perh_Ox})$	0
c	(1 / Pezh_Ox)
Diagonal	

Absorption Coefficient

a 0

Source Term

f $\text{beta_Ox} * \text{Da_Ox} * f_Ox$

Mass Coefficient

e_a 0

Damping or Mass Coefficient

d_a sigma_Ox

Conservative Flux Convection Coefficient

α	0	r
	0	z

Convection Coefficient

β	$-(1/r) * (S_i^2 / \text{Perh_Ox})$	r
	1	z

Conservative Flux Source

γ	0	r
	0	z

Show equation assuming:

Study 1, Time Dependent

$$e_a \frac{\partial^2 \theta_{RWGS}}{\partial t^2} + d_a \frac{\partial \theta_{RWGS}}{\partial t} + \nabla \cdot (-c \nabla \theta_{RWGS} - \alpha \theta_{RWGS} + \gamma) + \beta \cdot \nabla \theta_{RWGS} + a \theta_{RWGS} = f$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

Diffusion Coefficient

$(S_i^2 / \text{Perh_RWGS})$	0
c	(1/Perh_RWGS)
Diagonal	

Absorption Coefficient

a 0

Source Term

f beta_RWGS*Da_RWGS*f_RWGS

Mass Coefficient

e_a 0

Damping or Mass Coefficient

d_a sigma_RWGS

Conservative Flux Convection Coefficient

α	0	r
	0	z

Convection Coefficient

β	$-(1/r) * (S_i^2 / \text{Perh_RWGS})$	r
	1	z

Conservative Flux Source

γ	0	r
	0	z

Show equation assuming:

Study 1, Time Dependent

$$e_a \frac{\partial^2 \theta_{tai}}{\partial t^2} + d_a \frac{\partial \theta_{tai}}{\partial t} + \nabla \cdot (-c \nabla \theta_{tai} - \alpha \theta_{tai} + \gamma) + \beta \cdot \nabla \theta_{tai} + a \theta_{tai} = f$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Diffusion Coefficient

$S_i^2 \lambda_{da_i}$	0
c	λ_{da_i}
Diagonal	

▼ Absorption Coefficient

a 0

▼ Source Term

f 0

▼ Mass Coefficient

e_a 0

▼ Damping or Mass Coefficient

d_a 0

▼ Conservative Flux Convection Coefficient

α	0	r
	0	z

▼ Convection Coefficient

β	$-S_i^2 \lambda_{da_i} / r$	r
	0	z

▼ Conservative Flux Source

γ	0	r
	0	z

Initial conditions

Initial Values	
Initial value for y1:	
y1	y0H2_Ox
Initial time derivative of y1:	
$\frac{\partial y1}{\partial t}$	0
Initial value for y2:	
y2	y0O2_Ox
Initial time derivative of y2:	
$\frac{\partial y2}{\partial t}$	0
Initial value for y3:	
y3	y0H2O_Ox
Initial time derivative of y3:	
$\frac{\partial y3}{\partial t}$	0
Initial value for y4:	
y4	y0CO2
Initial time derivative of y4:	
$\frac{\partial y4}{\partial t}$	0
Initial value for y5:	
y5	y0H2
Initial time derivative of y5:	
$\frac{\partial y5}{\partial t}$	0
Initial value for y6:	
y6	y0CO
Initial time derivative of y6:	
$\frac{\partial y6}{\partial t}$	0
Initial value for y7:	
y7	y0H2O
Initial time derivative of y7:	
$\frac{\partial y7}{\partial t}$	0
Initial value for thetaOx:	
thetaOx	theta0_Ox
Initial time derivative of thetaOx:	
$\frac{\partial thetaOx}{\partial t}$	0
Initial value for thetaRWGS:	
thetaRWGS	theta0_RWGS
Initial time derivative of thetaRWGS:	
$\frac{\partial thetaRWGS}{\partial t}$	0

Initial value for θ_{tai} :

θ_{tai}

Initial time derivative of θ_{tai} :

$\frac{\partial \theta_{tai}}{\partial t}$

Boundary conditions centerline

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_1 - \alpha y_1 + \gamma) = g - q y_1$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_2 - \alpha y_2 + \gamma) = g - q y_2$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_3 - \alpha y_3 + \gamma) = g - q y_3$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla \theta_{Ox} - \alpha \theta_{Ox} + \gamma) = g - q \theta_{Ox}$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

CHC-RWGS wall

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_4 - \alpha y_4 + \gamma) = g - q y_4$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_5 - \alpha y_5 + \gamma) = g - q y_5$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_6 - \alpha y_6 + \gamma) = g - q y_6$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_7 - \alpha y_7 + \gamma) = g - q y_7$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla \theta_{RWGS} - \alpha \theta_{RWGS} + \gamma) = g - q \theta_{RWGS}$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

$$g = (S_i^2 / (\epsilon_{RWGS} L^2 v_{RWGS} \rho_{RWGS} C_{pgf_RWGS})) R_i U_{w_HE} (n_1 - n_2)$$

▼ Boundary Absorption/Impedance Term

$$q = 0$$

RWGS-Insulation wall

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_4 - \alpha y_4 + \gamma) = g - q y_4$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_5 - \alpha y_5 + \gamma) = g - q y_5$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_6 - \alpha y_6 + \gamma) = g - q y_6$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_7 - \alpha y_7 + \gamma) = g - q y_7$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla \theta_{RWGS} - \alpha \theta_{RWGS} + \gamma) = g - q \theta_{RWGS}$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

$$g = -(S_i^2 / (\epsilon_{RWGS} L_{vg_RWGS} \rho_{gf_RWGS} C_{pgf_RWGS})) R_i U_{w_HERWGS} (n_2 - n_3)$$

▼ Boundary Absorption/Impedance Term

$$q = 0$$

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla \theta_{tai} - \alpha \theta_{tai} + \gamma) = g - q \theta_{tai}$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

$$g = (S_i^2) U_{w_HERWGS} (R_i) (n_2 - n_3)$$

▼ Boundary Absorption/Impedance Term

$$q = 0$$

Ambient

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla \theta_{tai} - \alpha \theta_{tai} + \gamma) = g - q \theta_{tai}$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

$$g = -(S_i^2) (R_i) U_{w_HL} (n_3 - \theta_{a_a})$$

▼ Boundary Absorption/Impedance Term

$$q = 0$$

Inlet

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_1 - \alpha y_1 + \gamma) = g - q y_1$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g yfH2_Ox

▼ Boundary Absorption/Impedance Term

q 1

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_2 - \alpha y_2 + \gamma) = g - q y_2$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g yfO2_Ox

▼ Boundary Absorption/Impedance Term

q 1

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_3 - \alpha y_3 + \gamma) = g - q y_3$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g yfH2O_Ox

▼ Boundary Absorption/Impedance Term

q 1

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_4 - \alpha y_4 + \gamma) = g - q y_4$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g yfCO2

▼ Boundary Absorption/Impedance Term

q 1

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_5 - \alpha y_5 + \gamma) = g - q y_5$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g yfH2

▼ Boundary Absorption/Impedance Term

q 1

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_6 - \alpha y_6 + \gamma) = g - q y_6$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g yfCO

▼ Boundary Absorption/Impedance Term

q 1

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_7 - \alpha y_7 + \gamma) = g - q y_7$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g yfH2O

▼ Boundary Absorption/Impedance Term

q 1

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla \theta_{Ox} - \alpha \theta_{Ox} + \gamma) = g - q \theta_{Ox}$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g thetaf_Ox

▼ Boundary Absorption/Impedance Term

q 1

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla \theta_{RWGS} - \alpha \theta_{RWGS} + \gamma) = g - q \theta_{RWGS}$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g thetaf_RWGS

▼ Boundary Absorption/Impedance Term

q 1

Outlet

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_1 - \alpha y_1 + \gamma) = g - q y_1$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_2 - \alpha y_2 + \gamma) = g - q y_2$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_3 - \alpha y_3 + \gamma) = g - q y_3$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_4 - \alpha y_4 + \gamma) = g - q y_4$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_5 - \alpha y_5 + \gamma) = g - q y_5$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_6 - \alpha y_6 + \gamma) = g - q y_6$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla y_7 - \alpha y_7 + \gamma) = g - q y_7$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla \theta_{Ox} - \alpha \theta_{Ox} + \gamma) = g - q \theta_{Ox}$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Show equation assuming:

Study 1, Time Dependent

$$-\mathbf{n} \cdot (-c \nabla \theta_{RWGS} - \alpha \theta_{RWGS} + \gamma) = g - q \theta_{RWGS}$$

$$\nabla = \left[\frac{\partial}{\partial r}, \frac{\partial}{\partial z} \right]$$

▼ Boundary Flux/Source

g 0

▼ Boundary Absorption/Impedance Term

q 0

Parameters

Name	Expression
epsi_Ox	0.5
epsi_RWGS	0.5
dp	3.0e-3 [m]
ros_Ox	2e3 [kg/m^3]
ros_RWGS	2e3 [kg/m^3]
L	0.8 [m]
R_Ox	6.35e-3/2 [m]
R_RWGS	6.35e-3 [m]
Ac_Ox	πR_{Ox}^2
Ac_RWGS	$\pi (R_{RWGS}^2 - R_{Ox}^2)$
tortuosit...	$1/\sqrt{1 - \text{epsi_Ox}}$
tortuosit...	$1/\sqrt{1 - \text{epsi_RWGS}}$
dw_Ox	8.89e-4 [m]
diw	0.07 [m]
dw_RWGS	1.24e-3 [m]
R_i	$R_{RWGS} + diw$
S	L/R_{RWGS}
V_Ox	$Ac_{Ox} * L$
V_RWGS	$Ac_{RWGS} * L$
stabletime	4000

Name	Expression
yfH2_Ox	0.135
yfO2_Ox	0.865*0.21
yfH2O_Ox	0.0
y0H2_Ox	0.135
y0O2_Ox	0.865*0.21
y0H2O_Ox	0.0

Name	Expression
Wc_RWGS	Ac_RWGS*L*ros_RWGS [kg]
Wc_Ox	Ac_Ox*L*ros_Ox [kg]
Vm	0.024 [m^3/mol]
vg_RWGS	Qf_RWGS/Ac_RWGS [m/s]
vg_Ox	Qf_Ox/Ac_Ox [m/s]
SV_RWGS	10000 [1/h]
SV_Ox	10000 [1/h]
rogf_RW...	(Pt_RWGS*100000.0)/(R_g*Tf_RWGS) [mol/m^3]
rogf_Ox	(Pt_Ox*100000.0)/(R_g*Tf_Ox) [mol/m^3]
R_g	8.314 [(m^3*Pa)/(mol*K)]
Qf_RWGS	((GHSV_RWGS*Wc_RWGS*1000)/(3600*1000*1000)) [m^3/s]
Qf_Ox	((GHSV_Ox*Wc_Ox*1000)/(3600*1000*1000)) [m^3/s]
Pt_RWGS	1 [bar]
Pt_Ox	4.8 [bar]
GHSV_R...	SV_RWGS*1000*V_RWGS/Wc_RWGS [mL/(g*h)]
GHSV_Ox	SV_Ox*1000*V_Ox/Wc_Ox [mL/(g*h)]

Name	Expression
Tf_Ox	450+273.15 [K]
Tf_RWGS	400+273.15 [K]
Ta	50+273.15 [K]
Tad	Tf_Ox+(-deltaH_Ox/Cpgf_Ox) [K]
theta_a	Ta/Tad
thetaf_Ox	Tf_Ox/Tad
thetaf_R...	Tf_RWGS/Tad
T0_RWGS	350+273.15 [K]
T0_Ox	350+273.15 [K]
theta0_R...	T0_RWGS/Tad
theta0_Ox	T0_Ox/Tad
T0_i	(Ta+T0_RWGS)/2 [K]
theta0_i	T0_i/Tad

Name	Expression
deltaH_Ox	-242.0 [kJ/mol]
deltaH_R...	41.2 [kJ/mol]
B_eq	56.5995
deltaH_eq	36.5816 [kJ/mol]
Ea_RWGS	72.73 [kJ/mol]
Ea_Ox	93.067 [kJ/mol]
A_RWGS	1.53567e7 [mol/(kg*bar*s)]
A_Ox	78.56 [m^9/(kg*mol^2*s)]
B_CO	6.468e-3 [1/bar]
B_H2O	3.146e6
deltaH_CO	-60.31 [kJ/mol]
deltaH_H...	77.82 [kJ/mol]
gamma_...	Ea_RWGS/(8.314e-3*Tad)
gamma_...	Ea_Ox/(8.314e-3*Tad)
deltaH_C...	deltaH_CO/(8.314e-3*Tad)
deltaH_H...	deltaH_H2O/(8.314e-3*Tad)
deltaH_e...	deltaH_eq/(8.314e-3*Tad)

Name	Expression
Re_Ox	$vg_Ox \cdot dp \cdot \log M_Ox / \mu_{Ox}$
Pr_Ox	$Cp_{gf_Ox} \cdot \mu_{Ox} / (\lambda_{dagf_Ox} \cdot M_{gOx})$
Nu_Ox	$24 + 0.34 \cdot Re_Ox^{0.77}$

Name	Expression
kae_Ox	$\lambda_{dagf_Ox} \cdot (4 + Re_Ox \cdot Pr_Ox / 2)$ [kW/(m*K)]
kre_Ox	$\lambda_{dagf_Ox} \cdot (4 + Re_Ox \cdot Pr_Ox / (7 \cdot (2 - (1 - 2 \cdot (dp/R_Ox))^2)))$ [kW/(m*K)]
Dae_Ox	$\text{if}(Re_Ox < 1, \epsilon_{Ox} \cdot Dm_Ox / \text{tortuosity_Ox}, \epsilon_{Ox} \cdot (Dm_Ox / \text{tortuosity_Ox} + 0.5 \cdot dp \cdot vg_Ox))$
Dre_Ox	$\text{if}(Re_Ox < 1, \epsilon_{Ox} \cdot Dm_Ox / \text{tortuosity_Ox}, \epsilon_{Ox} \cdot (Dm_Ox / \text{tortuosity_Ox} + 0.1 \cdot dp \cdot vg_Ox))$
hw_Ox	$Nu_Ox \cdot \lambda_{dagf_Ox} / dp$
Uw_HL	$1e-3$ [kW/(m^2*K)]

Name	Expression
S_Ox	L/R_Ox
S_RWGS	$L/(R_RWGS - R_Ox)$
sigma_Ox	$(\epsilon_{Ox} \cdot \rho_{gf_Ox} \cdot Cp_{gf_Ox} + (1 - \epsilon_{Ox}) \cdot \rho_{Ox} \cdot Cps_Ox) / (\epsilon_{Ox} \cdot \rho_{gf_Ox} \cdot Cp_{gf_Ox})$
Pezm_Ox	$\epsilon_{Ox} \cdot vg_Ox \cdot L / Dae_Ox$
Perm_Ox	$\epsilon_{Ox} \cdot vg_Ox \cdot L / Dre_Ox$
Pezh_Ox	$\epsilon_{Ox} \cdot vg_Ox \cdot L \cdot \rho_{gf_Ox} \cdot Cp_{gf_Ox} / kae_Ox$
Perh_Ox	$\epsilon_{Ox} \cdot vg_Ox \cdot L \cdot \rho_{gf_Ox} \cdot Cp_{gf_Ox} / kre_Ox$
Da_Ox	$Wc_Ox \cdot A_Ox \cdot \rho_{gf_Ox}^2 / Qf_Ox$
Da_RWGS	$Wc_RWGS \cdot A_RWGS \cdot Pt_RWGS / (Qf_RWGS \cdot \rho_{gf_RWGS})$
beta_Ox	$-\Delta H_Ox / (Tad \cdot Cp_{gf_Ox})$
S_i	L/R_i

Name	Expression
CpCO2_...	$-2e-8 \cdot Tf_RWGS^2 + 5e-5 \cdot Tf_RWGS + 0.0256$ [kJ/(mol*K)]
CpH2_R...	$3e-9 \cdot Tf_RWGS^2 - 2e-6 \cdot Tf_RWGS + 0.0297$ [kJ/(mol*K)]
CpCO_R...	$1e-8 \cdot Tf_RWGS^2 - 7e-6 \cdot Tf_RWGS + 0.0301$ [kJ/(mol*K)]
CpH2O_...	$1e-8 \cdot Tf_RWGS^2 - 5e-6 \cdot Tf_RWGS + 0.0356$ [kJ/(mol*K)]
CpH2_Ox	$3e-9 \cdot Tf_Ox^2 - 2e-6 \cdot Tf_Ox + 0.0297$ [kJ/(mol*K)]
CpAir_Ox	$10^{-3} \cdot (2e-10 \cdot Tf_Ox^2 - 1e-8 \cdot Tf_Ox + 0.001) \cdot 29e-3$ [kJ/(mol*K)]
CpH2O_Ox	$1e-8 \cdot Tf_Ox^2 - 5e-6 \cdot Tf_Ox + 0.0356$ [kJ/(mol*K)]
Cp_{gf_Ox}	$yfH2_Ox \cdot CpH2_Ox + (yfO2_Ox / 0.21) \cdot CpAir_Ox + yfH2O_Ox \cdot CpH2O_Ox$ [kJ/(mol*K)]
Cps_RWGS	$-2.8e4 \cdot Tf_RWGS^{(-2)} + 1.742e-4 \cdot Tf_RWGS + 1.0446$ [kJ/(kg*K)]
Cps_Ox	$-2.8e4 \cdot Tf_Ox^{(-2)} + 1.742e-4 \cdot Tf_Ox + 1.0446$ [kJ/(kg*K)]

Name	Expression
miuCO2_...	$4e-8 \cdot T_f_RWGS + 6e-6$ [kg/(m*s)]
miuH2_R...	$2e-8 \cdot T_f_RWGS + 5e-6$ [kg/(m*s)]
miuCO_R...	$4e-8 \cdot T_f_RWGS + 7e-6$ [kg/(m*s)]
miuH2O_...	$4e-8 \cdot T_f_RWGS - 3e-6$ [kg/(m*s)]
miuH2_Ox	$2e-8 \cdot T_f_Ox + 5e-6$ [kg/(m*s)]
miuAir_Ox	$3e-8 \cdot T_f_Ox + 1e-5$ [kg/(m*s)]
miuH2O_...	$4e-8 \cdot T_f_Ox - 3e-6$ [kg/(m*s)]
miugf_Ox	$yfH2_Ox \cdot miuH2_Ox + (yfO2_Ox/0.21) \cdot miuAir_Ox + yfH2O_Ox \cdot miuH2O_Ox$ [kg/(m*s)]

Name	Expression
lamdaC...	$8e-8 \cdot T_f_RWGS - 4e-6$ [kW/(m*K)]
lamdaH2...	$5e-7 \cdot T_f_RWGS + 4e-5$ [kW/(m*K)]
lamdaC...	$6e-8 \cdot T_f_RWGS + 8e-6$ [kW/(m*K)]
lamdaH2...	$1e-7 \cdot T_f_RWGS - 2e-5$ [kW/(m*K)]
lamdaH2...	$5e-7 \cdot T_f_Ox + 4e-5$ [kW/(m*K)]
lamdaAir...	$6e-8 \cdot T_f_Ox + 9E-6$ [kW/(m*K)]
lamdaH2...	$1e-7 \cdot T_f_Ox - 2e-5$ [kW/(m*K)]
lamdagf_...	$yfH2_Ox \cdot lamdaH2_Ox + (yfO2_Ox/0.21) \cdot lamdaAir_Ox + yfH2O_Ox \cdot lamdaH2O_Ox$ [kW/(m*K)]
lamdaw_...	$0.0146 + 1.27e-5 \cdot (T_f_Ox - 273.15)$
lamda_i	$0.04e-3$ [kW/(m*K)]

Name	Expression
Dm_RWGS	$0.550e-4 \cdot (T_f_RWGS/273.15)^{1.75} \cdot (1/Pt_RWGS)$ [m^2/s]
Dm_Ox	$0.181e-4 \cdot (T_f_RWGS/273.15)^{1.75} \cdot (1/Pt_RWGS)$ [m^2/s]

Name	Expression
M_gOx	$yfH2_Ox \cdot Mg_H2 + (yfO2_Ox/0.21) \cdot Mg_Air$
Mg_H2	0.002 [kg/mol]
Mg_CO2	0.044 [kg/mol]
Mg_Air	$29e-3$ [kg/mol]
rogM_Ox	$rogf_Ox \cdot M_gOx$ [kg/m^3]

Variables

Name	Expression
n1	thetaOx
n2	thetaRWGS
n3	thetai
K_CO	$B_CO \cdot \exp(-\Delta H_COad / \theta_{RWGS})$ [1/bar]
K_H2O	$B_H2O \cdot \exp(-\Delta H_H2Oad / \theta_{RWGS})$
K_RWGS	$B_eq \cdot \exp(-\Delta H_eqad / \theta_{RWGS})$
DEN	$1 + K_CO \cdot P_t \cdot RWGS \cdot y_6 + K_H2O \cdot y_7 / y_5$
f_RWGS	$\exp(-\gamma_{RWGS} / \theta_{RWGS}) \cdot (y_4 - y_6 \cdot y_7 / (K_RWGS \cdot y_5)) / (DEN^2)$
f_Ox	$\exp(-\gamma_{Ox} / \theta_{Ox}) \cdot y_1^2 \cdot y_2$

Name	Expression
Cpgf_RW...	$\text{if}(t < \text{stabletime}, Cp_{Air_Ox}, yf_{CO2} \cdot Cp_{CO2_RWGS} + yf_{H2} \cdot Cp_{H2_RWGS} + yf_{CO} \cdot Cp_{CO_RWGS} + yf_{H2O} \cdot Cp_{H2O_RWGS})$ [kJ/(mol*K)]
miugf_R...	$\text{if}(t < \text{stabletime}, \mu_{Air_Ox}, yf_{CO2} \cdot \mu_{CO2_RWGS} + yf_{H2} \cdot \mu_{H2_RWGS} + yf_{CO} \cdot \mu_{CO_RWGS} + yf_{H2O} \cdot \mu_{H2O_RWGS})$ [kg/(m*s)]
lamdagf_...	$\text{if}(t < \text{stabletime}, \lambda_{Air_Ox}, yf_{CO2} \cdot \lambda_{CO2_RWGS} + yf_{H2} \cdot \lambda_{H2_RWGS} + yf_{CO} \cdot \lambda_{CO_RWGS} + yf_{H2O} \cdot \lambda_{H2O_RWGS})$
M_gRWGS	$\text{if}(t < \text{stabletime}, M_{g_Air}, yf_{CO2} \cdot M_{g_CO2} + yf_{H2} \cdot M_{g_H2})$ [kg/mol]
rogM_R...	$rogf_RWGS \cdot M_gRWGS$ [kg/m^3]
kae_RWGS	$\lambda_{dagf_RWGS} \cdot (4 + Re_RWGS \cdot Pr_RWGS / 2)$ [kW/(m*K)]
Re_RWGS	$vg_RWGS \cdot dp \cdot rogM_RWGS / \mu_{ugf_RWGS}$
Pr_RWGS	$Cpgf_RWGS \cdot \mu_{ugf_RWGS} / (\lambda_{dagf_RWGS} \cdot M_gRWGS)$
Nu_RWGS	$24 + 0.34 \cdot Re_RWGS^{0.77}$
kre_RWGS	$\lambda_{dagf_RWGS} \cdot (4 + Re_RWGS \cdot Pr_RWGS / (7 \cdot (2 - (1 - 2 \cdot (dp / R_RWGS))^2)))$ [kW/(m*K)]
Dae_RW...	$\text{if}(Re_RWGS < 1, \epsilon_{RWGS} \cdot D_{m_RWGS} / \text{tortuosity_RWGS}, \epsilon_{RWGS} \cdot (D_{m_RWGS} / \text{tortuosity_RWGS} + 0.5 \cdot dp \cdot vg_RWGS))$
Dre_RWGS	$\text{if}(Re_RWGS < 1, \epsilon_{RWGS} \cdot D_{m_RWGS} / \text{tortuosity_RWGS}, \epsilon_{RWGS} \cdot (D_{m_RWGS} / \text{tortuosity_RWGS} + 0.1 \cdot dp \cdot vg_RWGS))$
hw_RWGS	$Nu_RWGS \cdot \lambda_{dagf_RWGS} / dp$
Uw_HE	$(1 / hw_Ox + 1 / hw_RWGS + dw_Ox / \lambda_{daw_Ox})^{-1}$ [kW/(m^2*K)]
Uw_HER...	$(1 / hw_RWGS + dw_RWGS / \lambda_{daw_Ox})^{-1}$ [kW/(m^2*K)]
sigma_R...	$(\epsilon_{RWGS} \cdot rog_RWGS \cdot Cpgf_RWGS + (1 - \epsilon_{RWGS}) \cdot \sigma_{RWGS} \cdot Cps_RWGS) / (\epsilon_{RWGS} \cdot rog_RWGS \cdot Cpgf_RWGS)$
Pezm_R...	$\epsilon_{RWGS} \cdot vg_RWGS \cdot L / Dae_RWGS$
Perm_R...	$\epsilon_{RWGS} \cdot vg_RWGS \cdot L / Dre_RWGS$
Pezh_RW...	$\epsilon_{RWGS} \cdot vg_RWGS \cdot L \cdot rog_RWGS \cdot Cpgf_RWGS / kae_RWGS$
Perh_RW...	$\epsilon_{RWGS} \cdot vg_RWGS \cdot L \cdot rog_RWGS \cdot Cpgf_RWGS / kre_RWGS$
Bi_Ox	$Uw_HE \cdot R_Ox / kre_Ox$
Bi_RWGS	$Uw_HL \cdot R_RWGS / kre_RWGS$
beta_RW...	$-\Delta H_RWGS / (Tad \cdot Cpgf_RWGS)$

Name	Expression
n1	thetaOx
n2	thetaRWGS
K_CO	$B_CO \cdot \exp(-\Delta H_COad / \theta_{RWGS})$ [1/bar]
K_H2O	$B_H2O \cdot \exp(-\Delta H_H2Oad / \theta_{RWGS})$
k_RWGS	$B_eq \cdot \exp(-\Delta H_eqad / \theta_{RWGS})$
DEN	$1 + K_CO \cdot P_t \cdot RWGS \cdot y_{CO_RWGS} + K_H2O \cdot y_{H2O_RWGS} / y_{H2_RWGS}$
f_RWGS	$\exp(-\gamma_{RWGS} / \theta_{RWGS}) \cdot (y_{CO2_RWGS} - y_{CO_RWGS} \cdot y_{H2O_RWGS} / (K_RWGS \cdot y_{H2_RWGS})) / (DEN^2)$
f_Ox	$\exp(-\gamma_{Ox} / \theta_{Ox}) \cdot y_{H2_Ox}^2 \cdot y_{O2_Ox}$
y0CO2	if(t<stabletime,1,0.25)
y0H2	if(t<stabletime,1,0.75)
yfCO2	if(t<stabletime,1,0.25)
yfH2	if(t<stabletime,1,0.75)
yfCO	if(t<stabletime,1,0.0)
yfH2O	if(t<stabletime,1,0.0)
y0CO	if(t<stabletime,1,0.0)
y0H2O	if(t<stabletime,1,0.0)