The thermodynamics and reactor optimization of CO₂ methanation

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TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**THE THERMODYNAMICS AND REACTOR OPTIMIZATION OF
CO₂ METHANATION**

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A thesis submitted to the Nanyang Technological University in partial
fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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17 Jan 2019

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Date

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Chan Siew Hwa

Authorship Attribution Statement

This thesis contains material from 2 paper(s) published in the following peer-reviewed journal(s) where I was the first and/or corresponding author.

Chapter 2 is published as Bin Miao, Su Su Khine Ma, Xin Wang, Haibin Su and Siew Hwa Chan, *Catalysis mechanisms of CO₂ and CO methanation*. Catalysis Science & Technology, 2016. 6(12): p. 4048-4058.

The contributions of the co-authors are as follows:

- Prof Chan provided the initial project direction and edited the manuscript drafts.
- Prof Wang provided advices on the scope of the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Prof Chan and Prof Su Haibin.
- Dr Ma Su Su assisted the proof-reading and revise work.

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The contributions of the co-authors are as follows:

- Prof Chan suggested the materials area and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised by Prof Chan.
- I performed all modeling and calculation.

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Abstract

Power-to-Gas (PtG) is an emerging grid-scale energy storage technology by which the surplus renewable electricity and captured CO₂ are converted to synthetic natural gas as an energy carrier. In short, the off-grid, surplus electricity from renewable power sources such as wind and solar farms is utilized to electrolyze water via Solid-Oxide-Cell, and the generated hydrogen is then combined with CO₂ through the Sabatier process to produce methane. The transportation of methane is mature and energy-efficient within the existing natural gas pipeline or town gas network. Additionally, it would be ideal to make use of the reverse function of SOEC, the Solid-Oxide-Fuel-Cell, to generate electricity when the grid is short of power. The electricity generation is important to lower the levelized cost of the energy stored in the system. On the other hand, the CO₂ methanation ($\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$) is one of the crucial steps in the PtG technology. It utilizes the existing natural gas infrastructure to store and transport the renewable energy in a large-scale and long-distance. However, the strong exothermicity of the methanation process remains one of the major challenges for the scale-up of the technology, especially when the feedstocks are highly concentrated.

This work aims to tackle the thermal management dilemma between the thermodynamic and the kinetic limitation at various conditions to achieve optimal temperature control for the CO₂ methanation process. The methanation reaction mechanisms, kinetic rate equations, and thermodynamics are reviewed and adopted from literature. The focus of the thesis is on the fixed-bed reactor simulation and optimization. The homogeneous and heterogeneous heat and mass transfer models are built to mimic the transfer phenomena in the fixed-bed reactors as the optimization tool. Firstly, a control volume method was proposed to determine the theoretical optimal temperature profile along the axis of the fixed-bed reactor. The prime optimization criterion is to maximize the reactor single-pass yield to avoid the expensive post-processing steps such as gas separation and recirculation. After simultaneously considering of the thermodynamics and kinetic rate equations, the resultant temperature is a descending profile along the reactor axis at a gradient that is just enough to avoid equilibrium limitation meanwhile to maximize the kinetic of the catalyst. The so-called optimal temperature profile achieved by such balanced the thermodynamic limitation at high temperature and kinetic loss at low temperature to accomplish the maximum CH₄ yield. Nevertheless, the temperature profile posed challenges for the precise

control of the reactor temperature, particularly of how to eliminate the temperature runaway behavior at the entrance zone and the over-cooling phenomena at the rear end of the reactor.

A one-dimensional heterogeneous model that considering heat and mass transfer of the fixed-bed reactor is then established to realize the optimal temperature profile for the methanation process. A parametric study is conducted to investigate the effects of the inlet temperature, T_{in} and the heat transfer coefficient, h_{wall} on the reactor temperature profile and yield. Results found that the inlet temperature and heat transfer coefficient are effective in controlling the temperature profile to adapt the optimal temperature. Though, it is not easy to perfectly fit the temperature with the control of the T_{in} and h_{wall} only. The best-adapted case with root mean square error of 65.5 in the parametric study is almost reaching the thermodynamic prediction, or about 2.5% less than the optimal yield has been achieved. To generalize the optimization process, a dimensionless parameter that is based on the lump-sum approximation was proposed as the cooling-variable. The dimensionless parameter can be generally used in other strong exothermic process as an effective control variable.

Further, the economic model was built to evaluate the profitability of the large-scale deployment of the PtG technology. The model estimated the cost of building a hypothetical 100-MW PtG power plant with energy storage and power generation functions. Three schemes are investigated, i.e., Power-to-Hydrogen, Power-to-Methane, and Power-to-Power. The emphasis is on the effects of SOC cost and capacity factor to the Levelized Cost of Energy of the PtG plant. Besides, the plant's payback period and CO₂ emission are estimated. Results indicate that the PtG technology is profitable under certain scenarios whereas further improvement and optimization are necessary. Meanwhile, the study also found that without utilizing the fuel-cell function of the SOC, i.e., the power generation process using natural gas as fuel, the PtG plant is not able to recover the high cost of CAPEX & OPEX of SOC and the surplus electricity cost. The increase of the capacity factor of the plant is critical to the decrease of the LCOE. The CAPEX of PtG plant is almost twice the cost of the conventional natural gas power plant. The cost reduction of SOC plays a key role in the PtG commercialization.

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Abbreviations

AES	Auger electron spectroscopy
Btu	British thermal units
CRF	Capital Recovery Factor
DFT	Density functional theory
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
EJ	Exajoules, 10^{18} Joules
FTIR	Fourier Transform Infrared spectroscopy
GHSV	Gas Hourly Space Velocity
GtP	Gas-to-Power
GWh	Gigawatt hour
HHV	Higher Heating Value
LCOE	Levelized Cost of Electricity
LHHW	Langmuir-Hinshelwood-Hougen-Watson kinetic
LNG	Liquefied Natural Gas
Mtoe	Million Tons of Oil Equivalent
MW	Megawatt
NG plant	Natural Gas Power Plant
NPV	Net Present Value
PtG	Power-to-Gas
SOC	Solid Oxide Cell
SOEC	Solid Oxide Electrolysis Cell

SOFC	Solid Oxide Fuel Cell
SSITKA	Steady-State Isotope Transient Kinetic Analysis
STY	Space Time Yield
TCI	Total Cost of Investment
TWh	Terawatt hour, 10^9 Kilowatt hour
XRD	X-ray Diffraction

Symbols

Symbol	Description	Units
Latin Symbol		
r	Rate of reaction	$[mol/g/h]$ or $[mol/m^3/s]$
Rr	Reactor radius	$[m]$
C	Mole concentration	$[mol/m^3]$
n	Number of mole	$[mol]$
M	Molar mass	$[kg/mol]$
p	Partial pressure of species	$[bar]$
P	Total pressure	$[bar]$
G_0	Mass flux	$[kg/m^2/s]$
G^0	Gibbs free energy of formation	$[kJ/mol]$
z	Reactor axis direction	$[m]$
u	Superficial velocity	$[m/s]$
R	Universal gas constant	$[m^3 bar/K/mol]$
T	Temperature	$[K]$
h	Heat or mass transfer coefficient	$[W/m^2/K]$ or $[m/s]$
D	Gas diffusivity	$[cm^2/s]$
K	Thermal conductivity	$[W/m/K]$
C_p	Heat capacity	$[kJ/mol/K]$ or $[kJ/kg/K]$
J_H, J_D	Chilton-Colburn factor	
dp	Catalyst particle diameter	$[m]$

R_{cat}	Catalyst particle radius	$[m]$
w	Mass fraction	
Q	Volumetric flow rate	$[m^3/s]$
S_{cat}	Catalyst particle surface area per unit volume	$[m^2/m^3]$
A_V	Surface area per unit volume	$[m^2/m^3]$

Greek Symbol

ϵ	Packed-bed porosity	
ρ	Density	$[kg/m^3]$
η	Effectiveness factor	
μ	Viscosity	$[g/cm/s]$
σ	Characteristic diameter of the molecules	$[m]$
Ω	Collision integrals	
τ	Tortuosity	
ψ	Catalyst shape factor, sphere=1, cylindrical=0.92	
Φ	Weisz-Prater module	
Φ_T	Thiele modulus	
$\hat{\phi}$	Fugacity coefficient	

Subscripts

g	Gas phase
s	Solid phase
i	Species i
j	Reaction j

m	Mass
c	Coolant
p	Particle
eff	Effective
ave	Average
K	Knudsen diffusion

Chapter 1 Introduction

1.1 Motivation

The prosperity of modern civilization relies on the huge amount of energy consumption [1-4]. The majority of the energy consumption come from the primary energy, which is essentially the crude oil, coal and natural gas that are captured directly from natural resources [2]. The world total primary energy supply in 2016 is about 13,761 Mtoe (equivalent to about 576 EJ or 160,040 TWh). The global primary energy consumption growth is about 2.2% per year [3]. Secondary energy come from the transformation of primary energy. For example, in consideration of the transformation efficiency and other losses, the electricity generation sector consumes about 40% of the total primary energy captured per year [3]. The remaining of the annual primary energy supplies is consumed in the industry, transportation, non-energy uses and others [5]. But the current mode of energy consumption is not sustainable for two reasons: 1. Fossil-fuel is non-renewable with limited reserves, and 2. The combustion of fossil fuel generates environmental impact. The proved reserves of the oil and gas in 2017 is about 1697.1 billion barrels (equivalent to 10,379.8 EJ or 2,884,068.7 TWh), and 193.1 trillion cubic meters (equivalent to 7,724 EJ or 2,145,557.3 TWh), respectively [3]. The oil and gas reserves will approximately supply for 50 years and 52.6 years based on the current production rate. For coal, the average reserve-to-production ratio is longer, about 134 years [3]. The period may be long relative to a human lifetime, and the newly discovered resources diluted the anxiety of the energy depletion. However, the replacement of fossil fuel used in the modern industrial world has not been found, at least not in the large-scale. The depletion of primary energy will continue to intimidate the stability of the human society, economically and politically. On the aspect of environmental impact, the climate change, particularly the global warming and its induced events such as El Niño and La Niña phenomena, are believed to be caused by the greenhouse gas emission from human activities [6-9]. The effect of the greenhouse gas is rather cumulative and can only be observed in a long-term [7, 8]. The consequences of global warming at the earliest started to emerge in the ocean especially the Arctic area [10, 11]. For example, ocean warming has caused the change of the spatial distribution of fish communities [11], although the long-term effect remains unknown to human beings. Whether or not the ecosystem can cope with the rapid, irreversible climate change is a question mark.

Until now, about 60% of the Trillion tones CO₂ anthropogenic emissions budget has already been emitted since the industrialization [7]. Whereas in 2010 alone, the approximate annual greenhouse gas emission converted to CO₂-equivalent weight reached 49 Giga tones. Among the annual CO₂ equivalent emission, the US contributes to about 5.4 Gigatons and China contributes to about 2.2 Gigatons [12, 13]. By sectors, the industry, agriculture, buildings, and transportation are the main emission sectors, as can be seen from Figure 1.1 [14].

Figure 1.1 CO₂-equivalent emission from all sectors. [14] Other than fossil fuel combustion, human activity induced CO₂ also comes from agricultural (e.g., ammonia production), buildings (e.g., cement production) and other energy applications.

The indirect CO₂ emission is mainly from electricity and heat production. Electricity is driven the modern world ever since its discovery. As the biggest primary energy consumption sector, the total electricity generation capacity of the power sector is about 6,500 GW [15], generates 23,768 TWh electricity (average capacity factor about 41.7%) [4]. Among all the electricity generated, coal power plant contributes to about 44%, oil, and gas power plant contributes to 28%, and the remaining proportions are nuclear 13%, Hydropower 7%, and the rest 8% from biofuel, waste, solar and wind power [16]. Although remains as minority, the (almost) zero-emission renewable energy resources are playing and will continue to play a vital role in meeting current and future

energy needs [17]. They are also key components in the sustainable development of transportation and electricity generation sectors [18-20]. The new installation of solar and wind energy in 2016 to 2017 reach to 93.8 GW and 46.7 GW [21], and the new expansion of renewable electricity generation is around 114 TWh and 163 TWh, respectively [21]. By now, the cumulative installation of renewable energy (not including hydropower) reaches to 900GW, including solar power of about 300GW, wind power of about 500GW and the remaining are biomass related power generation technologies [15, 21]. The corresponding total electricity generation of the year from solar and wind powers are 328 TWh (equivalent to a capacity factor of 12.5%) and 958 TWh (equivalent to a capacity factor of 21.9%), respectively [2]. However, the high cost, intermittency, grid connection, and storage challenges, of the renewable energy remain to be addressed to achieve wider penetration in the energy market [19]. For example, wind energy faces seasonal variation. The energy supply can only be predicted by Weibull distribution rather than accurate production [22-24] whereas solar panel is restricted by the daily fluctuation and weather conditions [25, 26]. Small output renewable energy sources could be easily balanced within the energy network, but the large, incrementing percentage of renewable power highlights a substantial need for energy storage.

There is great potential and urgency for the development of energy storage solutions. A long-term, grid-scale energy storage system is urgently demanded to tackle the challenge of the integration of the fluctuating power supply and the hardly-balanced electricity grid [27]. Within the existing energy storage techniques, the electrical and electrochemical methods dominate the low and medium volume energy storage in terms of power capacity and dispatch duration. Whereas mechanical and chemical measures are suitable for large capacity, long duration storage [28, 29]. The comparison of the assorted energy storage system is shown in Figure 1.2.

Figure 1.2 Energy Storage System comparison in the scale of kW to GW [28]. The mechanical and chemical types of system dominate the large-scale, long period energy storage sector. Whereas batteries occupied the small-scale, prompt-response services.

Currently, hydroelectric is the most widely installed and reliable renewable energy source and contributes to about 16.6% of total electricity production in the world [27]. As one branch of hydroelectric power, the pumped-hydro is dominant as the existing energy storage technique. Briefly, water is pumped into a reservoir to store the electricity into the water potential when there is surplus electricity in the grid. The existing pumped-hydro storage capacity is around 118.6 GW globally [21]. But the deployment of the pumped-hydro plant is limited to certain geological and environmental conditions. The electrolysis of water using Solid Oxide Electrolyze Cell (SOEC) to produce hydrogen gas is another option, though at the moment hydrogen storage and transportation can be expensive due to high pressure and special storage material used [30]. Power-to-Gas technology that converts excess electricity to methane as energy storage intermediate through Sabatier reaction [31] ($4\text{H}_2 + \text{CO}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$) has drawn great attention to the academic and industrial area [32, 33]. The feedstocks for the methanation process are,

hydrogen, produced from water electrolysis [32-35] and CO₂, captured from the flue gas, biomass or other carbon-containing resources [31, 36, 37]. The facilities can be utilized to generate electricity by withdrawing natural gas from pipelines when the grid is short of power. The energy storage and the power generation functions of the Power-to-Gas technology are illustrated in Figure 1.3.

Figure 1.3 Power-to-Gas and Gas-to-Power schematic diagram. The surplus electricity is converted to methane and stored in the gas grid in the Power-to-Gas cycle. The reverse process is applicable when the grid is short of power. Methane is withdrawn from the gas grid to sustain the power generation process.

Besides, PtG that accompanied by carbon capture technology could be a key solution in tackling the challenge of climate change caused by greenhouse emission [38, 39]. The CO₂ is reused in the energy storage process, or even recycled internally as the energy carrier, which significantly reduces the carbon footprint of the technology. But most of the existing PtG pilot plants had only been operated for a short time and further work needed to prove their profitability [32]. The integration of PtG to the electricity and gas grid has not been established yet, due to the lack of existing prototypes and sufficient risk assessment. For the economic feasibility of Power-to-Gas plants, the cost of synthesized methane is still several times higher than that of conventional natural gas [33]. The economic competitiveness of Power-to-Gas plants counts on future technology break-through.

1.2 Objectives and Scope

The CO₂ methanation as one of the steps in the PtG process plays a key role in bridging the renewable hydrogen (green hydrogen) storage and the existing infrastructure. The thermal

management of the methanation process is complicated due to the strongly exothermic reaction and the dilemma between thermodynamic limitation and kinetic performance. This thesis attempts to build a deep understanding of the heat and mass transfer phenomena at the reactor level to solve the temperature control dilemma. Simulation work and parametric study are conducted in the thesis to achieve maximum yield of a single-stage fixed-bed reactor with balanced thermodynamics and kinetic performance. A cooling modulus is proposed to generalize the optimization strategy for the thermal management of other exothermic processes. Furthermore, the possibility of scaling-up of the PtG is of the interest of the thesis. Therefore the system level technological-economic feasibility is investigated in a hypothetical manner. The detail distribution of the above work scope in individual chapters is elaborated below.

Chapter 1 introduces the background and motivation of the project. The global warming and climate change phenomena induced by greenhouse gas emission requires an alternative solution to absorb the CO₂ emission. Meanwhile, the rapid developing but fluctuating renewable energy arises the demand for large-scale energy storage system. At this situation, the methanation technology becomes a necessity between the existing infrastructure and the water electrolysis technologies to solve the greenhouse gas emission and energy storage issues. The effect of Power-to-Gas under the realistic condition and large-scale implementation are the major motivations of this thesis.

Chapter 2 reviews the related aspects such as reaction mechanism and the corresponding intrinsic kinetics, reactor thermal management in the experimental and modeling areas. At first, the understanding of reaction mechanism is critical to the kinetics determine, hence the CO₂ and CO methanation mechanisms and deactivation mechanism are elaborately examined and discussed. Based on the mechanism study, the Langmuir-Hinshelwood Hougen-Watson (LHHW) kinetics from literature is adopted for the further parametric study. Finally, literature on the aspects of reactors hot-spot formation, thermal management are reviewed to understand the heat transfer and temperature controlling of the methanation process.

Chapter 3 introduces the methodology used in this thesis. Specifically, the Gibbs Energy minimization method is used for the thermodynamic calculation. The heat and mass transfer models are developed from existing finite element methods. The temperature dependent parameters are calculated from corresponding thermal and transfer theories.

Chapter 4 develops a control volume method to calculate the theoretical optimal temperature profile that maximizes the reactor yield. The model assumed accurately controlled temperature is achievable in the reactor. The optimal temperature balances the thermodynamics and kinetics performance via a descending profile along the equilibrium line. The optimal temperature profile is then used as a guidance for the reactor optimization in the subsequent chapters.

Chapter 5 presents a heat and mass transfer model to adapt the reactor temperature to the optimum temperature profile that is obtained in Chapter 4 to achieve the maximum product yield. Experimental data from the literature is used to validate the predictive capability of the transfer model. The model chooses inlet temperature and heat transfer coefficient as the control variables to optimize the temperature profile in the reactor. A dimensionless number is proposed to generalize the thermal management strategy for the optimum working conditions.

Chapter 6 presents a hypothetical study to evaluate the feasibility of Power-to-Gas plant as large-scale energy storage technology. Existing mature technologies such as natural gas power plant and electrolysis cells are taken as reference for the calculation of the plant cost. Realistic economic parameters are used to investigate the feasibility of the plant as the future commercial energy storage system.

Chapter 7 summarizes all the chapters in the thesis and discusses possible future works.

Chapter 2 Literature Review

From the first principle approach, the CO₂ and CO methanation mechanism is firstly thoroughly reviewed. The reaction mechanism, also called reaction schemes, is referred to the specific elementary steps of the molecule's evolution from reactants to products. It is the prerequisite to determine the intrinsic kinetics of the reaction. With the understanding of reaction schemes, a short summary of the widely accepted reaction kinetics is listed in the second part of the chapter. The literature review of reaction mechanism also revealed the necessity of effective thermal management to avoid the catalyst degradation due to hot spot. The third part of the literature review therefore focused on the reactor thermal management from both experimental and modeling approaches.

2.1 Reaction Mechanism

The development of high activity, high selectivity, and durable catalysts are of great importance for implementing large-scale energy storage facility. Great progress has been made on the catalyst metal, promoter and support material advancements [37, 40, 41]. Generally, Ni, Ru, Co, and Fe supported on Al₂O₃, SiO₂, TiO₂, ZrO₂, and CeO₂ are commonly used as methanation catalysts in various reaction conditions [37]. Particularly, Ni and Ru were found to be very selective to CH₄ production and were intensively studied [42, 43]. Promoter materials are added to provide auxiliary functions, such as sulfur-resistance, sintering-resistance and carbon-resistance properties [44-48]. Nevertheless, the in-depth discussion and a systematic categorization of existing debating mechanisms have not been done so far. A good understanding of the mechanism of methanation reaction will provide useful guide to achieve desired catalyst properties, such as good activity, selectivity, and stability. This review discussed CO₂ and CO methanation mechanisms through both experimental and computational aspects. The focus is given to Ni- and Ru-based catalysts for their great commercialization potential. There are four main sessions including the introduction and summary sessions. The second session discussed the well-accepted methanation mechanisms proposed from the 1970s to present according to their categories, i.e., associative methanation and dissociative methanation [37, 49, 50]. The third session is devoted to catalyst deactivation mechanisms, which include sulfur poisoning, surface carbon deposition, and catalyst metal sintering mechanisms. The reaction mechanism is all about the elementary steps. Specifically, there are three obstacles to be overcome: (1) What are the intermediates? (2) What are the

elementary steps, especially the rate-determining steps that lead to the intermediates? And (3) What are the active sites? To know what exactly happening during the reaction and further guide the catalyst design, the direct way is the *in-situ* observation with various spectroscopy techniques [51] and augmented by the computational modeling [52] of elementary steps. The existing proposed methanation mechanism can be divided into two categories: (1) Associative scheme and (2) Dissociative scheme.

CO₂ Methanation Mechanisms

In the arena of CO₂ methanation, two types of mechanisms have been proposed. One mechanism suggested that CO₂ associatively adsorbed with adatom H_{ad}H* forming oxygenate intermediates and subsequently hydrogenate to CH₄. The other mechanism described that CO₂ first dissociated to carbonyl (CO_{ad}) and O_{ad}, followed by carbonyl hydrogenation to CH₄. It has been found that the associative and dissociative mechanism schemes are correlated with the catalyst metal as well as support materials. To identify the inner link between reaction mechanism and the material, the literature is sorted according to the mechanism schemes. In each scheme, different catalysts and support materials are reviewed so that the readers could generalize the pattern behind the massive literature. The detailed discussion is presented in the following two sub-sessions.

CO₂ Associative Methanation

The CO₂ associative methanation involved the associative adsorption of CO₂ and H₂. Followed by the hydrogenation of associated species to form methane. Evidence from direct observation using *in-situ* infrared technique was found to support this mechanism, Aldana *et al.* studied CO₂ methanation on Ni-ceria-zirconia catalyst to reveal the reaction mechanism with *in-situ* fourier transform infrared spectroscopy (FTIR) [53]. The spectra of CO₂ methanation at 150°C showed carbonate (CO_{3ad}) on the support, and carbonyl (CO_{ad}) on the Ni metal, as shown in Figure 2.1 (A) spectrum a). With temperature increasing, carbonate hydrogenated to bicarbonate (HCO_{3ad}), and the bicarbonate quickly dehydrated to formate (HCOO_{ad}). On the other hand, carbonyl bands on Ni remain unchanged, as shown in Figure 2.1 (A) spectrum b) to f). The adatoms H_{ad} were believed to be provided by Ni-particle (not shown in the Figure). Upon the above observation, the authors proposed that the CH₄ and CO in the venting gas were produced by different mechanisms [53]. CH₄ is produced from successive hydrogenation of formate species while CO is produced from the CO₂ reduction at Ce³⁺ sites as a byproduct, as showed in Figure 2.1 (B) (highlighted in solid

and dash circle respectively). The overall reaction scheme is illustrated in Figure 2.1 (C-1): CH₄ production from hydrogenation of carbonate and formate species, and Figure 2.1 (C-2): CO production from CO₂ reduction at Ce³⁺ sites and adsorbed on Ni. The connection between formate and CH₄ formation can be found from Infrared data and Mass spectroscopy result. Schild *et al.* observed the depletion of formate signal leading to an increase in methane formation from their study of CO₂ methanation on Ni-zirconia catalyst with *in-situ* FTIR spectroscopy [54]. They concluded that formate is the essential intermediate for methane production [54].

Figure 2.1 (A): FTIR spectra for CO₂ methanation on Ni-Ceria-Zirconia catalyst (150 to 400 °C, H₂:CO₂=4:1). The formation of bicarbonate and formate corresponds to the formation of CH₄, whereas carbonyl is merely a spectator. Reaction temperature: a) 150 °C-1 min, b) 150 °C-30 min, c) 200 °C, d) 250 °C, e) 300 °C, f) 350 °C, g) 400 °C-1 min, and h) 400 °C-20min. (B): Transient experiment (at 400°C) on Ni-Ceria-Zirconia catalyst showed immediately ceased formation of CH₄ after H₂ turned off (solid line circle), and immediately ceased formation of CO after CO₂ turned off (dot circle line). Scheme (C-1): Methane produced from continuous hydrogenation of carbonate adsorbed on the support through formate and methoxy intermediates [53]. Scheme (C-2): Carbon monoxide initiated from CO₂ reduction at Ce³⁺ sites [53, 55].

The formate may have multiple functions, Westermann *et al.* regard formate as the precursor of both CH₄ and CO [56]. They studied CO₂ methanation mechanism over Ni supported on ultra-stable Y-type (USY) zeolite with *in-situ* IR spectroscopy. In the methanation condition, carbonate hydrogenated to formate and adsorbed onto Ni-particle at a temperature lower than 200°C. As the temperature increased to 300°C and higher, formate dehydrated to carbonyl and further hydrogenated to CH₄, or desorbed as CO. Pan *et al.* obtained similar results in the study of CO₂ methanation on Ni-Ceria catalyst with *in-situ* FTIR [57]. The spectra showed five types of adsorption species, among which monodentate carbonate and bicarbonate hydrogenated to formate. The formate then evolved to CH₄ and CO. The increasing CH₄ and carbonyl bands at the expense of formate bands was observed during the Temperature programmed study, indicating that formate is the major intermediate to methane production [57]. On the aspect of the computational study, Pan *et al.* conducted DFT calculation of the activation of the associative route (formate as intermediate) and the dissociative route (carbonyl as intermediate) of CO₂ methanation on Ni-alumina catalyst [58]. They found that surface hydroxyl (OH_{ad}) altered the pathway, where dissociative route became kinetically ($E_a=0.69$ eV) and thermodynamically (energy release=0.67 eV) favorable with hydroxylated catalyst surface. At the situation where hydroxyl was not available, formate became the major intermediate for methane production ($E_a=1.25$ eV) [58].

The associative mechanism is also applicable to the Ru-based catalyst. Prairie *et al.* investigated CO₂ methanation on the Ru-Al₂O₃ and Ru-TiO₂ catalyst with DRIFT spectroscopy [59]. The spectra showed formate (HCOO_{ad}) adsorbed on support, carbonyl (CO_{ad}) on Ru and Ru-oxide sites. The carbonyl was produced from reverse water gas shift (RWGS) of adsorbed CO₂ through formate species. Rate limiting step is thought to be the hydrogenation of carbonyl to CH₄. Upham *et al.* came to the conclusion with transient experiments on Ru-ceria catalyst [55]. Specifically, by introducing CO₂ before H₂, methane and CO were produced. If the injection sequence was reversed, ceria was reduced by H₂ firstly. The Ce³⁺ then reduced the CO₂ to CO, but CH₄ was not produced in this case. They proposed that methane is produced from associative hydrogenation of adsorbed CO₂ while CO was produced from CO₂ reduction over Ce³⁺ sites. On the aspect of computational calculation, Zhang *et al.* investigated CO₂ hydrogenation pathways over Ru(0001) surface [60]. The result showed that CO₂ direct dissociation was only thermodynamically favorable but with high energy barrier to occur ($E_a=1.20$ eV). The feasible pathway for the C-O

bond breaking was the formate (HCOO_{ad}) route ($E_{\text{a}}=0.37$ eV) and further dissociated to formyl (CHO_{ad}) intermediate ($E_{\text{a}}=0.41$ eV).

CO₂ Dissociative Methanation

It is possible that CO₂ directly dissociated to carbonyl (CO_{ad}) and O_{ad} as intermediate during methanation process. The CO_{ad} subsequently hydrogenate or further dissociate to C_{ad} and O_{ad} in the next step. *In-situ* infrared techniques provide direct observation of catalyst surface intermediates, Eckle *et al.* conducted the Steady-State Isotope Transient Kinetic Analysis (SSITKA) experiment to reveal reaction intermediates during CO and CO₂ methanation on the Ru-Al₂O₃, in the H₂-rich atmospheric pressure condition [61]. The isotope exchange from ¹²CO₂ to ¹³CO₂ resulted to the reducing intensity of ¹²CO_{ad} and the increasing intensity of the ¹³CO_{ad} band, which indicated that carbonyl is the intermediate during CO₂ methanation [61]. On the other hand, the slow response of formate bands during isotope exchanging excludes the formate species as major intermediate, as shown in Figure 2.2 (A) and (B) [61]. The overall reaction schemes are illustrated in Figure 2.2 (C-1) and (C-2). The key findings in SSITKA are consistent with temperature programmed desorption study, De Leitenburg *et al.* examined the ceria support effect during CO₂ methanation on the Noble-metal-based catalyst [62]. The high-temperature reduced-ceria (Ce^{3+}) promotes the CO₂ adsorption in the form of carbonyl (CO_{ad}) and oxidized-ceria (Ce^{4+}). The ceria-support provides the adsorbed carbonyl while metal particle provides the H_{ad} for the methanation process.

Figure 2.2 DRIFT spectra of CO_2 methanation on $\text{Ru-Al}_2\text{O}_3$. (190°C , $\text{H}_2:\text{CO}_2=5.3:1$), switching from (A) $^{12}\text{CO}_2$ reformate gas to (B) $^{13}\text{CO}_2$ reformate gas. The carbonyl and formyl bands quickly switched to new bands. The formate signal remained its $\text{H}^{12}\text{COO}_{\text{ad}}$ band and accumulated new $\text{H}^{13}\text{COO}_{\text{ad}}$ band. Scheme (C-1): CO_2 dissociated to CO_{ad} and O_{ad} on Ru sites. The CO_{ad} then evolved to methane in an associative way. Scheme (C-2): surface formate species accumulated rather than hydrogenated to CH_4 [61].

Akamaru *et al.* obtained the same result using DFT method in their study of CO_2 methanation on Ru-TiO_2 [63]. The calculation showed that adsorbed CO_2 firstly dissociated to carbonyl and O_{ad} on Ru-TiO_2 (with barrier $E_{\text{a}}=0.6$ eV), as has been observed by isotopic and Infrared experiment [61]. The subsequent methanation of carbonyl followed the hydrogen-assisted scheme with formyl intermediate (CHO_{ad} , $E_{\text{a}}=0.95$ eV) [63].

Discussion

The discrepancies of reaction mechanisms between associative methanation and dissociative methanation are related to reaction conditions. The isotope exchange experiment in ref. 33, as displayed in Figure 2.2(B), clearly showed the decay of carbonyl (CO_{ad}) and the accumulation of

formate (HCOO_{ad}) species during the CO_2 methanation, which support the CO_2 dissociative scheme [61]. However, the reaction condition is only limited to the low temperature (190°C) and H_2 -rich environment ($\text{H}_2:\text{CO}_2=5.3:1$). On a wider temperature range, Fujita *et al.* observed two methanation peaks during the temperature programmed reaction from 100 to 400°C on the $\text{Ni-Al}_2\text{O}_3$ catalyst (with $\text{H}_2:\text{CO}_2=9:1$) [64]. The first peak appeared at 150°C was attributed to the methanation of bridged-carbonyl (CO_{ad}) adsorbed on Ni , and the second peak appeared at 250°C was attributed to bidentate-formate (HCOO_{ad}) methanation on the support [64]. The high-temperature-peak at 250°C was in consistent with the FTIR spectra from ref. 25 (Aldana *et al.*), as shown in Figure 2 (A) [53]. But Aldana *et al.* did not observe low-temperature methanation [53]. This suggests not only the temperature but also the $\text{H}_2:\text{CO}_2$ ratio plays a key role. The CO_2 dissociative methanation is promoted in the H_2 -rich environment. The H_2 -rich environment enabled the prompt reduction of metal-oxide so that the CO_2 redox process is able to proceed. Most authors, however, examined the stoichiometric ($\text{H}_2:\text{CO}_2=4:1$) situation and observed the associative scheme [53, 54, 56, 57]. For the effect of support material, CO_2 adsorption on CeO_2 was much higher than that on Al_2O_3 [65]. This may contribute to the reverse water gas shift reaction at the metal-support interface, and affect the mechanism observed.

CO Methanation Mechanisms

In the area of CO methanation during pre-1970s, two types of methanation mechanisms were proposed. One mechanism involved the combination of H_{ad} with CO_{ad} to COH_{ad} , CHO_{ad} or CHOH_{ad} intermediates and followed by C-O bond breaking. The other mechanism involved direct dissociation of adsorbed CO_{ad} , forming surface-carbon (C_{ad}) as methanation intermediate [66].

CO Associative Methanation

Many researchers claimed that C-O direct bond breaking was not kinetically favorable without hydrogen-assisting [67]. Instead, H_{ad} combined with carbonyl to form either formyl (CHO_{ad}) or carbon-hydroxyl (COH_{ad}) to promote the C-O bond breaking, as illustrated in Figure 2.3 (C-1) and (C-2). Eckle *et al.* proposed the formyl (CHO_{ad}) route in their CO methanation on the Ru-based catalyst [61]. The SSITKA observed the surface intermediates signal change in the CO methanation process over Ru-zeolite and Ru-alumina catalyst. The DRIFT spectra showed prompt CO_{ad} signals change and followed by CHO_{ad} signal change after the switch of ^{12}CO to ^{13}CO feed, indicating the reaction sequence start with CO adsorption then hydrogenation of CO_{ad} to form

CHO_{ad} , as seen from Figure 2.3 (A) and (B). The steady-state exchange rate of CHO_{ad} species also found to be consistent with CH_4 formation rate [61]. The build-up of formate and carbonate band do not saturate throughout the experiment [68].

Figure 2.3 DRIFT spectra of CO methanation on $\text{Ru-Al}_2\text{O}_3$ (190°C , $\text{H}_2:\text{CO} > 100$), switching from (A) ^{12}CO feed gas to (B) ^{13}CO feed gas. The bands switches indicate that carbonyl and formyl (HCO_{ad}) are the major intermediates in CO methanation process. CO associative methanation to form Scheme (C-1): formyl[61] or Scheme (C-2): carbon hydroxyl (not observed in the IR data [67]).

On the aspect of Ni-based catalyst, Anderson *et al.* studied CO methanation on Ni(111) crystal through experimental and computational methods [67]. They found that CO direct dissociation on Ni(111) would not occur if the feed gas were properly cleaned to eliminate Ni-carbonyl ($\text{Ni}(\text{CO})_4$) contaminant. The C-O bond was only breakable at the step and defect sites with the hydrogen-assisted route. The reaction intermediate was thought to be COH_{ad} species. The Scanning Tunneling Microscopy (STM) measurement on Ni(111) observed carbon island near steps, whereas oxygen species were not detected. On the aspect of computational studies, for Ni(111) surface, Wang *et al.* calculated the elementary steps activation energy of CO methanation and

found that the E_a for CO_{ad} to evolve to C_{ad} , COH_{ad} and CHO_{ad} are 2.91, 1.93, and 1.70 eV respectively [69]. The result was in consistence with the study of Zhi *et al.*, in which CO prefer to adsorb at the catalyst hexagonal close-packed (hcp) site and convert to CHO_{ad} as dominant intermediate [70]. Similarly, Fajín *et al.* studied CO methanation on Ni(110) catalyst using the DFT method [71]. Among all the routes, the H-assisted CO dissociation through COH_{ad} ($E_a=1.42$ eV) species, and H-assisted CO dissociation through CHO_{ad} ($E_a=1.25$ eV) species are optimal scheme for C-O bond-breaking. On the supported catalyst, Wang *et al.* calculated CO methanation activation energy of each elementary steps over Ni- Al_2O_3 using DFT method [72]. Their results showed that hydrogen-assisted C-O bond breaking is energetically favorable than CO direct dissociation. The calculated activation energy (E_a) for CO dissociation on Ni_4 hollow site was 3.19 eV, which was higher than CO_{ad} desorption barrier, $E_a=2.03$ eV. Hydrogen-assisted dissociation at the same location, $\text{CHO}_{\text{ad}} \rightarrow \text{HC}_{\text{ad}} + \text{O}_{\text{ad}}$ ($E_a=1.32$ eV), was energetically achievable.

CO Dissociative Methanation

The CO dissociative methanation suggested that C-O bond breaking is taking place directly at the active sites, before the successive hydrogenation steps. The other scheme for CO dissociation is through CO disproportionation. With *in-situ* FTIR technique, Panagiotopoulou *et al.* investigated active sites of CO methanation over the Ru- TiO_2 catalyst [49]. The *in-situ* FTIR spectra of temperature programmed reaction showed linearly and bridged bonded carbonyls adsorbed on Ru, Ru oxide, and metal-support interface as shown in Figure 2.4 (A). The Ru-oxide spectra indicated that CO firstly dissociative adsorbed as C_{ad} and O_{ad} . Followed by C_{ad} hydrogenation. In their subsequent work, they confirmed that both the dissociative and associative methanation pathways occurred with different temperature and hydrogen content ranges [50]. At low-temperature (200°C), the dissociative scheme prevailed. In addition, at a higher temperature (350°C) the associative methanation become dominated, as shown in Figure 2.4 (B)-1 and -2 [50]. On the aspect of computational studies, DFT calculation provided evidence of CO dissociation on step sites by calculating the activation energy. Tison *et al.* conducted Ultra-high vacuum (UHV) experiments and DFT calculation of CO dissociation over Ru-crystal [73]. The STM under UHV condition showed step decoration, which was assigned as evidence of CO dissociation at the step sites (4-fold hollow sites). The oxygen adatoms were observed at the terrace, where the 3-fold hollow sites are present. Their DFT calculation confirmed that the CO dissociation over 4-fold

hollow sites is energetically feasible. Vendelbo *et al.* conducted CO dissociation over Ru with UHV apparatus and DFT calculation [74]. The calculation results suggested that CO dissociation was preferable than desorption on Ru step sites.

Figure 2.4 (A): FTIR spectra of CO temperature programmed methanation on Ru-TiO₂ (25 to 450°C, H₂:CO=10:1). The spectra showed carbonyl adsorbed on Ru-oxide and Ru sites. The carbonyl-Ruⁿ⁺ band reduced as temperature increasing. (B)-1 and (B)-2: FTIR spectra of CO methanation on Ru-TiO₂ (200°C, 350°C, H₂:CO=0 to 24:1). The carbonyl was observed on Ru-oxide and Ru sites. The metal oxide band reduced with the increase of H₂ partial pressure [49]. (C): The illustration of CO dissociative methanation scheme.

Transient experiments were carried out to examine the CO methanation mechanisms. Araki and Poniec studied CO methanation over Ni film at temperatures of 250~350°C [75]. They observed a short induction period of CH₄ formation after CO and H₂ mixture admitted to the Ni film while

CO₂ almost immediately produced. The CO₂ formation without induction period can be observed even without H₂ present [75]. They concluded that CO₂ formation should pass through a fast route, most probably via CO disproportionation, also known as Boudouard Reaction [75]. The isotope-traced experiment is shown in Figure 2.5 (A) and (B), in which H₂ and ¹²CO mixture were admitted to ¹³C-coated Ni-film at 250°C. The Mass spectroscopy detected immediate ¹³CH₄ production followed by ¹²CH₄ and ¹²CO₂ formation, which clearly showed that H₂ firstly combined with surface carbon to form ¹³CH₄. The ¹²CO₂ formation indicated that CO dissociation was an easy process and not necessary required hydrogen assistant [75]. The conclusion was supported by Madden and Ertl in their earlier study of CO decomposition on a Ni(110) surface [76], where CO started to dissociate to C_{ad} and O_{ad} at a temperature as low as 177°C, and the O_{ad} is subsequently taken away by CO [76]. Goodman *et al.* conducted CO methanation kinetic study over Ni single crystal [42]. The Auger electron spectroscopy (AES) observation supported the pathway of surface carbide or CH_x species as major intermediate. The surface carbon is formed through CO disproportionation since O_{ad} element is not detected on the surface [42].

Figure 2.5 (A): Mass spectroscopy of CO methanation on Ni-film (250°C , $\text{H}_2:\text{CO}=5:1$): admitting ^{12}CO and H_2 onto the ^{13}C -coated Ni-film produced $^{13}\text{CH}_4$ gas followed by $^{12}\text{CH}_4$ and $^{12}\text{CO}_2$, as illustrated in (B). The $^{13}\text{CH}_4$, $^{12}\text{CH}_4$ are formed from hydrogenation of adsorbed $^{13}\text{C}_{\text{ad}}$, $^{12}\text{C}_{\text{ad}}$. The $^{12}\text{CO}_2$ is produced from ^{12}CO disproportionation (Boudouard reaction) [75].

Discussion

CO is more active than CO_2 in the methanation process. On the Ni film, CO_2 is almost instantly produced from CO disproportionation ($\text{H}_2:\text{CO}=5$, $T=250^\circ\text{C}$) [75]. Besides, the leftover surface carbon is able to hydrogenate to CH_4 quickly, as shown in isotope-traced experiment in Figure 6 [75]. In addition, the metal-oxide was observed as evidence for CO dissociative methanation on the Ru- TiO_2 at 200°C with various H_2 content ($\text{H}_2:\text{CO}=0$ to 24) [50]. On the other hand, CHO_{ad}

was observed on the Ru-Al₂O₃ participating the methanation process as strong evidence of associative methanation scheme ($H_2:CO > 100$, $T = 190^\circ C$) [67]. The above evidences suggest that both associative and dissociative methanation contributes to a certain portion to the CH₄ production at respective reaction conditions. Since the associative CO methanation was only observed at very high H₂ content, It could be possible that the associative adsorption of CO and H₂ followed an Eley–Rideal mechanism where H₂ insert to bridged-CO_{ad} directly. It's worth mentioning that only bridged-CO_{ad} can be effectively hydrogenated while linear-CO_{ad} retarded the methanation process [77]. The dissociative route requires under-coordinate sites to break the C-O bond and the reductive environment (either H₂- or CO-rich environment) to regenerate the active sites from the oxide state.

Deactivation Mechanism

Catalyst deactivation is a complex process that combined with many mechanisms together, among which poisoning, coking, and sintering are great concerns in the methanation process [78]. The poisoning effect principally caused by the strong chemisorption of species on the active sites and blocked the sites [79]. For instance, the existing possible mechanisms of sulfur poisoning was described as sulfur preferentially adsorbed on active sites and hence block the reaction on that site [80]. Adsorbed sulfur also affects the adjacent active site by weakening the electronic density, hence alters the site activity towards certain products [80]. Coking is a mechanical process, in which carbon filament or whisker physically (1) fouling the metal, (2) block the pores, and (3) disintegrate the catalyst metal and support [81]. The temperature has a great impact on the carbon morphology: (1) surface carbide is formed below 325°C, (2) graphite carbon starts to occur upon CO decomposition at 425°C, and (3) filamentous and crystalline graphitic carbon occurs above 550°C [81]. The catalyst deactivation mechanism also varies with catalyst metal and support materials. The focus of this work is majorly on the Ni and Ru catalyst with various support materials.

Sulfur Poisoning

Sulfur poisoning mechanism was widely studied in many areas [80]. In the methanation aspect, Legras *et al.* examined the sulfur poisoning mechanism on Ni-Al₂O₃ with SSITKA and *in-situ* FTIR techniques [82]. They introduced H₂S to the catalyst after CO methanation. The sulfur species seem to inhibit the CO adsorption without disturb CH₄ production. The authors proposed

that carbonyl (CO_{ad}) or C_{ad} (generated from CO methanation) at the step sites protected the sites from sulfur poisoning [82], as illustrated in Figure 2.6 (C). In this case, S species adsorbed on terrace sites, inhibiting CO adsorption, whereas CH_4 formation sites were not affected, as evidenced in Figure 2.6 (A) and (B). In the absence of methanation before S introducing, S species attached to step sites easily and caused 10-fold catalyst deactivation [82]. The same phenomena were observed on the Ru-based catalyst, where carbon deposited catalyst showed better sulfur-resistance property [83]. Bartholomew *et al.* proposed the site competing model in their work [84]. The higher H_2 to CO ratio resulted in lower carbon coverage hence stronger sulfur poisoning effect. Refer to the sites poisoned by sulfur species, defects and steps have greater priority than terraces [84]. Rostrup-Nielsen and Pedersen examined sulfur poisoning of Boudouard reaction and Methanation reaction on Ni catalyst [85]. They pre-sulfide the catalyst pellets in various temperature to test sulfur coverage variations. They found that both Boudouard reaction and Methanation reaction shared the same reaction intermediate, most likely surface carbon [85]. Moreover, the non-linear poisoning effect indicated that sulfur poisoned several nickel atoms at the same time [85]. It was found that only 3% monolayer sulfur completely deactivated the Ni crystal catalyst in their CO dissociation test [86].

Figure 2.6 The effect of sulfur to the active sites. Introducing H_2S to the $\text{Ni-Al}_2\text{O}_3$ after CO methanation (A): S species occupied CO adsorption sites, which result to a quick decay of ^{12}CO signal in the isotope exchange experiment (SSITKA) [82], (B): S species has a negligible effect on CH_4 isotope exchange, which indicates that S species has not poisoned the CH_4 formation sites [82], and (C): Active carbon protects step sites from being occupied by sulfur species.

The morphology of sulfur species varies, Erikson *et al.* examined the H_2S concentration effect [87]. Their findings showed that the catalyst deactivation rate decreased with H_2S concentration, due to the formation of multilayer sulfide. As a contrast, surface sulfide (2-D sulfide) that formed with ppb level H_2S deactivate catalyst more severely. Surface sulfide poisoning effect with ppb level H_2S was studied by Fitzharris *et al.* [88] over Ni catalyst and by Agrawal *et al.* [83] over Ru catalyst. They found that surface sulfide had lower energy barrier of formation hence bond to the catalyst surface strongly. The sulfur poisoning does not affect the activation energy of the methanation process, indicating that sulfur poisoning is surface geometric effect other than electronic effect [83]. Czekaj *et al.* conducted DFT calculation of stability of various sulfur species

on the Ni catalyst and support [89]. The result showed that there are many stable structures exist on the catalyst surface, among which carbonyl sulfide and hydrogen sulfide were the most stable species. Sulfide species not only existed on the supported Ni particle but also attached to the support.

Figure 2.7 Surface scanning of deactivated catalyst taken from the methanation reactor in Güssing (Austria) and of poisoned at 400°C. (A): Without contacting air: the poisoning species on the deactivated catalyst are thiophene (C_4H_4S) and S instead of H_2S [87]. (B): After contacting air, the thiophene and S spectra shifted to H_2S [87].

The remaining sulfide species on the support after catalyst reactivation can cause re-poisoning of the catalyst [89]. Struis *et al.* showed that the sulfur poisoning effect was not due to H_2S only [90]. The sulfur K-edge X-ray adsorption near edge structure indicated that industrial methanation catalyst had been poisoned by thiophene (C_4H_4S) rather than H_2S , as shown in Figure 2.7 that contacting the specimen with the air may transform the poisoning species. To enhance the sulfur tolerance, Yuan *et al.* examined the sulfur tolerances of SiO_2 supported Ni and Ni-Ru methanation catalyst using experimental and computational approaches [44]. Their results showed that sulfur poisons the catalyst by blocking the active sites as well as enhancing the sintering and oxidation of Ni particle. Ru promoted sulfur-resistance by weakening the bond between S and Ni. Lee *et al.* studied the sulfur tolerance effect of Rh-Ni binary metal using the DFT method [91]. The result

showed that the sulfur adatom could increase the activation barrier for CO dissociation. The binary metal catalyst reduces sulfur adsorption strength hence resists sulfur poisoning. Yan *et al.* prepared Ni catalyst via plasma decomposition technique and discussed the sulfur-resistance effect of the catalyst [92]. They found that the lesser defect sites on plasma-decomposed catalyst result to the better sulfur-resistance performance.

Carbon Deposition and Metal Sintering

Carbon deposition has been intensively studied in the methanation area with temperature range from 200 °C to 450 °C and steam reforming area with temperature range from 600 to 900°C [81]. In the thermodynamics equilibrium calculation, the carbon formation is favorable in the high-temperature range (above 450 °C) [93]. However, carbon deposition was observed at a much lower temperature due to some mechanisms [94]. McCarty *et al.* conducted CO temperature programmed reaction at the temperature of 227 ± 50 °C over Ni-Al₂O₃ catalyst and characterized 4-types of surface carbons, namely (1) atomic carbon C_α, (2) amorphous carbon C_β, (3) bulk Ni-carbide C_γ, and (4) crystalline graphitic carbon.[94] The atomic carbon C_α and the initial Ni-carbide C_γ were active carbon whereas amorphous carbon C_β and crystalline carbon were relatively stable. Nonetheless, the amorphous carbon (C_β) was found active to methanation to some extent on Rh-based catalyst [95]. Figure 2.8 (A) showed the CH₄ production peak during the temperature-programmed reaction. With the increase of carbon coverage, more carbon accumulated on the catalyst surface, as illustrated in Figure 2.8 (B) [94]. The step edges on the metal catalysts are the growth centres of carbon whisker [96]. It was observed on TEM that the nucleation and growth of graphene layers are accompanied by the restructuring of the metal step edges [96]. In the methanation of lean hydrogen synthesis gas where H₂:CO_x between 0.3 to 1.8, the metal particle morphology is changed by carbon deposits [97]. Czekaj *et al.* investigated the mechanism of carbon whisker growth on Ni-Al₂O₃ through in-situ XPS and High-Resolution Transmission Electron Microscopy (HRTEM) techniques. The carbon whisker associated with Ni particle, and caused detachment of Ni particle from support, as can be seen in Figure 2.8 (A) and (B) [97].

For the reason of the inactivation of active carbon, Alstrup *et al.* proposed a whisker carbon growth model, in which unstable carbide initiated the growth [98]. During the induction period, the unstable carbide evolved and caused Ni particle reconstruction. The unstable carbide then decomposed to filamentous carbon and metal. The carbon filament grew up with surface-carbon

migration [98]. Gupta *et al.* proposed another carbon inactivation model. They observed active and inactive carbon after carbon deposited on the catalyst surface [99]. The inactive carbon was initially active, converted to inactive with time and elevated temperature ($>252^{\circ}\text{C}$). The inactive carbon eventually converted to graphitic form and blocked active sites [99]. Goodman *et al.* deposited surface carbon using Boudouard reaction in a various temperature range [42]. The high-temperature deposited ($>427^{\circ}\text{C}$) surface carbon presented in the graphitic form. Heating in hydrogen can hardly remove the graphic carbon [42].

Figure 2.8 (A): Mass spectra (CH_4) of deposited surface carbon methanation on $\text{Ni-Al}_2\text{O}_3$. The two peaks indicate the activity of two kinds of surface carbon species, i.e., atomic carbon C_α and

amorphous carbon C_β . (B): Carbon inactivation pathways [94] from left to right: very active atomic carbon C_α migrate [100] to step sites forming amorphous carbon C_β (active), or atomic carbon C_α , the former converted to elemental carbon and the latter to bulk carbide C_γ .

Computational studies provide useful insight on the carbon deposition mechanism. Abild-Pedersen *et al.* studied the mechanism of carbon nanofiber formation using DFT calculation over Ni single crystal [100]. They found that the Ni edge sites were the preferred sites for graphite growth. Surface carbon is able to diffuse along step edge sites to the graphite perimeter to fill the graphite growth. Helveg *et al.* summarized the mechanisms of whisker carbon growth on Ni catalyst [101]. The classic mechanisms that involved temperature gradient or concentration gradient induced whisker growth are investigated by HRTEM observation and DFT calculations. Surface steps acted as carbon growth centre. The stronger bond between carbon and graphene acted as the driving force. Carbon transported from step sites to free metal surface through surface diffusion or sub-surface diffusion [101].

Figure 2.9 The detachment of Ni induced by carbon whisker growth. (A): The HRTEM image showed the association of Ni particles with carbon whisker on the Ni- Al_2O_3 catalyst after 137 hours methanation [100]. (B): Illustration of carbon whisker growth and Ni particle detachment from the catalyst support [101].

The rapid loss of methanation activity of Ni-based catalyst during the first 5 hours can be attributed to the metal size growth [102, 103]. Agnelli *et al.* studied low-temperature (230°C) metal sintering process during CO hydrogenation over supported Ni catalyst with DRIFT technique [102]. They observed the evolution of metal particle size distribution when the reaction temperature is far below Tammann Temperature (591°C for Ni), which means no physical sintering has taken place.

They attributed this sintering process to Ni-carbonyl ($\text{Ni}(\text{CO})_4$) species migrating on the silica surface, as showed in Figure 2.10, where catalyst particle size growth (A) corresponding to the Ni-carbonyl band formation (B) Mirodatos *et al.* showed that higher CO pressure contributed to Ni carbonyl formation, which further enhanced the metal sintering [104]. Shen *et al.* studied the catalyst deactivation caused by Ni-carbonyl formation and diffusion [103]. They suggested using the thermodynamic calculation to predict the $\text{Ni}(\text{CO})_4$ formation. Specifically, equilibrium partial pressure of $\text{Ni}(\text{CO})_4$ lesser than 10^{-6} Pa was found as a safe zone for the $\text{Ni-Al}_2\text{O}_3$ catalyst [103]. Rostrup-Nielsen *et al.* concluded that in the range of low-temperature methanation, sintering of Ni catalyst was due to Ni-carbonyl ($\text{Ni}(\text{CO})_4$) formation and migration [105]. High-temperature (above 600 °C) methanation prohibited the Ni-carbonyl formation but thermal sintering dominant [105].

Figure 2.10 The Ni metal sintering induced by Ni-carbonyl. (A): The DRIFT spectra of CO methanation on Ni-SiO_2 (230°C, $\text{H}_2:\text{CO}=2:1$) showed the formation of surface Ni-carbonyl species (the sub-carbonyl peak) corresponding to the catalyst deactivation (due to Ni-particle smoothing) process [102]. (B): Ni-carbonyl migration induced Ni metal sintering.

Summary and Perspectives

The recent study on CO_2 and CO methanation mechanisms and catalyst deactivation mechanisms are discussed through experimental and computational approaches. The following issues were addressed: (1) What are the intermediates on the catalyst surface? (2) What are the elementary

steps that lead to the intermediates? (3) What are the active sites? For the CO₂ methanation, intermediates in the associative scheme include carbonate (CO_{3ad}), bicarbonate (HCO_{3ad}), formate (HCOO_{ad}), and carbonyl (CO_{ad}) species. Researchers claimed that hydrogenation of these surface species reduced the barrier of C-O bond breaking. The active sites are located at the metal-support interface. On the other hand, the dissociative pathway involved carbonyl (CO_{ad}) as intermediate, which resulted from direct C-O bond breaking at the under-coordinated sites, i.e., step and kink sites. The active sites reduce C-O bond breaking barrier so that CO₂ direct dissociation is possible at these locations. For the CO methanation: some researchers concluded that direct C-O bond breaking is not energetically feasible. CO and H₂ associatively adsorbed as formyl (CHO_{ad}) or carbon-hydroxyl (COH_{ad}) species so that the barrier is reduced. Nevertheless, some other researchers observed surface carbon (C_{ad}) as the result of CO direct dissociation or disproportionation. In both associative and dissociative schemes, under-coordinated sites are the critical active sites, and the rate-limiting step is either the C-O bond breaking or C_{ad} hydrogenation. For the deactivation mechanisms: (1) Sulfur poisoning results from the strong chemisorption of Sulfur species on the active sites, (2) Carbon deposition is induced by the migration and nucleation of inactive carbons. The elevated temperature and the long period of the absent of H_{ad} species induced the inactivation of the active carbon. The fouling of surface carbon caused metal detachment from the support material. (3) The metal sintering is caused by the migration of metal-carbonyl and other transportable species.

For the prospect in the mechanism study, first of all, the debating mechanisms should be uncovered clearly based on the respective active metals, supports, and reaction conditions so that catalysts optimization and kinetics determine is possible. It is suggested to focus on model catalyst testing, where the effects of support and promoter materials can be eliminated. Secondly, the catalysts micro-level morphology should be well-controlled to enhance the kinetics of the rate-determining elementary step. This requires the advancement of catalyst synthesis method to achieve the desired combination of active sites. Thirdly, increase the durability of the catalyst for commercialization and large-scale implementation. Strong metal-support interaction to counter the carbon detachment effect could be an effective approach. Lastly, explore the optimum reaction temperature, H₂:CO_x ratio, and pressure to maximize the methanation output.

The effects of the catalyst shape and size to the reaction mechanism is not covered in this thesis. This is because reaction mechanism is more of sites-dependent (micro-scale) rather than structure-dependent (macro-scale or porous-scale) [106]. Although, reaction mechanism can be structure-dependent due to the local temperature and/or concentration differences, which requires further investigation from both modeling and experimental works.

In conclusion, the CO₂ and CO methanation process have been extensively studied, but the exact mechanism is still under debate. The literature review showed that both associative and dissociative methanation hold solid evidence in proving their validity in respective reaction conditions. Despite numerous approaches and claims made, more works are necessary to draw a clearer boundary between the two mechanisms. All in all, the development of the high activity, high selectivity, and durable methanation catalysts are the key factors to the large-scale implementation of Power-to-Gas to tackle intermittency of renewable energy sources. The breakthrough in this area, as well as other technologies such as Solid Oxide Electrolysis Cell, Carbon Capture and Storage, are of great vital for the sustainable development of the future world.

2.2 Reaction Kinetics

With the discussion in the reaction mechanisms in the previous chapter, it is noticed that the intrinsic reaction kinetics expressions are dependent on the reaction schemes (i.e., the elemental steps). For example, the associate CO₂ methanation and the dissociate CO₂ methanation have different reaction schemes and hence different kinetics expression. Meanwhile, the catalyst metal, i.e., nickel and ruthenium, may affect the specific reaction routes due to the distinct adsorption/desorption energy on the activate sites. The power law kinetics, on the other hand, are more of “best-fitted” rate equations without much of consideration on the reaction schemes. The variables in a power law kinetics are temperature and partial pressure of the reactants and products. The constants in the power law kinetics are rather fitted according to the measured reactor conditions and the reaction rates. The power law kinetics are easier to be determined but lesser adaptive to a broader range of reaction conditions. Thus, the power law kinetics are not used in this study as the optimization requires the investigation of wide range of reaction conditions. Instead, the intrinsic kinetics are more suitable for this purpose. More specific, the kinetics on the nickel-based alumina support catalyst are chosen in this study because of the plentiful literature of the mature catalyst.

The CO₂ methanation process may involve three major reactions, i.e., the CO₂ and CO methanation, and the Water-Gas-Shift reaction [107]. The chemical balance equations are shown below:

Reaction kinetics is about the rate of the reactions. What parameters are affecting the reaction rate? Collision Theory provides a qualitative explanation of chemical reactions and the rates at which they occur [108]. The reactants need to collide so that to react, hence any factor that affects the frequency of the collision will determine the reaction rate. Generally, the reaction rate depends on the temperature, pressure, and the concentration of the reactants [108]. Reactants concentration can be represented by temperature and partial pressure of the species. The rate equation becomes:

$$r_j \propto function(T, p_i)$$

Where r_j is the rate of reaction j , T is reaction temperature and p_i is the partial pressure of specie i .

The power law kinetics adjusts the rate constant and reaction order to adapt the measured reaction rate and the reaction conditions, without the necessity to know the true elementary steps of the reaction. The effectiveness of power-law kinetics is adequate but limited to the reaction conditions at which the parameters were measured [109]. On the other hand, the Langmuir-Hinshelwood-Hougen-Watson (LHHW) type kinetics represents a category of reactions that happened on the catalyst surface where the reactants are adsorbed and meet at the catalyst reaction sites. To establish the LHHW kinetic, the reaction mechanism or scheme need to be determined or proposed. The effectiveness of LHHW kinetics is adaptable to a wider range of parameters and suitable for parametric study [109].

The earlier kinetic studies are mainly for the determination of the reaction mechanism. The kinetic measurement experiments are mostly in small scale, well controlled in the micro level. Weatherbee and Bartholomew derived Langmuir-Hinshelwood intrinsic kinetics to identify the mechanism of the CO₂ methanation under Ni-based catalyst [110]. Their work showed that the methanation is achieved by dissociative adsorption of CO₂ to CO and atomic oxygen followed by dissociation of adsorbed CO to atomic carbon and atomic oxygen, the atomic carbon is then hydrogenated to methane, as can be illustrated in Figure 2.11 in the CO₂ dissociative scheme [110]. Klose and Baerns studied the CO methanation on the Ni-based catalyst supported on the alumina [111]. Their kinetic study indicates that the possible CO methanation pathway is by the CO dissociative adsorption and subsequent hydrogenation of the surface carbon and surface oxygen intermediates as can be illustrated in Figure 2.11 in the CO dissociative scheme [111]. Xu and Froment [107] examined the intrinsic rate equation of CO, CO₂ methanation and Water-Gas-Shift reaction on a Ni-based catalyst and tried to reveal the reaction mechanism from the kinetic rate-limiting steps. Their study shows that the non-dissociative path could be the real mechanism in their study conditions. The associative mechanism was also found by other authors, as can be illustrated in Figure 2.11 in the CO₂ and CO associative schemes [112]. However, the kinetic model is not able to unambiguously discriminate the specific reaction route. Kopyscinski *et al.* developed LHHW type kinetics from their steady-state integral reactor and found that the surface carbon hydrogenation is the rate-limiting step [113]. The more delicated mechanism study is

then shifted to XRD, DRIFTS, and other *in-situ* techniques. The detail discussion and review about methanation mechanism was shown in the later part of this chapter. All the possible reaction schemes are summarised and illustrated in Figure 2.11:

Figure 2.11 CO₂ associative and dissociative methanation scheme : in the associative scheme, the first and the second C-O bond breaking are both assisted by adatom H_{ad}. Whereas in the dissociative scheme, the first C-O bond dissociated directly on the catalyst, and the second C-O bond breaking refers to the discussion of CO associative and dissociative methanation scheme: the associative scheme is assisted by H_{ad}, whereas dissociative scheme occurred directly on the catalyst surface.

In recent years, kinetic study focused on the catalyst performance improvement and reactor simulation application [114]. From a practical point, Stefan *et al.* compared and adapted rate equations from literature to fit for the dynamics operation of simulation work with the wider range of temperature and pressure [114]. Their study concludes that the selection of the rate equation should follow the catalyst Ni-content as the prime indicator [114]. Indeed, intuitively the number of active sites on the catalyst surface should affect the reaction rate significantly. Zhang *et al.* [115] expanded Xu's and Klose' work to a commercial Ni-based catalyst with 50% metal loading in a plug-flow reactor. They adapted the rate constant to their experimental work and expanded

the temperature range to 250 ~ 360 °C [115]. Koschany *et al.* [109] examined the various kinetic equations in a differential reactor. They found that the power law rate equation is adequate for most of the reaction conditions but overestimates the rates while approaching to equilibrium conditions at high temperature [109]. A summary of rate equations are listed as below whereas the detail parameters and constants are attached in the Appendix A5 at the back of the thesis:

Table 2.1 CO₂ and CO methanation rate equation summary

Reaction	Rate Equation	Reference
CO ₂ LHHW	$r = \frac{\frac{k_{CO_2}}{p_{H_2}^{3.5}} \left[p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_{eq,CO_2}} \right]}{(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O} / p_{H_2})^2}$	Xu <i>et al.</i> [107]
<p>where rate constant $k_{CO_2} = k_{CO_2}^0 \exp\left(-\frac{E_{CO_2}}{RT}\right)$, and equilibrium constant $K_{eq,CO_2} = K_{eq,CO_2}^0 \exp\left(-\frac{\Delta H_{eq,CO_2}}{RT}\right)$, K_{CO}, K_{H_2}, K_{CH_4}, K_{H_2O} are the adsorption constant of the species.</p>		
CO ₂ LHHW	$r = \frac{k_{CO_2} \cdot p_{H_2}^{0.5} p_{CO_2}^{0.5} \left(1 - \frac{p_{CH_4} p_{H_2O}^2}{p_{CO_2} p_{H_2}^4 K_{eq,CO_2}}\right)}{\left(1 + K_{OH} \frac{p_{H_2O}}{p_{H_2}^{0.5}} + K_{H_2} p_{H_2}^{0.5} + K_{mix} p_{CO_2}^{0.5}\right)^2}$	Koschany <i>et al.</i> [109]
CO ₂ Power Law	$r = \frac{k_{CO_2} \cdot p_{H_2}^{n_{H_2}} p_{CO_2}^{n_{CO_2}} \left(1 - \frac{p_{CH_4} p_{H_2O}^2}{p_{H_2}^4 p_{CO_2} K_{eq,CO_2}}\right)}{\left(1 + K_{OH} \frac{p_{H_2O}}{p_{H_2}^{0.5}}\right)}$	Koschany <i>et al.</i> [109]
CO LHHW	$r = \frac{\frac{k_{CO}}{p_{H_2}^{2.5}} \left[p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_{eq,CO}} \right]}{(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O} / p_{H_2})^2}$	Xu <i>et al.</i> [107]
CO LHHW	$r = \frac{k_{CH_2} K_c K_H^2 p_{CO}^{0.5} p_{H_2}}{[1 + K_c p_{CO}^{0.5} + K_H p_{H_2}^{0.5}]^3}$	Klose <i>et al.</i> [111]
CO LHHW	$r = \frac{k_{CO} K_c p_{CO}^{0.5} p_{H_2}^{0.5}}{(1 + K_c p_{CO}^{0.5} + K_{OH} p_{H_2O} p_{H_2}^{-0.5})^2}$	Kopyscinski <i>et al.</i> [113]

The reaction rate and schemes may vary with reaction conditions such as temperature ranges, the partial pressure of the reactants and products. Also, the reaction schemes may totally different on different types of catalyst surface and support materials. The study in this thesis is limited in the

Ni-based alumina supported catalyst. The kinetic parameters are adopted from Xu and Froment's work.

2.3 Reactor Thermal Management

In the exothermic reactor, the axial temperature profile sometimes attains a local maximum, which is referred to as hot spot [116]. The temperature gradient of hot spot and its surrounding can exceed the order of 100 °C [116]. As has been review from the catalyst deactivation mechanism section, the coking and metal sintering are thought to be induced by the extreme temperature gradient (or hot spot) in the reactor [81]. The coking is responsible for the fouling of the effective active sites, pores blocking, and the metal disintegrate from the support. The metal sintering leads to the catalyst deactivation due to the metal surface losses. In the system level, the temperature runaway behavior can be a severe safety hazard if the hot spot is not confined in a certain range. Therefore, reactor thermal management is of great important for the operation of exothermic reactors.

As for the reason of hot spot formation, extensive works have been done. Nguyen and Balakotaiah developed a heterogeneous model to investigate the relationship between flow maldistributions and hot spots formation in the fixed-bed reactor [117]. They proposed that the interphase resistances may lead to the formation of high temperature stream [117]. The heat of the stream is then transfered to catalyst particles at certain location [117]. Agrawal *et al.* examined the mechanism for hot spot formation through a 3D heterogeneous model [118]. They found that hot spot may occur even in perfectly uniform packed bed [118]. Their model showed that heat and mass transfer resistance between gas and solid phase has a major influence on the maldistributions of the stream transversely [118]. In the transversal direction, hot zones are observed by infrared cameras [116], and their existence are attributed to the effect of interaction among diffusion processes, reaction rate, global coupling and catalyst non-uniformity [116, 119]. Several ways of avoiding the hot spot formation are proposed: 1. The dilution of reactant concentration. 2. Reduce the conversions by limiting the temperature or catalyst activity. 3. Reduce the interphase resistance by using smaller size catalyst. 4. The control of the inlet temperature or the catalyst loading near the entrance. 5. Increase the bed conductivity by mixing with inert high conductivity particles [118].

With the basic understanding of the hot spot formation, the detail literature review on the aspects of methanation industrial reactor, laboratory scale reactor and reactor simulation are conducted in the subsequent sections.

Industrial Reactors

There is no industrial level Power-to-Gas plant established so far. Instead, demonstration projects and pilot scale reactors are running in several institutes [120-122]. For example, the prototype plant constructed in Tohoku University aims to recycle the CO₂ with electrolytic hydrogen that produced from surplus solar power [120]. Audi e-gas plant demonstrated a 6 MW pilot-scale methanation reactor to harness the CO₂ from a biogas plant using alkaline electrolyzer to produce hydrogen [121]. The energy source of the e-gas plant is called green electricity, which ultimately is the surplus electricity from the grid. And the product methane is directly distributed to the CNG vehicles. The technological and economic aspects of the PtG project were examined by these works [123, 124]. The authors found that the current water electrolysis based PtG project is not competitive with conventional natural gas or even biomethane. The cost of SNG strongly depends on the annual operation time (i.e., the capacity factor) and the electricity price [123-125].

Similar technologies, such as the Fischer-Tropsch process [126, 127] and syngas methanation process [128, 129] have been operated commercially for many years. The Fischer-Tropsch technology produces long chain hydrocarbon mixture from CO/H₂ mixture (also known as syngas) on the Cobalt and Iron catalysts. The final products may be further separated or upgraded to other chemicals depends on market prices [127]. Interestingly the primary goal of the FT process is to avoid the methanation in the reactor, as methane is considered byproduct [127]. Nowadays, the commercial operations of FT plants are mainly located in South Africa and Malaysia, where cheap coal and natural gas resources can be found [127, 130, 131]. The reactors and thermal management technologies used in the FT process are also usable to the syngas methanation process for the purpose of coal and biomass gasification [128]. The advantages of SNG are the well-established distribution infrastructure and the wider end-use technologies [128].

For the FT process and the methanation process, two types of reactor are commonly used in the industrial scale reactor, i.e., fixed-bed reactor and fluidized-bed reactor. From the aspect of the cooling system, each type has many sub-settings that vary with application. For instance, the cooling system can be internally or externally arranged. The arrangement of the cooling system

will further induce isothermal, adiabatic, or non-isothermal behavior in the reactors and different segment of the reactors. For the fixed-bed reactor, there are a few ways of loading the catalyst and layout the cooling system, as illustrated in Figure 2.12 [132]. Figure 2.12 (a) shows a reactor cooling system embedded in the bulk packed bed. The cooling system is on-site controlled and provides an isothermal working condition for the entire reactor [113]. The Figure 2.12 (b) shows a multi-segment cooled fixed-bed reactor where each segment of the reactor is working adiabatically [132]. Overall, the reactor is working at a discretized descending temperature pattern, and each segment reached equilibrium condition before the heat-exchanger, which can be described in Figure 2.13 (a). In the methanation application, Tanja *et al.* proposed two-plant concept according to their study which utilizes multi-stage cooling strategy to gradually reduce the temperature to achieve higher CH₄ yield from the reactor outlet [133]. Multi-step reactors could achieve the similar functionality, the Lurgi process [134] and TREMP process [135] are examples of this category. Höhle *et al.* demonstrated three high-temperature methanation pilot plants in which two of them are multi-stage adiabatic reactors, and the other one is stepped-cooled single-stage reactor [136]. Sometimes the catalysts are loaded inside multi-tubes, and the tubes are cooled internally or externally, as seen in Figure 2.12 (c) and (d). Because of the much higher axial to diameter ratio, the isothermal and adiabatic conditions are not maintained in these tubes. Instead, temperature profile along the tube axis is optimized to achieve maximum production [136].

Figure 2.12 Several types of fixed-bed methanation reactor with the cooling design. The deep grey color represents the catalyst, and the blue color represent the cooling channel.

The temperature pattern of the multi-stage reactors and single-stage reactors can be represented by the following diagram [136]. Figure 2.13 (a) shows the temperature profile of three adiabatic reactors working in a multi-stage series. Each of these reactors converts a fraction of the reactants until the equilibrium state achieved. The products from the previous reactor are then cooled down in the heat exchanger before the next stage. The final stage reactor converts the product gas until certain yield as per requirement of the products end-use. Figure 2.13 (b) shows the continuous temperature profile in the single-stage reactor. The temperature profile along the reactor axis is descending to avoid the arrival of the equilibrium state, at which the reaction ceased to proceed to the desired direction.

Figure 2.13 Temperature profile of methanation reactor corresponding to products yield in the (a) multi-stage adiabatic reactors and (b) single-stage non-isothermal reactor comparison with equilibrium temperature-yield profile [136].

Intuitively, the fluidized-bed reactors are thought to be suitable for the strong exothermic process because of the well thermal mixing in the reactor is good for the hot-spot elimination. But the isothermal condition in the reactor will either face thermodynamic limitation if the temperature is set to be high or kinetic limitation if the reactor temperature is low. The multi-stage fluidized-bed reactor or single-stage fluidized-bed reactor with multi-stage cooling and recirculation system become the unavoidable design to increase the production yield. Figure 2.14 (a) shows an FT process fluidized-bed reactor with two-stage cooling and recirculation system arrangement [127]. The cooling and recycling in the reactor are merely for the increase of the yield. Figure 2.14 (b) and (c) are showing a similar reactor but with different catalyst phases. In the (b) case, multi-stage reactor arrangement is necessary to achieve higher yield. Whereas in the (c) case, wax phase product is separated from the slurry phase catalyst (catalyst will be recycled back) and the gas products are recycled [127]. For the non-isothermal condition, Kopyscinski *et al.* investigated the performance of a fluidized-bed reactor in the CO methanation reaction [137, 138]. They found that the CO conversion mainly happens in the first 20mm of the fluidized-bed. Because of the high reaction rate in this section of the reactor, the mass transfer limitation is the rate-limiting step at this portion. Meanwhile, the temperature difference of 100K was observed in the reactor [137, 138].

Figure 2.14 Schematic diagram of the fluidized-bed reactor. (a) Circulating fluidized bed reactor (b) Sasol fluidized beds (c) Slurry phase reactor [127].

Structured Reactors and Modeling

Lab-scale reactors can be flexibly designed because of the small volume. Also, the demand for precise temperature control requires more effective thermal control devices to be equipped. On the aspect of reactor modeling, innovations can be applied without too much concerns about the complicated manufacturing, high cost and the lifespan of the sophisticated reactor. Structured reactors, such as multi-channel reactor [139-141], tubular reactor with internal or external cooling channels [142-144], membrane reactor [145-147] have been investigated by researchers, either by experiments or simulations. A schematic diagram is shown in Figure 2.15 to illustrate the various structured-reactors in the existing literature. The diagram is simplified as only the reacting zone (orange color) and the cooling zone (blue color) are displayed.

Figure 2.15 Structured fixed-bed reactor design. (a) the multi-channel reactor, reacting zone and cooling zone are alternant arranged. (b1-3) Tubular reactors are cooled externally, internally or

both applied. The orange color is the reacting zone, and the blue color represents the cooling zone. The red arrows represent the heat transfer direction.

The multi-channel reactor is characterized by the alternant laid reacting zone and cooling zone, as illustrated in Figure 2.15 (a). The reacting channel can be slot shape or slab shape. The catalyst is coated, sprayed on the channel to promote fluent flow or directly loaded as particle form [141]. The reactor body is made of metal to effectively conduct the heat to the cooling channels [139, 141]. In the cooling channel, the cooling potential of air, steam, and water and various flow rate were examined by researchers [140]. The heat removal rate of air and steam were found to be similar, whereas evaporation of water has the highest cooling potential [140]. With the increment of the coolant flow rate, extinguishment of the reactor was observed [140]. Kreitz *et al.* investigated the dynamic operation of a micro-structured fixed-bed reactor [148]. The fluctuating supply of feedstocks lead to large temperature gradients and the lower methane selectivity. Buffer storage and multi-stage reactors are suggested to ensure the feedstock stability [148].

The lab-scale tubular reactors are very close to industrial scale reactor and can be easily scaled-up by increasing the number of tubes. The catalysts are loaded simply as packed-bed. The cooling system of tubular reactor is relatively simpler than that of multi-channels. Double tube, internal tubes or both are applied as cooling measures, as illustrated in Figure 2.15 (b1-3), and the design varies with the temperature control demand [142-144]. If simply observed from the shape, a membrane reactor can be categorized as a special case of the tubular reactor. The membrane reactors separate the reactants from each other to control the reaction rate, especially at the entrance where reactants concentration is high [145]. The permselective membrane filters out the product to push the reaction to the forward direction [146]. The chemical equilibrium is pushed forward due to the Le Châtelier's Principle. The increment of CO₂ conversion of 18% was observed in the water permeation membrane reactor for the Sabatier reaction [146]. The H₂ permselective membrane can be used for the distribution supply of the feedstocks [147]. Currie *et al.* found that the separation supply of H₂ results in a more uniform temperature distribution in the methanation reactor [147]. The uniform temperature leads to the higher yield and eliminate the CO/solid carbon formation. However, as a trade-off the H₂ utilization rate is lower in the outlet stream since not all the H₂ penetrates through the membrane [147].

On the other hand, the catalyst dilution [143, 149, 150], monolithic shaped catalyst [151, 152], catalyst shape distribution [153], are used to enhance the heat transfer in the catalyst bed, as

illustrated in Figure 2.16. At the entrance zone of the reactor, the local hot-spot in the center portion of the catalyst bed or catalyst particle is inevitable unless lesser heat is generated. By means of catalyst dilution, the local temperature runaway behavior can be avoided [143, 149]. The catalyst bed is diluted with inert material such as alumina beads to reduce the heat generation at the segment. The catalyst dilution may reduce the productivity of the reactor but unlikely a major issue. The temperature and the reactants concentration at the entrance zone is relatively high so that the catalyst dilution will not affect the overall reactor productivity severely. The catalyst dilution can also be inherited from the catalyst shape. For example, the monolithic catalyst provides artificial internal channels to guide the flow meanwhile reduce the catalyst loading, as illustrated in Figure 2.16 (a) [151, 152, 154, 155].

Figure 2.16 Catalyst morphology modification as temperature control methods. (a) The catalyst can be a monolithic entity with internal flow channels like honeycomb or capillary tube [151]. The monolithic catalyst replaced the incompact catalyst bed to provide effective heat transfer through the backbone of the honeycomb. (b) the packed-bed is diluted [149] or distributed [153] with different shape/activity catalysts to achieve step-controlled temperature profile along the reactor axis

For monolithic catalyst, Kiewidt and Thöming simulated the heat and mass transfer phenomena in a sponges-structure supported catalyst [154]. A 2-D pseudo-homogeneous model was established to investigate the temperature distribution in the axial and radial direction. The high porosity of the sponge structure promoted the heat and mass transfer between catalyst phase and gas phase, which is good for the overall yield and temperature management in the exothermic reactor [154]. The limitation of the model is the lack of computational fluid dynamics calculation to allow for explicit representation of heat and mass transfer between catalyst surface and gas phase [154]. Their pareto-optimal analysis shows that the monolithic sponges as catalyst support is more suitable for small-scale, unsteady-state operations [155].

Another approach is to load various shape of catalyst in different segment of the reactor to alter the gas flow pattern, as illustrated in Figure 2.16 (b) [153]. The catalyst shape distribution changes the local catalytic activity and the heat transfer effectiveness [153]. However, the method is only suitable for steady-state operation. Also, due to lower catalyst loading, the inert pellet mixing also reduces the reactor performance [153]. In practice, the non-uniform catalysts are commonly seen on Fischer-Tropsch reactors for the optimization of hydrocarbon formation [156]. The bed temperature runaway is found to be completely prevented in the optimum case and the long chain hydrocarbon selectivity (C_5^+) is enhanced [156]. On the steam methane reforming (the reverse of methanation) reactor, catalyst dilution by adsorbent is one of the useful reactor design strategies for the thermal optimization [150].

All in all, the temperature control methods reviewed in the above section can be generalized as the following two points: 1. Enhancing of the heat removal rate, and 2. Inhibiting of the heat generation rate, either through experiments or modelling approaches. The specific formulation of the modeling on the simulation of heat and mass transfer phenomena in the methanation reactor is discussed in the next chapter.

Chapter 3 Methodology

The focus of the thesis is on the fixed-bed reactor simulation. To achieve the optimum balance between thermodynamics and kinetics performance, reactor scale simulation is established. Specifically, the homogeneous and heterogeneous heat and mass transfer models are built to mimic the transfer phenomena in the bulk fluid and in the porous media. For the chemical reaction, the thermodynamics of CO_2 and CO methanation is studied as the guide line for the kinetics performance optimization. Gibbs energy minimization method is adopted to calculate the equilibrium composition of the reaction. An illustration of the modeling components for the fixed-bed reactor is shown in Figure 3.1. Briefly, the fixed-bed reactor model consists of transfer equations and reaction kinetics equations. The temperature/concentration dependent parameters in the transfer model and reaction kinetics are inherited from literature.

Figure 3.1 Fixed-bed reactor modeling components.

3.1 Thermodynamic

Gibbs Energy Minimization

The Gibbs free energy minimization method provides guidance for the equilibrium condition gas composition of the reaction [157, 158]. The method simply minimizes the summation of the Gibbs free energy of the species before and after the balance equation at any given pressure and temperature. At the minimum Gibbs energy situation, the composition of the reactants and products should reach an equilibrium, in which the forward reaction rate equals to the backward reaction rate. The ratio of each reactant and products can be determined.

The Gibbs function of the system is given by:

$$nG = \sum_{i=1}^N n_i \bar{G}_i + RT \sum n_i \ln\left(\frac{\hat{f}_i}{f_i^0}\right) \quad (3.1)$$

The equation is simplified according to reference [159], for the gas phase reactions, $\hat{f}_i = \hat{\Phi}_i y_i P$. The function is then derived into this form:

$$nG(T, P) = \sum n_i \Delta G^0 + \sum n_i RT \ln p + \sum n_i RT \ln y_i + \sum n_i RT \ln \hat{\Phi}_i \quad (3.2)$$

Where n_i is the number of moles of species i , ΔG^0 is the standard Gibbs free energy of formation of species i , R is the universal gas constant, p is the total pressure of the gas mixture, y_i is the mole fraction of species i in the gas mixture, $\hat{\Phi}_i$ is the fugacity coefficient of species i in the gas mixture. The Gibbs free energy of formation can be calculated from JANAF table [160] or NIST Chemistry Webbook [161] for thermodynamic properties.

Gao *et al.* have systematically scanned the reaction conditions of CO₂ and CO methanation process in their paper [93]. Briefly, both the CO₂ and CO methanation reaction favor low temperature and high pressure thermodynamically [93]. The term favor here means higher conversion fraction but not higher reaction rate. To fully understand the thermodynamic process, an Excel model [159] and a MATLAB model are established to replicate the Gibbs Energy Minimization method. The Gibbs energy function is minimized in Excel using Solver plugin with GRG nonlinear optimizer. Another minimizer used is MATLAB is *fmincon()* function in order to automate the calculation and visualize the result easily.

Thermodynamic Equilibrium

The Gibbs free energy minimization method provides effective guidance for the reaction condition selection. The equilibrium model results and discussion are shown here rather than in the subsequent chapter for the convenience of reference.

Figure 3.2 shows the equilibrium gas composition of CO₂ methanation reaction corresponding to a reaction temperature at the stoichiometric H₂ to CO₂ ratio. The diagram indicates that at high temperature, the reaction moves to the methane reforming direction and at a low temperature, the reaction moves to the CO₂ methanation direction.

Figure 3.2 CO₂ methanation gas composition when reaching to equilibrium. The diagram shows that the CH₄ yield favors low temperature from thermodynamic point of view. Also, to prevent the formation of CO, the equilibrium temperature should not exceed 450 °C and above

Figure 3.3 shows the CH₄ yield corresponding to the reaction temperature at the equilibrium condition at various H₂ to CO₂ ratio. At the same reaction temperature, CH₄ yield favors higher hydrogen ratio. This diagram also shows that for reaction pressure at 1 bar, the ratio at 4, it is very hard to reach 100% yield unless the reaction temperature can drop to 150°C and below. The new issue arises because of the poor kinetic performance at low temperature.

Figure 3.3 The CH₄ yield with various H₂:CO₂ ratio. At the same temperature condition, the CH₄ yield favors higher H₂:CO₂ ratio

Figure 3.4 shows that at the same temperature, CH₄ yield favors higher total pressure. The result indicates that to avoid poor kinetic performance at low temperature, increase the reaction pressure is an option. The only issue remaining is the hot-spot formation at the entrance zone due to the strong heat generation.

Figure 3.4 CH₄ yield and reaction pressure. The 100% CH₄ yield is moving toward higher temperature with higher reaction pressure.

Equilibrium Constant

The equilibrium constant in the kinetic equation is calculated from the integration of the van't Hoff equation.

$$\frac{d\ln(K_{eq})}{dT} = \frac{\Delta H_R^0}{RT^2} \quad (3.3)$$

Where K_{eq} is the equilibrium constant of a reaction, T is the reaction temperature, ΔH^0 is the standard enthalpy change of a reaction, R is the universal gas constant. A detail derivation and explanation of the van't Hoff equation can be found in the Thermodynamics textbook page 818 and 819 [162].

The derived results are shown below, and it is used throughout this thesis. The validity of the temperature dependent constant is from 298K to 700K, however, compared with other works, the equation gives acceptable accuracy even beyond the range [163].

$$K_{eq-CO_2 \text{ methanation}} = \exp(-20.8 + 1.81 \ln T - 2.93e-2T + 2.45e-5T^2 - 1.19e-8T^3 + 2.49e-12T^4 + 1.88e+4T^{-1})$$

$$K_{eq-CO \text{ methanation}} = \exp(-9.78 - 1.26 \ln T - 1.95e-2T + 1.89e-5T^2 - 9.61e-9T^3 + 2.07e-12T^4 + 2.34e+4T^{-1})$$

$$K_{eq-RWGS} = \exp(-11 + 3.08 \ln T - 9.81e-3T + 5.69e-6T^2 - 2.27e-9T^3 + 4.19e-13T^4 - 4.65e+3T^{-1})$$

3.2 Reactor Simulation

Simulation works can provide useful guidance to the reactor design and thermal management. The major components in the reactor simulation are the mathematical representation of reaction rate, mass transfer, heat transfer, and momentum transfer equations. The reaction rate is essentially algebraic expression of reactants partial pressure (P_i) and reaction temperature (T). Different from rate equation, the mass transfer, heat transfer and momentum transfer equations are essentially Ordinary Differential Equations (ODEs) or Partial Differential Equations (PDEs) that derived from control volume methods [164]. Figure 3.1 shows the interactions between kinetic, mass, heat, and momentum equations. Briefly, the kinetic equation receives inputs of P_i and T from mass and heat transfer equations and returns outputs of reactants concentration update (ΔC_i) and heat generation ($r_j \Delta H$) to the respective transfer equations. The momentum equation receives inputs from inlet pressure and provides superficial velocity to the mass and heat transfer equations. The minor effects, such as temperature dependent of material properties, heat and momentum transfer due to mass diffusion, boundary conditions are neglected in the schematic diagram. The ODEs or PDEs are then solved by numerical methods.

Figure 3.1 Schematic diagram of reactor simulation components and their major interactions.

The Power-to-Gas plants absorb the surplus power from renewable sources as energy storage buffer. However, the key component of PtG system, the Solid Oxide Electrolysis Cell, is not capable to work in the dynamic condition without rapid degradation of the stack material. Hence, small-scale buffer storage of the fluctuating electricity is necessary to maintain the SOEC's consistent working. The modeling of this thesis is thereby restricted to steady state simulation.

Momentum Equation Simplification

In this study sophisticated momentum conservation model is not necessary. Hence, the Ergun equation was implemented as a simplified model to calculate the pressure gradient along the packed-bed [108]. The superficial velocity was then calculated from the local pressure accompanied by ideal gas law and mass conservation law. The ideal gas law that connects to the concentration and local pressure is shown below:

$$C_i = \frac{n}{V} = \frac{p_i}{RT} [\text{mol/m}^3] \quad (3.4)$$

Where p_i is the partial pressure of the reactant i , R is the universal gas constant.

At each segment of the reactor, the mass flow into the segment must flow out. The mass conservation equation shows below:

$$\frac{dG_0}{dz} = 0, \text{ or } \rho \times u = \text{constant} [\text{dimensionless}] \quad (3.5)$$

Where G_0 is the mass flow rate per unit cross-sectional area with the unit of $[\text{kg/m}^2/\text{s}]$. The total mass flow rate is determined by the inlet gas flow rate. The combination of ideal gas law and mass conservation law gives the pressure dependent superficial velocity:

$$u = \frac{G_0 \cdot RT}{PM_{ave}} [\text{m/s}] \quad (3.6)$$

Pseudo-homogeneous Model

For the mass and heat transfer, the simplest form of the model can be represented by a set of initial value problem (IVP) ODEs. The radial direction transfer phenomena are sum up into the axial direction. The ODEs are then solved by integrating the equations along the axial direction and substituting the initial value, as shown in the schematic diagram of Figure 1.2. Researchers investigated the accuracy of the 1D model. Schlereth and Hinrichsen constructed a pseudo-homogeneous plug-flow model, where Ergun equation is used as an empirical momentum equation to predict the pressure drop in the porous media [145]. They found that 1D pseudo-homogeneous model can provide an effective guide to the condition design and optimization [145]. The only drawback of the pseudo-homogeneous model is super sensitive of the results to the inlet temperature and the cooling temperature due to the lack of the 2nd order terms and the mass transfer limitation. The slight increment of the cooling temperature will cause a temperature runaway behavior [145].

The higher dimension is not necessary for the small radius fixed-bed reactor. The reactor diameter larger than 6cm starts to affect the equilibrium shift due to the poor heat transfer in the radial direction [145]. The radial direction temperature difference of 2K to 10K was experimentally observed by researchers in the pilot-scale fixed-bed reactor with reactor diameters from 2cm to 8cm [165]. Based on these results, one can safely lump-up the radial direction into the 1D model.

Figure 1.2 *The schematic diagram of a one-dimensional Pseudo-homogeneous model. At steady-state, the transfer model is represented by a set of ODEs to be integrated along the axis direction.*

Homogeneous Model Assumptions

1. For the heat and mass transfer equation, the reactor is assumed to be one-dimensional. The radial direction transfer phenomena are assumed to be negligible compared with the ones in axial direction.
2. For the heat transfer equation, the heat removal rate is assumed to be limited by the heat transfer coefficient h_{wall} since the heat conduction coefficient in the solid is much larger than the heat convection in the free air.
3. In the mass transfer equation, the diffusion terms are negligible compared with the bulk fluid transfer terms.
4. For the momentum transfer, the reactor is assumed to be running at plug-flow mode. The velocity field is simply calculated from ideal gas law and mass conservation equation.

The 1-D, first-order, pseudo-homogeneous heat transfer equation is shown below [145]:

$$u\rho_{ave}C_{p,mix}\frac{dT}{dz} = \sum_1^3 (-\Delta H)r_j\eta_j - h_{wall}A_V(T - T_c) \quad (3.7)$$

Where u is the superficial velocity along reactor axis direction, $C_{p,mix}$ is the heat capacity of fluid gas, z is the axis dimension, ρ_{ave} is the density of the gas mixture, r_j is the volumetric reaction rate of j^{th} reaction, ΔH is the reaction enthalpy, A_V is the reactor surface area per unit volume, T_c is the cooling temperature.

The 1-D, first-order mass transfer equation in the reactor:

$$\rho u \frac{dw_i}{dz} = M_i \sum_{j=1}^3 r_j \eta_j \quad (3.8)$$

where u is the superficial velocity along reactor axis direction, w_i is the mass fraction, M_i is the molar mass of species i , r_j is the volumetric reaction rate of j^{th} reaction, η_j is the effectiveness factor of reaction j^{th} .

Heterogeneous Model

To tackle the sensitivity issues, the diffusion terms need to be established in the solid phase. Hence the solid phase and gas phase need to be separated into two equations. The separation of the two phases, i.e., the catalyst surface and the bulk fluid, also created heat and mass transfer barriers between phases, which is good for the stabilization of the model. For the mass transfer phenomena within the catalyst particle, the mass diffusion is represented by an empirical equation, i.e., the effectiveness factor. The temperature within the catalyst particle is assumed to be constant. The schematic diagram of the heterogeneous model is shown in Figure 1.3.

Figure 1.3 The schematic diagram of a one-dimensional heterogeneous model. The gas phase and solid phase balance equations are separated into two groups in the heterogeneous model. In the gas phase, convection dominant the transfer mechanism whereas diffusion terms are negligible. In the solid phase, diffusion is the main transfer mechanism. The chemical reaction occurs on the solid phase.

Heterogeneous Model Assumptions

1. The reactor is assumed to be one-dimensional. In the gas phase, the radial direction transfer phenomena are assumed to be negligible compared with the ones in axial direction. In the solid phase, the major transfer mode is by molecule diffusion (for mass transfer) and conduction (for heat transfer).
2. The chemical reactions are assumed to be happened in the solid phase only.
3. The external cooling term is assumed to be linked to the gas phase equation.
4. The transfer between gas phase and solid phase is by effective heat and mass diffusion, h_{heat} and h_{mass} , which are calculated from Chilton-Colburn factor.

The mass balance equations in the gas phase and solid phase are:

$$\rho_{ave} u \frac{\partial w_{g,i}}{\partial z} = \rho_{ave} D_i \left(\frac{\partial^2 w_{s,i}}{\partial z^2} \right) + \rho_{ave} h_{mass,i} S_{cat} (w_{s,i} - w_{g,i}) \quad (3.9)$$

$$0 = \rho_{ave} h_{mass,i} S_{cat} (w_{g,i} - w_{s,i}) + M_i \sum_{j=1}^3 r_j \eta_j \quad (3.10)$$

Where $\rho_{ave} = \frac{pM_{ave}}{RT}$ is the average density of the gas mixture, which is derived from ideal gas law and constant pressure assumption and is temperature dependent. In the ρ_{ave} equation, M_{ave} is the average mole mass of the gas mixture based on mole fraction. The term u is the superficial velocity of the gas mixture in the fixed-bed. To follow the mass conservation, $\rho_{ave} \times u$ is constant and equal to the entrance mass flux G_0 . The term $w_{g,i}$ and $w_{s,i}$ are the mass fraction of the specie i in the gas phase and solid phase (To be clarified with the previous homogeneous mass fraction term w_i , which represents the mass fraction of specie i in both gas phase and porous medium). The term $h_{m,i}$ is the mass transfer coefficient, S_{cat} is the surface area of catalyst bead per unit volume. D_i is the effective mass diffusivity. The η_j and r_j are the effectiveness factor and volumetric reaction rate of j .

The energy balance equations in the gas phase and solid phase are:

$$\rho_{ave} u C_{p,mix} \frac{\partial T}{\partial z} = h_{heat} S_{cat} (T_s - T_g) + h_{wall} A_V (T_c - T_g) \quad (3.11)$$

$$0 = k \left(\frac{\partial^2 T_s}{\partial z^2} \right) + h_{heat} S_{cat} (T_g - T_s) + \sum_1^3 (-\Delta H) r_j \eta_j \quad (3.12)$$

Where $C_{p,mix}$ is the heat capacity of the gas mixture. The term h is the heat transfer coefficient of the fluid. T_g , T_s and T_c are temperature in the gas phase, solid phase, and cooling temperature, respectively. The term k is the thermal conductivity of the catalyst particle. The term h_{wall} is the effective heat transfer coefficient between the reactor wall and the cooling system. The term A_V is the surface area of the reactor outer surface per unit volume.

Boundary conditions:

For both the gas and solid phase, there is no source and flux term at the inlet and outlet position. In the infinitesimal length of the reactor segment before the inlet and beyond the outlet of the reactor, the temperature and mass fraction remain constant, i.e., zero gradient, as shown below:

$$\begin{aligned} \frac{\partial T_g}{\partial z} = 0, \quad \frac{\partial w_g}{\partial z} = 0 \\ \frac{\partial T_s}{\partial z} = 0, \quad \frac{\partial w_s}{\partial z} = 0 \end{aligned} \quad (3.13)$$

The inlet temperature and mass fraction are set to be constant as follows:

$$T = T_{inlet}, \quad w = w_{i,inlet} \quad (3.14)$$

For the reactor outer surface boundary condition, the cooling term (heat sink) $h_{wall}A_V(T_c - T_g)$ is already integrated in to the balance equation because the one-dimensional system has no outer surface.

3.3 Transfer Properties

Viscosity

The temperature dependent viscosity of gas molecule can be estimated from Chapman-Enskog theory [166]. The viscosity is written in the form of Lennard-Jones parameters as:

$$\mu = 2.6693 \times 10^{-5} \frac{\sqrt{M_i T}}{\sigma^2 \Omega_\mu} [\text{g/cm/s}] \quad (3.15)$$

Where M_i is the mole mass of the molecule, σ is the characteristic diameter of the molecules, Ω_μ is the collision integrals. The characteristic diameter of the molecules can be found from the table of Lennard-Jones Potential Parameters and Critical Properties. The collision integrals and the Lennard-Jones Potential Parameters can be both found in the reference Table E.1 and E.2 [166]. Typical values of viscosity can be found in Appendix A2.

Binary Diffusivity and Knudsen Effect

The diffusivity of one molecule relative to the other can be obtained from kinetic theory and corresponding-states arguments [166]. The approximate form of binary diffusivity of two-component system can be shown:

$$D_{AB} = 0.0018583 \sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \frac{1}{p \sigma_{AB}^2 \Omega_{D,AB}} [\text{cm}^2/\text{s}] \quad (3.16)$$

Where M_A and M_B are the mole mass of species A and B, p is the total pressure, $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$, σ_i is the characteristic diameter of the molecules, $\Omega_{D,AB}$ is the collisional integral.

The mass transfer in the porous catalyst particle can be affected by the Knudsen effect if the pore size is small. The Knudsen diffusivity of a species is represented by the function below:

$$D_{K,i} = 4850 d_p \sqrt{\frac{T}{M}} [\text{cm}^2/\text{s}] \quad (3.17)$$

The pore radius of the alumina supported catalyst is within the range of 20 to 200 angstrom [167], at which both the Knudsen diffusivity and the molecular diffusivity affect the mass transfer of the molecules in the porous media. The effective diffusivity of a species in the porous particle with other gas mixture can be represented by:

$$D_{i,eff} = \frac{\epsilon}{\tau} \left(\frac{1}{D_{i,mix}} + \frac{1}{D_K} \right) [\text{cm}^2/\text{s}] \quad (3.18)$$

Where ϵ is the porosity of the particle and τ is the tortuosity of the particle. The relationship between porosity and tortuosity can be found from the following simulation work [168] expressed as:

$$\tau = \frac{(1 + \epsilon)^2}{\epsilon(1 + \epsilon)^2 + 4\epsilon^2(1 - \epsilon)} \quad (3.19)$$

The typical values of porosity and tortuosity can be found from Figure 1.4.

Figure 1.4 The porous media tortuosity corresponding to the porosity.

Thermal Conductivity

A semi-empirical method of calculating thermal conductivity of the gas is shown in the following equation [166]:

$$k = \left(C_p + \frac{5}{4} R \right) \frac{\mu}{M_i} \text{ [W/m/K]} \quad (3.20)$$

Where C_p [J/mole/K] is the heat capacity, R [J/mol/K] is universal gas constant, M_i [kg/mol] is the mole mass of the species i , μ [kg/m/s] is dynamic viscosity.

Effective Heat Transfer Coefficient

The heat transfer between bulk fluid and catalyst pellets is hard to determine from experiments. The heat transfer coefficient for forced convection in the packed bed is determined by Chilton-Colburn factor [169]:

$$h_{heat} = J_H \frac{C_p G_0}{Pr^{2/3}} \text{ [W/m}^2\text{/K]} \quad (3.21)$$

Where $J_H = \begin{cases} 0.91 Re^{-0.51} \psi & (if Re < 50) \\ 0.61 Re^{-0.41} \psi & (if Re > 50) \end{cases}$, Pr is Prandtl number with typical value 0.71 for gases

is assumed in this work, C_p is heat capacity of the gas mixture, G_0 is the superficial mass flux which defined as mass flow rate divided by the cross-section area of the reactor tube, ψ is catalyst shape factor with a defined value of 1 for sphere shape and 0.92 for cylindrical shape.

The Reynolds number in the porous bed is defined as: $Re = \frac{d_p G_0}{(1-\epsilon)\mu\psi}$, where d_p is the particle diameter, ϵ is the bed porosity.

Effective Mass Transfer Coefficient

The mass transfer coefficient between bulk fluid and catalyst pellets is estimated using the following equation [169]:

$$h_{eff} = J_D \frac{G_0}{\rho(Sc)^{2/3}} \text{ [m/s]} \quad (3.22)$$

Where J_D is Chilton-Colburn j-factor and $J_D = J_H$, G_0 is again the superficial mass flux, ρ is the density of the fluid, Sc is the Schmidt number with typical value 0.71 is assumed.

3.4 Mass Transfer Limitation

Weisz–Prater criterion

Weisz–Prater criterion is used to estimate the mass transfer limitation in the entrance zone. Zhao and Sun studied the high-temperature methanation mass transfer effect and found that for the Weisz-Prater module lower than 1.31 the mass transfer limitation does not significantly affect the reaction rate [170]. The Weisz-Prater module for sphere shape catalyst can be found below:

$$\Phi_{W-P} = r_j \frac{R_{cat}^2}{C_i D_{i,eff}} \quad (3.23)$$

Where Φ_{W-P} is Weisz-Prater module, r_j is the volumetric rate of reaction j , R_{cat} is the radius of catalyst particles, C_i is the mole concentration of transfer limiting species, $D_{i,eff}$ is the effective diffusivity of transfer limiting species. The entrance zone Weisz-Prater module of various temperature is shown in Figure 1.5. The dash lines represent the Weisz-Prater module of the CO₂, CO methanation and the Reverse-Water-Gas-Shift reaction corresponding to the various temperature at the entrance zone species concentration. The green line represents the adopted threshold value when the mass transfer effect become the rate limitation step [170]. The diagram indicates that at temperature lower than 850K the mass transfer is not limiting the three reaction rates. Other than the entrance zone, the mass transfer is unlikely the bottleneck.

Figure 1.5 Weisz-Prater Module of methanation reactionAt the entrance zone at various temperature. The solid green line corresponds to the mass transfer limitation criteria above which the mass transfer become the rate limiting step.

Effectiveness Factor

In situation when the temperature is higher than 850K, the mass transfer phenomena in the catalyst particle are represented by the empirical equation, Thiele modulus and effectiveness factor. The Thiele modulus is shown in the following function [171]:

$$\Phi_T = \frac{dp}{2} \sqrt{\frac{M_{CO_2} r_{CO_2}}{D_{CO_2}^{eff} \rho_{CO_2}}} \quad (3.24)$$

The effectiveness factor in terms of Thiele modulus can be found in the following equation:

$$\eta = \frac{3}{\Phi_T} \left(\frac{1}{\tanh \Phi_T} - \frac{1}{\Phi_T} \right) \quad (3.25)$$

Where Φ_T is the Thiele modulus, M_i is the mole mass of species, r is the reaction rate, D_i^{eff} is the effective diffusivity in the porous media, ρ is the density of the gas.

Chapter 4 Optimal Temperature Profile from Thermodynamics and Kinetics

Abstract

In this chapter a control volume method is proposed to calculate the theoretical optimal temperature profile along the reactor axis to yield maximum methane conversion of given length reactor and catalyst rate equations. The reaction thermodynamics is considered in the control volume integration via iteration. The deduced optimum temperature profile descends along the reactor axis at a gradient that is just enough to avoid equilibrium condition meanwhile fully utilize the kinetics of the catalyst. The temperature profile balances the dilemma between thermodynamic limitation at high temperature and kinetic loss at low temperature. Though, the temperature profile also poses challenges for the precise control of the reactor temperature, which will be addressed in the following chapter.

4.1 Introduction

In this chapter, the fixed-bed reactor temperature profile along the axis is optimized from thermodynamics and kinetics calculation. The rational of the optimization is to maximize the reactor volumetric throughput by balancing the contradiction between thermodynamic limitation and kinetics performance at different temperature. Thermodynamically, the methanation reaction benefits from low temperature whereas the kinetics performance is extremely poor at low temperature. Hence the optimum temperature profile that compromises both thermodynamics and kinetic performance is especially important and is to be done prior to other reactor-level optimization.

The CO₂ methanation reaction is a strongly exothermic process. The extreme temperature and hot-spot formation at the entrance area remains one of the challenges for methanation reactor design. The high temperature leads to the formation of carbon deposition (above 450 °C) [93, 94] and catalyst sintering (above 600 °C) [105, 172]. Besides, at high temperature, the equilibrium state constrains the upper boundary of the max attainable conversion of the reactants [93]. For example, the attainable CH₄ yield at 1 bar pressure and 400 °C is about 85%. The yield drops significantly to around 50% at 550 °C, as can be seen from Figure 4.1. The higher reaction pressure is favorable to the increase of CH₄ yield. But the rise of reaction pressure may result in uncontrollable temperature runaway behavior due to the high concentration of the reactants.

To inhibit the formation of hot-spot, many strategies have been investigated by researchers. Daniel *et al.* implemented multi-steps catalyst dilution in the reactor by mixing inert quartz fillings at the entrance zone to eliminate the hot-spot [143]. The spike shape temperature profile was successfully avoided, and the entire reactor temperature was maintained at about 300 °C [143]. Essentially, the heat generation in the entrance zone is stretched to a longer segment so that the heat can be dissipated timely. The temperature control can be external, Bremer *et al.* developed dynamics algorithm to confine the start-up period temperature peak below 750 K to avoid catalyst degradation and the CO formation [173]. The dynamics control of the cooling media temperature along reactor axis successfully prevented the formation of temperature peak, and the selectivity of CH₄ reached to almost 100% [173].

However, the low-temperature operation significantly reduces the kinetic performance and result in a poor reactor yield per unit time and volume. At a low temperature where CH₄ equilibrium

theoretical yield could reach 100%, the reaction rate is very low [145]. The remnant 10% of the conversion would take large reactor volume to convert.

Figure 4.1 Equilibrium yield of CH₄ at various pressure, H₂ : CO₂ ratio, and temperature. The higher pressure and higher hydrogen fraction are favorable to the CH₄ yield.

A practical approach is to maintain a relatively high temperature at the entrance or in the first stage of the reactor to obtain the high kinetic performance. The rear portion of the reactor should be confined at low temperature to obtain high conversion. In an optimal situation at which the reactor temperature control system is ideal, the temperature profile along the reactor axis should be following the profile of continuous descending line along the equilibrium CH₄ yield, as is illustrated by the arrows in Figure 4.2. To fully utilize the catalyst activity at high temperature, the temperature of the subsequent reactor segment is just low enough to drive the reaction to the forward direction. The descending gradient of the temperature profile is affected by feed gas space velocity, catalyst activity, the amount of catalyst loaded and the diffusion limitation.

Figure 4.2 Schematic diagram of optimal temperature profile along reactor axis derived from equilibrium condition. The profile descends along equilibrium temperature to give space for forwarding reaction.

4.2 Methods

Assumptions

1. Heat transfer model is not considered in this method. i.e., the temperature profile is assumed to be achievable by novel means of thermal management technic without occurring of over-heating or over-cooling segment.
2. The reactor is assumed to be running at plug-flow mode. The velocity field is simply calculated from ideal gas law and mass conservation equation, as discussed in Chapter 3, Momentum Equation Simplification.
3. The LHHW kinetics is assumed to be representing the true reaction rate of the catalyst.

Optimal Temperature Profile

As per discussion in the previous chapter, there exists an optimal temperature profile along reactor axis at given reaction condition that give maximum throughput and 100% CH₄ yield. A control volume method is proposed here to calculate the optimum temperature profile. The homogeneous mass transfer equation: $\rho u \frac{dw_i}{dz} = M_i \sum_j^3 \eta r_j$ is re-arranged to the form that the temperature dependent reaction rate can be determined for each iteration: $dz = \frac{\rho u dw_i}{\sum_j^3 \eta r_j M_i}$. The dz is replaced with Δl and dw_i is replaced with Δw_i in the infinitesimal segment of the reactor for the purpose of better representation. For the optimization of methanation, the major objective is to maximize the methane formation, hence the Δw_i is set to Δw_{CH_4} which represent the formation of methane in an infinitesimal segment. The methane formation rate is the summation of methane formation rates.

The differential equation in the control volume become:

$$\Delta l = \frac{\rho u \Delta w_{CH_4}}{\sum_j^3 \eta r_j M_{CH_4}} [\text{m}]. \quad (4.1)$$

Where u is the superficial velocity $u = \frac{Q}{A}$, in which Q is the volumetric flow rate and A is the effective cross-sectional area of the reactor, ρ is gas density at standard condition, Δw_{CH_4} is the mass fraction of CH₄ changes, η is the effectiveness factor to represent the mass transfer limitation in the catalyst sphere, $r(T, p)$ is the reaction rate of CH₄ formation at temperature T and partial pressure p , M_{CH_4} is the molar mass of CH₄. The correlation of temperature T at which the rate is maximized, and the accumulation of the Δl is the output of Equation 4.1.

Generally, the physical representation of the equation is the length (Δl) required to produce the infinitesimal amount of CH_4 (Δw_{CH_4}) in the given conditions of effectiveness factor (η), volume flow rate (Q), and the reaction rate ($r(T, C)$). The equation eventually established the relationship between axis location z (accumulation of Δl) and T , in which T is calculated from the maximization of reaction rate $r(T, C)$. Considering the sintering effect (start at around 923K [105]) and the rapid reaction rate at high-temperature zone, extremely high temperature is to be avoided. The 823K is selected as upper-temperature limit to all the cases to avoid the mass transfer limitation [170]. The upper-temperature limit was selected based on the Weisz-Prater criterion that was discussed in Chapter 2 [170].

The total length to get 100% CO_2 conversion is the summation of all the Δl . The schematic diagram of the control volume and the infinitesimal length (Δl) can be found in Figure 4.3.

Figure 4.3 The entrance zone starts from high-temperature to enhance the reaction rate. Although the yield of CH_4 is low, the reaction is rapid in the forward direction before it reaches to an equilibrium state. The temperature needs to be reduced just before the equilibrium reached. The temperature at the rear zone should be low enough to allow the full conversion.

Kinetics and Thermodynamics

The kinetic data is adopted from Xu and Froment's LHHW rate equations [107]. The kinetic constants and parameters can be found in Appendix A5. The rate equations are shown in the table below for quick reference.

Reaction	Balance Equation	Rate Equation
CO ₂ methanation	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O,$ $\Delta H_{298K} = -165.0 \text{ [kJ/mol]}$	$r = \frac{\frac{k_{CO_2}}{p_{H_2}^{3.5}} \left[p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_{eq,CO_2}} \right]}{\left(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2}} \right)^2}$
CO methanation	$CO + 3H_2 \leftrightarrow CH_4 + H_2O,$ $\Delta H_{298K} = -206.1 \text{ [kJ/mol]}$	$r = \frac{\frac{k_{CO}}{p_{H_2}^{2.5}} \left[p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_{eq,CO}} \right]}{\left(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2}} \right)^2}$
Water-Gas-Shift	$CO + H_2O \leftrightarrow CO_2 + H_2,$ $\Delta H_{298K} = -41.2 \text{ [kJ/mol]}$	$r = \frac{\frac{k_{WGS}}{p_{H_2}} \left[p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_{eq,WGS}} \right]}{\left(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2}} \right)^2}$

The equilibrium temperature profile is calculated from the Gibbs Energy Minimization method using the following equation:

$$nG(T, P) = \sum n_i \Delta G^0 + \sum n_i RT \ln P + \sum n_i RT \ln y_i + \sum n_i RT \ln \hat{\Phi}_i \quad (4.2)$$

Where n_i is the number of moles of species i , ΔG^0 is the standard Gibbs free energy of formation of species i , R is the universal gas constant, P is the total pressure of the gas mixture, y_i is the mole fraction of species i in the gas mixture, $\hat{\Phi}_i$ is the fugacity coefficient of species i in the gas mixture. The Gibbs free energy of formation can be calculated from JANAF table [160] or NIST Chemistry Webbook [161] for thermodynamic properties.

The Gibbs energy function is minimized in Excel using Solver plugin with GRG nonlinear optimizer. More explicitly, the objective function is minimized by adjusting variables n_i to achieve Gibbs energy minimization for the given parameters (T and P). The initial value of n_i are the stoichiometric number of the methanation reaction. All other settings of the optimizer are set to default values. The Gibbs energy of formation of all species are iterated with the change of temperature and pressure before minimization. The GRG solver is a local optimizer which may

lead to a local minimum result. The calculation is then verified with literature from Gao *et al.* [93]. The results of basic cases are matched with their work very well.

Transfer Model

The reactor is assumed as plug flow. The bulk fluid species concentration is assumed to be fully mixed within each section, i.e., no concentration gradient along the radial direction. The diffusion limitation in the reactor is represented by the effectiveness factor as inner-particle transfer model. Effectiveness factor is determined from the following equation:

$$\eta = \frac{3}{\phi^2} (\phi \coth \phi - 1) \quad (4.3)$$

where ϕ is Thiele modulus and is defined as $\phi = \sqrt{\frac{\text{reaction rate}}{\text{diffusion rate}}} = \frac{dp}{2} \sqrt{\frac{M_{CO_2} r_{CO_2}}{D_{CO_2}^{eff} \rho_{CO_2}}}$

The effective diffusivity of the species in the gas mixture and the micro-pore is calculated with the following equation:

$$D_{eff,i} = \frac{\epsilon}{\tau} \left(\frac{1}{D_{i,mix}} + \frac{1}{D_{K,i}} \right)^{-1} [\text{cm}^2/\text{s}] \quad (4.4)$$

where D_i is the binary diffusivity of species i to the mixture gas, and $D_K = \frac{d}{3} \left(\frac{8RT}{\pi M_i} \right)^{1/2} [\text{cm}^2/\text{s}]$ is the Knudsen diffusion of species i in the porous catalyst beads [174]. ϵ is the porosity and τ is the tortuosity of the catalyst beads. The simulation is solved and visualized in MATLAB.

4.3 Results and Discussion

Figure 4.4 shows the optimum temperature profile along the reactor axis for a one-meter reactor at 1 bar and 10 bar at 2000 to 6000 1/h GHSV. The plateau at the inlet zone is due to kinetic limitation at the 823K upper limit temperature. The temperature profile is descending rapidly at the front half of the reactor and majority of the reaction is taken place at this portion. The lower portion of the reactor has relative flat temperature profile due to the kinetic limitation at low concentration and low temperature. High activity catalyst should be loaded at this zone to convert the remnant amount of the reactants, or otherwise, the reactor space is almost idling at these locations.

Figure 4.4 Optimal Temperature Profile along reactor axis predicted from thermodynamic descending temperature and Xu's kinetic.

Figure 4.5 shows the relationship between CH_4 yield along the reactor axis and the temperature profile along the reactor axis. The square marker indicates the inlet of the reactor and the circle marker indicates the outlet of the reactor, and the reactor axis scale is not displayed in the figure. The vertical portion of the solid line, at both 1 bar and 10 bar cases, corresponds to the plateau portion in Figure 4.4 above, where kinetic limitation delays the temperature descending. The curved portion of the solid line shows that the optimum temperature lies at the region where is not too close or too far from the equilibrium temperature profile. The reaction encounters thermodynamic limitation if the line is too close to equilibrium line and is limited by kinetics if it is too far away from the equilibrium line. Overall, the single-pass yield for space velocity at 6000

1/h at 1 bar and 10 bar cases shown in the figure are 84.6% which corresponds to the 3.26 kW CH₄ production and 90.05% which corresponds to the 34.67 kW CH₄ production.

Figure 4.5 The optimum temperature profile and the CH₄ yield compare with equilibrium temperature profile. The vertical portion of the solid lines is limited by the kinetics of the catalyst, and the curved portion is limited by the thermodynamic equilibrium state.

The space-time yield of this reactor is reducing all along the reactor because the reaction is approaching equilibrium at the entrance location, as shown in Figure 4.6 (a). This result indicates that it is better to run the reactor at very high temperature and high space velocity to maximize the throughput of the reactor if CH₄ yield is not a concern in the subsequent application. But it will result in the low conversion of the feedstock and high cost of post-processing stage for the gas separation. Figure 4.6 (b) shows that only 20% CH₄ yield can be achieved if the maximization of

the space-time yield (STY) is the criteria. The maximization of STY is studied in a similar model and discussed in Appendix B2.

Figure 4.6 The Space-Time Yield (STY) with respect to reactor axis and CH₄ yield. (a) The Space-Time Yield (STY) corresponds to the reactor axis. The STY drops with reactor length increases. This indicates that the shorter the reactor, the better the STY performance. But the maximization of STY will lead to a poor methanation rate and expensive post-processing. (b) The STY corresponding to CH₄ yield of the outlet. The maximum STY is located at the position where CH₄ yield is about 20%.

The mole fraction of the reactants produced from the optimum temperature profile is shown in Figure 4.7. It can be found that almost all the reaction appears at the entrance zone of the reactor. The same situation was found by other researchers from the experimental work [137, 138]. The result is also tally with the phenomenon of hot-spot formation at the entrance of the reactor.

Figure 4.7 The mole fraction of the gas composition along reactor axis. Almost all the reaction appears at the entrance zone of the reactor, which leads to temperature runaway behavior if heat removal is not performed well.

Figure 4.8 shows the heat generation along the reactor axis. Most of the heat is generated at the entrance zone, which creates a challenge for the heat management in the real reactor operation. This figure also provides guidance on how much heat should be removed to keep the reactor stable. Without proper cooling, the temperature runaway will occur at the entrance zone.

Figure 4.8 The heat flux on the radial direction along the reactor axis. The axis is in log-scale for clear display because the heat generation is congested at the entrance region. (GHSV=6000 [1/h], P=1 bar)

With several parametric studies, the plot in Figure 4.9 shows that at a certain length, it is always beneficial to increase the space velocity to gain higher CH₄ production rate, as shown in Figure 4.9 (a). However, the conversion fraction of the CH₄ reduces as the increase of the gas flow rate, as shown in Figure 4.9 (b).

Figure 4.9 The effect of space velocity on CH_4 productivity and yield. (a) The relationship between CH_4 production (in terms of heating value) and GHSV. (b) The CH_4 yield and the corresponding GHSV. The reactor length is fixed at 1 meter, and the pressure is fixed at 1 bar.

The reactor throughput corresponds to the increase in pressure is shown in Figure 4.10. The plot shows that it is always beneficial to increase the reaction pressure to gain higher CH_4 production rate and higher CH_4 yield. One concern is that the heat generation is significantly increased due to the higher concentration. The yield is approaching 100% at certain high pressure but maybe involving long-chain hydrocarbon formation as in the Fischer-Tropsch reaction [126, 175]. Hence the effect of higher pressure to the methanation is not discussed here.

Figure 4.10 The parametric study on the effect of pressure. The heating value of the CH₄ produced is always increasing with the increase of pressure because of higher concentration in the gas. Also, the CH₄ yield is increasing with the increase of pressure and approaching 90% at 10 [bar].

4.4 Conclusion

In this work, a control volume method is proposed to tackle the dilemma between thermodynamic limitation and kinetic performance during the CO_2 and CO methanation process. The theoretical optimal temperature profile to produce maximum CH_4 yield for a single-stage reactor for various reaction conditions is obtained from this method. Specifically, the optimum temperature profile enables the reactor to approach to equilibrium at the entrance zone to utilize the full potential of the catalyst kinetic. The single-pass yield for the space velocity of 6000 1/h at 1 bar and 10 bar cases are 84.6% and 90.05%. The equivalent CH_4 production of the 1 bar and 10 bar cases are 3.26 kW and 34.67 kW. The parametric sensitivity study shows that the higher space velocity is beneficial to the CH_4 productivity but is detrimental to the CH_4 yield. The higher pressure will enhance the CH_4 productivity and the yield but may lead to the formation of long chain hydrocarbons.

The study reveals two possible distinct optimization strategies. One strategy, as has been discussed in this chapter, is to maximize the CH_4 yield with the descending temperature profile. The strategy is useful when the gas purity is a critical property for the subsequent applications. The other strategy is to maximize the total throughput of the reactor without concerning of the yield. In the case, the space-time-yield (STY) is maximized, and the CH_4 yield reduces to about 20%. The product mixture will majorly contain H_2 , CH_4 and some remnant CO , CO_2 . The discussion of the STY maximization is attached in Appendix B2.

The limitation of this work could be the requirement of high heat removal rate to maintain the temperature profile at the reactor entrance. If not well controlled, the temperature runaway may happen. It could be easier to obtain the temperature profile by separating the reactor into multi-stages and uses different cooling strategies to remove the heat. The realistic operation of the reactor is studied in the next chapter where heat and mass transfer models are implemented to validate the optimum operation window and to obtain the maximum yield of the product.

Chapter 5 Fixed-bed Reactor Optimization

Abstract

In this chapter, a 1-D, single-stage reactor model that contains heat and mass transfer phenomena is implemented to validate the effectiveness of the optimum temperature profile determined in the previous chapter. The optimization model utilizes the inlet temperature and heat transfer coefficient as the control variables to adapt the optimum temperature profile. The parametric study results show that the inlet temperature and heat transfer coefficient are effective in controlling the reactor temperature. The best-adapted case in the parametric study almost reaches the thermodynamic prediction, about 2.5% less than the theoretical maximum yield is achieved. A dimensionless number is then proposed to generalize the thermal management technic for the indication of optimal working conditions. The dimensionless number is also applicable to other strong exothermic reactions.

5.1 Introduction

The CO₂ methanation reaction, also known as Sabatier reaction, is a strongly exothermic process. The heat generation creates a lot of issues, such as reactor temperature runaway, carbon fouling, and catalysts deactivation. In the laboratory scale, researchers proposed structured reactors such as micro-channel or multi-channel reactors [139, 140], membrane reactor [145, 146] to tackle the problem of temperature runaway in the reactor. The temperature control of these reactors is rather rigorous and accurate, but the delicate structure of the reactors may not easy to scale up. The various types of tubular reactors and packed-bed loaded catalyst are more suitable for large-scale implementation. Tubular reactors are simply cooled internally or externally with cooling jackets, channels [142-144], or simply heat conducting rods [176] or a combination of the above methods. In the cooling channels, various coolants are applied to conduct the heat [140]. The local hot-spot among catalyst particles are controlled by means of catalyst dilution and structured catalysts, by which the heat is either prevented from generation or conducted out effectively [143, 149, 151-153].

However, the above means of thermal management are mainly for hot-spot elimination. The overall productivity of the reactor may not be optimized in these situations. Also, the modification of the reactor shape and catalyst loading are not adaptable to the dynamic change of the operation condition and feed gas compositions. The studies of the adjustable parameters are more practical for the realistic reactor control. Kiewidt and Thöming conducted the optimization of the single-stage reactor simulation and achieved the optimum temperature profile of CO₂ methanation in a single-pass operation based on Semenov number adjustment [144]. They found the Semenov can be an effective dimensionless number to balance the kinetic performance and thermodynamic limitation of the exothermic process. Their study indicates that for a given length of the reactor (represented by Da_I), there exist optimal thermal conductivity of the reactor wall (represented by Se number) to maximize the productivity of the reactor [144]. The optimum Se number corresponds to a set of parameters that result to the optimum temperature profile along the reactor axis [144]. The inlet temperature could be an effective variable in controlling the CO₂ conversion. The parametric study from Chein *et al.* indicates that there exist optimal inlet temperature that maximizes the CO₂ conversion while other conditions remain constant [177].

In this chapter, a one-dimensional heterogeneous model is implemented to validate the feasibility of our previous temperature profile in the optimizing the reactor yield. The previous optimal temperature profile is shown in Figure 5.1 for reference. The goal of this chapter is first to adapt the modeling temperature to the optimum temperature profile and second to achieve the maximization of the product yield. Among all the parameters, the inlet temperature and heat transfer coefficient are adopted as the control variables to realize the thermal management in a single-stage reactor. Further, the combination of the two control variables is generalized to a dimensionless number called cooling modulus as the universal optimization indicator.

Figure 5.1 Optimal temperature profile corresponding to CH_4 yield in the single-stage non-isothermal reactor (1-meter length) comparison with equilibrium temperature-yield profile.

5.2 Methods

Assumptions

The assumptions made in the model are generally based on order-of-magnitude approximation. For instance, the bulk flow in the porous media is neglected in the solid phase transfer equation for its minor effect. The turbulence flow in the fixed-bed is simplified as plug-flow since conservation law is always applicable. Intuitively, the chemical reaction is majorly occurred on the catalyst surface (i.e., the solid phase) rather than in the free flow gas. Based on the above justifications, the following assumptions are applied to the model.

1. In the solid phase, the major transfer mechanism is diffusion. The velocity terms are neglected in the solid phase balance equations.
2. The reactor heat loss is assumed to be conducted by the gas phase fluid. Hence the heat sink term is within the heat transfer balance equation of the gas phase.
3. The reactor is assumed to be running at plug-flow mode. The velocity field is simply calculated from ideal gas law and mass conservation equation, as discussed in Chapter 3, Momentum Equation Simplification.
4. The chemical reaction is happened on the catalyst surface only, so the reaction source only exists on the solid phase.

Transfer Model

Based on the above assumptions, the one-dimensional heterogeneous model was established as follow:

The mass balance equation in the gas phase and solid phase:

$$\rho_{ave} u \frac{\partial w_{g,i}}{\partial z} = \rho_{ave} D_i \left(\frac{\partial^2 w_{s,i}}{\partial z^2} \right) + \rho_{ave} h_{m,i} S_{cat} (w_{s,i} - w_{g,i}) \quad (5.1)$$

$$0 = \rho_{ave} h_{m,i} S_{cat} (w_{g,i} - w_{s,i}) + M_i \sum \eta_j r_j \quad (5.2)$$

Where $\rho_{ave} = \frac{p\bar{M}}{RT}$ is the average density of the gas mixture, which is derived from ideal gas law and constant pressure assumption and is temperature dependent. In the ρ_{ave} equation, $\bar{M}$ is the average mole mass of the gas mixture based on mole fraction. The term u is the superficial velocity of the gas mixture in the fixed-bed. To follow the mass conservation, $\rho_{ave} \times u$ is constant and equal to the entrance mass flux G_0 . The term $w_{g,i}$ and $w_{s,i}$ are the mass fraction of the specie i in the gas phase and solid phase. The term $h_{m,i}$ is the mass transfer coefficient, S_{cat} is the surface area of catalyst bead per unit volume. D_i is the effective mass diffusivity. The η_j and r_j are the effectiveness factor and reaction rate of rate j .

The energy balance equation in the gas phase and solid phase:

$$u \rho_{ave} C_{p,mix} \frac{\partial T}{\partial z} = h S_{cat} (T_s - T_g) + h_{wall} A_V (T_c - T_g) \quad (5.3)$$

$$0 = k \left(\frac{\partial^2 T_s}{\partial z^2} \right) + h S_{cat} (T_g - T_s) + \sum (-\Delta H) \eta_j r_j \quad (5.4)$$

Where $C_{p,mix}$ is the heat capacity of the gas mixture. The term h is the heat transfer coefficient of the fluid. T_g , T_s and T_c are the temperature in the gas phase, solid phase and cooling temperature. The term k is the thermal conductivity of the catalyst particle. The term h_{wall} is the effective heat transfer coefficient between the reactor wall and the cooling system. The term A_V is the surface area of the reactor outer surface per unit volume. The control volume model and the important transfer parameters of the above equations are illustrated in Figure 5.2.

Figure 5.2 Illustration of control volume in the heterogeneous transfer model and the list of critical transfer parameters.

The mass transfer coefficient between bulk fluid and the catalyst surface is shown below:

$$h_{eff} = J_D \frac{G_0}{\rho (Sc)^{2/3}} \text{ [m/s]} \quad (5.5)$$

The heat transfer coefficient between bulk fluid and catalyst surface is shown below:

$$h_{heat} = J_H \frac{c_p G_0}{Pr^{2/3}} \text{ [W/m}^2\text{/K]} \quad (5.6)$$

For the pressure distribution along the reactor, the pressure drop due to the friction of the fixed-bed was neglected. There is no momentum conservation equation for simplifying purpose. Instead, the mass conservation was obeyed as follow:

$$\frac{dG_0}{dz} = 0, \text{ or } \rho \times u = \text{constant} \quad (5.7)$$

Where G_0 is the mass flow rate per unit cross-sectional area in the unit of $[\text{kg/m}^2\text{/s}]$.

The combination of ideal gas law and mass conversation law gives the pressure dependent superficial velocity:

$$u = \frac{G_0 \cdot RT}{PM_{ave}} \text{ [m/s]} \quad (5.8)$$

Boundary conditions:

For the solid phase, there is no source and flux term at the inlet and outlet position. In the infinitesimal length of the reactor segment before the inlet and beyond the outlet of the reactor, the temperature and mass fraction remain constant, i.e., zero gradient, as shown:

$$\frac{\partial T_s}{\partial z} = 0, \quad \frac{\partial w_s}{\partial z} = 0 \quad (5.9)$$

For the gas phase inlet heat and mass transfer boundary conditions equal to the inlet conditions, i.e., the inlet gas temperature and the inlet gas mass fraction:

$$T = T_{inlet}, \quad w = w_{i,inlet} \quad (5.10)$$

For the gas phase outlet, no source and flux applied result to zero gradient boundary conditions:

$$\frac{\partial T_g}{\partial z} = 0, \quad \frac{\partial w_g}{\partial z} = 0 \quad (5.11)$$

For the reactor outer surface boundary condition, the cooling term (heat sink) $h_{wall}A_V(T_c - T_g)$ is already integrated in the balance equation because the one-dimensional system has no outer surface.

Kinetic

To keep the consistency from our previous thermodynamic calculation, the kinetic data is again taken from Xu and Froment's LHHW rate equations [107]. The detail kinetic constants and parameters can be found in Appendix A5. It has been found by researchers that the kinetic rates of Xu and Froment's work are underestimating the CO₂ methanation at low temperature [114, 115, 176]. Indeed, the catalyst activity is affected by firstly the catalytic metal, i.e., Nickle or Ruthenium, and secondly the loading amount of the metal (Xu and Froment used 15.2% Ni-Mg-Al₂O₃ catalyst), and thirdly the micro-morphological aspects of the metal particle and the support materials. Experimental adaptation of the kinetic rate equation is usually necessary for the currently available commercial catalyst. But within this thesis, the parameters from Xu and Froment are adopted for consistency.

Table 5.1 Kinetic rate equation from Xu and Froment

Reaction	Balance Equation	Rate Equation
CO ₂ methanation	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O,$ $\Delta H_{298K} = -165.0 \text{ [kJ/mol]}$	$r = \frac{\frac{k_{CO_2}}{p_{H_2}^{3.5}} \left[p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_{eq,CO_2}} \right]}{\left(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2}} \right)^2}$
CO methanation	$CO + 3H_2 \leftrightarrow CH_4 + H_2O,$ $\Delta H_{298K} = -206.1 \text{ [kJ/mol]}$	$r = \frac{\frac{k_{CO}}{p_{H_2}^{2.5}} \left[p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_{eq,CO}} \right]}{\left(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2}} \right)^2}$
Water-Gas-Shift	$CO + H_2O \leftrightarrow CO_2 + H_2,$ $\Delta H_{298K} = -41.2 \text{ [kJ/mol]}$	$r = \frac{\frac{k_{WGS}}{p_{H_2}} \left[p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_{eq,WGS}} \right]}{\left(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2}} \right)^2}$

Lump-sum Approximation

To generalize the effect of the inlet temperature T_{in} and the heat transfer coefficient h_{wall} , an approximated lump-sum model is proposed to combine T_{in} and h_{wall} into one parameter called cooling modulus. The modulus is used to approximate the thermal accumulation within the reactor as an indicator of reactor extinguishment and super-heating.

There are two basic assumptions to make to establish the lump-sum model. Firstly, the model assumed that the heat removal of the reactor is mainly by the reactor wall convection, whereas the amount of heat carried out by the outflow is negligible. Secondly, the model also assumed that the heat generation is approximately affected by the inlet temperature, as illustrated in Figure 5.3.

Lump-sum Approximation

Figure 5.3 The schematic of the lump-sum model For the consideration of thermal accumulation in the reactor. The model assumes that the heat removal of the reactor is mainly by the reactor wall conduction, whereas the amount of heat carried out by the outflow is negligible. The model also assumes that the heat generation is approximately affected by the inlet temperature.

Based on the above discussion and assumptions, the cooling modulus is defined as follow:

$$\begin{aligned} \text{Cooling Modulus} &= \frac{\text{Cooling Rate}}{\text{Heating Rate}} = \frac{\Delta T \cdot h_{\text{wall}} \cdot A_v}{r \cdot (-\Delta H)} = \frac{\Delta T \cdot h_{\text{wall}} \cdot (2/Rr)}{r(T_{\text{in}}, p_{i,\text{in}}) \cdot (-\Delta H)} \\ &\equiv \frac{[W/m^3]}{[W/m^3]} \end{aligned} \quad (5.12)$$

Where the ΔT is the temperature difference between the reactor wall and the coolant, h_{wall} is the heat transfer coefficient of the reactor wall, $r(T_{\text{in}}, C_{i,\text{in}})$ is the reaction rate at the entrance of the reactor determined by the inlet temperature and inlet reactant partial pressure, Rr is the reactor radius. For the definition of ΔT , the approximate representation of the temperature difference is assumed to be $(T_{\text{max,eq}} - T_c)$, in which $T_{\text{max,eq}} = 823K$, and $T_c = 473K$.

Transfer Model Validation

The heterogeneous transfer model is validated by the elaborate experimental data from Ducamp *et al* [176]. Figure 5.4 shows that the axial temperature profile of the model is fitted very well with the experimental results at the same working conditions. The inlet temperature of the compared three cases are 498K, 523K, and 548K. The reaction pressure is 4 bar, and the gas composition is $\text{H}_2:\text{CO}_2:\text{Ar}=4:1:10$. The metal loading of the experimental catalyst is 14~17% commercial catalyst with BET-surface area of $150 \text{ m}^2/\text{g}$. The root-mean-square error of the curve fitting at 498K, 523K and 548K are 35.7, 28.5 and 21.5, respectively.

Figure 5.4 Model validation of One-dimensional heterogeneous model with experimental data.[176, 178] The outlet CO_2 conversion of 86.9%, 89.5%, 89.4% of the model is slightly higher than the experimental results of 83% to 86% at the same situation probably possibly because of the kinetic modification and the radial direction heat transfer of the tubular reactor.

5.3 Results and Discussion

The effect of inlet temperature and heat transfer coefficient of the reactor wall is investigated in the heat and mass transfer model. Other parameters used in the model are listed in Table 5.2.

Table 5.2 Parameters in the Temperature Optimization Modeling

Parameters	Value	Unit
Reactor Diameter	2.13	[cm]
Reactor Length	1	[m]
Reactor Volume	0.358	[Liter]
Catalyst Density	1370	[kg/m ³]
Catalyst Diameter	1	[mm]
Bed Porosity	0.4	1
Bed Density	$1370 \times (1 - 0.4) = 822$	[kg/m ³]
H ₂ : CO ₂ ratio	4	1
Space Velocity, GHSV	2000	[1/h]
Inlet Temperature, T_{in}	250~370	[°C]
Cooling Temperature, T_c	250	[°C]
Pressure	1	[bar]
Heat Transfer Coefficient	6~36	[W/m ² /K]

Figure 5.5 shows the CH₄ yield corresponding to the inlet temperature T_{in} and the heat transfer coefficient h_{wall} of the reactor wall. In Figure 5.5 (a) the effect of heat transfer coefficient h_{wall} to the yield of the outlet CH₄ vary with the inlet temperature. For the low inlet temperature, for example 573K shown in the figure in the blue dotted line with ‘plus’ marker, the high h_{wall} will cause the extinguishment of the reactor. The phenomena are not observed in the high inlet temperature in the study range. Instead, there exists optimal h_{wall} to maximize the yield of the reactor. For instance, the CH₄ yield is maximized at $h_{wall}=22$ [W/m²/K] when $T_{inlet}=613$ K. The

increase of the h_{wall} from 5 to 20 [W/m²/K] is favorable for the yield due to the elimination of thermodynamic limitation. But the further increase of the h_{wall} is not beneficial to the product yield, probably attributed to the rapid chill down of the reactor, especially at the rear end of the reactor.

Figure 5.5 (b) shows that if the reactor is successfully ignited the CH₄ yield is not sensitive to the inlet temperature. The blue dotted line with ‘plus’ marker in Figure 5.5 (b) shows an over-heating case where the yield is restricted by the equilibrium state. For the boundary of reactor extinguishment and ignition, catalyst performance can be a critical factor. The ignition temperature of commercial Ni-based (loading from 14~17%) was found to be as low as 500K [176]. But in this study, the catalyst ignition temperature is around 550K due to the underestimating of the reaction rate at low temperature [114, 115, 176].

Figure 5.5 Parametric study on the effect of inlet temperature and cooling rate. (a) The relationship between reactor outlet yield and heat transfer coefficient of the wall. The blue dash line with plus marker shows a case of over-cooling at which the reaction did not reach to equilibrium throughout the reactor. (b) The relationship between reactor outlet yield and the inlet temperature. The blue dash line with plus marker shows an over-heating situation of which equilibrium state restricted the reactor yield.

Figure 5.6 shows the best adapted temperature profile (green dash-dot line) corresponding to the reactor axis and CH₄ yield. The figure also shows the equilibrium (solid red line) and optimal (black solid line) temperature profiles as a reference. Figure 5.6 (a) shows that at almost the entire

reactor the adapted temperature is slightly higher than the optimum temperature profile. Near the outlet, the adapted temperature is dropped down below the optimum temperature. The figure indicates that the control of T_{in} and h_{wall} is not sufficient to achieve the perfect adaptation to the optimum temperature profile. Figure 5.6 (b) shows that the best adapted temperature profile is almost following along the equilibrium line until the outlet. The outlet CH_4 yield of 86.8% is very close to the optimum yield of 89.3%, which indicates that the temperature control method is effective, even though not perfect. The root mean square error between the best adapted profile and the optimum temperature profile is 65.5. To achieve better performance, the multi-steps cooling strategy could be feasible. For example, a smaller value of h_{wall} near the reactor outlet may helpful to increase the yield. Another method could be the increase of the catalyst loading at the downstream of the reactor to enhance the catalytic activity.

Figure 5.6 The best adapted temperature profile corresponding to reactor axis and CH_4 yield and compare with equilibrium (blue dash line) and optimal (solid black line) conditions.

As a comparison, Figure 5.7 shows the temperature profile of the reactor extinguishment situation and reactor super-heating situation. The inlet temperatures of both cases are 573K but vary on the heat transfer coefficient. The former case yield is restricted by the poor kinetic performance, and

the latter case yield is limited by the equilibrium state due to the high temperature at the outlet. In Figure 5.7 (a1), the cooling rate h_{wall} value of 24 [W/m²/K] seems too high to ignite the reaction. The corresponding outlet CH₄ yield is only 40%. On the other hand, the (a2) shows the low h_{wall} value that failed to remove the heat in the reactor timely and result to a high outlet temperature and low yield. Even so, the corresponding outlet yield of the super-heating situation reached 70%, which imply that the prime optimization goal should be the avoidance of reactor extinguishment.

Figure 5.7 The temperature profile of the reactor extinguishment situation and reactor super-heating situation. At the extinguishment situation: (a1) shows that the temperature along axis did not reach to an optimal temperature profile. (b1) shows that the reaction did not reach to equilibrium and result to a low CH₄ yield. At the super-heating situation: (a2) shows that the temperature along the axis is much higher than the optimum temperature. (b2) shows that the temperature hit the limitation of the equilibrium state.

Figure 5.8 shows the effect of cooling modulus and heat transfer coefficient on the CH₄ yield. It can be found in (a) that the cooling modulus is an effective parameter to discriminate the reactor ignition and extinguishment situations. The boundary value cooling modulus > 7 represents a

group of a combination of T_{in} and h_{wall} that lead to the extinguishment of the reactor (yield <50%). For the value below 7, however, the effect of cooling modulus to the yield is not consistent. Rather, the effect of cooling modulus is slightly dependent on T_{in} . This indicate that the cooling modulus is not a very effective indicator once the reactor is ignited successfully.

At this region of operation, the h_{wall} is a more effective parameter for the optimization of the yield, as shown in the Figure 5.8(b) the marker congested zone. The effect of h_{wall} at this zone is not sensitive to the inlet temperature. The phenomenon is probably because of the strong exothermic process is hard to quench once start-up.

Figure 5.8 The effect of cooling modulus and heat transfer coefficient on the outlet yield at various temperature. (a) The cooling modulus is a good indicator of reactor ignition and extinguishment. (b) The h_{wall} can be a good optimization variable but is not able to predict the ignition combination of T_{in} and h_{wall} .

Figure 5.9 shows the gas composition along the reactor axis of the best-adapted case in the parametric study. At inlet temperature 633 K and heat transfer coefficient of 22 [W/m²/K], the reactor generates a yield of 86.8%. As a reference, the optimum temperature profile at the same situation generates a yield of 89.3%. The gas composition shows that the reaction mainly occurs at the entrance of the reactor.

Figure 5.9 The mole fraction of the gas composition along reactor axis. ($P=1$ bar, $T_{in}=633K$, $h_{wall}=22$ [W/m²/K], $GHSV=2000$ 1/h. The outlet yield=86.8%, Optimal yield=89.3%).

5.4 Conclusion

In this chapter, a one-dimensional heterogeneous model was built to investigate the heat and mass transfer phenomena in the methanation reactor — the model chooses inlet temperature and the heat transfer coefficient as the control variables to adapt the temperature to the optimum temperature profile that was calculated from the previous chapter. The best-adapted temperature profile achieved CH₄ yield of 86.8% which is very close to the theoretical optimal yield of 89.3%. The performance loss may come from the over-cooling segment near the outlet of the reactor.

The flat trend of the yield plot upon successful ignition implies that the prime goal of the reactor optimization is the prevention of extinguishment rather than quenching down the reactor. A dimensionless number called cooling modulus was proposed as the indicator to discriminate the ignition and extinguishment situations. The cooling modulus should not exceed 7 to avoid the extinguishment of the reactor. The cooling modulus is useful in determining the combination of T_{in} and h_{wall} that will maintain the high yield of the reactor.

Overall, the inlet temperature and heat transfer coefficient are the most convenient and adaptable means to optimize the reactor performance from the realistic point of view. But the two parameters are not sufficient to achieve perfect fitting to the optimum temperature profile. At the inlet, it is very hard to gain immediate equilibrium without the risk of over-heating behavior. At the rear portion of the reactor, the temperature drops to so low that the kinetics is limiting the reactor yield.

To achieve better performance, the multi-steps cooling strategy could be useful to maintain the kinetic performance to a longer extent. Another possible method could be the increase of the catalyst loading at the downstream of the reactor to enhance the catalytic activity. Whichever technic is taken, the exothermic temperature control is a complicated process and requires a dynamic method to fit the various operation conditions.

Chapter 6 The Scale-Up of Power-to-Gas Technology

Abstract

Power-to-Gas (PtG) is a grid-scale energy storage technology by which electricity is converted into gas fuel as an energy carrier. PtG utilizes surplus renewable electricity to generate hydrogen from Solid-Oxide-Cell, and the hydrogen is then combined with CO₂ in the Sabatier process to produce the methane. The transportation of methane is mature and energy-efficient within the existing natural gas pipeline or town gas network. Additionally, it is ideal to make use of the reverse function of SOC, the Solid-Oxide-Fuel-Cell, to generate electricity when the grid is weak in power. This study estimated the cost of building a hypothetical 100-MW PtG power plant with energy storage and power generation capabilities. The emphasis is on the effects of SOC cost, fuel cost and capacity factor to the Levelized Cost of Energy of the PtG plant. The net present value of the plant is analyzed to estimate the lowest affordable contract price to secure a positive present value. Besides, the plant payback period and CO₂ emission are estimated.

6.1 Introduction

Intermittency remains one of the major obstacles for the grid connection of renewable energy. The excess electricity produced from the fluctuating power sources, if not stored, is curtailed to stabilize the electricity grid [179, 180]. The large-scale (in the scale of GWh or TWh), seasonal storage of renewable electricity is vital to the full utilization and stabilization of renewable power sources. Among the existing energy storage technologies, pumped-hydro energy storage systems are the most prevalent [21]. The surplus electricity is stored in the gravitational energy of water. The water is released for power generation in the turbine when the peak demand is arrived. But the system is only suitable for certain geographical locations where large water reservoir exists [181]. Batteries, with high round-trip efficiency, can provide prompt response to the grid electricity fluctuation. However, at current stage, batteries cannot store enough energy in reasonably sized facilities or at an affordable cost to balance the seasonal fluctuation. Power-to-Gas (PtG) technology that converts surplus electricity into hydrogen or methane could be a feasible method to mitigate the intermittency dilemma [33, 182]. The first step in the PtG process is to produce hydrogen from water and renewable power via electrolysis. The produced hydrogen can either be used directly or consumed in the second stage to produce methane. The synthetic hydrogen/methane can be stored over long periods of time or transported to other places.

The main disadvantage of the current PtG project is the high cost. The investment of the PtG facilities is capital intensive, the facilities need to be fully utilized to recover the capital expenditure (CAPEX). However, the PtG capacity factor is highly affected by the intermittency supply of the renewable power. For example, the solar and wind power capacity factor all over the world ranges from 3% to 30% [1]. This low utilization rate leads to the high levelized cost of the synthetic gases. The solid oxide cell based PtG could be used as power generation plant (via the fuel cell mode) during the trough periods of renewable power. Eventually the PtG plant is a dual function facility used for energy storage or power generation at different periods. Further feasibility study needs to be conducted with realistic grid management data as input.

A simple illustration of the PtG plant is shown in Figure 1.3. Briefly, the PtG plant consists of energy storage and power generation processes. In the energy storage process, the plant absorbs surplus electricity from the grid or off-grid renewable power to produce hydrogen or methane subsequently. The produced gas fuels can be either stored, sold or converted to other fuel, depends

on the infrastructure availability. In the power generation process, the plant generates electricity with stored hydrogen or methane (from gas grid) when the power grid is short of electricity. For simplicity, the CO₂ storage and water recycling paths are not shown in the figure.

In the technology and economic aspects, the PtG process is comprehensively reviewed by the following works [33, 123, 182-184]. A summary of these works is shown here: The pilot-scale PtG plants have been established in Japan, Germany, Denmark and Switzerland [182]. Currently, the cheapest and mature electrolyzer is the alkaline type, and PEM electrolyzer could be the near future option, whereas solid oxide electrolysis is still in the emerging stage [123]. The PtG facilities show the potential to improve the stability of the grid while connecting with renewable power sources. However, the market mechanism is not clear [183, 184]. The PtG is not economically efficiency to recover the high CAPEX and OPEX of the plant [184]. The cost of synthesized methane is still several times higher than that of conventional natural gas [33]. The high cost could be attributed to the low utilization rate, the generation costs of H₂ and methane were found to strongly depend on the capacity factor and the electricity price [123]. Overall, to commercialize the PtG technology technical and economic barriers must be overcome.

In the system level, the overall efficiency of PtG plant has been investigated by modeling studies. It was found that the electrical efficiency of power to methane ranges from 71.64% to 81.08%, varies with thermal management strategies [185]. The efficiency of SOEC-based, high-temperature methanation process integrated with effective thermal reuse system can reach to 86% [186]. On the other hand, rather than water electrolysis to generate pure hydrogen, the direct co-electrolysis of water and CO₂ to produce syngas (mainly CO+H₂) were investigated as CO₂ mitigation solution [187, 188]. The SOEC-based co-electrolysis converted approximately 67% of the CO₂ into syngas [187]. During the process, the reverse water gas shift reaction and the co-electrolysis are both contributing to the CO production [188, 189]. The syngas produced from co-electrolysis can be further converted to methane [190], methanol [191] and Dimethyl Ether (DME) [192] in the subsequent chemical reactor to obtain higher economic values.

The electrolyzer is the key bridge between electricity and chemical fuel. Currently, the Alkaline Electrolysis Cells (AEC), Polymer Exchange Membrane Electrolysis Cells (PEMEC), and Solid Oxide Electrolysis Cells (SOEC) are the most attractive future hydrogen generation technologies [193, 194]. Among the three technologies, only SOC is suitable for seamless switch between

electrolysis and power generation mode without obvious degradation of the material, which is adaptable to the intermittent supplied energy sources [195, 196]. Furthermore, the electrical-to-hydrogen efficiency of SOEC can be higher than 100% in the endothermic operation model [195, 197-199]. The SOFC can be fed with H₂, CO, syngas, biogas, and even with hydrocarbon fuels directly [200-202]. The low efficient fuel purification and separation processes can be avoided. The AEC and PEMEC are not reversible to be power generation facilities. Besides, the AFC and PEMFC are sensitive to the impurities in the feed gas, especially the CO and CO₂ that produced from methane reforming [203, 204]. The purification and separation process, on the other hand, will significantly reduce the hydrogen utilization rate, the hydrogen recovery rate in the PSA is only 50% to satisfy the demand of hydrogen purity of 99.99% for low-temperature fuel cell usages [205, 206]. Comparison of main characteristics of AEC, PEMEC, and SOEC can be summarised in Table 1.

Table 6.1 Characteristics of AEC/FC, PEMEC/FC, and SOEC/FC systems.

	AEC/FC	PEMEC/FC	SOEC/FC
Operating Temperature (°C)	60~80	50~80	650~1000
Pressure (bar)	<30	<30	<25
Capital Cost (€ /kW)	1000~1200	1860~2320	>2000
PtG (H ₂) efficiency	60% [207]	60% [208]	95% [197, 198]
PtG (CH ₄) efficiency	48%*	48%*	74%*
GtP (from H ₂) efficiency	60% [203, 208]	60% [204]	60% [209]
GtP (from CH ₄) efficiency	24% ^{&§}	24% ^{&§}	50%
PtP round-trip efficiency	36% ⁺	36% ⁺	57% ⁺

* Methanation efficiency 78%, based on HHV [123]. [&] Methane reforming efficiency 80% [210]. [§] Purification and PSA recovery rate 50% [205, 206]. ⁺ Power to H₂ combine with H₂ to Power, storage losses neglected

This study evaluates the capital and operational cost of building a hypothetical 100-MW PtG plant. The plant is assumed to be constructed in Singapore, in which the country is planning to raise its solar power to 1 GW in the coming decades to fulfill the commitment of CO₂ reduction of 36% by 2030 [211]. The evaluation is based on parameters from similar technologies or reasonable assumptions. The emphasis is on establishing the relationship between Levelized Cost of Energy

(LCOE) of the PtG plant with respect to several factors, such as SOC cost, fuel price and power generation capacity factor. Three different PtG schemes with various energy storage intermediates are considered in this study. In the first scheme, excess power is converted to hydrogen and injected into town gas pipeline directly (Power-to-H₂). In the second scheme, additional methanation process is performed to increase the volumetric heating value of the product, and the produced gas is sold to the town gas system (Power-to-CH₄). The third scheme considers hydrogen storage in the plant, and the hydrogen is later converted back to electricity when needed (Power-to-Power). The three PtG schemes are illustrated in Figure 6.1. To fully utilize the facility and the investment, the plants would run on the power generation mode when electricity is needed. A sensitivity study on the major variables is conducted to test the effectiveness of these factors.

Figure 6.1 Three different Power-to-Gas schemes.

6.2 Methodology

Assumptions

For the economic aspects, the existing commercial technologies are taken as references for the cost estimation. The Solid-Oxide-Cell (SOC) cost is referenced from the following reports [212-214]. The estimated mass production cost of the SOC system is in the range of 1000 to 2000 US\$/kW by 2020 [212, 213]. The cost of the methanation plant is estimated from the commercial Coal-to-SNG plant from literature [215]. Specifically, the cost of unnecessary components in the Coal-to-SNG plant is subtracted from the total cost, which leads to a cost of 270 US\$/kW [215]. The estimation is tally with the approximation range of 210~444 US\$/kW methanation reactor from the work of Jens *et al.* [216]. The similar ranges of cost estimation are reported by other biomass-SNG and coal-SNG plant studies [217, 218]. The SOC and Methanation system unit cost is then multiplied the capacity of 100-MW to obtain the total cost of the Power-to-Gas plant. The land lease cost, infrastructure and development cost, annual fixed operating cost and variable cost of the PtG plant are taken from the reported 400-MW Natural Gas power plant [24]. Finally, the discount rate of the capital is assumed to be 7.13% over 20 years [24]. The capital is assumed to be injected into the project at the time zero, which is the worst-case scenario.

The energy input of the energy storage process is taken from local solar power. The local solar power is assumed to have a much larger capacity than 100-MW so that the PtG plant can be fully used. However, the utilization of solar power is limited to its local environmental and geographical factors, the peak sun hour on average in Singapore is around 4.55 hours per day, which approximately equivalent to a capacity factor of 19% [219, 220]. For the power generation process, the Energy Market Authority (EMA) estimated averaged capacity factor of power plants in Singapore is ranged from 58.5% to 63.4% for the period of 2019~2020 [24]. As the PtG power plant that is running on both energy storage and power generation mode, there may exist overlapping between energy storage and power generation period due to the fluctuating demand in the power grid. To simply the calculation, the capacity factors of 10% and 50% are assumed for the energy storage and the power generation processes, respectively. The gas pipeline capacity is assumed to be large enough to store and retrieve sufficient CH₄ during energy storage and power generation periods. During the energy storage process, the SOEC electrolysis efficiency is

assumed to be 95% [197, 198]. In the fuel cell mode, the SOFC efficiency (including the internal methane reforming and gas recirculating) is assumed to be 50% [221].

Economic Calculations

The capital cost is annualized according to the discount rate and the year of the loan. The Levelized Cost of Electricity (LCOE) is then calculated from the annualized capital cost and the operation cost divided by the energy produced (including the electricity and the gases) of the year. Variable cost and fuel cost are directly added to the LCOE. The annualized cost A and the LCOE of the plant are computed based on equations (6.1) and (6.2) [222]:

$$A = C \times CRF + F_{O\&M} + (V_{O\&M} + C_{fuel} \times H_{fuel}) \times 8760 C_f \quad (6.1)$$

$$LCOE = \frac{[(C \times CRF) + F_{O\&M}]}{8760 \times C_f} + V_{O\&M} + (C_{fuel} \times H_{fuel}) \quad (6.2)$$

Where C is the capital cost of the plant [US\$], CRF is the capital recovery factor that converts the present value into a stream of equal annual payments over the period of t , which defined as $[i(1+i)^t]/[(1+i)^t - 1]$, i is the discount rate of the capital, $F_{O\&M}$ is the fixed operating and maintenance cost, $V_{O\&M}$ is the variable operating and maintenance cost [US\$/MWh], C_{fuel} is the cost of the fuel, and H_{fuel} is the heat rate of the fuel [Btu/kWh], C_f is the capacity factor.

To evaluate the effect of electricity selling price on the profitability of the plant, the net present value (NPV) is calculated. The NPV is calculated from equation (6.3) [223]:

$$NPV = NCF \times PW - C \quad (6.3)$$

Where NPV is net present value, NCF is the net cash flow, PW is the present worth factor that convert the discrete payments of the future to present value over the period of t , which defined as $[(1+i)^t - 1]/[i(1+i)^t]$, i is the annual discount rate of the capital, C is the capital cost of the plant at time zero. The cashflow is monthly based, so the annual discount rate is converted to monthly rate using this equation: $i_{month} = (1+i)^{1/12} - 1$.

The cumulative cash flow is calculated from equation (6.4):

$$C_{n+1} = C_n \times (1+i) - A_{outflow} + A_{inflow} \quad (6.4)$$

Where C_n and C_{n+1} are the remaining of the acquisition cost of the plant at period n and $n+1$, A_{out} and A_{in} are the annual cash flow out and cash flow in.

All the algebra equations are solved and visualized in MATLAB.

Parameters

Based on the discussion in the Assumption section of this chapter, a summary of parameters is listed in Table 6.2. Sensitivity studies are conducted to evaluate the effect of key variables.

Table 6.2 Summary of Parameters for Economic Feasibility Study

Names	Value	Names	Value
SOEC electrical efficiency	95% [197, 198, 219]	Discounted rate, period	7.13%, 20 years [24]
SOFC electrical efficiency	50% [221]	Plant lifespan	20 years
Methanation thermal efficiency	78% [185]	NG unit price	7.5 US\$/GJ
Natural Gas plant efficiency	48% [24]	NG HHV	55.5 MJ/kg
Energy storage capacity factor ^{&}	10% [24, 219, 220]	NG plant cost	890 US\$/kW [24]
Power generation capacity factor ^{&}	50% [24, 219, 220]	Heat rate of NG plant	7108.7 Btu/kWh
Land lease and preparation cost*	14.3 million US\$ [24]	Surplus renewable electricity price	30 US\$/MWh [219]
Owner's cost*	17.0 million US\$ [24]	Annual fixed operating cost	3.8 million US\$/year [24]
Grid connection cost *	17.2 million US\$ [24]	Plant variable cost	5.7 US\$/MWh [24]
Methanation system cost	270 US\$/kW [215, 216]	Electricity contract price	130 US\$/MWh [224]
SOC system cost	1500 US\$/kW [212, 213]	Gas contract price	100 US\$/MWh [225]
SG\$/US\$ ratio	0.74	Hydrogen storage (30 bar)	5 US\$/kWh [226]

*All summed under 'Land and others' term, detail list of each term see reference [24].

[&] Refer detail discussion in the assumption portion.

6.3 Results and Discussion

Sensitivity Study

At first, the effect of key variables variation on the LCOE changes is examined. The sensitivity study varies the key variable in the range of $\pm 50\%$ from its base value and controls the remaining parameters as constant. Figure 6.2 shows the effect of fuel price, SOFC capacity factor, and SOFC efficiency on the LCOE. The result of Figure 6.2 (a) shows that the fuel price has a strong impact on the LCOE of the plant, the variation of $\pm 50\%$ of the fuel price lead to the LCOE variation of $\pm 30\%$. On the other hand, Figure 6.2 (b) shows that the effect of the increasing SOFC capacity factor on the LCOE is strong at the lower value. But the further increases of the capacity factor will not reduce the LCOE significantly. Figure 6.2 (c) shows that the effect of SOFC efficiency on the LCOE is almost linear, the increase of SOFC efficiency of 20% will lead to the LCOE reduce about 10%. However, the further improvement of SOFC efficiency to above 60% is not practical in the system level. Overall, the stable supply of low-cost fuel and the maintaining of high capacity factor are the most important factors to the further reduction of the LCOE of PtG plant.

Figure 6.2 Sensitivity study of the effect of (a) fuel price, (b) SOFC capacity factor, and (c) SOFC efficiency to the LCOE.

Figure 6.3 shows the effect of (a) capital discount rate, (b) renewable electricity capacity factor and (c) renewable electricity price on the LCOE. The variation of the dependent variable of 50%

result to the LCOE variation of less than 10% indicates that the three variables have minor effects on the LCOE of the energy produced from PtG plant.

Figure 6.3 Sensitivity study of the effect of (a) capital discount rate, (b) renewable electricity capacity factor, and (c) renewable electricity price to the LCOE.

Plant Economic Study

Overall, the capital costs of the hypothetical 100-MW Power-to-Gas plants are 185.4, 196.8 and 208.5 million US\$ for the Power-to-H₂, Power-to-CH₄ and Power-to-Power cases, respectively. The referenced 100-MW NG plant costs around 89.1 million US\$ to build. The energy storage process captures 92.2 GWh of surplus electricity annually and stores the energy in the form of hydrogen (83.2GWh), methane (64.9GWh) or electricity (39.5GWh). The CO₂ emission is about 30.9% lesser than the state-of-the-art NG power plant per MWh electricity produced. The summarized results are tabulated in Table 6.3.

Table 6.3 Comparison Between Power-to-Gas cases with Natural Gas Power Plant

100-MW Power Plant	Power-to-H ₂	Power-to-CH ₄	Power-to-Power	Natural Gas Plant
Capital Cost [million US\$]	185.4	208.5	196.8	89.1
Capacity Factor	50%+10%	50%+10%	50%+10%	60%
Electricity Generation [GWh/year]	438.0+83.2 (H ₂)	438.0+64.9(CH ₄)	438.0+39.5(electricity)	525.6

Fixed Surplus Electricity [GWh/year]	92.2	92.2	92.2	N.A.
CO ₂ Emission [kg/MWh]	343.6	356.1	338.7	490.0

The annual cost breakdown of the PtG plants is illustrated in the stacked-bar chart in Figure 6.4. Among all the cases, the major component of the annual cost is the fuel consumption of the power generation process. For the PtG capital cost, the main portion is the Solid-Oxide-Cell cost. The capital cost of PtG is almost doubled than that of the NG plant due to the higher cost of power generators (SOC system cost is 1500 US\$/kW, whereas NG plant cost is 890 US\$/kW). On the other hand, the energy efficiency of SOC (50% for SOFC and 95% for SOEC) is higher than NG plant (48%), which result in a lower fuel cost in the PtG plants. Overall, the annualized cost of PtG plants is slightly higher than that of a conventional NG plant.

Figure 6.4 The annualized cost breakdown of the PtG plants and the Natural Gas Plant.

As has been found in the sensitivity study, the fuel cost has a strong effect on the LCOE of the plant. The increase of NG price to 15 US\$/GJ will significantly increase the PtG LCOE to above US\$140/MWh, as shown in Figure 6.5. Hence the stable supply of low-cost fuel is critical to the power generation process. For simplification, the reference NG plant LCOE is calculated based

on 7.5 US\$/GJ consistently rather than increases with NG price increase. The discussion of fuel price is beyond the scope of this study.

Figure 6.5 The effect of fuel price on the LCOE.

The LCOE of PtG reduces rapidly with the increase of the power generation capacity factor, as shown in Figure 6.6. The LCOE of PtG plant could be more competitive than NG plant if the capacity factor can be raised to 55% and above. The result indicates that the full utilization of the facility is crucial to the profitability of the plant. However, further increase of the power generation capacity factor is hard to achieve due to the peak regulation and the possible overlapping with the renewable surplus power. For the energy storage process, the renewable power supply period could be much longer than 10% in the region such as Europe and the US attribute to geographical

vastness and variety of energy types. The additional energy storage capacity factor would benefit the dropping of the PtG LCOE.

Figure 6.6 The relationship between Levelized Cost of Energy of PtG plants and the capacity factor of the power generation process.

With the development of the technology, the SOC unit cost is expected to be further reduced. Figure 6.7 shows the relationship between LCOE and the unit cost of SOC. The result shows that the PtG LCOE decreases gradually with the decrease of SOC unit cost. The Power-to-H₂ exhibits lower LCOE than the NG plant at the SOC cost lower than 1700 US\$/kW. The result reveals that the SOC-based power plant could be comparable to a NG plant if the mass production of SOC is

established. However, the currently available commercial SOC cost is still higher than 2000 US\$/kW [227]. This emerging technology requires more effort in research and development.

Figure 6.7 The relationship between Levelized Cost of Energy of PtG plants and the Solid-Oxide-Cell cost.

The net present value of the PtG plants corresponding to various electricity contract price is shown in Figure 6.8. The electricity contract price is defined as the selling price of the electricity to the grid. The lower the contract price, the higher the competitiveness of the power plant. The lowest contract price to secure zero net present value for Power-to-H₂, Power-to-Power and Power-to-CH₄ are 120, 124 and 129 US\$/MWh, respectively. The Power-to-H₂ plant shows the best economic performance attribute to the lower capital cost and highest efficiency. The profitability

divergence within the three PtG cases indicates that the conversion of energy carrier (from H_2 to CH_4 or back to electricity) is not preferable in the economic sense. If possible, local consumption of the hydrogen is recommended instead of transporting the hydrogen or further convert it to other fuel.

Figure 6.8 Net present value corresponding to the various electricity contract price.

Based on the net present value estimation, the lowest electricity contract price is assumed to be 130 US\$/MWh. The corresponding cumulative cash flow of PtG plant in 20 years period is shown in Figure 6.9. The results show that the payback period of Power-to- H_2 and Power-to-Power are 13 to 15 years, whereas Power-to- CH_4 is almost not profitable in the period of 20 years. Due to the lack of information, the exact contract price is unknown. In the local electricity market, the

latest electricity tariff is 188.9 US\$/MWh [224]. According to the grid owner's website [228], approximately 75.9% of the electricity tariffs goes to the power generation company, which is around 143.3 US\$/MWh. Meanwhile, the LCOE of the local state-of-the-art NG plant is found to be 116 US\$/MWh [24]. Hence the selection of 130 US\$/MWh as payback period estimation variable is feasible and competitive. The PtG plant is more of a grid stabilizer than a power generator. The PtG plant could provide grid services to balance peak-demand and the surplus renewable power. By this approach, the large-scale integration of solar power to the grid will be possible. The PtG plant enables the higher utilization of solar energy by peak-supply shaving from day time to night-time, which eliminated the duck-curved power generation patterns.

Figure 6.9 The cumulative cash flow of PtG plant in 20 years period.

Figure 6.10 compares the CO₂ emission of the PtG plants and other power generation technologies [229]. The CO₂ emission of the PtG is around 339~356 kg/MWh. As a reference, the median CO₂ emission of coal-based power plant and NG power plant are 820 and 490 kg/MWh, respectively [14, 229]. The CO₂ emission of PtG plant is 30.9% lower compared with the NG plant. The CO₂ reduction is attributed to the energy storage process, where surplus renewable energy is stored to replace fuel consumption. The carbon footprint could be further reduced with a longer period of the renewable power supply.

Figure 6.10 The CO₂ emission per unit MWh energy produced of various power generation technologies [9].

6.4 Conclusion

This study evaluated the feasibility of a hypothetical 100-MW Power-to-Gas plant, which converts surplus renewable electricity into gas form and converts it back to electricity when necessary. The purpose of this study is to explore the possibility of PtG as a large-scale energy storage system to mitigate the intermittency issue of renewable power sources.

Based on the assumptions and references from literature, the PtG plant with energy storage and power generation processes is profitable at certain situations. Specifically, the affordable lowest contract price of the PtG plant to achieve above-zero net present value for Power-to-H₂, Power-to-Power and Power-to-CH₄ are 120, 124 and 129 US\$/MWh, respectively. Based on the local electricity market price, a contract price of 130 US\$/MWh is feasible and competitive, which corresponds to the payback period of 13 and 15 years for the Power-to-H₂ and Power-to-Power scenario. Among all the control variables, it is found that the fuel price, SOFC capacity factor and SOFC efficiency are the most influencing variables to the LCOE of the plant, whereas the effects of capital discount rate, SOEC capacity factor and renewable electricity price are relatively minor. Moreover, the CO₂ emission of the PtG plant is significantly dropped (30.9% per each MWh electricity generated) compared with the state-of-the-art NG plant.

For the improvement of the PtG profitability, the increase of the SOFC capacity factor with proper grid management will make the plant comparable to NG plant in the economic sense. However, the capacity factor is hard to increase because of the peak-shaving in the grid. Cautions should be exercised on the overlapping of the energy storage and the power generation process that may cut down the capacity factor to a lower level. The further development of SOC to have a lower cost, say below 1000 US\$/kW, to achieve higher revenue and shorter payback time is more important and practical to justify for the application of PtG plants. The scale-up of the plant may further reduce the unit cost and make this technology promising.

For the limitation of the study, the operating mode of PtG plant may differ from NG plant. Hence the fixed operating cost and variable cost of the plant should be studied in detail in a separate work. Moreover, SOCs are normally constructed modularly rather than centralized, the land usage of PtG plant should be evaluated differently. The assumed SOC lifespan of 20 years could be another issue, especially when the SOC is frequently switching between electrolysis mode and fuel cell mode. As an emerging power generation technology, the recycling costs of SOC is another

important topic to be explored. For the PtCH₄ case, another concern is the CO₂ sources. It is costly to obtain high purity CO₂ continually if the plant is open-looped, and the CO₂ is eventually ejected again to the atmosphere. Close-loop PtCH₄ where CO₂ is internally stored could be a solution, economic aspect should be investigated on the storage and recycling of the CO₂.

All in all, the PtG plant with energy storage and power generation process may play a vital role in the era of renewable energy. The combination of different types of the energy storage system to tackle the short-term and long-term power fluctuation might be the key to the future of renewable energy.

Chapter 7 Conclusion

Large-scale energy storage that balances the fluctuation of the power source is vital to the grid connection of the intermittent supplied renewable energy. The emerging Power-to-Gas technology that utilizes the existing infrastructure as storage and reuses greenhouse gas as feedstock has drawn the attention of the industry and researchers. Methanation as one step of the PtG process plays a key role in bridging of the renewable hydrogen storage and the natural gas grid. This thesis investigated the CO₂ and CO methanation process from the micro level to system level covered various aspects such as reaction mechanism, reaction kinetic, reaction thermodynamic, and the heat and mass transfer phenomena. The micro level studies are relying on the literature, whereas modeling approaches investigate the thermodynamics and transfer phenomena. The emphasize of this thesis was given to the thermal management of the strong exothermic process and to the tackling of the various challenges that aroused from the heat release.

As a general summary, three major questions are solved in this thesis. Firstly, the optimum temperature profile along the reactor axis is calculated from thermodynamic perspective. The temperature profile balanced the dilemma between thermodynamic limitation and kinetics performance at different temperature zone and achieved maximization of catalyst performance theoretically. Secondly, to enable the rigorous control of the temperature profile, a general heat transfer modulus was proposed to simplify the temperature control parameters. The dimensionless modulus can be applied to other strong exothermic process as an effective thermal management indicator. Thirdly, in the macro-level, the economic feasibility of large-scale Power-to-Gas plant was investigated, and promising results were discovered innovatively. The detail summary of each task is unfolded in the subsequent sections.

7.1 Summary of review

The reaction kinetics is one of the key components in the modeling study. However, the reaction kinetics and mechanisms are intimately related. The rate equation is hardly complete without a good understanding of the reaction elementary steps. Besides, mechanism study is useful to guide the catalyst design process to overcome the rate-limit-step. From the literature review, it has been found that the barrier for prompt methanation mainly lies on the chemical bond breaking of the first oxygen in the CO₂ methanation and the hydrogenation of the carbon species on the catalyst surface. The reaction scheme controversy focused on how the carbon-oxygen bond breaks, with

or without the surface hydrogen association. For the deactivation of the catalyst, it was found that the sulfur poisoning of the key active sites, carbon deposition, and catalytic metal sintering are the major reasons. To avoid the catalyst deactivation, feedstock purification and reaction conditions controlling are the most effective measures.

In the practical operation, how to confine the reactor temperature runaway behavior is of the most challenging part. The internally or externally cooled tubular reactors are widely adopted in the industrial CO methanation process. Researchers propose the innovative multi-channel, micro-channel reactors in the laboratory scale. Additionally, thermal management is not only about heat removal and hot-spot elimination. How to balance the kinetic performance and thermodynamic limitation at the different temperature range is more important for the effective use of the reactor space.

7.2 Summary of modeling

A control volume method was proposed to tackle the dilemma between thermodynamic limitation and kinetic performance of the CO₂ and CO methanation process. The theoretical optimal temperature profile to produce maximum CH₄ yield for a single-stage reactor for various reaction conditions is obtained from this method. The single-pass CH₄ yield for the 1 bar and 10 bars are 84.6% (3.26 kW CH₄ production) and 90.05% (34.67 kW CH₄ production), respectively. The optimum temperature profile provides competent guidance for the reactor thermal management. According to the author's knowledge and literature review, there is only handful previous works attempt to tackle this dilemma from this direction.

The validation of the optimum temperature profile was the conducted with a one-dimensional, heterogeneous heat and mass transfer model. The model chooses the heat transfer coefficient of the reactor wall, h_{wall} and the inlet temperature, T_{in} as the control variables to adjust the reactor temperature profile. The parametric study was conducted to find the optimum inlet temperature and cooling rate. It was found that the control of the h_{wall} and T_{in} is not sufficient to perfectly adapt the optimum temperature without occurring of over-heating and over-cooling here and there. Nonetheless, the yield is only 2.5% lower than the optimum case. The results indicate that the over-cooling near the outlet is more destructive to the product yield. The reaction is almost ceased at the low temperature and low concentration near the outlet. The proposed cooling modulus is an effective parameter to discriminate the ignition and extinguishment situations of the reactor to

filter out the combination of variables that cause the extinguishment of the reactor. The cooling modulus can also be readily used (with kinetics adapted to the new catalyst) to other strong exothermic process at which thermodynamics and kinetics dilemma occurred.

In a broader context, the system level economic estimation provides a simple but effective guide on the feasibility of Power-to-Gas technology. It was found that the PtG as energy storage is restricted by the high investment cost and low utilization rate. The proposed PtG & GtP schemes tackled the low utilization issue by utilizing the power generation function of SOC to recover the high investment cost. Coupling with advanced grid management system, the PtG & GtP plant could play a key role in the large-scale energy storage sector.

7.3 Future work

For the aspect of reactor cooling system design and optimization, the control of the temperature profile to fully utilize the reactor space is important. A possible research direction could be the investigation of the dynamically controlled multi-steps cooling system to achieve accurate heat removal in different segments of the reactor. In particular, the future work should pay attention to the thermal management of the outlet segment to achieve faster conversion of the remnant 10% of the reactants.

On the aspect of reactor design, the delicate multi-channel, micro-channel reactor, and membrane reactor could be popular if the catalyst performance can be enhanced and the catalyst deactivation mechanism can be fully understood. Due to the space limitation in the narrow channels, the catalyst kinetics should be greatly improved to achieve massive methanation transformation. The improvement of the low-temperature activity and the high-temperature stability of the catalyst are critical to these reactors. Also, the catalyst reloading for these sophisticated reactors is not easy. The on-site catalyst re-generation mechanism should be addressed to avoid the total replacement of the catalyst.

Other than that, on the aspect of catalyst development, the high activity non-noble metal catalyst, support material, and the metal-support interaction are to be investigated thoroughly. Besides, it is still important to fully understand the reaction mechanism to reveal the rate-limiting-step of the reaction under different catalyst and reaction conditions. The reaction mechanism may differ from catalyst type and support materials. The *in-situ* observation technic should be used to study the

elementary steps. The catalyst development is the key to the large-scale implementation of Power-to-Gas technology.

7.4 Final closing

As a closing, the commercialization of Power-to-Gas as large-scale energy storage relies on the break-through of many research works and technologies. Not only the methanation process but also the electrolysis process. The integration of electrolyzer and methanation reactor may also generate another level of complexity, which requires further investigation. With the rapid development of renewable energy, to tackle the intermittency problem, there exist opportunities and urgency for the energy storage system. More importantly, the current energy system that heavily relies on fossil fuel consumption needs to be revolutionized to a more sustainable, reliable, and nonpollution mode.

Appendix A Parameters

A1 JANAF thermodynamics data (NIST webbook for thermodynamic calculation)

The temperature dependence of heat capacity is calculated in the function below:

$$\text{Heat capacity: } C_p(T) = R(a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4) \text{ [J/mol/K]}$$

$$\text{Enthalpy: } H^0(T) = R(a_1T + a_2\frac{T^2}{2} + a_3\frac{T^3}{3} + a_4\frac{T^4}{4} + a_5\frac{T^5}{5} + b_1) \text{ [J/mol]}$$

$$\text{Entropy: } S^0(T) = R(a_1\ln T + a_2T + a_3\frac{T^2}{2} + a_4\frac{T^3}{3} + a_5\frac{T^4}{4} + b_2) \text{ [J/mol/K]}$$

$$\text{Gibbs Free Energy: } \Delta G = \Delta H - T\Delta S \text{ [J/mol]}$$

The parameters in the above equations are tabulated below.

Table A.1 JANAF thermodynamics data

JANAF Data	a1	a2	a3	a4	a5	b1(a6)	b2(a7)	H0(297.15)
CH4	5.15E+00	-1.37E-02	4.92E-05	-4.85E-08	1.67E-11	-1.02E+04	-4.64E+00	-8.97E+03
C2H6	4.29E+00	-5.50E-03	5.99E-05	-7.08E-08	2.69E-11	-1.15E+04	2.67E+00	-1.01E+04
H2	2.34E+00	7.98E-03	-1.95E-05	2.02E-08	-7.38E-12	-9.18E+02	6.83E-01	0.00E+00
CO2	2.36E+00	8.98E-03	-7.12E-06	2.46E-09	-1.44E-13	-4.84E+04	9.90E+00	-4.73E+04
H2O	4.20E+00	-2.04E-03	6.52E-06	-5.49E-09	1.77E-12	-3.03E+04	-8.49E-01	-2.91E+04
CO	3.58E+00	-6.10E-04	1.02E-06	9.07E-10	-9.04E-13	-1.43E+04	3.51E+00	-1.33E+04
C	2.55E+00	-3.22E-04	7.34E-07	-7.32E-10	2.67E-13	8.54E+04	4.53E+00	8.62E+04
C-	2.50E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.99E+04	3.96E+00	7.07E+04
C+	2.62E+00	-5.54E-04	1.06E-06	-9.24E-10	3.01E-13	2.17E+05	3.83E+00	2.18E+05
O2	3.78E+00	-2.97E-03	9.85E-06	-9.68E-09	3.24E-12	-1.06E+03	3.66E+00	0.00E+00

A2 Temperature Dependent of Viscosity

The viscosity is written in the form of Lennard-Jones parameters as:

$$\mu = 2.6693 \times 10^{-5} \frac{\sqrt{M_i T}}{\sigma^2 \Omega_\mu} [\text{g/cm/s}]$$

Typical values of the temperature-dependent viscosity of gases used in this thesis are tabulated for references.

Table A.2 Viscosity of Gases

μ [g/cm/s]	473K	523K	573K	623K	673K	723K	773K	823K
CO ₂	2.21E-04	2.40E-04	2.56E-04	2.73E-04	2.88E-04	3.04E-04	3.20E-04	3.33E-04
H ₂	1.21E-04	1.30E-04	1.38E-04	1.44E-04	1.53E-04	1.59E-04	1.66E-04	1.66E-04
CH ₄	1.58E-04	1.70E-04	1.81E-04	1.92E-04	2.04E-04	2.14E-04	2.24E-04	2.31E-04
H ₂ O	1.62E-04	1.70E-04	1.93E-04	2.17E-04	2.25E-04	2.48E-04	2.71E-04	2.80E-04
CO	2.50E-04	2.68E-04	2.83E-04	3.05E-04	3.17E-04	3.38E-04	3.49E-04	3.64E-04
N ₂	1.72E-04	1.83E-04	1.98E-04	2.07E-04	2.21E-04	2.29E-04	2.42E-04	2.50E-04

A3 Binary Diffusivity and Knudsen Diffusivity

The approximate form of binary diffusivity of two-component system can be shown:

$$D_{AB} = 0.0018583 \sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right) \frac{1}{p \sigma_{AB}^2 \Omega_{D,AB}}} \text{ [cm}^2\text{/s]}$$

The typical values of binary diffusivity of gases at different temperature are tabulated for references.

D _{i,j} [cm ² /s] @ 573K	CO ₂	H ₂	CH ₄	H ₂ O	CO	N ₂
CO ₂		1.4600	0.3980	0.3978	0.3631	0.3598
H ₂			1.6532	1.9436	1.7442	1.7036
CH ₄				0.5352	0.5091	0.5034
H ₂ O					0.5330	0.5299
CO						0.4773
N ₂						

D _{i,j} [cm ² /s] @ 673K	CO ₂	H ₂	CH ₄	H ₂ O	CO	N ₂
CO ₂		1.4954	0.4146	0.4180	0.3762	0.3719
H ₂			1.6873	2.0120	1.7754	1.7341
CH ₄				0.5709	0.5230	0.5123
H ₂ O					0.5683	0.5623
CO						0.4773
N ₂						

D _{i,j} [cm ² /s] @ 773K	CO ₂	H ₂	CH ₄	H ₂ O	CO	N ₂
CO ₂		1.5263	0.4280	0.4437	0.3811	0.3872
H ₂			1.7175	2.0801	1.8296	1.7871
CH ₄				0.5999	0.5423	0.5311
H ₂ O					0.5901	0.5823
CO						0.4912
N ₂						

D _{i,j} [cm ² /s] @ 873K	CO ₂	H ₂	CH ₄	H ₂ O	CO	N ₂
CO ₂		1.5536	0.4376	0.4577	0.3951	0.3872

H ₂			1.7700	2.1371	1.8757	1.8321
CH ₄				0.6247	0.5581	0.5466
H ₂ O					0.6087	0.6048
CO						0.5032
N ₂						

D _{i,j} [cm ² /s] @ 973K	CO ₂	H ₂	CH ₄	H ₂ O	CO	N ₂
CO ₂		1.6011	0.4537	0.4767	0.4066	0.3985
H ₂			1.7700	2.2157	1.8757	1.8713
CH ₄				0.6456	0.5717	0.5599
H ₂ O					0.6298	0.6194
CO						0.5135
N ₂						

The typical values of binary diffusivity of gases relative to the gas mixture are tabulated for references.

D _{i,mix} [cm ² /s]	473K	573K	673K	773K	873K	973K
CO ₂	0.5699	0.5957	0.6152	0.6333	0.6463	0.6673
H ₂	1.6331	1.7009	1.7408	1.7881	1.8337	1.8668
CH ₄	0.6816	0.7198	0.7416	0.7638	0.7874	0.8002
H ₂ O	0.7384	0.7879	0.8263	0.8592	0.8866	0.9174
CO	0.6902	0.7253	0.7440	0.7669	0.7882	0.7995
N ₂	0.5699	0.5957	0.6152	0.6333	0.6463	0.6673

The Knudsen diffusivity of a species is represented by the function:

$$D_{K,i} = 4850 d_p \sqrt{\frac{T}{M_i}} [\text{cm}^2/\text{s}]$$

The typical values of Knudsen diffusivity of gases in the porous particle are tabulated for references.

D _{i,K} [cm ² /s] d _{pore} =100 [nm]	473K	573K	673K	773K	873K	973K
CO ₂	0.7459	0.8209	0.8897	0.9535	1.0133	1.0698
H ₂	0.1993	0.2194	0.2378	0.2548	0.2708	0.2859

CH ₄	0.1590	0.1750	0.1897	0.1966	0.2160	0.2281
H ₂ O	0.2637	0.2902	0.3145	0.3371	0.3583	0.3782
CO	0.2486	0.2736	0.2966	0.3178	0.3378	0.3566

A4 Thermal Conductivity

The typical values of thermal conductivity of gases are tabulated for references.

$$k = \left(C_p + \frac{5}{4} \frac{R}{M} \right) \mu \text{ [W/m/K]}$$

K [W/m/K]	473K	573K	673K	773K	873K	973K
CO ₂	0.02778	0.03353	0.03896	0.04441	0.04947	0.05429
H ₂	0.23918	0.27707	0.30807	0.33813	0.37431	0.39843
CH ₄	0.05473	0.06832	0.08300	0.09798	0.11508	0.12932
H ₂ O	0.04290	0.05190	0.06135	0.07519	0.08551	0.09622
CO	0.03599	0.04133	0.04689	0.05223	0.05742	0.06309

A5 Kinetic Parameters

Xu and Froment's rate equation and parameters:

$$r_{CO_2} = \frac{\frac{k_{CO_2}}{p_{H_2}^{3.5}} \left[p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_{eq,CO_2}} \right]}{(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O} / p_{H_2})^2}$$

where rate constant $k_{CO_2} = k_{CO_2}^0 \exp\left(-\frac{E_{CO_2}}{RT}\right)$, and equilibrium constant $K_{eq,CO_2} = K_{eq,CO_2}^0 \exp\left(-\frac{\Delta H_{eq,CO_2}}{RT}\right)$. Other adsorption constants are listed below:

$$r_{CO} = \frac{\frac{k_{CO}}{p_{H_2}^{2.5}} \left[p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_{eq,CO}} \right]}{(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O} / p_{H_2})^2}$$

where rate constant $k_{CO} = k_{CO}^0 \exp\left(-\frac{E_{CO}}{RT}\right)$, and equilibrium constant $K_{eq,CO} = K_{eq,CO}^0 \exp\left(-\frac{\Delta H_{eq,CO}}{RT}\right)$. Other adsorption constants are listed below:

$$r_{WGS} = \frac{\frac{k_{WGS}}{p_{H_2}} \left[p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_{eq,WGS}} \right]}{\left(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2}}\right)^2}$$

Table A.3 Kinetic Parameters and Other Fitted Versions

	Xu (15.2% Ni)	Ducamp (14~17% Ni)	Zhang	Unit
$k_{CO_2}^0$	1.0208×10^{15}	4.61×10^{13}	N.A.	$mole \times Bar^{0.5} / (g \ h)$
E_{CO_2}	243.9	209.9	N.A.	$kJ/mole$
K_{eq,CO_2}^0	1.11e11			Bar^2
$\Delta H_{eq,CO_2}$	182.4			$kJ/mole$
K_{CO}^0	8.23×10^{-5}	3.14×10^{-10}	8.23×10^{-5}	Bar^{-1}
ΔH_{CO}	-70.65	120.2	-70.65	$kJ/mole$
$K_{H_2}^0$	6.12×10^{-9}		6.12×10^{-9}	Bar^{-1}

ΔH_{H_2}	-82.9		-82.9	<i>kJ/mole</i>
$K_{CH_4}^0$	6.65×10^{-4}		6.65×10^{-4}	<i>Bar⁻¹</i>
ΔH_{CH_4}	-38.28		-38.28	<i>kJ/mole</i>
$K_{H_2O}^0$	1.77×10^5		1.77×10^5	<i>l</i>
ΔH_{H_2O}	88.68		88.68	<i>kJ/mole</i>
k_{CO}^0	4.2248×10^{15}	2.083×10^{13}	1.59×10^{17}	<i>mole $\times$ Bar^{0.5}/(g h)</i>
E_{CO}	240.1	218.9	248	<i>kJ/mole</i>
$K_{eq,CO}^0$	7.846×10^{12}			<i>Bar²</i>
$\Delta H_{eq,CO}$	220.2			<i>kJ/mole</i>
$K_{H_2}^0$	6.12×10^{-9}			<i>Bar⁻¹</i>
ΔH_{H_2}	-82.9			<i>kJ/mole</i>
k_{WGS}^0	1.955×10^6	1.12×10^7	7.83×10^6	<i>mole $\times$ Bar⁻¹/(g h)</i>
E_{WGS}	67.13	59.4	62	<i>kJ/mole</i>
$K_{eq,WGS}^0$	1.412×10^{-2}			<i>Bar²</i>
$\Delta H_{eq,WGS}$	-37.72			<i>kJ/mole</i>

Hwang's power law kinetic parameters:

$$r_{CO_2} = \rho \frac{k K_{CO_2} K_{H_2}^4 p_{CO_2} p_{H_2}^4}{(1 + K_{CO_2} p_{CO_2} + K_{H_2} p_{H_2})^5} \left(1 - \frac{p_{CH_4} p_{H_2O}^2}{p_{CO_2} p_{H_2}^4 K_{eq}} \right)$$

	Hwang (27.2% Ni)	Unit
k	$1.0635 \times 10^{11} \cdot \exp(-113497.4/RT)$	<i>mole/(g h)</i>
K_{CO_2}	$9.099 \times 10^{-7} \cdot \exp(69691.8/RT)$	<i>Bar⁻¹</i>
K_{H_2}	$9.6104 \times 10^{-4} \cdot \exp(39942/RT)$	<i>Bar⁻¹</i>
K_{eq}	$1.11 \times 10^{11} \cdot \exp(-182400/RT)$	<i>Bar⁻²</i>

Appendix B Additional Discussion

B2 Space Time Yield Maximization

Continued the discussion from Chapter 4, the results reveal another optimization direction that may be useful in the multi-stage reactor. The goal is now maximizing the space-time yield (STY) by shortening the reactor or increasing the space velocity. A One-Dimensional homogeneous model was built to investigate this direction. All the settings can be found from Chapter 5, the inlet temperature is now set to be 823K. The space velocity sweeps from 1×10^5 [1/h] up to 3×10^6 [1/h].

Figure B.0.1 (a) and (b) shows the STY of the optimum temperature profile corresponding to the CH_4 yield and reactor axis. The maximum STY exists at where the outlet CH_4 yield is only 20%, and the corresponding reactor length is 0.014 meter. By increase the GHSV to 1.2×10^6 [1/h], the maximum STY is achieved at a 1-meter reactor, as shown in Figure B.0.1 (c). Generally, the space-time yield (STY) is maximized when the equilibrium condition is achieved at the outlet of the reactor. The reactor length and the gas hourly space velocity (GHSV) have the same effect on STY.

Figure B.0.1 The maximization of Space-Time Yield (STY). (a) The STY and the corresponding attainable CH_4 Yield at the outlet. (b) The STY and the corresponding reactor length. (c) The Space-Time-Yield of CH_4 at the reactor outlet with respect to GHSV. The maximum STY equivalent to the feed gas GHSV 1,200,000 [1/h] or 60 kW CH_4 productivity for the 1-meter reactor.

Figure B.0.2 (a) shows the temperature profile of the Max-STY situation compared with the equilibrium line (shown in blue dash line) and the optimum temperature profile (shown in solid black line). The Max-STY temperature profile did not reach the equilibrium line due to kinetics or mass transfer limitation at the high temperature, as shown in (a) the black circle marker. The Figure B.0.2 (b) shows the temperature profile along the reactor axis at the Max STY situation as a reference. The temperature difference along reactor axis is not high probably because of the strong reverse reaction at the region near the equilibrium profile. Also, the reverse water gas shift reaction consumed some of the heat generated from methanation.

Figure B.0.2 The Max STY temperature profile compared with the equilibrium conditions. The Max STY did not reach to equilibrium line, probably because of the kinetics or mass transfer limitation at the high-temperature zone.

List of Publication

Journal Paper

Bin Miao, Su Su Khine Ma, Xin Wang, Haibin Su and Siew Hwa Chan, *Catalysis mechanisms of CO₂ and CO methanation*, Catalysis Science & Technology, 2016, **6**, 4048.

Bin Miao and Siew Hwa Chan, *The economic feasibility study of a 100-MW Power-to-Gas Plant*, International Journal of Hydrogen Energy, 2019.

Bin Miao and Siew Hwa Chan, *Thermodynamic Optimal Temperature Profile in a Single-Stage Methanation Reactor*, Journal paper preparing to be submitted to Chemical Engineering Science.

Conference Paper

Oral presentation

Bin Miao and Siew Hwa Chan, *A study of Closed-loop and Open-loop Power-to-Gas Plant, the Economical Assessment*, presented in HYPOTHESIS 2018, Singapore.

Bin Miao and Siew Hwa Chan, *The Profitability Estimation of a 100 MW Power-to-Gas Plant*, presented in ICRED2018, Nagoya, awarded as the best presenter, accepted in Energy Procedia.

Reference

1. Administration, U.S.E.I., *International Energy Outlook 2018*. 2018, Energy Information Administration: WASHINGTON DC.
2. Agency, I.E. *Key World Energy Statistics 2018*. 2018; Available from: <https://webstore.iea.org/key-world-energy-statistics-2018>.
3. BP, *BP Statistical Review of World Energy*. 2018.
4. Administration, E.I. *International Energy Statistics, Total Electricity Net Generation 2016*. 2016 Dec 03]; Available from: <https://www.eia.gov/beta/international/rankings/#?product=2-12&cy=2016>.
5. *World Energy Balance (2016)*. 2016; Available from: <https://www.iea.org/Sankey/>.
6. Edenhofer, O., R. Pichs-Madruga, Y. Sokona, E. Farahani, S. Kadner, K., A.A. Seyboth, I. Baum, S. Brunner, P. Eickemeier, B. Kriemann, J. Savolainen, S. Schlömer, C. von Stechow, T. Zwickel and J.C., and M. (eds.), *Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. 2014.
7. Allen, M.R., et al., *Warming caused by cumulative carbon emissions towards the trillionth tonne*. Nature, 2009. **458**: p. 1163.
8. Matthews, H.D., et al., *The proportionality of global warming to cumulative carbon emissions*. Nature, 2009. **459**: p. 829.
9. Cai, W., et al., *Increased frequency of extreme La Niña events under greenhouse warming*. Nature Climate Change, 2015. **5**: p. 132.
10. Gattuso, J.-P., et al., *Contrasting futures for ocean and society from different anthropogenic CO₂ emissions scenarios*. Science, 2015. **349**(6243): p. aac4722.
11. Fossheim, M., et al., *Recent warming leads to a rapid borealization of fish communities in the Arctic*. Nature Climate Change, 2015. **5**: p. 673.
12. Feng, K., et al., *Drivers of the US CO₂ emissions 1997–2013*. Nature Communications, 2015. **6**: p. 7714.
13. Liu, Z., et al., *Reduced carbon emission estimates from fossil fuel combustion and cement production in China*. Nature, 2015. **524**: p. 335.

14. Schlömer S., T.B., L. Fulton, E. Hertwich, A. McKinnon, D. Perczyk, J. Roy, R. Schaeffer, R. Sims, P. Smith, and R. Wiser, *Climate Change 2014: Mitigation of Climate Change*. 2014, Cambridge University Press: Cambridge, United Kingdom and New York, NY, USA.
15. REN21, *Renewables 2017 Global Status Report*. 2017, REN21.
16. Agency, I.E. *World Balance 2016*. 2018 [cited 2018 Dec 04]; Available from: <https://www.iea.org/Sankey/#?c=World&s=Balance>.
17. Miao, B., et al., *Catalysis mechanisms of CO₂ and CO methanation*. Catalysis Science & Technology, 2016. **6**(12): p. 4048-4058.
18. Chu, S. and A. Majumdar, *Opportunities and challenges for a sustainable energy future*. Nature, 2012. **488**(7411): p. 294-303.
19. Turner, J.A., *A Realizable Renewable Energy Future*. Science, 1999. **285**(5428): p. 687-689.
20. *Global Wind Energy Council*. 2015; Available from: <http://www.gwec.net/>.
21. Agency, I.R.E., *Renewable Capacity Statistics 2018*. 2018, International Renewable Energy Agency.
22. Burton, T., et al., *Wind energy handbook*. 2001: John Wiley & Sons.
23. Barton, J.P. and D.G. Infield, *Energy storage and its use with intermittent renewable energy*. IEEE Transactions on Energy Conversion, 2004. **19**(2): p. 441-448.
24. Brinckerhoff, W.P., *Review of the Vesting Contract Technical Parameters*. 2016, WSP Parsons Brinckerhoff.
25. Denholm, P. and R.M. Margolis, *Evaluating the limits of solar photovoltaics (PV) in traditional electric power systems*. Energy Policy, 2007. **35**(5): p. 2852-2861.
26. Parida, B., S. Iniyan, and R. Goic, *A review of solar photovoltaic technologies*. Renewable and Sustainable Energy Reviews, 2011. **15**(3): p. 1625-1636.
27. Díaz-González, F., et al., *A review of energy storage technologies for wind power applications*. Renewable and Sustainable Energy Reviews, 2012. **16**(4): p. 2154-2171.
28. Sprake, D., et al., *Housing Estate Energy Storage Feasibility for a 2050 Scenario*. 2017.
29. Ibrahim, H., A. Ilinca, and J. Perron, *Energy storage systems—Characteristics and comparisons*. Renewable and Sustainable Energy Reviews, 2008. **12**(5): p. 1221-1250.
30. Sternberg, A. and A. Bardow, *Power-to-What? - Environmental assessment of energy storage systems*. Energy & Environmental Science, 2015. **8**(2): p. 389-400.

31. Sabatier, P. and J.B. Senderens, *New methane synthesis*. Comptes Rendus Hebdomadaires Des Seances De L Academie Des Sciences, 1902. **134**: p. 514-516.
32. Gahleitner, G., *Hydrogen from renewable electricity: An international review of power-to-gas pilot plants for stationary applications*. International Journal of Hydrogen Energy, 2013. **38**(5): p. 2039-2061.
33. Schiebahn, S., et al., *Power to gas: Technological overview, systems analysis and economic assessment for a case study in Germany*. International Journal of Hydrogen Energy, 2015. **40**(12): p. 4285-4294.
34. Jentsch, M., T. Trost, and M. Sterner, *Optimal Use of Power-to-Gas Energy Storage Systems in an 85% Renewable Energy Scenario*. Energy Procedia, 2014. **46**(0): p. 254-261.
35. Graves, C., et al., *Sustainable hydrocarbon fuels by recycling CO₂ and H₂O with renewable or nuclear energy*. Renewable and Sustainable Energy Reviews, 2011. **15**(1): p. 1-23.
36. Yang, H., et al., *Progress in carbon dioxide separation and capture: A review*. Journal of Environmental Sciences, 2008. **20**(1): p. 14-27.
37. Gao, J., et al., *Recent advances in methanation catalysts for the production of synthetic natural gas*. RSC Advances, 2015. **5**(29): p. 22759-22776.
38. Steven J. Davis, Ken Caldeira, and H.D. Matthews, *Future CO₂ Emissions and Climate Change from Existing Energy Infrastructure*. Science, 2010. **329**(5997): p. 1330-1333.
39. Meehl, G.A., et al., *How Much More Global Warming and Sea Level Rise?* Science, 2005. **307**(5716): p. 1769-1772.
40. Wang, W., et al., *Recent advances in catalytic hydrogenation of carbon dioxide*. Chemical Society Reviews, 2011. **40**(7): p. 3703-3727.
41. Aziz, M.A.A., et al., *CO₂ methanation over heterogeneous catalysts: Recent progress and future prospects*. Green Chemistry, 2015. **17**(5): p. 2647-2663.
42. Goodman, D.W., et al., *Kinetics of the hydrogenation of CO over a single crystal nickel catalyst*. Journal of Catalysis, 1980. **63**(1): p. 226-234.
43. Kelley, R.D. and D.W. Goodman, *Catalytic methanation over single crystal nickel and ruthenium: Reaction kinetics on different crystal planes and the correlation of surface carbide concentration with reaction rate*. Surface Science, 1982. **123**(2-3): p. L743-L749.

44. Yuan, C., et al., *The SiO₂ supported bimetallic Ni–Ru particles: A good sulfur-tolerant catalyst for methanation reaction*. Chemical Engineering Journal, 2015. **260**: p. 1-10.
45. Wentrcek, P.W., et al., *Deactivation of alumina-supported nickel and ruthenium catalysts by sulfur compounds*. Journal of Catalysis, 1980. **61**(1): p. 232-241.
46. Li, Y., G. Lu, and J. Ma, *Highly active and stable nano NiO-MgO catalyst encapsulated by silica with a core-shell structure for CO₂ methanation*. RSC Advances, 2014. **4**(34): p. 17420-17428.
47. Liu, J., et al., *Intercorrelation of structure and performance of Ni-Mg/Al₂O₃ catalysts prepared with different methods for syngas methanation*. Catalysis Science and Technology, 2014. **4**(2): p. 472-481.
48. Zhi, G., et al., *Effect of La₂O₃ modification on the catalytic performance of Ni/SiC for methanation of carbon dioxide*. Catalysis Communications, 2011. **16**(1): p. 56-59.
49. Panagiotopoulou, P., D.I. Kondarides, and X.E. Verykios, *Mechanistic Study of the Selective Methanation of CO over Ru/TiO₂ Catalyst: Identification of Active Surface Species and Reaction Pathways*. Journal of Physical Chemistry C, 2011. **115**(4): p. 1220-1230.
50. Panagiotopoulou, P., D.I. Kondarides, and X.E. Verykios, *Mechanistic aspects of the selective methanation of CO over Ru/TiO₂ catalyst*. Catalysis Today, 2012. **181**(1): p. 138-147.
51. Somorjai, G.A., *Modern surface science and surface technologies: An introduction*. Chemical Reviews, 1996. **96**(4): p. 1223-1235.
52. Norskov, J.K., et al., *Towards the computational design of solid catalysts*. Nat Chem, 2009. **1**(1): p. 37-46.
53. Aldana, P.A.U., et al., *Catalytic CO₂ valorization into CH₄ on Ni-based ceria-zirconia. Reaction mechanism by operando IR spectroscopy*. Catalysis Today, 2013. **215**: p. 201-207.
54. Schild, C., et al., *CO₂ hydrogenation over nickel/zirconia catalysts from amorphous precursors: On the mechanism of methane formation*. Journal of Physical Chemistry, 1991. **95**(16): p. 6341-6346.
55. Upham, D.C., et al., *CO₂ methanation by Ru-doped ceria: the role of the oxidation state of the surface*. Catalysis Science & Technology, 2015. **5**(3): p. 1783-1791.

56. Westermann, A., et al., *Insight into CO₂ methanation mechanism over NiUSY zeolites: An operando IR study*. Applied Catalysis B: Environmental, 2015. **174-175**: p. 120-125.
57. Pan, Q., et al., *In situ FTIR spectroscopic study of the CO₂ methanation mechanism on Ni/Ce_{0.5}Zr_{0.5}O₂*. Catalysis Science & Technology, 2014. **4**(2): p. 502-509.
58. Pan, Y.X., C.J. Liu, and Q.F. Ge, *Effect of surface hydroxyls on selective CO₂ hydrogenation over Ni-4/gamma-Al₂O₃: A density functional theory study*. Journal of Catalysis, 2010. **272**(2): p. 227-234.
59. Prairie, M.R., et al., *A fourier transform infrared spectroscopic study of CO₂ methanation on supported ruthenium*. Journal of Catalysis, 1991. **129**(1): p. 130-144.
60. Zhang, S.T., et al., *Hydrogenation mechanism of carbon dioxide and carbon monoxide on Ru(0001) surface: a density functional theory study*. Rsc Advances, 2014. **4**(57): p. 30241-30249.
61. Eckle, S., H.G. Anfang, and R.J. Behm, *Reaction Intermediates and Side Products in the Methanation of CO and CO₂ over Supported Ru Catalysts in H₂-Rich Reformate Gases*. Journal of Physical Chemistry C, 2011. **115**(4): p. 1361-1367.
62. De Leitenburg, C., A. Trovarelli, and J. Kašpar, *A temperature-programmed and transient kinetic study of CO₂ activation and methanation over CeO₂ supported noble metals*. Journal of Catalysis, 1997. **166**(1): p. 98-107.
63. Akamaru, S., et al., *Density functional theory analysis of methanation reaction of CO₂ on Ru nanoparticle supported on TiO₂ (1 0 1)*. Applied Catalysis A: General, 2014. **470**: p. 405-411.
64. Fujita, S.i., et al., *Mechanisms of methanation of carbon dioxide and carbon monoxide over nickel/alumina catalysts*. Applied Catalysis A, General, 1993. **104**(1): p. 87-100.
65. Tada, S., et al., *Ni/CeO₂ catalysts with high CO₂ methanation activity and high CH₄ selectivity at low temperatures*. International Journal of Hydrogen Energy, 2012. **37**(7): p. 5527-5531.
66. Mills, G.A. and F.W. Steffgen, *Catalytic Methanation*. Catalysis Reviews, 1974. **8**(1): p. 159-210.
67. Andersson, M.P., et al., *Structure sensitivity of the methanation reaction: H₂-induced CO dissociation on nickel surfaces*. Journal of Catalysis, 2008. **255**(1): p. 6-19.

68. Eckle, S., Y. Denkwitz, and R.J. Behm, *Activity, selectivity, and adsorbed reaction intermediates/reaction side products in the selective methanation of CO in reformat gases on supported Ru catalysts*. Journal of Catalysis, 2010. **269**(2): p. 255-268.
69. Wang, J., et al., *The selectivity and activity of catalyst for CO hydrogenation to methanol and hydrocarbon: A comparative study on Cu, Co and Ni surfaces*. Surface Science, 2016. **645**: p. 30-40.
70. Zhi, C., et al., *Insight into the mechanism of methane synthesis from syngas on a Ni(111) surface: a theoretical study*. RSC Advances, 2015. **5**(82): p. 66742-66756.
71. Fajín, J.L.C., J.R.B. Gomes, and M.N.D.S. Cordeiro, *Mechanistic Study of Carbon Monoxide Methanation over Pure and Rhodium- or Ruthenium-Doped Nickel Catalysts*. Journal of Physical Chemistry C, 2015. **119**(29): p. 16537-16551.
72. Wang, Y., et al., *Mechanism of CO methanation on the Ni4/ γ -Al₂O₃ and Ni₃Fe/ γ -Al₂O₃ catalysts: A density functional theory study*. International Journal of Hydrogen Energy, 2015. **40**(29): p. 8864-8876.
73. Tison, Y., et al., *Scanning Tunneling Microscopy Evidence for the Dissociation of Carbon Monoxide on Ruthenium Steps*. Journal of Physical Chemistry C, 2012. **116**(27): p. 14350-14359.
74. Vendelbo, S.B., et al., *Self Blocking of CO Dissociation on a Stepped Ruthenium Surface*. Topics in Catalysis, 2010. **53**(5-6): p. 357-364.
75. Araki, M. and V. Ponc, *Methanation of carbon monoxide on nickel and nickel-copper alloys*. Journal of Catalysis, 1976. **44**(3): p. 439-448.
76. Madden, H.H. and G. Ertl, *Decomposition of carbon monoxide on a (110) nickel surface*. Surface Science, 1973. **35**: p. 211-226.
77. Fujita, S.-i., et al., *Mechanisms of methanation of CO and CO₂ over Ni*. Industrial and Engineering Chemistry Research, 1991. **30**(6): p. 1146-1151.
78. Forzatti, P. and L. Lietti, *Catalyst deactivation*. Catalysis Today, 1999. **52**(2-3): p. 165-181.
79. Bartholomew, C.H., *Mechanisms of catalyst deactivation*. Applied Catalysis A: General, 2001. **212**(1-2): p. 17-60.
80. Oudar, J., *Sulfur Adsorption and Poisoning of Metallic Catalysts*. Catalysis Reviews, 1980. **22**(2): p. 171-195.

81. Bartholomew, C.H., *Carbon deposition in steam reforming and methanation*. Catalysis Reviews Science and Engineering, 1982. **24**(1): p. 67-112.
82. Legras, B., et al., *Impact and Detailed Action of Sulfur in Syngas on Methane Synthesis on Ni/gamma-Al₂O₃ Catalyst*. Acs Catalysis, 2014. **4**(8): p. 2785-2791.
83. Agrawal, P.K., J.R. Katzer, and W.H. Manogue, *Methanation over transition-metal catalysts*. Journal of Catalysis, 1982. **74**(2): p. 332-342.
84. Bartholomew, C.H., G.D. Weatherbee, and G.A. Jarvi, *SULFUR POISONING OF NICKEL METHANATION CATALYSTS .1. INSITU DEACTIVATION BY H₂S OF NICKEL AND NICKEL BIMETALLICS*. Journal of Catalysis, 1979. **60**(2): p. 257-269.
85. Rostrup-Nielsen, J.R. and K. Pedersen, *SULFUR POISONING OF BOUDOUARD AND METHANATION REACTIONS ON NICKEL CATALYSTS*. Journal of Catalysis, 1979. **59**(3): p. 395-404.
86. Engbæk, J., et al., *CO dissociation on Ni: The effect of steps and of nickel carbonyl*. Surface Science, 2008. **602**(3): p. 733-743.
87. Erekson, E.J. and C.H. Bartholomew, *Sulfur poisoning of nickel methanation catalysts: II. Effects of H₂S concentration, CO and H₂O partial pressures and temperature on reactivation rates*. Applied Catalysis, 1983. **5**(3): p. 323-336.
88. Fitzharris, W.D., J.R. Katzer, and W.H. Manogue, *Sulfur deactivation of nickel methanation catalysts*. Journal of Catalysis, 1982. **76**(2): p. 369-384.
89. Czekaj, I., et al., *Sulphur poisoning of Ni catalysts used in the SNG production from biomass: Computational studies*. Catalysis Today, 2011. **176**(1): p. 429-432.
90. Struis, R.P.W.J., et al., *Sulphur poisoning of Ni catalysts in the SNG production from biomass: A TPO/XPS/XAS study*. Applied Catalysis A: General, 2009. **362**(1-2): p. 121-128.
91. Lee, K., C. Song, and M.J. Janik, *Density functional theory study of sulfur tolerance of CO adsorption and dissociation on Rh–Ni binary metals*. Applied Catalysis A: General, 2010. **389**(1–2): p. 122-130.
92. Yan, X.L., et al., *Enhanced sulfur resistance of Ni/SiO₂ catalyst for methanation via the plasma decomposition of nickel precursor*. Physical Chemistry Chemical Physics, 2013. **15**(29): p. 12132-12138.

93. Gao, J., et al., *A thermodynamics analysis of methanation reactions of carbon oxides for the production of synthetic natural gas*. RSC Advances, 2012. **2**(6): p. 2358-2368.
94. McCarty, J.G. and H. Wise, *Hydrogenation of surface carbon on alumina-supported nickel*. Journal of Catalysis, 1979. **57**(3): p. 406-416.
95. Nishizawa, K., et al., *Methanation of carbon deposited directly from CO₂ on rhodium-bearing activated magnetite*. Journal of materials science, 1994. **29**(3): p. 768-772.
96. Helveg, S., et al., *Atomic-scale imaging of carbon nanofibre growth*. Nature, 2004. **427**(6973): p. 426-429.
97. Czekaj, I., et al., *Characterization of surface processes at the Ni-based catalyst during the methanation of biomass-derived synthesis gas: X-ray photoelectron spectroscopy (XPS)*. Applied Catalysis A: General, 2007. **329**: p. 68-78.
98. Alstrup, I., *A new model explaining carbon filament growth on nickel, iron, and Ni-Cu alloy catalysts*. Journal of Catalysis, 1988. **109**(2): p. 241-251.
99. Gupta, N.M., et al., *MECHANISM OF CO AND CO₂ METHANATION OVER RU-MOLECULAR-SIEVE CATALYST*. Journal of Catalysis, 1979. **60**(1): p. 57-67.
100. Abild-Pedersen, F., et al., *Mechanisms for catalytic carbon nanofiber growth studied by ab initio density functional theory calculations*. Physical Review B - Condensed Matter and Materials Physics, 2006. **73**(11).
101. Helveg, S., J. Sehested, and J.R. Rostrup-Nielsen, *Whisker carbon in perspective*. Catalysis Today, 2011. **178**(1): p. 42-46.
102. Agnelli, M., et al., *CO hydrogenation on a nickel catalyst: II. A mechanistic study by transient kinetics and infrared spectroscopy*. Journal of Catalysis, 1998. **175**(1): p. 117-128.
103. Shen, W.M., J.A. Dumesic, and C.G. Hill Jr, *Criteria for stable Ni particle size under methanation reaction conditions: Nickel transport and particle size growth via nickel carbonyl*. Journal of Catalysis, 1981. **68**(1): p. 152-165.
104. Mirodatos, C., H. Praliaud, and M. Primet, *Deactivation of Nickel-based Catalysts during CO Methanation and Disproportionation*. Journal of Catalysis, 1987. **107**(2): p. 275-287.
105. Rostrup-Nielsen, J.R., K. Pedersen, and J. Sehested, *High temperature methanation: Sintering and structure sensitivity*. Applied Catalysis A: General, 2007. **330**: p. 134-138.

106. Wang, F., et al., *Active Site Dependent Reaction Mechanism over Ru/CeO₂ Catalyst toward CO₂ Methanation*. Journal of the American Chemical Society, 2016. **138**(19): p. 6298-6305.
107. Xu, J. and G.F. Froment, *Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics*. AIChE Journal, 1989. **35**(1): p. 88-96.
108. Coker, A.K., *Modeling of chemical kinetics and reactor design*. Vol. 1. 2001: Gulf Professional Publishing.
109. Koschany, F., D. Schlereth, and O. Hinrichsen, *On the kinetics of the methanation of carbon dioxide on coprecipitated NiAl(O)_x*. Applied Catalysis B: Environmental, 2016. **181**: p. 504-516.
110. Weatherbee, G.D. and C.H. Bartholomew, *Hydrogenation of CO₂ on group VIII metals. II. Kinetics and mechanism of CO₂ hydrogenation on nickel*. Journal of Catalysis, 1982. **77**(2): p. 460-472.
111. Klose, J. and M. Baerns, *Kinetics of the methanation of carbon monoxide on an alumina-supported nickel catalyst*. Journal of Catalysis, 1984. **85**(1): p. 105-116.
112. Van Herwijnen, T., H. Van Doesburg, and W.A. De Jong, *Kinetics of the methanation of CO and CO₂ on a nickel catalyst*. Journal of Catalysis, 1973. **28**(3): p. 391-402.
113. Kopyscinski, J., *Production of synthetic natural gas in a fluidized bed reactor. understanding the hydrodynamic, mass transfer, and kinetic effects*. 2010, ETH/PSI.
114. Rönsch, S., et al., *Global reaction kinetics of CO and CO₂ methanation for dynamic process modeling*. Chemical Engineering & Technology, 2016. **39**(2): p. 208-218.
115. Zhang, J., et al., *Kinetic investigation of carbon monoxide hydrogenation under realistic conditions of methanation of biomass derived syngas*. Fuel, 2013. **111**: p. 845-854.
116. Marwaha, B. and D. Luss, *Hot zones formation in packed bed reactors*. Chemical Engineering Science, 2003. **58**(3): p. 733-738.
117. Nguyen, D. and V. Balakotaiah, *Flow maldistributions and hot spots in down-flow packed bed reactors*. Chemical Engineering Science, 1994. **49**(24, Part 2): p. 5489-5505.
118. Agrawal, R., D.H. West, and V. Balakotaiah, *Modeling and analysis of local hot spot formation in down-flow adiabatic packed-bed reactors*. Chemical Engineering Science, 2007. **62**(18): p. 4926-4943.

119. Stanek, V. and J. Szekely, *Three-dimensional flow of fluids through nonuniform packed beds*. AIChE Journal, 1974. **20**(5): p. 974-980.
120. Hashimoto, K., et al., *The production of renewable energy in the form of methane using electrolytic hydrogen generation*. Energy, Sustainability and Society, 2014. **4**(1): p. 17.
121. Rieke, S., *Erste industrielle power-to-gas-anlage mit 6 megawatt*. GWF–Gas| Erdgas, 2013: p. 660-664.
122. Bajohr, S., et al., *Kopplung der ptg-technologie mit thermochemischer biomassevergasung: Das kic-projekt, demosng*. Gas Energie, 2014. **155**: p. 470-475.
123. Götz, M., et al., *Renewable Power-to-Gas: A technological and economic review*. Renewable Energy, 2016. **85**: p. 1371-1390.
124. Gutiérrez-Martín, F. and L.M. Rodríguez-Antón, *Power-to-SNG technology for energy storage at large scales*. International Journal of Hydrogen Energy, 2016. **41**(42): p. 19290-19303.
125. Connolly, D., B.V. Mathiesen, and I. Ridjan, *A comparison between renewable transport fuels that can supplement or replace biofuels in a 100% renewable energy system*. Energy, 2014. **73**: p. 110-125.
126. Dry, M.E., *The Fischer-Tropsch process: 1950-2000*. Catalysis Today, 2002. **71**(3-4): p. 227-241.
127. Steynberg, A.P., *Chapter 1 - Introduction to Fischer-Tropsch Technology*, in *Studies in Surface Science and Catalysis*, A. Steynberg and M. Dry, Editors. 2004, Elsevier. p. 1-63.
128. Kopyscinski, J., T.J. Schildhauer, and S.M.A. Biollaz, *Production of synthetic natural gas (SNG) from coal and dry biomass – A technology review from 1950 to 2009*. Fuel, 2010. **89**(8): p. 1763-1783.
129. Rönsch, S., et al., *Review on methanation – From fundamentals to current projects*. Fuel, 2016. **166**: p. 276-296.
130. Dry, M.E., *High quality diesel via the Fischer–Tropsch process – a review*. Journal of Chemical Technology & Biotechnology, 2002. **77**(1): p. 43-50.
131. Schulz, H., *Short history and present trends of Fischer–Tropsch synthesis*. Applied Catalysis A: General, 1999. **186**(1): p. 3-12.
132. Davis, B.H., *Fischer–Tropsch synthesis: Overview of reactor development and future potentialities*. Topics in Catalysis, 2005. **32**(3): p. 143-168.

133. Schaaf, T., et al., *Methanation of CO₂ - storage of renewable energy in a gas distribution system*. Energy, Sustainability and Society, 2014. **4**(1): p. 2.
134. U.S. Department of Energy, O.o.F.E., *Practical Experience Gained During the First Twenty Years of Operation of the Great Plains Gasification Plant and Implications for Future Projects*. 2006, U.S. Department of Energy.
135. Topsøe, H. *Topsøe Recycle Energy-efficient Methanation Process*. 2018; Available from: <https://www.topsoe.com/research/research-activities-papers/sng>.
136. Höhle, B., et al., *Methane from synthesis gas and operation of high-temperature methanation*. Nuclear Engineering and Design, 1984. **78**(2): p. 241-250.
137. Kopyscinski, J., T.J. Schildhauer, and S.M.A. Biollaz, *Methanation in a fluidized bed reactor with high initial CO partial pressure: Part I—Experimental investigation of hydrodynamics, mass transfer effects, and carbon deposition*. Chemical Engineering Science, 2011. **66**(5): p. 924-934.
138. Kopyscinski, J., T.J. Schildhauer, and S.M.A. Biollaz, *Fluidized-Bed Methanation: Interaction between Kinetics and Mass Transfer*. Industrial & Engineering Chemistry Research, 2011. **50**(5): p. 2781-2790.
139. Brooks, K.P., et al., *Methanation of carbon dioxide by hydrogen reduction using the Sabatier process in microchannel reactors*. Chemical Engineering Science, 2007. **62**(4): p. 1161-1170.
140. Belimov, M., D. Metzger, and P. Pfeifer, *On the temperature control in a microstructured packed bed reactor for methanation of CO/CO₂ mixtures*. AIChE Journal, 2017. **63**(1): p. 120-129.
141. Liu, Z., et al., *Total methanation of syngas to synthetic natural gas over Ni catalyst in a micro-channel reactor*. Fuel, 2012. **95**: p. 599-605.
142. Hou, B., et al., *Optimization and simulation of the Sabatier reaction process in a packed bed*. AIChE Journal, 2016. **62**(8): p. 2879-2892.
143. Türks, D., et al., *Methanation of CO₂ on Ni/Al₂O₃ in a Structured Fixed-Bed Reactor—A Scale-Up Study*. Catalysts, 2017. **7**(5): p. 152.
144. Kiewidt, L. and J. Thöming, *Predicting optimal temperature profiles in single-stage fixed-bed reactors for CO₂-methanation*. Chemical Engineering Science, 2015. **132**: p. 59-71.

145. Schlereth, D. and O. Hinrichsen, *A fixed-bed reactor modeling study on the methanation of CO₂*. Chemical Engineering Research and Design, 2014. **92**(4): p. 702-712.
146. Ohya, H., et al., *Methanation of carbon dioxide by using membrane reactor integrated with water vapor permselective membrane and its analysis*. Journal of Membrane Science, 1997. **131**(1-2): p. 237-247.
147. Currie, R., M.W. Fowler, and D.S.A. Simakov, *Catalytic membrane reactor for CO₂ hydrogenation using renewable streams: Model-based feasibility analysis*. Chemical Engineering Journal, 2019. **372**: p. 1240-1252.
148. Kreitz, B., G.D. Wehinger, and T. Turek, *Dynamic simulation of the CO₂ methanation in a micro-structured fixed-bed reactor*. Chemical Engineering Science, 2019. **195**: p. 541-552.
149. Hwang, S. and R. Smith, *Heterogeneous catalytic reactor design with optimum temperature profile I: application of catalyst dilution and side-stream distribution*. Chemical Engineering Science, 2004. **59**(20): p. 4229-4243.
150. Rajasree, R., V.R. Kumar, and B.D. Kulkarni, *Performance Enhancement of Steam Methane Reforming Using Tubular Packed-Bed Microreactors and Dilution by Adsorbent*. Energy & Fuels, 2006. **20**(2): p. 463-472.
151. Schlereth, D., P.J. Donaubauer, and O. Hinrichsen, *Metallic Honeycombs as Catalyst Supports for Methanation of Carbon Dioxide*. Chemical Engineering & Technology, 2015. **38**(10): p. 1845-1852.
152. Schlereth, D. and O. Hinrichsen, *Comparison of a Pseudocontinuous, Heterogeneous 2D Conductive Monolith Reactor Model to a 3D Computational Fluid Dynamics Model*. Industrial & Engineering Chemistry Research, 2014. **53**(28): p. 11550-11556.
153. Hwang, S., P. Linke, and R. Smith, *Heterogeneous catalytic reactor design with optimum temperature profile II: application of non-uniform catalyst*. Chemical Engineering Science, 2004. **59**(20): p. 4245-4260.
154. Kiewidt, L. and J. Thöming, *Multiscale modeling of monolithic sponges as catalyst carrier for the methanation of carbon dioxide*. Chemical Engineering Science: X, 2019. **2**: p. 100016.

155. Kiewidt, L. and J. Thöming, *Pareto-optimal design and assessment of monolithic sponges as catalyst carriers for exothermic reactions*. Chemical Engineering Journal, 2019. **359**: p. 496-504.
156. Mazidi, S.K., M.T. Sadeghi, and M.A. Marvast, *Optimization of Fischer-Tropsch Process in a Fixed-Bed Reactor Using Non-uniform Catalysts*. Chemical Engineering and Technology, 2013. **36**(1): p. 62-72.
157. Adhikari, S., S. Fernando, and A. Haryanto, *A Comparative Thermodynamics and Experimental Analysis on Hydrogen Production by Steam Reforming of Glycerin*. Energy & Fuels, 2007. **21**(4): p. 2306-2310.
158. Ozkara-Aydinoglu, S., *Thermodynamics equilibrium analysis of combined carbon dioxide reforming with steam reforming of methane to synthesis gas*. International Journal of Hydrogen Energy, 2010. **35**(23): p. 12821-12828.
159. Lwin, Y., *Chemical Equilibrium by Gibbs Energy Minimization on Spreadsheets*. Vol. 16. 2000.
160. Malcolm W. Chase, Jr., *NIST-JANAF thermochemical tables*. 1998: Fourth edition. Washington, DC : American Chemical Society ; New York : American Institute of Physics for the National Institute of Standards and Technology, 1998.
161. Technology, N.I.o.S.a. *NIST Chemistry WebBook*. 2018; Available from: <https://webbook.nist.gov/chemistry/#>.
162. Çengel, Y.A., *Thermodynamics : an engineering approach*. 2008: Sixth edition. Boston : McGraw-Hill Higher Education, [2008] ©2008.
163. Hou, K. and R. Hughes, *The Kinetics of Methane Steam Reforming Over a Ni/ α -Al₂O₃ Catalyst*. Vol. 82. 2001. 311-328.
164. Deen, W.M., *Analysis of Transport Phenomena*. 1998: Oxford University Press, USA.
165. Park, N., et al., *Modeling of a pilot-scale fixed-bed reactor for iron-based Fischer–Tropsch synthesis: Two-dimensional approach for optimal tube diameter*. Fuel, 2014. **122**(0): p. 229-235.
166. R. Byron Bird, W.E.S., Edwin N. Lightfoot, *Transport Phenomena*. 1960: John Wiley & Sons.
167. Trimm, D. and A. Stanislaus, *The control of pore size in alumina catalyst supports: a review*. Applied Catalysis, 1986. **21**(2): p. 215-238.

168. Kong, W., et al., *A Simple Expression for the Tortuosity of Gas Transport Paths in Solid Oxide Fuel Cells' Porous Electrodes*. *Energies*, 2015. **8**(12): p. 12406.
169. Chan, S.H., D.L. Hoang, and O.L. Ding, *Transient performance of an autothermal reformer—A 2-D modeling approach*. *International Journal of Heat and Mass Transfer*, 2005. **48**(19): p. 4205-4214.
170. Zhao, L.-J. and Q. Sun, *Calculations of effectiveness factors and the criteria of mass transfer effect for high-temperature methanation (HTM) catalyst*. *International Journal of Low-Carbon Technologies*, 2015. **10**(3): p. 288-293.
171. Renken, A. and L. Kiwi-Minsker, *Catalytic reaction engineering principles*. *Catalysis: From Principles to Applications*, 2012: p. 67-109.
172. Miao, B., et al., *Catalysis mechanisms of CO₂ and CO methanation*. *Catalysis Science & Technology*, 2016. **6**(12): p. 4048-4058.
173. Bremer, J., K.H.G. Rätze, and K. Sundmacher, *CO₂ methanation: Optimal start-up control of a fixed-bed reactor for power-to-gas applications*. *AIChE Journal*, 2017. **63**(1): p. 23-31.
174. Schechter, R.S., *Transport Phenomena* (Bird, R. Byron; Stewart, Warren E.; Lightfoot, Edwin N.). *Journal of Chemical Education*, 1961. **38**(9): p. A640.
175. Henrici-Olivé, G. and S. Olivé, *The Fischer-Tropsch Synthesis: Molecular Weight Distribution of Primary Products and Reaction Mechanism*. *Angewandte Chemie International Edition in English*, 1976. **15**(3): p. 136-141.
176. Ducamp, J., A. Bengaouer, and P. Baurens, *Modelling and experimental validation of a CO₂ methanation annular cooled fixed-bed reactor exchanger*. *The Canadian Journal of Chemical Engineering*, 2017. **95**(2): p. 241-252.
177. Chein, R.Y., W.Y. Chen, and C.T. Yu, *Numerical simulation of carbon dioxide methanation reaction for synthetic natural gas production in fixed-bed reactors*. *Journal of Natural Gas Science and Engineering*, 2016. **29**: p. 243-251.
178. Hwang, H.T., et al., *A membrane-based reactive separation system for CO₂ removal in a life support system*. *Journal of Membrane Science*, 2008. **315**(1-2): p. 116-124.
179. Bird, L., et al., *Wind and solar energy curtailment : A review of international experience*. *Renewable & sustainable energy reviews*, 2016. **65**: p. 577-586.

180. Li, C., et al., *Comprehensive review of renewable energy curtailment and avoidance: A specific example in China*. Renewable and Sustainable Energy Reviews, 2015. **41**: p. 1067-1079.
181. DOE. *Pumped-Storage Hydropower*. 2019; Available from: <https://www.energy.gov/eere/water/pumped-storage-hydropower>.
182. Bailera, M., et al., *Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO₂*. Renewable and Sustainable Energy Reviews, 2017. **69**: p. 292-312.
183. Walker, S.B., et al., *Economic analysis with respect to Power-to-Gas energy storage with consideration of various market mechanisms*. International Journal of Hydrogen Energy, 2016. **41**(19): p. 7754-7765.
184. Liu, W., F. Wen, and Y. Xue, *Power-to-gas technology in energy systems: current status and prospects of potential operation strategies*. Journal of Modern Power Systems and Clean Energy, 2017. **5**(3): p. 439-450.
185. Stempien, J.P., et al., *Production of sustainable methane from renewable energy and captured carbon dioxide with the use of Solid Oxide Electrolyzer: A thermodynamics assessment*. Energy, 2015. **82**: p. 714-721.
186. Giglio, E., et al., *Power-to-Gas through High Temperature Electrolysis and Carbon Dioxide Methanation: Reactor Design and Process Modeling*. Industrial & Engineering Chemistry Research, 2018. **57**(11): p. 4007-4018.
187. Stempien, J.P., et al., *Energy and exergy analysis of Solid Oxide Electrolyser Cell (SOEC) working as a CO₂ mitigation device*. International Journal of Hydrogen Energy, 2012. **37**(19): p. 14518-14527.
188. Ni, M., *2D thermal modeling of a solid oxide electrolyzer cell (SOEC) for syngas production by H₂O/CO₂ co-electrolysis*. International Journal of Hydrogen Energy, 2012. **37**(8): p. 6389-6399.
189. Ni, M., *An electrochemical model for syngas production by co-electrolysis of H₂O and CO₂*. Journal of Power Sources, 2012. **202**: p. 209-216.
190. Chen, B., H. Xu, and M. Ni, *Modelling of SOEC-FT reactor: Pressure effects on methanation process*. Applied Energy, 2017. **185**: p. 814-824.

191. Schwabe, F., et al., *Concept, design, and energy analysis of an integrated power-to-methanol process utilizing a tubular proton-conducting solid oxide electrolysis cell*. International Journal of Hydrogen Energy, 2018.
192. Sun, X., et al., *Thermodynamics analysis of synthetic hydrocarbon fuel production in pressurized solid oxide electrolysis cells*. International Journal of Hydrogen Energy, 2012. **37**(22): p. 17101-17110.
193. Jan Pawel Stempien, Q.S., Siew Hwa Chan, *Solid Oxide Electrolyzer Cell Modeling: A Review*. Journal of Power Technologies, 2013. **93**.
194. Schmidt, O., et al., *Future cost and performance of water electrolysis: An expert elicitation study*. International Journal of Hydrogen Energy, 2017. **42**(52): p. 30470-30492.
195. Nguyen, V.N., et al., *Long-term tests of a Jülich planar short stack with reversible solid oxide cells in both fuel cell and electrolysis modes*. International Journal of Hydrogen Energy, 2013. **38**(11): p. 4281-4290.
196. Graves, C., et al., *Eliminating degradation in solid oxide electrochemical cells by reversible operation*. Nature Materials, 2014. **14**: p. 239.
197. Brisse, A., J. Schefold, and M. Zahid, *High temperature water electrolysis in solid oxide cells*. International Journal of Hydrogen Energy, 2008. **33**(20): p. 5375-5382.
198. Laguna-Bercero, M.A., *Recent advances in high temperature electrolysis using solid oxide fuel cells: A review*. Journal of Power Sources, 2012. **203**: p. 4-16.
199. Pan, Z., et al., *Experimental and thermodynamics study on the performance of water electrolysis by solid oxide electrolyzer cells with Nb-doped Co-based perovskite anode*. Applied Energy, 2017. **191**: p. 559-567.
200. Ge, X.M., et al., *Solid Oxide Fuel Cell Anode Materials for Direct Hydrocarbon Utilization*. Advanced Energy Materials, 2012. **2**(10): p. 1156-1181.
201. Murray, E.P., T. Tsai, and S.A. Barnett, *A direct-methane fuel cell with a ceria-based anode*. Nature, 1999. **400**: p. 649.
202. Park, S., J.M. Vohs, and R.J. Gorte, *Direct oxidation of hydrocarbons in a solid-oxide fuel cell*. Nature, 2000. **404**: p. 265.
203. McLean, G.F., et al., *An assessment of alkaline fuel cell technology*. International Journal of Hydrogen Energy, 2002. **27**(5): p. 507-526.

204. Cheng, X., et al., *A review of PEM hydrogen fuel cell contamination: Impacts, mechanisms, and mitigation*. Journal of Power Sources, 2007. **165**(2): p. 739-756.
205. Ribeiro, A.M., et al., *A parametric study of layered bed PSA for hydrogen purification*. Chemical Engineering Science, 2008. **63**(21): p. 5258-5273.
206. Moon, D.-K., et al., *Pressure Swing Adsorption Process for Recovering H₂ from the Effluent Gas of a Melting Incinerator*. Industrial & Engineering Chemistry Research, 2014. **53**(40): p. 15447-15455.
207. Zeng, K. and D. Zhang, *Recent progress in alkaline water electrolysis for hydrogen production and applications*. Progress in Energy and Combustion Science, 2010. **36**(3): p. 307-326.
208. Carmo, M., et al., *A comprehensive review on PEM water electrolysis*. International Journal of Hydrogen Energy, 2013. **38**(12): p. 4901-4934.
209. Kirubakaran, A., S. Jain, and R.K. Nema, *A review on fuel cell technologies and power electronic interface*. Renewable and Sustainable Energy Reviews, 2009. **13**(9): p. 2430-2440.
210. Lutz, A.E., et al., *Thermodynamics analysis of hydrogen production by steam reforming*. International Journal of Hydrogen Energy, 2003. **28**(2): p. 159-167.
211. Authority, E.M. *Facilitating the Entry of Solar Energy into Singapore*. 2018; Available from: https://www.ema.gov.sg/solar_photovoltaic_systems.aspx.
212. Roberto Scataglini, A.M., Max Wei, Shuk Han Chan, Timothy Lipman, David Gosselin, Anna D'Alessio, Hanna Breunig, Whitney G. Colella, and Brian D. James, *A Total Cost of Ownership Model for Solid Oxide Fuel Cells in Combined Heat and Power and Power Only Applications* 2015, Environmental Energy Technologies Division.
213. Institute, B.M., *Manufacturing Cost Analysis of 100 and 250 kW Fuel Cell Systems for Primary Power and Combined Heat and Power Applications*. 2016, Battelle Memorial Institute.
214. Mark Weimar, L.C., David Gotthold, Greg Whyatt, *Cost Study for Manufacturing of Solid Oxide Fuel Cell Power Systems*. 2013, Pacific Northwest National Laboratory.
215. Chandel., M. and E. Williams., *Synthetic Natural Gas (SNG): Technology, Environmental Implications, and Economics*. 2009.

216. Baier, J., G. Schneider, and A. Heel, *A Cost Estimation for CO₂ Reduction and Reuse by Methanation from Cement Industry Sources in Switzerland*. *Frontiers in Energy Research*, 2018. **6**(5).
217. Aranda, G., A. van der Drift, and R. Smit, *The economy of large scale biomass to substitute natural gas (bioSNG) plants*. 2014: ECN.
218. Zwart, R., et al., *Production of synthetic natural gas (SNG) from biomass*. Report for Energy Research Center of the Netherlands. Available online: <http://www.ecn.nl/docs/library/report/2006/e06018.pdf> (accessed on 3 June 2013), 2006.
219. Tilak K. Doshi, N.S.D.S., Nguyen Phuong Linh, Teo Han Guan, *The Economics of Solar PV in Singapore 2011*, Energy Economics Division.
220. Data.gov.sg. *Sunshine Duration- Monthly Mean Daily Duration*. 2018 [cited 2018 June 13]; Available from: <https://data.gov.sg/dataset/sunshine-duration-monthly-mean-daily-duration>.
221. Singhal, S.C., *Solid oxide fuel cells for stationary, mobile, and military applications*. Solid State Ionics, 2002. **152-153**: p. 405-410.
222. Boubault, A., et al., *Levelized cost of energy (LCOE) metric to characterize solar absorber coatings for the CSP industry*. *Renewable Energy*, 2016. **85**: p. 472-483.
223. Miller, F.P., A.F. Vandome, and M.B. John, *Net Present Value*. 2011: VDM Publishing.
224. Authority, E.M. *Electricity Tariffs*. 2019 [cited 2019 11 Jan]; Available from: https://www.ema.gov.sg/Residential_Electricity_Tariffs.aspx.
225. Citygas. *Gas Tariffs*. 2019 [cited 2019 11 Jan]; Available from: <https://www.citygas.com.sg/useful-info/gas-tariffs/>.
226. Suhaib Muhammad, A. and A. John. *Low-cost storage options for solar hydrogen systems for remote area power supply*. in *WHEC16: 16 World Hydrogen Energy Conference*. 2006. France.
227. Administration, E.I., *Cost and Performance Characteristics of New Generating Technologies, Annual Energy Outlook 2018*. 2018.
228. SPgroup. *Tariff Rates*. 2018 [cited 2018 13 Jan]; Available from: <https://www.spgroup.com.sg/what-we-do/billing>.
229. Technology, T.P.O.o.S.a., *Carbon Footprint of Electricity Generation*. 2011, The Parliamentary Office of Science and Technology.