

**DESIGN DEVELOPMENT OF
INTEGRATED METHANE PYROLYSIS AND REFORMING
PROCESSES FOR LOW-CARBON AMMONIA PRODUCTION**

BY
MUHAMAD REDA GALIH PANGESTU

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

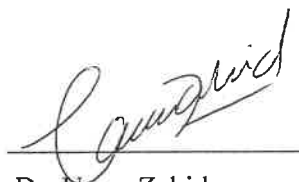
MAY 2024

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

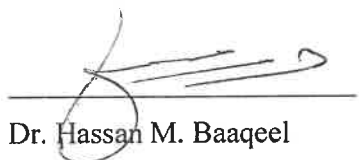
COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES

This thesis, written by **MUHAMAD REDA GALIH PANGESTU** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate & Interdisciplinary Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMICAL ENGINEERING**



Dr. Umer Zahid

(Advisor)



Dr. Hassan M. Baaqeel

Chairman, Department of Chemical
Engineering



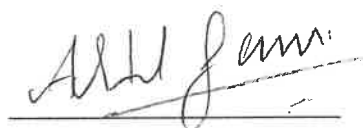
Dr. Eid Musaad Al-Mutairi

(Member)



Prof. Suliman Saleh Al-Homidan

Dean, College of Graduate &
Interdisciplinary Studies



Dr. Abdul Gani Abdul Jameel

(Member)

Date



© Muhamad Reda Galih Pangestu

2024

Dedicated to my parents, my family, and society

ACKNOWLEDGMENTS

In the name of Allah, the Most Gracious, the Most Merciful. All the praises and thanks be to Allah ﷻ who has given me the chance and ability to complete my master's study at King Fahd University of Petroleum and Minerals (KFUPM). May blessings and peace be continuously bestowed upon Prophet Muhammad ﷺ, his families, his companions, and the people who follow his pathway.

I am truly grateful and thankful to my thesis advisor, Dr. Umer Zahid, for his guidance, patience, and encouragement to me over the past few years. I would like to convey great gratefulness to my thesis committee members Dr. Eid Musaad Al-Mutairi and Dr. Abdul Gani Abdul Jameel for their support and recommendations during the time of this effort.

I want to reveal my admiration for the Chemical Engineering Department of KFUPM especially to our chairman, Dr. Hassan Mohammed Baaqeel, that facilitate me to finish and spread our thesis work. Thanks to all my friends from the Chemical Engineering Department for providing me with incredible accompaniment. My grateful also for my workplace, PT Pupuk Kujang Cikampek for allowing me to pursue higher degree in KFUPM.

My profound gratitude goes to my parents, my wife, and my daughters who were extremely patient during my study at KFUPM when they needed me the most. Thanks a lot also to Indonesian community in KFUPM for their encouragement and continuous support during this study period. To all other individuals who have contributed to the success of this work, from the bottom of my heart, I say thank you and may Allah bless you all.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	v
TABLE OF CONTENTS	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF ABBREVIATIONS	xiii
ABSTRACT	xiv
مستخلص	xvi
CHAPTER 1 INTRODUCTION.....	1
1.1 Background	1
1.2 Problem Statement	4
1.3 Objectives	5
1.4 Thesis Outline	6
1.5 Completion Timeline	7
CHAPTER 2 LITERATURE REVIEW	8
2.1 Hydrogen from Steam Methane Reforming (SMR)	8
2.2 Hydrogen from Methane Pyrolysis	9
2.2.1 Reaction Mechanism, Energy, and Hydrogen Yield	9
2.2.2 Thermodynamics Analysis.....	12
2.3 Process Development and Challenges	13
2.3.1 Feed Pretreatment	14
2.3.2 Solid–Gas Separation and Product Purification	16

2.4	Catalyst for Methane Pyrolysis	17
2.4.1	Solid Catalyst	17
2.4.2	Molten Catalyst (Metals and Salts).....	20
2.5	Reactor Design and Maturity	24
2.5.1	Fluidized Bed Reactor.....	24
2.5.2	Moving Bed Reactor	26
2.5.3	Liquid Metal Bubble Column Reactor.....	27
2.5.4	Plasma Reactors	29
2.6	Solid Carbon Types, applications, and current Market.....	31
2.7	Techno-Economic Study for Methane Pyrolysis	33
CHAPTER 3 METHODOLOGY		36
3.1	Model Basis and Assumptions.....	36
3.2	Model Validation and Sensitivity Analysis	37
3.3	Economic Analysis	38
CHAPTER 4 PROCESS DESIGN DEVELOPMENT		39
4.1	Conventional SMR-Ammonia (Base model).....	39
4.1.1	Desulfurization section	41
4.1.2	Reformer and Water Gas Shift (WGS) section.....	42
4.1.3	CO ₂ Removal and Methanation Section	44
4.1.4	Ammonia Synthesis	45
4.1.5	Refrigerant Loop	46
4.2	Integration of MP-SMR-Ammonia (Proposed Model).....	49
4.2.1	Methane Pyrolysis Kinetic	51

4.2.2	Operating Condition Selection.....	52
4.2.3	MP Reactor Sizing Optimization	54
CHAPTER 5 RESULTS AND DISCUSSIONS.....		61
5.1	Base Model Reactor Validation	61
5.2	MP Reactor Kinetic Validation.....	64
5.3	Product and CO ₂ Emission.....	68
5.4	Energy Analysis	70
5.5	Economic Analysis	72
CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS.....		79
6.1	Conclusions.....	79
6.2	Recommendations.....	80
REFERENCES.....		81
VITAE.....		91

LIST OF TABLES

Table 1.1 Completion Timeline	7
Table 2.1 Energy and stoichiometry reaction comparison for several hydrogen production technologies. Enthalpy data are taken from the National Institute of Standards and Technology (NIST) [30,33]	10
Table 2.2 Typical composition of natural gas. Data taken from sample analysis result of a laboratory control in West Java, Indonesia in April 2022 [65]	15
Table 2.3 Type of catalyst and its performance in MP with regard to the carbon coproduct	21
Table 2.4 Solid carbon type, applications, market size (MT: metric ton) [96]	33
Table 2.5 Hydrogen cost from MP TEA studies. All H ₂ costs are shown without solid carbon revenue included.....	34
Table 3.1 Natural Gas Composition.....	36
Table 3.2 Design specification for Integrated SMR-MP-Ammonia Plant Model.....	37
Table 4.1 Major unit operation models and specification	56
Table 4.2 Material balance of proposed integration model with 50% NG split ratio	58
Table 5.1 Validation of key parameters of ammonia converter model with actual plant data	63
Table 5.2 Key parameter summary for investment analysis comparison between base and proposed model	73
Table 5.3 Annual revenue comparison of based and proposed model in no CO ₂ tax scenario	77

LIST OF FIGURES

Figure 1.1	Percent share of hydrogen production by fuel source in 2021 and 2022. This figure was adapted with permission from [4]. Copyright 2023 International Energy Agency (IEA).	2
Figure 1.2	Projected ammonia application and demand in 2030 and 2050 for different scenarios. Adapted from [10]. Copyright 2023 International Energy Agency (IEA)	3
Figure 2.1	Different production pathways for producing 1 ton of H ₂ . Carbon dioxide from SMR does not include the combustion or flue gas.....	11
Figure 2.2	Hydrogen yield profile for 1 kmol/hr methane feed into MP Gibbs Reactor under different pressure and temperature conditions based on Aspen Plus simulation.....	12
Figure 2.3	Process design of MP process for hydrogen production.....	14
Figure 2.4	Temperature ranges of different catalyst types for MP. Adapted with permission from [52]. Copyright 2015 Springer Science Business Media Dordrecht	18
Figure 2.5	Activation energy of several type of solid and molten catalyst and comparison with non-catalytic energy required. Drawn based on table from [37]	23
Figure 2.6	(a) FBR design for MP proposed by US DOE. Reprinted with permission from [77]. Copyright 2021 Elsevier and (b) MBR design proposed by BASF. Redrawn based on [30]	26
Figure 2.7	Concept design of LMBCR for MP. Reprinted with permission from [23]. Copyright 2018 Elsevier	28

Figure 2.8	Thermal plasma arc reactor for MP. Adapted with permission from [89]. Copyright 2023 Elsevier	30
Figure 2.9	Type of carbon coproduct in MP based on catalyst used and reaction temperature. This figure was redrawn based on several literatures from [92,93]. CNT: Carbon nanotube and CNF: Carbon nanofiber.....	31
Figure 4.1	Simplified SMR Ammonia Urea process block diagram. SMR reaction happens in the Primary Reformer section.	40
Figure 4.2	Natural Gas Feed Pretreatment	40
Figure 4.3	Desulfurization Section.....	41
Figure 4.4	Process flow diagram of Reformer Section. SMR reaction happens in the Primary Reformer (“PRIMREFM”) and air injection in the secondary reformer (“SECREFR”).....	43
Figure 4.5	Flow diagram of Water Gas Shift Section	44
Figure 4.6	Ammonia synthesis reactor (NH ₃ converter) configuration with 3 PFR bed model in series and intercoolers to control each bed inlet temperature	46
Figure 4.7	Refrigerant loop process flow diagram.....	48
Figure 4.8	Proposed design of MP integration in SMR-ammonia-urea production plant.	50
Figure 4.9	Sensitivity analysis to determine the optimal number of tubes in the MP reactor using existing dimensions of the SMR primary reformer tubes	54
Figure 4.10	Methane pyrolysis section.....	55
Figure 4.11	Proposed integration model flowsheet design through Aspen Plus	57
Figure 5.1	Validation of Primary and Secondary Reformer with actual plant data	62

Figure 5.2	Ammonia converter outlet gas composition compared with the actual plant data.....	64
Figure 5.3	MP kinetic model under high-pressure conditions at a constant temperature of 600°C (Figure 5.3a) and 1,000°C (Figure 5.3b), compared with the equilibrium state.....	65
Figure 5.4	Keipi experimental data for non-catalytic MP process at atmospheric pressure and temperature range of 390 – 1,170 °C. The red box shows the highest methane conversion at the highest temperature range (900 – 1,170 °C)	67
Figure 5.5	MP kinetic reactor models compared with the Catalan model with the same reactor type and thermodynamic properties (RKS-BM) in Aspen Plus v11	67
Figure 5.6	Products and CO ₂ emission in different split ratio.....	69
Figure 5.7	Energy and products profile for various split ratio	70
Figure 5.8	Energy distribution profile comparison of base case model (split ratio = 0) and integration model at different NG feed spit ratio	71
Figure 5.9	Total capital cost breakdown in direct and indirect cost.....	73
Figure 5.10	Operating cost breakdown comparison for each model.....	74
Figure 5.11	Cash flow comparison for base and proposed model when CO ₂ tax USD 8/ton applied.....	75
Figure 5.12	Sensitivity analysis of CO ₂ tax and carbon black price for the similar profitability of proposed and based model.....	77

LIST OF ABBREVIATIONS

<i>AE</i>	: Alkaline electrolysis
<i>BFW</i>	: Boiler feed water
<i>CNFs</i>	: Carbon nanofibers
<i>CNTs</i>	: Carbon nanotubes
<i>FBR</i>	: Fluidized bed reactor
<i>HTS</i>	: High temperature shift reactor
<i>LTS</i>	: Low temperature shift
<i>LMBCR</i>	: Liquid metal bubble column reactor
<i>MBR</i>	: Mixed bed reactor
<i>MP</i>	: Methane pyrolysis
<i>MTPD</i>	: Metric ton per day
<i>NG</i>	: Natural gas
<i>PEM</i>	: Polymer electrolyte membrane
<i>SMR</i>	: Steam methane reforming
<i>TEA</i>	: Techno-economic analysis
<i>TRL</i>	: Technology Readiness Level

ABSTRACT

Full Name : Muhamad Reda Galih Pangestu

Thesis Title : Design Development of Integrated Methane Pyrolysis and Reforming Processes for Low-Carbon Ammonia Production

Major Field : Chemical Engineering

Date of Degree : May 2024

Industrial ammonia production, primarily through steam methane reforming (SMR), significantly contributes to greenhouse gas emissions. To limit global temperature rise to below 1.5 °C, modifying existing plants is essential. Methane pyrolysis (MP) offers a solution by enabling hydrogen or ammonia production without carbon dioxide emissions, while producing marketable solid carbon. This study examines the technical and economic feasibility of integrating MP into a conventional SMR-ammonia plant by splitting the natural gas (NG) feed between the MP and SMR sections. Operating at 33 bar and 1,400°C, the MP section achieves a 71.2% conversion rate, producing carbon black as a co-product. The integrated model shows reduced CO₂ emissions and lower energy consumption compared to a baseline SMR-only plant. With a 50% NG feed split to MP, the model produces 773 metric tons per day of ammonia with 35% lower CO₂ emission intensity. Sensitivity analysis indicates the economic viability of the integrated model under various scenarios. Considering current and projected Middle Eastern prices for NG, ammonia, carbon black, and a CO₂ tax, the 50% NG feed split scenario is approximately 48 million

USD more profitable annually than the baseline model. This profitability is enhanced by additional revenue from carbon black sales and potential steam export. The levelized cost of ammonia from the proposed model is 187 USD/ton if carbon black revenue is considered and 240 USD/ton without it.

مستخلص

الاسم الكامل: محمد رضا غاليه بانجستو

عنوان الرسالة: تطوير تصميم عمليات البيروليز والتحويل المتكاملة للميثان لإنتاج الأمونيا ذات الكربون المنخفض

المجال الرئيسي: الهندسة الكيميائية

تاريخ الحصول على الدرجة: ذو القعدة 1445 هـ

يُعتبر إنتاج الأمونيا الصناعي من خلال إصلاح الميثان البخاري (SMR) مساهماً كبيراً في انبعاثات غازات الاحتباس الحراري. وللدخول من ارتفاع درجة الحرارة العالمية إلى أقل من 1.5 درجة مئوية، فإن تعديل المصانع الحالية أمر ضروري. يوفر التحلل الحراري للميثان (MP) حلاً من خلال إنتاج الهيدروجين أو الأمونيا دون انبعاثات ثاني أكسيد الكربون، مع إنتاج الكربون الصلب القابل للتسويق. تدرس هذه الدراسة الجدوى الفنية والاقتصادية لدمج التحلل الحراري للميثان في مصنع الأمونيا التقليدي المعتمد على إصلاح الميثان البخاري من خلال تقسيم إمداد الغاز الطبيعي بين قسمي التحلل الحراري للميثان وإصلاح الميثان البخاري. يعمل قسم التحلل الحراري للميثان عند ضغط 33 بار ودرجة حرارة 1400 درجة مئوية، محققاً معدل تحويل للميثان بنسبة 71.2%، مع إنتاج الكربون الأسود كمنتج ثانوي. تم تصميم مفاعل التحلل الحراري للميثان ليكون قابلاً للتبادل مع الأنابيب الاحتياطية من مفاعل إصلاح الميثان البخاري، بالإضافة إلى وحدة لاسترداد الميثان وتدقيق إعادة التدوير لتحسين إنتاجية المنتجات. يظهر النموذج المدمج انخفاضاً في انبعاثات ثاني أكسيد الكربون واستهلاكاً أقل للطاقة مقارنة بالمصنع الأساسي المعتمد على إصلاح الميثان البخاري فقط. مع تقسيم 50% من إمداد الغاز الطبيعي إلى التحلل الحراري للميثان، ينتج النموذج 773 طناً مترياً يومياً من الأمونيا مع انخفاض بنسبة 35% في كثافة انبعاثات ثاني أكسيد الكربون. تشير تحليلات الحساسية إلى الجدوى الاقتصادية للنموذج المدمج تحت سيناريوهات مختلفة. بالنظر إلى الأسعار الحالية والمتوقعة في الشرق الأوسط للغاز الطبيعي والأمونيا والكربون الأسود وضريبة ثاني أكسيد الكربون، فإن سيناريو تقسيم 50% من إمداد الغاز الطبيعي يُظهر ربحية أكبر بنحو 48 مليون دولار سنوياً مقارنة بالنموذج الأساسي. تتعزز هذه الربحية بالإيرادات الإضافية من مبيعات الكربون الأسود وإمكانية تصدير البخار. يبلغ التكلفة المثلى لإنتاج الأمونيا من النموذج المقترح (50% تكامل) حوالي 187 دولاراً للطن إذا تم اعتبار إيرادات الكربون الأسود و240 دولاراً للطن دون اعتبارها.

CHAPTER 1

INTRODUCTION

1.1 Background

Ammonia (NH_3) stands out as one of the most widely manufactured industrial chemicals worldwide with nearly 200 million tons of production in 2022 [1]. To date, approximately 70% of ammonia finds its primary use in fertilizers, with the remaining portion dedicated to diverse industrial applications, including plastics, refrigerants, explosives, synthetic fibers, and potential fuel for clean energy transitions [2]. However, as depicted by Figure 1.1, the current production of hydrogen, the main ammonia reactant, heavily relies on fossil fuels, with over 60% of the production occurring through natural gas-based steam methane reforming (SMR) and the remaining portion primarily through coal gasification. This heavy dependence on fossil fuels and technologies has rendered ammonia one of the most emissions-intensive commodities in heavy industry. The Congressional Research Service (CRS) reports that ammonia production represents 15-20% of all carbon dioxide (CO_2) emissions from the chemical sector [2,3].

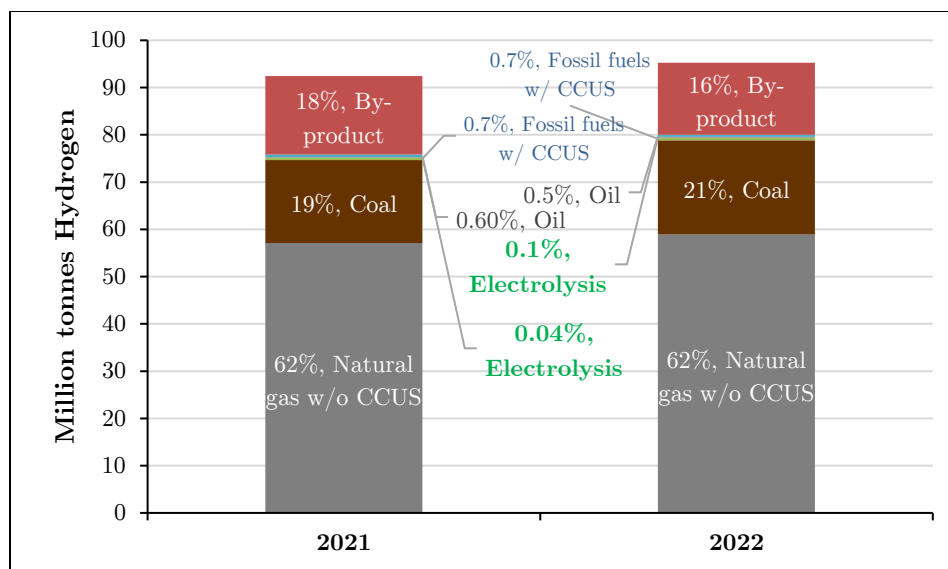


Figure 1.1 Percent share of hydrogen production by fuel source in 2021 and 2022. This figure was adapted with permission from [4]. Copyright 2023 International Energy Agency (IEA).

SMR is an endothermic reaction of methane (CH_4) with steam (H_2O) in the presence of a nickel-based catalyst at the temperature range of 800 – 1,000 °C to produce hydrogen (H_2) and carbon monoxide [5]. SMR is usually followed by a water gas shift (WGS) reaction for converting CO into CO_2 [6]. The H_2 produced is then used to react with nitrogen (N_2) from the air to produce ammonia via the Haber-Bosch process. The CO_2 generated as a byproduct is typically used to produce urea fertilizer if the ammonia and urea plants are coupled. However, for a single ammonia production facility, the CO_2 is mostly vented, some of them are stored and sold in liquid phase. The CO_2 that vented into the atmosphere are greatly contributed to greenhouse gas (GHG) emissions [1–3]. If methane or natural gas itself is used as fuel to reach the SMR temperature, the emission would be higher [5,7].

On a different front, in 2020, approximately 70 – 80% of ammonia applications were designated for fertilizer purposes, with urea-based fertilizers constituting around 57 – 67% of the overall fertilizer production from ammonia [8,9]. Notably, data from the

International Energy Agency (IEA) [10] as depicted in Figure 1.2, show that the demand profile for ammonia is poised to transform in the coming years, particularly with the adoption of sustainable development or net-zero emission scenarios.

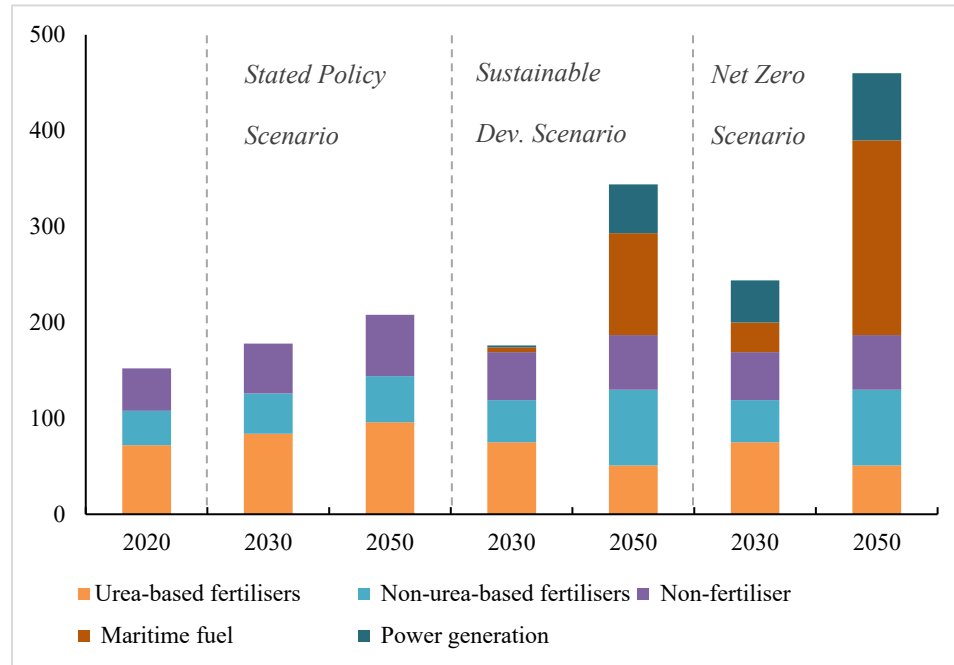


Figure 1.2 Projected ammonia application and demand in 2030 and 2050 for different scenarios. Adapted from [10]. Copyright 2023 International Energy Agency (IEA)

Despite becoming alternative low carbon maritime fuel, ammonia process production through SMR still leaves significant amount of CO₂ emission. To address this issue, several companies have implemented strategies such as constructing CO₂ liquid plants, dry ice plants, or developing carbon capture technology [6,11]. In Saudi Arabia, green ammonia will be produced by NEOM project with annual capacity of 1.2 million tons in 2025, while blue ammonia is currently produced by SABIC-Agri nutrient and Aramco. However, both blue and green ammonia are currently contributing less than 1% from total hydrogen production in 2022. Therefore, alternative novel solution is required to reach the decarbonization goal faster.

A novel solution to mitigate CO₂ emissions in SMR-Ammonia plant is by integration of methane pyrolysis (MP) into existing SMR-Ammonia process plants. MP reaction happened in a temperature range of 500 – 1,600 °C depending on the type of catalyst used [12,13]. The hydrogen produced via MP can be reacted with nitrogen to synthesize ammonia, while the solid carbon can be utilized as a valuable byproduct. Some literature called this process as *turquoise hydrogen* or *turquoise ammonia* [7,13].

This thesis proposes the integration of MP with existing SMR-ammonia plants as a pathway to low-carbon ammonia production. It will investigate various schemes and scenarios for splitting the natural gas feed and configuring the integrated process using Aspen Plus software. A techno-economic analysis (TEA) will be conducted to evaluate the economic feasibility of the proposed integration, considering capital and operational costs. The results will provide insights into the environmental and economic benefits of integrating MP with existing SMR-ammonia plants, paving the way for a more sustainable ammonia production industry.

1.2 Problem Statement

Industrial ammonia plants that mostly use SMR technology were chosen because of their proven reliability and efficiency. However, their contribution to 1.5% of GHG emissions should be mitigated with a novel approach that not only has lower emissions but also a competitive price. Moreover, the imposition of CO₂ taxes and penalties on GHG is becoming increasingly prevalent worldwide as part of efforts to mitigate climate change. These policies aim to internalize the environmental costs associated with carbon emissions and incentivize industries to adopt cleaner technologies and practices. Currently, CO₂ tax

rates worldwide vary from 0 – 156 USD/ton-CO₂ [14]. In the Middle East, the CO₂ tax rate averages around 4 – 8 USD/ton-CO₂ [15].

MP process is a promising approach but still has some constraints to reach maturity as SMR technology. The key distinction lies in the additional requirement of steam in SMR for the water gas shift reaction, resulting in the production of CO₂ as a byproduct. In contrast, MP exclusively utilizes methane as a feedstock, yielding a lower hydrogen output compared to SMR from the same quantity of methane [16]. Integrating these two technologies into an existing SMR-ammonia plant would gain some benefits if optimum design and configuration were applied. Based on the stoichiometry reaction, solid carbon as a co-product of MP would be produced three times as much as hydrogen. The solid carbon co-product type in MP such as carbon black, carbon nanotubes (CNTs), carbon nanofibers (CNFs), and graphite depends on the temperature reaction and the catalyst used [17]. Carbon black experiencing the largest market demand among other types with prices currently ranging from 0.8 to 2.1 USD/kg [18]. Utilizing the right solid carbon type in the reaction would help in the marketing and revenue of the plant.

1.3 Objectives

The aim of this study is to perform a comprehensive techno-economic analysis (TEA) of methane pyrolysis technology integrated into existing SMR-ammonia plants. The goal is to attain ammonia production with reduced emissions and enhanced cost competitiveness. Specifically, the research objectives are as follows:

- a. **Optimize Design and Configuration:** Investigate various schemes and scenarios for splitting natural gas feed, configuring the integration process, and determining the most efficient design for the integration plant.
- b. **Quantify Greenhouse Gas Reduction:** Calculate CO₂ equivalent (CO₂e) emission for selected scenarios and compare with the conventional SMR-Ammonia plant to quantify GHG reduction.
- c. **Evaluate Economic Viability:** Conduct a comprehensive techno-economic analysis to determine the economic feasibility of the integrated process, considering factors such as production costs, carbon taxes, and potential carbon credit revenues in the evolving global policy landscape.

1.4 Thesis Outline

- **Chapter 1 Introduction:** consists of background information, problem statement, objectives, outline and completion timeline.
- **Chapter 2 Literature Review:** presents an important review of the prevailing literature on methane pyrolysis process for hydrogen or ammonia production.
- **Chapter 3 Methodology:** comprises the methodology of this study. This chapter describes the simulation procedure including the assumptions and design for achieving the required goals of this study.
- **Chapter 4 Process Design Development:** this chapter delves into the design considerations of the proposed integration model, spanning from upstream operations such as feed splitting to adjustments of purge gas and any additional sections required.

- **Chapter 5 Results and Discussions.** This chapter presents the simulation results, validates the model, analyzes product yields and emissions, conducts energy and economic comparisons between the conventional and proposed models, and engages in discussions around the implications of these results.
- **Chapter 6 Conclusions:** presents the concluding remarks and suggestions for further studies.

1.5 Completion Timeline

The anticipated timeline for the completion of the proposed research project is shown in Table 1.1. The timeline is divided into four main phases: literature review, research methodology development, simulation, validation & analysis, and thesis writing.

Table 1.1 Completion Timeline

Task	Start Date	Finish Date	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun
Literature Review	Aug-23	Nov-23											
Learning Aspen Plus v11	Aug-23	Nov-23											
Methane Pyrolysis (MP) Simulation	Sep-23	Oct-23											
Generate SMR-Ammonia Simulation	Oct-23	Dec-23											
Integrate MP and SMR Simulation	Dec-23	Feb-24											
Validation and Optimatoin	Dec-23	Jan-24											
Thesis Writing	Sep-23	May-24											
Manuscrip Writing and Submission	Oct-23	Jun-24											
Conference	May-24	Jun-24											
Thesis Defense	May-24	Jun-24											

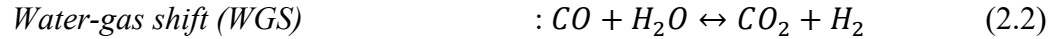
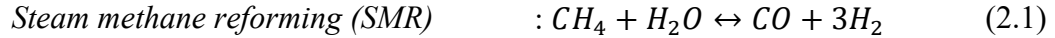
This work has been accepted for oral presentation at two prestigious conferences. The first is the Middle East Process Engineer Conference (MEPEC), taken place in Saudi Arabia from 6 – 8 May 2024. The second one is the European Symposium on Computer Aided Process Engineering (ESCAPE), set to be held in Florence, Italy, from June 2nd to 6th, 2024.

CHAPTER 2

LITERATURE REVIEW

2.1 Hydrogen from Steam Methane Reforming (SMR)

Natural gas (mainly methane) is reacted with steam (H_2O) with the help of catalysts at a pressure and temperature within 20–40 bar and 800–1,000 °C with the molar steam to carbon ratio maintained at approximately 2.5–3.5 to produce syngas (H_2 and CO) [19]. Carbon monoxide (CO) is then converted to CO_2 and H_2 in a water-gas shift (WGS) reactor to produce more hydrogen [20]. The main reactions are as follows:



SMR can handle substantial hydrogen capacities ranging from 130,000 to 300,000 tons/year, and these capacities are readily available in the commercial domain [6]. The associated hydrogen production costs from this technology typically fall within the range of 0.7 to 2.1 USD/kg, with variations primarily dependent on factors, such as natural gas prices (constituting 70%–80% of the cost), plant capacity, and the integration of a carbon capture facility [21]. Notably, achieving a carbon capture of 85% in the SMR process would result in an increase in the hydrogen price to approximately 1.14 USD/kg [6].

The emissions intensity of using natural gas in the SMR process ranges from 9.7 to 13.7 kg CO_2 eq/kg H_2 produced (without CCS), whereas with 85% carbon capture, the emission drops significantly to approximately 2 kg CO_2 /kg H_2 [22]. These data highlight

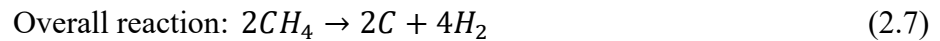
the environmental implications of and the potential for mitigating carbon emissions by integrating carbon capture into the SMR process.

2.2 Hydrogen from Methane Pyrolysis

Methane pyrolysis or methane decomposition process is an alternate way to produce hydrogen from methane through a catalytic or non-catalytic reaction in a temperature range of 600 – 1,600 °C without emitting carbon dioxide [23,24]. Methane (CH₄) undergoes a splitting process into its elementary components: solid carbon and hydrogen gas. Presently, numerous researchers are directing significant attention towards this technology, recognizing it as a promising avenue for the production of clean hydrogen [25–28].

2.2.1 Reaction Mechanism, Energy, and Hydrogen Yield

The mechanism of MP has been studied since the 1970s, and most researchers agree that the process entails a free-radical mechanism, with the initial reaction step involving the dissociation of CH₄ into a methyl radical (CH₃•) and a hydrogen atom [29,30]. The most well-known mechanism was proposed by Chen et al. [29,31] with the reactions are shown below.



Chen et al. [31] reported that, during the thermal decomposition of methane at 606–830 °C, hydrogen, and ethane (C₂H₆) are the main products of the reaction along with the formation of solid carbon. Typically, the formation of intermediate products, such as C₂H₆, C₂H₄, and C₂H₂, is faster than methane dehydrogenation. However, the product selectivity will mainly correspond to hydrogen and solid carbon, as shown in reaction (11) if the time and temperature increase [25].

Methane is known for its thermodynamic stability owing to the strong carbon-hydrogen (C-H) bonds within its molecular structure. Breaking these bonds during MP requires overcoming a considerable energy barrier, which results in an endothermic process [12]. Water molecules, which are central to water electrolysis, exhibit stability attributed to the oxygen-hydrogen (O-H) bonds. The energy required to break these bonds during electrolysis is also significant and represents an endothermic reaction [32]. The reactions for hydrogen production via MP, water electrolysis, and SMR are listed in Table 2.1.

Table 2.1 Energy and stoichiometry reaction comparison for several hydrogen production technologies. Enthalpy data are taken from the National Institute of Standards and Technology (NIST) [30,33]

Method	Reaction	Enthalpy (kJ/mol)
Methane Pyrolysis	$\frac{1}{2}CH_4(g) \rightarrow H_2(g) + \frac{1}{2}C(s)$	$\Delta H_{298\text{ K}}^0 = 37.7$
Water Electrolysis	$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$	$\Delta H_{298\text{ K}}^0 = 285.8$
Steam Methane Reforming	$\frac{1}{4}CH_4(g) + \frac{1}{2}H_2O(l) \rightarrow \frac{1}{4}CO_2(g) + H_2(g)$	$\Delta H_{298\text{ K}}^0 = 63.4$

Table 2.1 shows that the enthalpy energy per 1 mol of hydrogen production for MP was the lowest compared with SMR + WGS and water electrolysis. Water electrolysis requires seven times more energy to produce 1 mol of hydrogen than MP. The SMR + WGS reaction yields 0.5 ton-H₂/ton-CH₄ by utilizing steam or water as an additional

reactant, whereas MP yields 0.25 ton-H₂/ton-CH₄ without any additional reactant. A comparison of the yields and mass balances is shown in Figure 2.1.

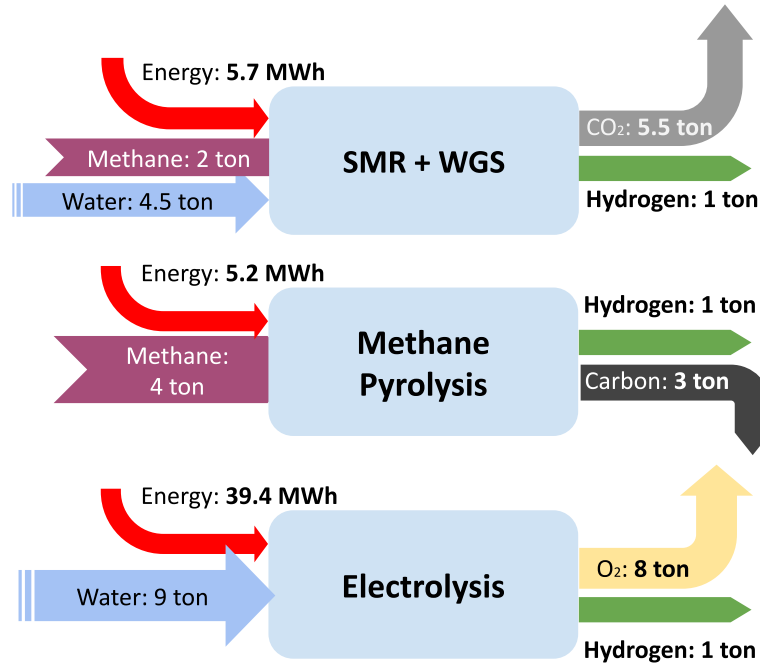


Figure 2.1 Different production pathways for producing 1 ton of hydrogen. Carbon dioxide from SMR does not include the combustion or flue gas.

SMR + WGS requires 2 tons of methane, 4.5 tons of steam, and 5.7 MWh of energy to produce 1 ton of hydrogen while emitting 5.5 tons of CO₂. MP, which uses 4 tons of methane and 5.2 MWh of energy, avoids steam input, and produces 3 tons of solid carbon as a potentially useful byproduct. On the other hand, electrolysis requires the highest energy (39.4 MWh) and water (9 tons) per ton of hydrogen, but has environmental benefits owing to the utilization of renewable electricity and the generation of oxygen.

2.2.2 Thermodynamics Analysis

The temperature required for MP is comparable to that of SMR, typically ranging between 600 and 1,600°C. Higher temperatures are advantageous for MP because the process is endothermic [34]. However, as shown in Figure 2.2, the pressure needs to be optimized. This shows that achieving high methane conversion becomes more challenging at higher pressures.

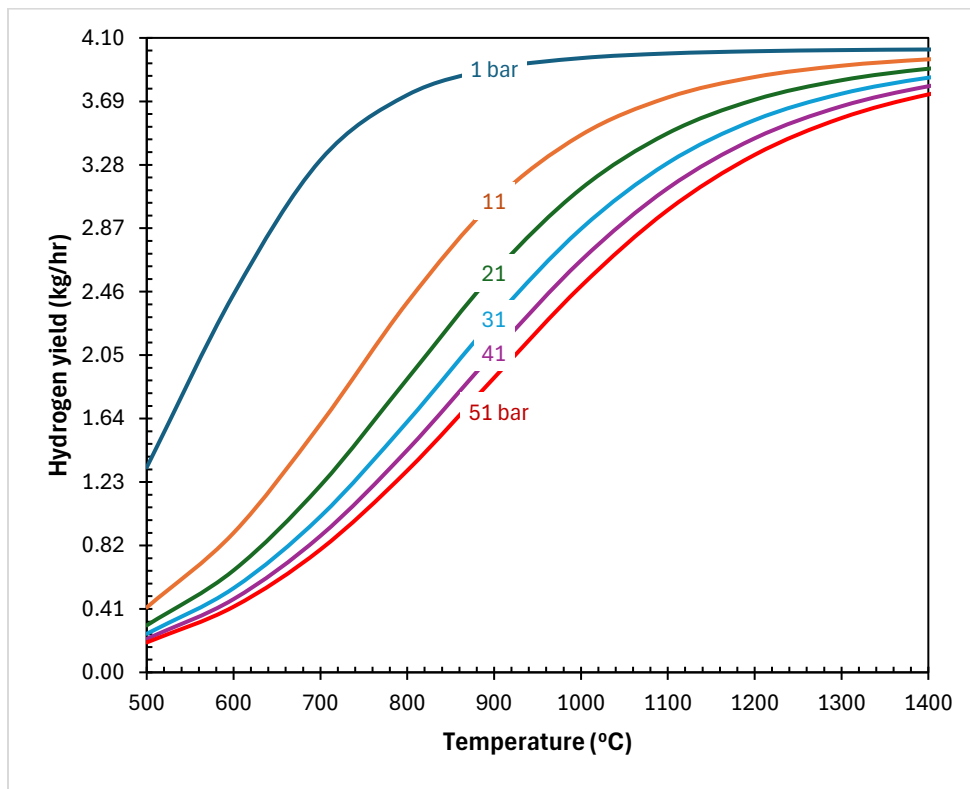


Figure 2.2 Hydrogen yield profile for 1 kmol/hr methane feed into MP Gibbs Reactor under different pressure and temperature conditions based on Aspen Plus simulation

Methane conversion and the reaction rate both will increase with temperature. This is because higher temperatures provide more kinetic energy to methane molecules, allowing them to reach the activation energy and break the C-H bonds. The higher the temperature, the more CH_4 decomposes into H_2 and carbon. The results in Figure 3 also show that, as the pressure increases, the reaction rate and methane conversion decrease.

This is because higher pressures increase the collision frequency and partial pressure of the reactants, shifting the equilibrium to the left according to Le Chatelier's principle. The higher the pressure, the more methane molecules remain intact, and less hydrogen and carbon are produced [35].

Temperature and pressure would also influence the catalyst performance. Higher temperatures cause the catalyst to deactivate faster. For instance, catalysts based on nickel deactivate rapidly over 600 °C. [36]. Conversely, increasing the pressure helps the catalyst survive, resulting in a longer lifetime. Higher pressures lead to higher hydrogen partial pressure and reduced catalyst deactivation [37]. Popov et al. [38] demonstrated that elevating the pressure from 1 to 10 bar while maintaining a constant temperature of 600 °C resulted in a rise in hydrogen yield from 26 to 40 mol/g-catalyst. Furthermore, this adjustment led to an extension in the lifespan of the Ni-Cu catalyst, from 17 to 40 hours.

2.3 Process Development and Challenges

Despite not requiring a WGS and CO₂ removal unit, such as SMR, the MP process still requires the downstream separation of solid carbon and unreacted natural gas components to achieve high hydrogen purity. Moreover, there should be some pretreatment for the upstream process. The following section elaborates on this process and its associated challenges. The general configuration of MP technologies for large-scale hydrogen production is shown in Figure 2.3.

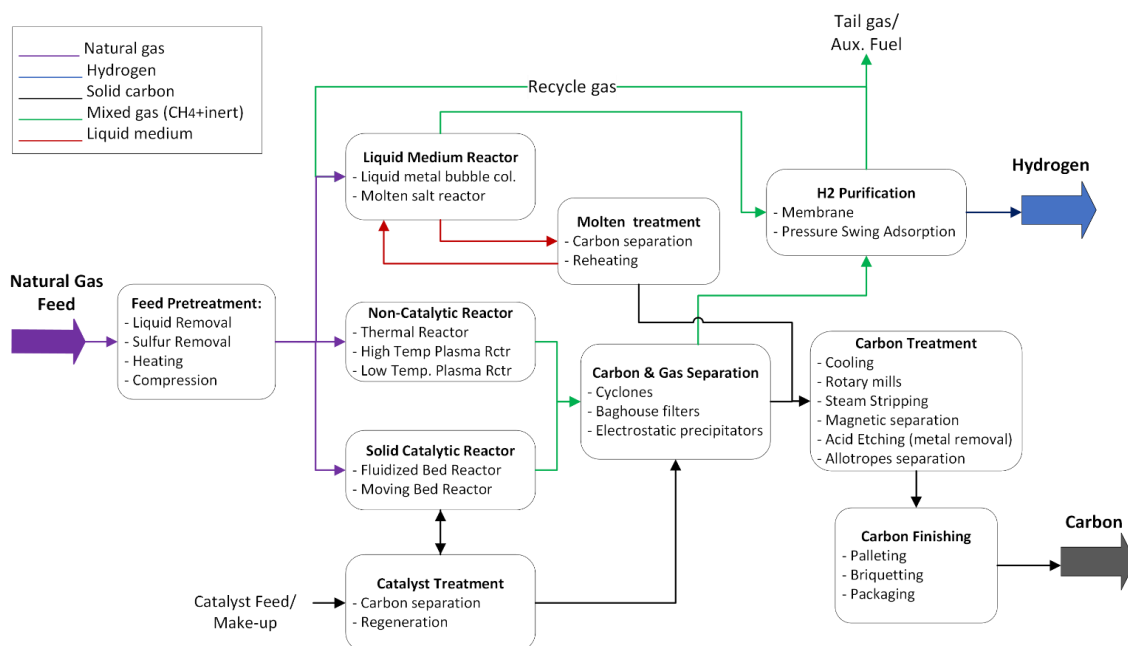


Figure 2.3 Process design of MP process for hydrogen production.

The sole feedstock required for the MP process is natural gas (purple block/line). Prior to its entry into the primary reactor, it needs to be pretreated. This involves a condensate/liquid and sulfur removal unit from the natural gas feed stream coupled with preheating and compression, if necessary. After pretreatment, the reactor type varies based on the technology and catalyst employed. Solid catalysts align well with fluidized bed reactors (FBRs) or moving bed reactors (MBRs), whereas liquid metal catalysts find application in liquid bubble reactors. Noncatalytic reactors with higher temperatures can also use conventional heat sources or plasma energy. The details of the feed pretreatment and reactor product post-treatment are discussed in the following section.

2.3.1 Feed Pretreatment

Several studies focusing on MP have employed pure methane as the feed, primarily to assess methane conversion or hydrogen yield [12,34]. However, in practical industrial applications, the feed typically comprises commercial natural gas, which contains 80%–

95% methane along with heavier hydrocarbons (C2, C3, C4), carbon dioxide, and a small amount of sulfur compounds [39,40]. Table 2.2 presents an illustrative example of the composition of commercial natural gas.

Table 2.2 Typical composition of natural gas. Data taken from sample analysis result of a laboratory control in West Java, Indonesia in April 2022 [65]

COMPONENTS	AMOUNT	UNIT
CH ₄	82.07	vol, %
C ₂ H ₆	2.99	vol, %
C ₃ H ₈	3.05	vol, %
n-C4	0.79	vol, %
i-C4	0.62	vol, %
n-C5	0.18	vol, %
i-C5	0.26	vol, %
C6	0.34	vol, %
CO ₂	5.57	vol, %
N ₂	4.12	vol, %
Ar	0.01	vol, %
H ₂ S	3.28	vol, ppm

Considering the composition, it is imperative to incorporate a feed pretreatment section upstream of the methane pyrolysis reactor, especially when using a catalytic process, as sulfur can severely impair most catalysts [41,42]. This sulfur removal unit is also usually found in typical SMR technology. The desulfurization step prevents catalyst poisoning in the downstream reactor. It is not mandatory to use a desulfurization unit in a noncatalytic reactor. However, another pretreatment process for gas–liquid separation, such as a flash drum, still needs to be considered to remove any liquid or condensate in the natural gas before it enters the suction compressor. It is also practical to have a preheating unit in which the heat from the reactor effluent stream can be utilized to heat the incoming fresh feed by recovering heat energy from the reactor outlet stream.

2.3.2 Solid–Gas Separation and Product Purification

Reactor effluent from the MP process contains hydrogen, unreacted natural gas, and solid carbon [24]. Consequently, the incorporation of a solid–gas separation unit is essential. Various technologies, such as cyclones, baghouse filters, or electrostatic precipitators, are viable options for achieving this separation [45]. Cyclones are cost-effective and suitable for large volumes, baghouse filters excel in capturing fine particulate matter, and electrostatic precipitators are efficient in removing particles of various sizes and can handle high-temperature gas streams [45,46]. The choice of technology depends on factors, such as the gas stream characteristics, carbon particle size, cost considerations, and required separation efficiency.

Subsequent stages involve the purification of hydrogen and solid carbon. Unreacted gases can be separated from hydrogen through various available technologies, such as PSA, cryogenic methods, or specific types of membrane separation [34]. Once separated, the produced hydrogen can be cooled and stored, whereas the unreacted feed gas can be recycled back into the reactor or used as an additional fuel for combustion to provide endothermic energy to the reactor. Similarly, some amount of hydrogen produced can also serve as a combustion fuel to provide the necessary endothermic energy to the MP reactor in the case of deficient natural gas flow after hydrogen separation, or if the process decides to recycle unreacted methane back to the reactor. In addition, if a catalytic process and sulfur removal unit are employed in the upstream feed pretreatment section, as discussed earlier, a small amount of the hydrogen stream from the product can be sent to the natural gas feed for desulfurization. This will reduce the overall hydrogen production yield, but will result in better combustion and cleaner flue gas emissions.

Solid carbon coproduct purification is required to generate additional revenue from the overall MP process. Different purification methods can be used, depending on the type of reactor and catalyst used. For example, magnetic separation can be used to separate solid carbon from metal particles in metal-based catalytic processes [34]. Washing or steam stripping methods can be used to remove salt residues from solid carbon in a molten salt medium reactor [47]. After purification, solid carbon can be cooled, packaged as pellets, or stored for various applications. However, the fate of the separated metal catalyst and salts prompts a crucial question: Can these components be recycled in the process? Although theoretically possible, numerous studies have indicated the substantial deactivation of metal catalysts owing to carbon deposits, rendering the regeneration process challenging [48]. The details of the catalyst development for MP are discussed in the following section.

2.4 Catalysts for Methane Pyrolysis

The catalysts used in MP can be categorized based on their physical state: solid, liquid (molten), and gas. Gas-phase catalysts using halogens, such as bromine and chlorine, were recently reported to provide an alternate option for the MP process [64]. However, in the section below, the catalyst development will mainly focus on the solid and molten catalysts, as they have been investigated deeply and developed by big companies to reach commercial scale.

2.4.1 Solid Catalysts

Several types of solid catalysts show promising activity for the methane pyrolysis reaction. Nickel (Ni) based catalysts have the highest activity compared to cobalt-based (Co), iron-based (Fe), molybdenum (Mo), and carbon-based catalysts [30,49,50]. Cobalt

and other metals such as platinum (Pt) and palladium (Pd) show promising activity for MP, but they are not well developed due to the higher cost. Nickel-based catalysts could lower the temperature up to 500 °C while iron based usually need more than 700 °C [51]. Temperature range comparison from different catalysts is shown in Figure 2.4.

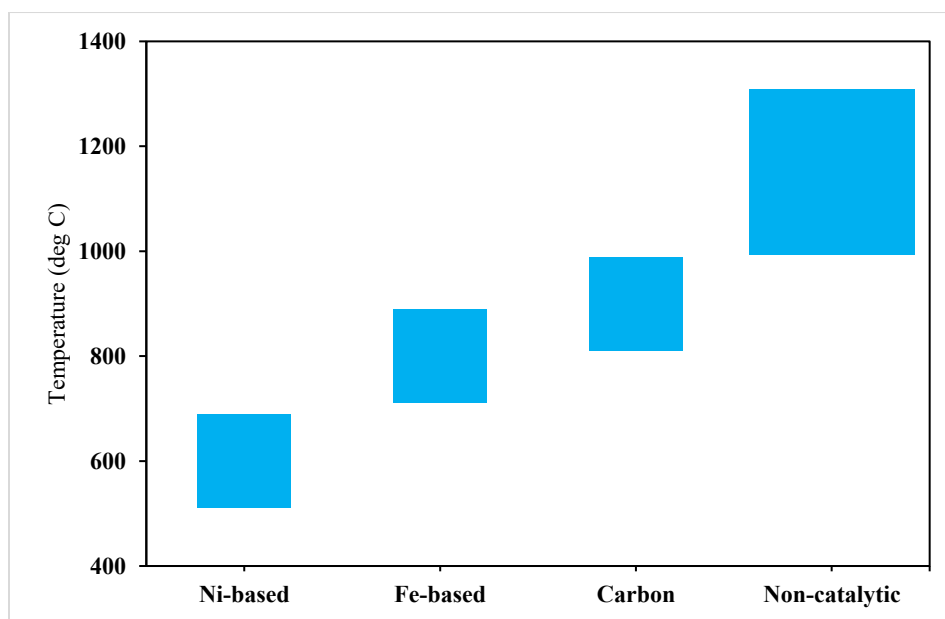


Figure 2.4 Temperature ranges of different catalyst types for MP. Adapted with permission from [52]. Copyright 2015 Springer Science Business Media Dordrecht

Selecting the catalyst for commercial use is not about the high activity and low material cost only, but the stability and catalyst lifetime also need to be considered [41,53]. Despite nickel-based catalysts showing the highest activity and lowest temperature conditions, nickel is quickly deactivated at temperatures above 600 °C due to carbon deposit accumulation and sintering [36,37,54]. Overcoming this challenge, the researchers who want to keep the solid phase catalyst, combine the nickel with another compound and add the support to increase the stability. The addition of supports which are usually from metal oxides will change the pore structure, surface area, and catalyst composition which

would affect the activity and stability of the overall catalyst [55]. Metal oxides support that common in practice are Al_2O_3 , MgO , SiO_2 , etc. [55].

The fundamental factor influencing catalytic activity is the concentration of active metal particles. In their research, Sikander et al. created nickel catalysts using hydrotalcite through co-precipitation, adjusting the nickel concentration levels [56]. The catalyst composed of 40% nickel concentration demonstrated the highest methane conversion rate, exceeding 80% over 7 hours at 650 °C. Nevertheless, an excessive concentration of nickel resulted in diminished catalyst performance, attributed to the formation of larger nickel particles and continuous development of the bulk NiO phase during the reduction process. Additionally, the catalyst's spinel-like structure played a critical role in promoting the growth of elongated and uniform carbon nanofibers (CNF).

Tezel and colleagues employed a commercial calcium silicate material in the synthesis of a bimetallic Ni-Fe catalyst, with the addition of Al_2O_3 as a supplementary support [57]. They vary the ratio of Fe in Ni/ Al_2O_3 from 0 to 0.61. The results show that the addition of Fe delayed the deactivation of the Ni/ Al_2O_3 catalyst but lowered the initial methane conversion at 600 °C. The highest methane conversion was 69% at 700 °C with the highest Fe/Ni ratio (0.61). Another similar study in bimetallic catalysts was found by doping other metals into Ni-based catalysts [42].

Several research investigations have documented the utilization of promoters to enhance the durability of catalysts. For example, adding potassium into Ni/ Al_2O_3 catalysts has demonstrated an enhancement in stability and resistance to carbon deposition [58]. However, the extended duration of the solid catalyst's lifespan or catalyst activity in MP

remains in the order of hours, most of them are below 10 hours [42]. This duration is notably distant from the endurance standards of industrial catalysts, such as the nickel catalyst in SMR, which can persist for 8 – 10 years [59].

Addressing the deactivation challenges posed by the ongoing accumulation of solid carbon co-products can involve employing catalyst regeneration as an alternative strategy. Depending on the nature of the poison, certain catalysts can be reactivated after encountering deactivation or poisoning [60,61]. Exploring the potential of a fluidized bed reactor configuration that facilitates the continuous regeneration of solid catalysts appears to be a promising approach, a topic that will be detailed in the subsequent section. Additionally, researchers have found the utilization of an alternative catalyst state, such as a liquid or molten catalyst, to be a promising solution worth investigating.

2.4.2 Molten Catalysts (Metals and Salts)

Employing molten media provides an alternative strategy for tackling the problem of solid carbon sticking to the catalyst and reactor walls while simultaneously preventing the potential transportation of carbon as dust alongside hydrogen and methane [62]. However, high-activity metal catalysts, such as Ni, Co, and Fe, also have high melting point temperatures; for example, the melting point of Ni is higher than 1450 °C. This has led researchers to investigate metals with lower melting points. For instance, Wang et al. [63] studied the application of pure molten metal of magnesium as a catalyst for MP, leading to only 30% of the equilibrium conversion at 700 °C. The achieved conversion was limited by the operational temperature range because increasing the temperature was not possible owing to magnesium evaporation at higher temperatures.

Table 2.3 Type of catalyst and its performance in MP with regard to the carbon coproduct

Material	Type of catalyst	T (°C)	X-CH ₄ (%)	Life (Hr)	Carbon type	Ref.
Ni _{0.4} /hydrotalcite	Solid metal	650	80	7	CNF	[56]
Ni-Fe/Al ₂ O ₃	Solid bimetal alloy	650	69	210	CNF	[64]
Ni/2MgO.Al ₂ O ₃	Solid metal	600	64	4.5	CNT	[65]
9Ni-1Co/ Al ₂ O ₃ .TiO ₂	Solid bimetal alloy	650	69	1	CNT	[66]
K ₂ CO ₃ /Carbon	Solid salt and carbon	850	90	1.5	CF	[67]
Activated Carbon	Solid carbon	900	67	< 1	Spherical carbon	[68]
Carbon Black	Solid carbon	900	52	1.25	Spherical carbon	[68]
Mg	Molten metal	700	30	75	Amorphous carbon	[63]
Ni _{0.17} Bi _{0.83}	Molten metal alloy	1065	95	170	Graphite	[69]
Ni _{0.27} -Bi _{0.73} /NaBr	Molten metal alloy + salt	1000	37.5	20	Carbon black, CNT	[47]
MnCl ₂ -KCl	Molten salts	1050	55	30	Graphitic sheets	[70]
NaBr-KBr+Mn-Co/Al ₂ O ₃	Molten metal alloy + salt	1000	10.4	24	Amorphous carbon, graphite	[71]

T, temperature; *X*, conversion; *CNF* (Carbon nanofiber); *CNT* (Carbon nanotube); *CF* (Carbon fiber)

One solution to counteract the melting point of the pure molten metal is to use a molten metal alloy catalyst [72]. The active catalyst metal (Ni, Co, Pt, Pd), when dissolved in Bi, Ga, In, Sn, and Pb, produces a stable molten catalyst alloy for MP [37]. Upham et al. [69] conducted a comparative analysis of the catalytic activity across a diverse range of metal alloys using a screening reactor-based approach. These results indicate that the combination of Ni and Bi is a promising molten alloy. At a temperature of 1,065°C, Ni_{0.17}Bi_{0.83} exhibits the highest H₂ production rate, while Ni_{0.27}Bi_{0.73} achieves an impressive 95% conversion rate. In terms of stability, molten Ni/Bi catalysts have been reported to maintain good activity for up to 170 h [42].

Despite the various operational advantages of using molten metals in MP, there are certain constraints. Some metals tend to evaporate at elevated temperatures because of their

high vapor pressures. This evaporation can lead to the condensation of vapor within the pores of the carbon particles. Consequently, carbon becomes highly contaminated and requires thorough purification before it can be used for commercial purposes. For instance, for molten Ni-Bi alloys, Rahimi et al. [72] obtained 83% weight of metal contamination in the carbon, whereas Zeng et al. [73] obtained 0.21% weight of Te contamination.

The combination of molten metals and salts has been studied to overcome the heavy metal contamination of solid carbon [37]. The most common molten salts reported in the literature include KBr, NaBr, NaCl, NaF, KCl, MnCl₂, and FeCl₂ [74]. Molten salts exhibit a reduced vapor pressure, and carbon contaminated with salt is more amenable to purification due to its pronounced solubility in water [39]. According to Rahimi et al. [72], increasing the molten salt volume reduces metal contamination in carbon, but increases the salt content. For instance, reducing the molten salt height from 240 to 110 mm resulted in a substantial rise in Ni and Bi concentrations within the carbon. Specifically, the Ni content increased from 0.04 wt.% to 0.55 wt.%, while the Bi content escalated from 0.62 wt.% to 3.30 wt.% [72].

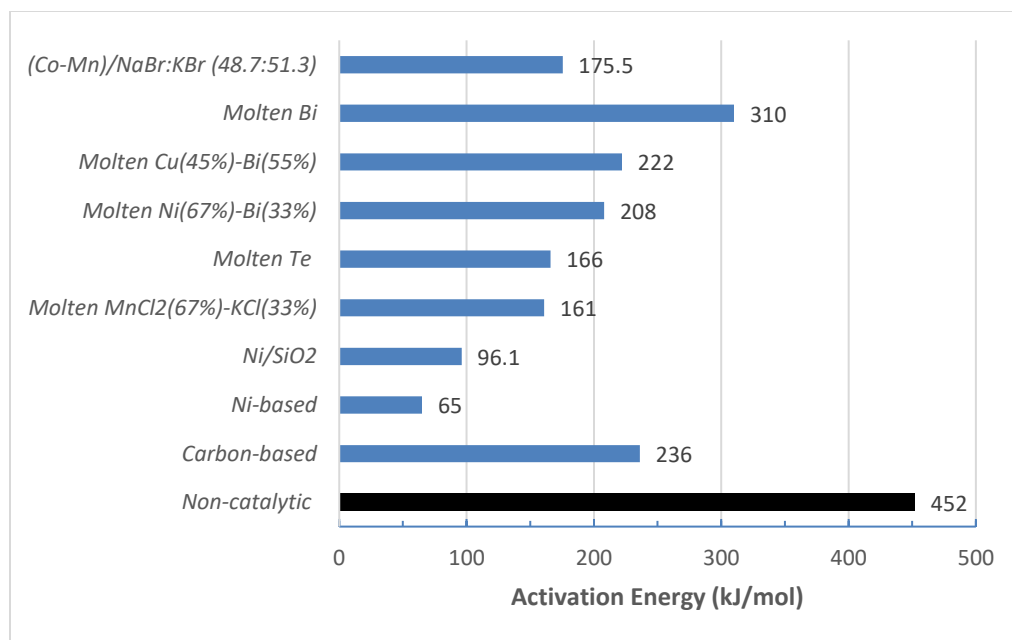


Figure 2.5 Activation energy of several type of solid and molten catalyst and comparison with non-catalytic energy required (Drawn based on table from [37])

Figure 2.5 illustrates the activation energies required for various catalysts in MP, including solid metals, molten metals, molten salts, and carbon-based catalysts. Despite these drawbacks, nickel-solid-based catalysts exhibit the lowest activation energy. In general, molten metals tend to exhibit higher activities than molten salts. The combination of molten media (metals and salts) provides promising results and effectively minimizes the metal contamination in the carbon coproduct. Notably, as shown in Table 4, the lifetime of the molten catalyst is generally longer than that of the solid catalyst [42].

Although carbon-based catalysts can also be utilized, their reported activities are lower than those of other catalysts [37]. However, the use of carbon as a catalyst has the main advantage of the absence of metal contamination in solid carbon coproducts. In addition, carbon catalysts are less expensive than metal-based catalysts. In the following section, the possibility of reactor design and the maturity level rank of the technology type are discussed with a combination of suitable catalyst-type selection.

2.5 Reactor Design and Maturity

Researchers have extensively examined and proposed various reactor designs. For solid catalysts, the prevalent choice involves employing an FBR or MBR with diverse configurations to regenerate and circulate the solid catalyst. In the case of molten catalysts, the utilization of bubble column reactors has been widely reported. Additionally, some researchers have proposed alternative reactor types and designs that do not involve catalysts. The following section presents the most commonly employed reactor designs that have been developed and are ready for commercial use in terms of their technology readiness level (TRL), which varies between 5 and 11, based on the International Energy Agency (IEA) standards [75].

2.5.1 Fluidized Bed Reactor

FBRs are among the most widely used reactor types for MP because they offer reasonable heat and mass transfer rates, good temperature control, and easy carbon separation. An FBR can continuously add and withdraw solid catalyst particles; therefore, the pressure drop owing to carbon coproduct accumulation does not increase significantly [76]. Figure 2.6(a) illustrates an example of an FBR design by U.S. Department of Energy researchers [77], wherein a layer of bed material, such as catalyst particles, undergoes fluidization induced by a gas stream. This results in the creation of a turbulent, well-mixed environment. The natural gas feed is injected into the reactor and catalytically decomposed to produce hydrogen gas and solid carbon. Carbon particles are either entrained by the gas stream and collected in a downstream filter or deposited on the bed material and removed periodically [51].

Several studies have demonstrated the feasibility and performance of FBRs for MP at different scales under different conditions. In the 1960s, Universal Oil Products pioneered a laboratory plant known as HYPRO to transform methane and gaseous hydrocarbon feedstocks into hydrogen and carbon. This innovative system harnessed a circulating fluidized bed design, enabling MP in one reactor and catalyst regeneration in the other through the combustion of deposited carbon. Employing a Ni/Al₂O₃ catalyst at temperatures ranging from 815–1,093 °C, the HYPRO process remarkably achieved methane conversion surpassing 90% [78]. Notably, the heat generated during catalyst regeneration served as the primary energy source for the endothermic process, whereas the catalyst circulation rate played a crucial role in regulating the temperature of the MP reactor. Such reactors have recently experienced a resurgence in interest, prompting the development of novel concepts that incorporate the fundamental principles established by the groundbreaking HYPRO process.

The National Energy Technology Laboratory of the U.S. Department of Energy (DOE) [40] reported a prototype of high-pressure FBR with a height of approximately 186 cm, operated at 700 °C, and used their proprietary catalyst. They achieved a methane conversion of 80%–90% after 50 h of operation; however, the methane conversion declined to approximately 60% in the following 65 h of operation. The coproducts were CNFs and CNTs.

The FBR is a promising technology for MP because it can produce high-quality hydrogen and carbon with low energy consumption and environmental impacts. However, there are still some challenges and limitations that need to be addressed, such as the optimal design and operation of the reactor, the selection and regeneration of the bed material, and

the prevention and mitigation of carbon deposition and agglomeration. Further research and development are required to overcome these challenges and scale up the technology for commercial applications.

2.5.2 Moving Bed Reactor

An MBR is similar to an FBR in terms of the moving solid particle or catalyst. However, in an MBR, solid particles or catalysts are not fluidized by feed or gas streams. The MBR is the first type of continuous catalyst regeneration technology used to remove and regenerate coke deposits from catalysts [79]. This is a promising solution for carbon accumulation and catalyst deactivation during MP. A compelling MBR concept was developed by BASF, as depicted in Figure 2.6(b) [30].

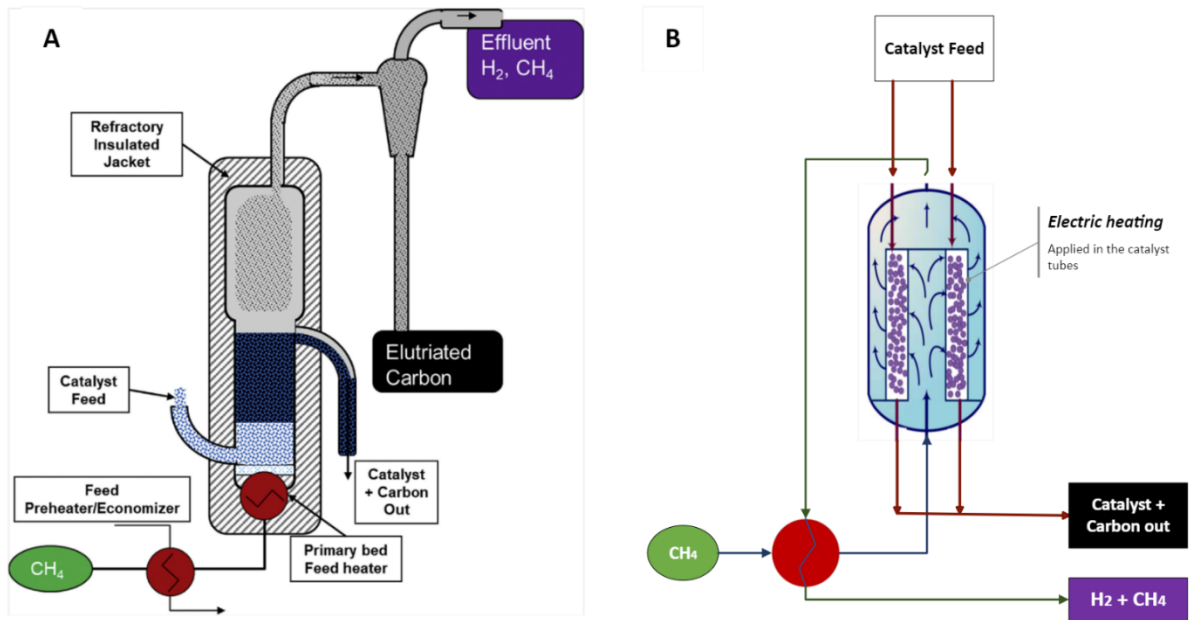


Figure 2.6 (a) FBR design for MP proposed by US DOE. Reprinted with permission from [77]. Copyright 2021 Elsevier and (b) MBR design proposed by BASF. Redrawn based on [30]

In an MBR, natural gas and carbon granules (or any solid catalyst) flow in opposite directions throughout the reactor. The reactor configuration involves feeding natural gas at the bottom while introducing catalyst particles at the top. Electric heating is applied directly to the carbon within the reaction zone, releasing heat, which is then transferred to the feed gas. Consequently, MP occurs. The carbon produced from the reaction accumulates on the carbon/catalyst particles and is continuously removed from the bottom of the reactor [30].

The gas product cools at the top of the reactor by contacting the fresh cold solid catalyst particles. Consequently, the outlet gas preheats the catalyst prior to entering the reactor and undergoing electric heating. MBRs have significant advantages. They facilitate sufficient heat transfer of the gas and catalyst, eliminate back-mixing, and make the residence time controllable [79]. The laboratory-scale MBR developed by BASF for MP uses carbon as a catalyst, and the reactor operating temperature is 1,300–1,400°C. There are plans to scale up the MBR design to a pilot plant by 2025 [80].

2.5.3 Liquid Metal Bubble Column Reactor

The concept of the LMBCR was introduced by Tyrer in 1931 [81]. This concept has been developed by several researchers, to increase the hydrogen yield and energy efficiency. The overall concept of the LMBCR is illustrated in Figure 8. Natural gas or methane is fed from the bottom to the molten medium through the inlet tube. To enhance the liquid–gas interaction, a sparger may be employed to break the gas bubbles [37]. As these bubbles ascend within the molten medium, methane undergoes heating and cracks into solid carbon and hydrogen gas [82]. Owing to the substantial difference in density between carbon and the molten medium, two distinct behaviors are observed. Carbon rises

to the surface, buoyed by buoyancy forces, or descends deeper into the melt under the influence of gravity. Consequently, carbon collection is more manageable [83].

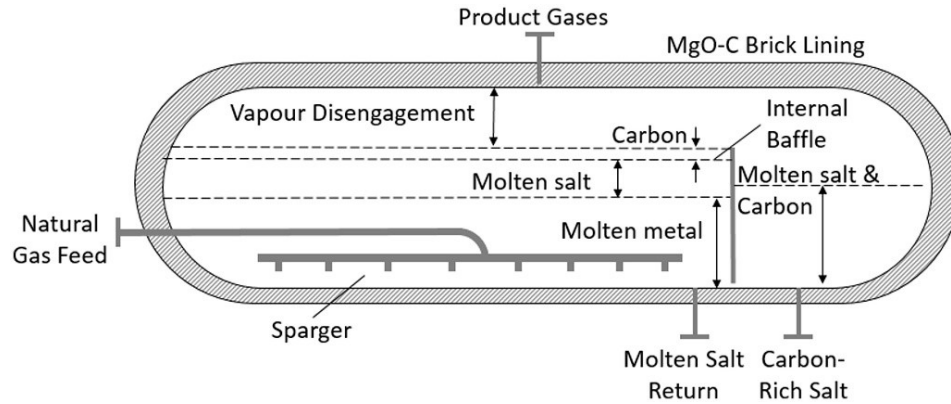


Figure 2.7 Concept design of LMBCR for MP. Reprinted with permission from [23]. Copyright 2018 Elsevier

The Karlsruhe Institute of Technology used liquid tin as a molten medium, and reported that the carbon powder coproduct floats on the surface of liquid tin and a hydrogen yield of 78% is achieved at a temperature of 1,175 °C [84]. For a large-scale implementation, Catalan et al. [85] recommended the molten tin medium at 1,100 °C in a vertical type of reactor with a length of more than 14 m and a diameter of approximately 3 m with an inlet natural gas pressure of 57.8 bar. The designed reactor could achieve a minimum gas holdup of 25%-vol and a methane conversion of 65%. However, achieving a gas holdup of 25%-vol required high pressure in the vertical reactor. Parkinson et al. [48] suggested a horizontal reactor alignment, as illustrated in Figure 2.7, because horizontal vessel reactors are better at maximizing gas volumetric hold-up than vertical bubble column reactors, owing to their larger cross-sectional area for gas injection. The required pressure is lower, leading to lower capital costs for the reactor.

As mentioned in the Catalyst section, liquid molten media can be a combination of metals and salts. The concept design of the LMBCR in Figure 2.7 shows an example of combining the molten alloy metal Ni-Bi and molten salts $\text{MgCl}_2\text{-NaCl}$ for easier separation of solid carbon [48]. The Shell Company has been working on the technology since 2017 that involves the use of molten salt catalysis. In this process, titanium gettering was employed to convert hydrogen into titanium hydride. Subsequently, titanium hydride was separated and reheated to obtain pure hydrogen [86].

2.5.4 Plasma Reactors

Plasma is the fourth state of matter, and is distinct from solids, liquids, and gases. It is a hot ionized gas composed of positively charged ions and free electrons. Plasmas are characterized by their ability to conduct electricity and respond to electromagnetic fields. They are commonly found in stars, lightning, and certain industrial applications that require elevated temperatures. Plasma is formed when energy is added to a gas. Energy injection commonly occurs through an electric field [87]. Plasma reactors use ionized gases or plasma to initiate chemical reactions at high temperatures. Plasma can be classified into two main categories: thermal and nonthermal. Thermal plasma shows a temperature balance among all particles, with electron and gas temperatures reaching 10,000 K. Thermal plasmas are highly ionized and have a dense charge. On the other hand, nonthermal plasma has a significant temperature gap between the electrons and ions (nonequilibrium). While the electron temperatures can reach several thousand Kelvin, gas and ion temperatures usually remain in the range of hundreds of Kelvin [88].

Different types of plasma reactors can be used for MP depending on the nature and characteristics of the plasma. Some common types include dielectric barrier discharge,

microwave, and arc plasma reactors [25]. Each type of plasma reactor has advantages and disadvantages in terms of methane conversion, product selectivity, energy efficiency, and operational stability.

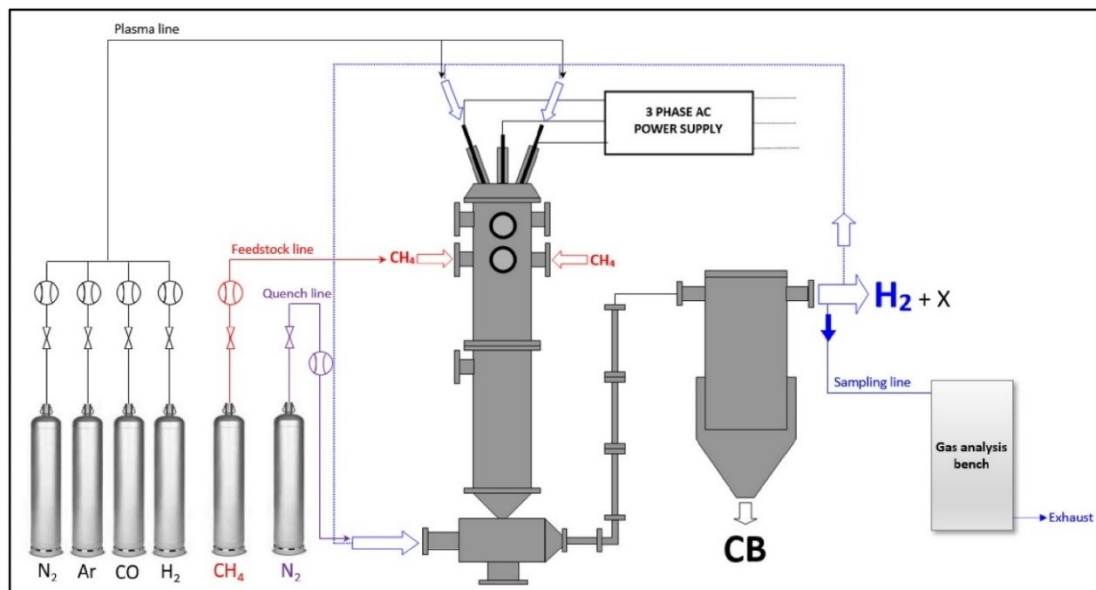


Figure 2.8 Thermal plasma arc reactor for MP. Adapted with permission from [89]. Copyright 2023 Elsevier

One of the most promising approaches is the use of a thermal plasma arc reactor developed by Fulcheri et al. [89], as shown in Figure 2.8. This plasma reactor utilizes either nitrogen or a hydrogen–nitrogen mixture as the plasma gas, whereas methane is injected independently. Torches equipped with graphite electrodes deliver power inputs ranging from 60 to 69 kW. This plasma reactor achieves methane conversion exceeding 99%, with a high hydrogen selectivity of 95% while also producing valuable carbon black coproducts at an operating temperature of 1,670 °C and atmospheric pressure. The reactor was developed by Monolith for commercial-scale production. In 2021, Monolith commenced the development of its inaugural commercial-scale production plant in Nebraska, United States, which can produce 5,000 t of hydrogen annually. This technology falls in the TRL

rank of 8–9 and has good potential for commercialization [90]. For nonthermal plasma, Gasplas and Cambridge University conducted a bench-scale test at an atmospheric pressure reactor powered with a double-vortex 6-kW microwave at 177–377 °C and achieved a methane conversion of 87% but lower hydrogen yield and selectivity compared with the thermal plasma [91].

2.6 Solid Carbon Types, applications, and current Market

During MP, different types of solid carbon and hydrogen are produced. The variation in the solid carbon type is due to several factors, such as the reaction temperature, residence time, catalytic or noncatalytic process, and type of catalyst used [92]. Figure 2.9 summarizes the major types of solid carbon produced by MP.

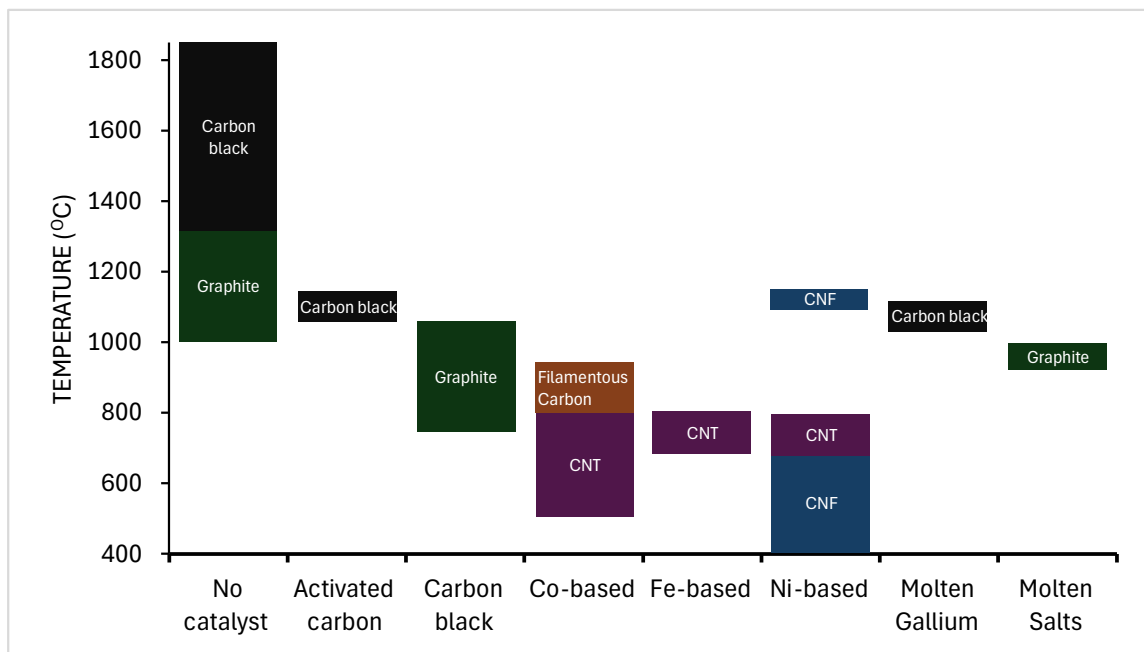


Figure 2.9 Type of carbon coproduct in MP based on catalyst used and reaction temperature. This figure was redrawn based on several literatures from [92,93]. CNT: Carbon nanotube and CNF: Carbon nanofiber

The type of carbon material from the noncatalytic reaction is mainly carbon black if the MP reaction temperature is approximately 1,300–1,800 °C and graphite if the MP reaction temperature is lower than 1,300 °C [89,90]. Carbon materials from solid-metal catalysts differ depending on the main metal used. Nickel-based catalysts produce CNFs when the reactor temperature ranges from 400 to 700 °C and CNTs when the reactor temperature ranges from 700 to 800 °C. Some reported experiments also claim that CNFs are produced at temperatures above 1,000 °C. Iron- and cobalt-based catalysts mostly produce CNTs at their optimal temperatures (less than 800 °C). A study also found filamentous carbon type produced by Co-based catalysts at 800–900 °C [17].

Utilizing activated carbon as a catalyst for MP will produce carbon black along with hydrogen at the optimum temperature (approximately 1,100 °C), whereas using carbon black as a catalyst will produce mainly graphite at the temperatures of approximately 800–1,000 °C [17,92]. For molten metals or molten salt catalysts, carbon black was produced when molten gallium was used at a temperature of 1,119 °C [94]. Graphite has also been reported in several studies that utilize molten metals or salt media. For example, molten Ni-Bi with an MP reaction temperature of approximately 1,000 °C produced graphitic carbon[93]. The combination of FeCl₃ with NaCl-KCl was also observed in graphitic carbon materials at an operating temperature of 1,000 °C [95].

After determining the type of carbon coproduct in MP, the market size and value of solid carbon should also be determined. Table 2.4 outlines various potentially valuable carbon products and details their industrial applications, market pricing, size, and significance.

Table 2.4 Solid carbon type, applications, market size, and price (MT: metric ton) [96]

Carbon type	Applications	Expected Price	Market
Carbon black	Tires, inks, coating, direct carbon fuel cells, construction material, and plastic	\$0.4–2/kg	16.4M MT (2022)
Graphite	Lithium batteries	\$10/kg	250K MT (2020)
Carbon fiber	Construction, automotive, aerospace, wind turbine, carbon-reinforced composites	\$25–113/kg	100K MT (2020)
Carbon nanotubes	Polymers, plastics, electronics, lithium-ion batteries	\$0.10–600/gr	20K MT (2022)
Needle coke	Graphite electrodes in electric arc steel furnaces	\$1.5/kg	1.5M MT (2014)

The range of potential carbon products is diverse and includes carbon black, CNTs, CNFs, and needle-like coke. The pricing of carbon products can vary significantly, and is influenced by carbon characteristics and impurities. Among these, carbon black is the most established product with high market demand [96]. To elaborate on this economic aspect, several studies are reviewed in the techno-economic section.

2.7 Techno-Economic Study for Methane Pyrolysis

Techno-economic analysis (TEA) was used to compare the viability of the MP process with that of current hydrogen production technologies, such as SMR, with or without CCS [23]. The techno-economic aspects of MP are complex and depend on various factors, such as the type of reactor and catalyst used, the cost of natural gas, and the type and price of solid carbon produced [91]. Based on several TEA studies, as shown in Table 2.5, MP is more expensive than SMR when solid carbon revenue is not considered [23].

Table 2.5 Hydrogen cost from MP TEA studies. All H₂ costs are shown without solid carbon revenue included.

H ₂ Production Technology	Cost of H ₂	Ref.
SMR-CCS technology	\$1.40–\$2.50/kg	[77]
MP with molten salt (KCl-MnCl ₂) bubble-column reactors	\$1.80/kg	[39]
MP with molten media (Ni-Bi metal and salt) reactors	\$1.70/kg	[48]
MP with FBR using solid Fe-based catalysts	\$3.20–3.50/kg	[77]
MP with hot cyclone reactor and liquid Zn	\$2.50/kg of crude (94%) H ₂ , and \$3.40/kg pure (99%+) H ₂	[97]

To match the cost competitiveness of SMR with CCS (SMR-CCS), a minimum carbon coproduct revenue of \$0.2/kg for the solid carbon produced [48] or a minimum of 20% of produced carbon selling at \$1.20–1.50/kg is required [77]. Another study claimed that, if all carbon produced can be marketed within the range of \$0.3–0.8/kg, the MP hydrogen price could be lower than that of hydrogen from SMR without CCS (< \$1.00/kg) [39]. This underscores the pivotal role of carbon coproducts in MP.

Based on the solid carbon market price and demand in Table 2.4 and these techno-economic studies, it is possible to satisfy the carbon price requirement (approximately \$0.2–2/kg); however, the size of the solid carbon market is relatively low. As indicated in Table 5, excluding carbon black and needle coke, specific carbon markets could reach saturation before fulfilling a portion of the total demand in the hydrogen market.

Another potential scenario in which MP could prove more profitable than SMR is the widespread implementation of a CO₂ tax. Additionally, Brandon et al. [94] performed TEA and demonstrated that the molten gallium MP process can effectively compete with SMR when the carbon tax falls within the range of EUR 50–100 per ton. This conclusion aligns

with similar findings from a TEA conducted by Parkinson et al. [23], indicating that, to make MP as economically profitable as SMR, an approximate CO₂ tax of \$21 per ton is necessary. In practical terms, this equates to an equivalent hydrogen cost of \$1.45/kg for both the SMR and pyrolysis processes.

CHAPTER 3

METHODOLOGY

Aspen Plus v11 and its associated Aspen Process Economic Analyzer (APEA) v11 were employed to conduct a techno-economic analysis through simulation to evaluate the feasibility and economic viability of the proposed MP integration in the SMR-ammonia-urea production process.

3.1 Model Basis and Assumptions

Several assumptions are taken into consideration:

- The model is assumed to operate under steady-state conditions.
- A constant NG feed with a mass flow rate of 517 tpd (ton per day), pressure of 11 bar, and temperature of 32 °C is used. The fixed composition of this feed is detailed in Table 3.1.

Table 3.1 Natural Gas Composition

Component	mol % dry
CH ₄	91.04%
C ₂ H ₆	2.88%
N ₂	2.54%
CO ₂	1.83%
C ₃ H ₈	1.01%
I-C ₄	0.35%
N-C ₄	0.35%
Sulfur	30 ppmv

- Based on this NG feed amount, the SMR-ammonia-urea plant model was built with a design capacity of 1,725 tpd urea and an approximate surplus of 20 tpd NH₃.

- The methane pyrolysis model was built with a capacity of half the NG flow rate (258.5 tpd) to achieve a maximum splitting ratio of 50%.
- The Redlich-Kwong-Soave with Boston-Mathias alpha function (RKS-BM) method is used for thermodynamic property calculations.
- Air composition is fixed at 78 mol% N₂, 21 mol% O₂, and 1 mol% argon.
- The MP reactor was modeled using a kinetic reactor.

3.2 Model Validation and Sensitivity Analysis

Model validation was conducted for the kinetic reactors, particularly the MP reactor model. This validation utilized experimental data from Keipi et al. [98]. Another key parameter within a different process section was also validated using reference plant design data.

Several sensitivity analyses were conducted to explore the impact of varying integration schemes on key performance metrics such as production quantity, CO₂ emissions, and energy consumption. Multiple sets of design specifications were utilized, as outlined in Table 3.2, to maintain consistency across these analyses and ensure that other parameters remained within the designated design range.

Table 3.2 Design specification for Integrated SMR-MP-Ammonia Plant Model

Design specifications	Parameter	Target	Vary
DS-1	S/C (mass) inlet primary reformer	4.044	Steam feed controller
DS-2	H/N (mole) inlet NH ₃ converter	2.90	Air feed controller
DS-3	NH ₃ /CO ₂ (mole) inlet urea reactor	2.0	NH ₃ feed controller

3.3 Economic Analysis

The Aspen Process Economic Analyzer (APEA) v11 was employed to conduct the economic analysis. The investment analysis will compare two distinct cases. The base case model presumes an average annual production gap of 15% between the ammonia and urea plants. This will be juxtaposed with the proposed integration model, which assumes a 15% integration level or the NG splitting ratio in MP. Both the base and proposed models are premised on the assumption that the facilities are newly constructed (grass-root facilities) in the Middle East area. The economic assumptions were formulated based on current trends observed globally, as well as specifically in the United States and the Middle East. These assumptions include:

- Natural gas price: \$2.00/MMBTU
- Ammonia and urea selling prices: \$550/ton and \$390/ton, respectively.
- The carbon black price is 0.8 – 2.1 USD/kg.
- CO₂ tax policy in the Middle East is 8 USD/ton-CO₂.
- Operating days per year: 330 days
- Expected plant lifetime: 25 years.

Sensitivity analysis on carbon black price and CO₂ tax with the annual revenues of both models will also be presented and discussed. These will provide a comprehensive framework for the economic analysis, facilitating a robust comparison between the base case and the proposed integration model.

CHAPTER 4

PROCESS DESIGN DEVELOPMENT

This chapter outlines the process design for integrating MP into an existing SMR-ammonia production plant utilizing NG as feedstock. To understand the integrated process comprehensively, we will first explore the conventional ammonia production process employing SMR technology. Subsequently, we will delve into the proposed integration of MP within the conventional plant design.

4.1 Conventional SMR-Ammonia (Base model)

Various technologies offered by different licensors (such as KBR, Linde, Topsoe, Casale, etc.) exist for the production of ammonia from NG, each with proven commercial viability [99]. In this investigation, we adopt the ammonia production technology developed by KBR, which incorporates two reformers (primary and secondary) with air injection in the secondary reformer. Figure 4.1 show a schematic representation of a typical process flow diagram for the production of ammonia and urea from NG feedstock. The ammonia production process encompasses a pretreatment stage, reformer operation, water-gas shift reaction, CO₂ removal, methanation, NH₃ synthesis loop, and refrigeration (inclusive of a hydrogen recovery unit). Alongside NG, the requisite raw materials include steam and air.

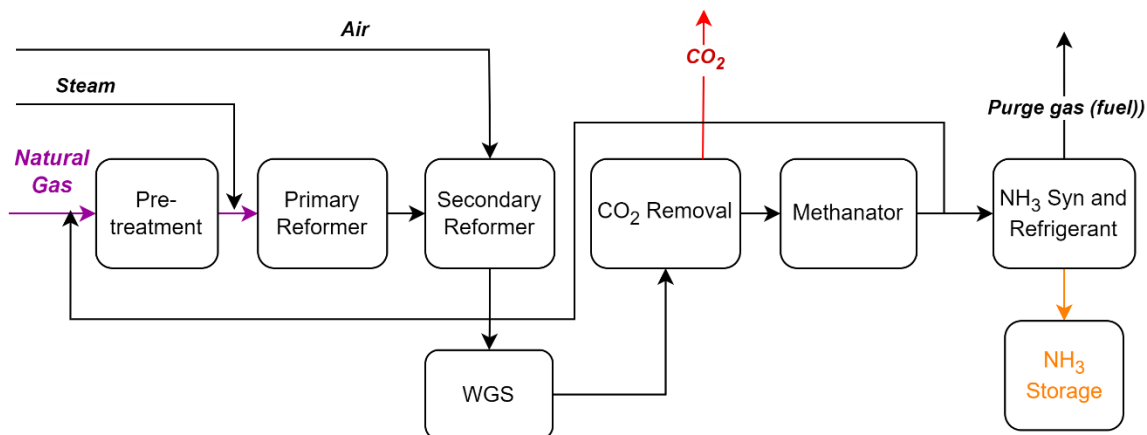


Figure 4.1 Simplified SMR-Ammonia-Urea process block diagram. SMR reaction happens in the Primary Reformer section.

The NG feed typically originates from a supplier at a moderate pressure range of 10 – 12 bar and slightly above ambient temperature (30 – 35 °C). Its composition primarily comprises methane along with other heavier components (C2+), CO₂ gas, and small amounts of sulfur. Converting the NG into hydrogen and ammonia necessitates several reaction processes involving operating pressure and temperature adjustments. Figure 4.2 shows the upstream or pretreatment process of NG feed.

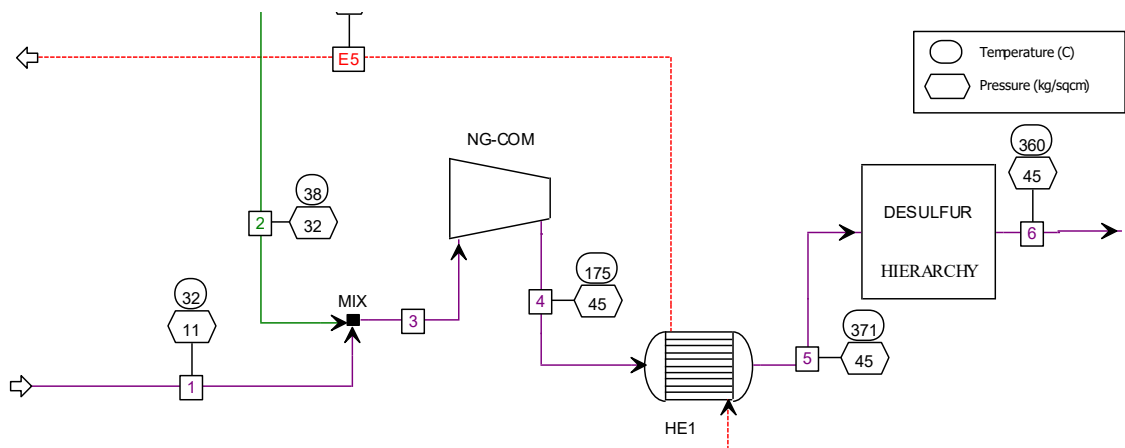


Figure 4.2 Natural Gas Feed Pretreatment

Dry NG feed is mixed with small portion of syngas product recycle and compressed by NG-COM to increase the pressure from 11 bar to 45 bar. Compressed NG then heated with excess heat of SMR reactor to increase the NG temperature to approximately 371 °C. This treatment done to suit the feed and operating condition for desulfurization section. In the subsequent subsection, key process sections will be elucidated in detail to provide a comprehensive understanding of the potential for integrating MP process.

4.1.1 Desulfurization section

The most prevalent method for sulfur removal involves two distinct steps: hydrogenation and adsorption [44,100]. Initially, the NG is combined with a hydrogen-rich gas, typically sourced from a methanation reactor's recycled syngas product outlet. This mixture undergoes a hydrogenation reaction, converting sulfur compounds into hydrogen sulfide (H_2S). This reaction typically occurs at a 30 – 45 bar pressure and is facilitated by a cobalt-molybdenum catalyst at temperatures ranging from 290 – 370 °C (Reactions 4.1 and 4.2).

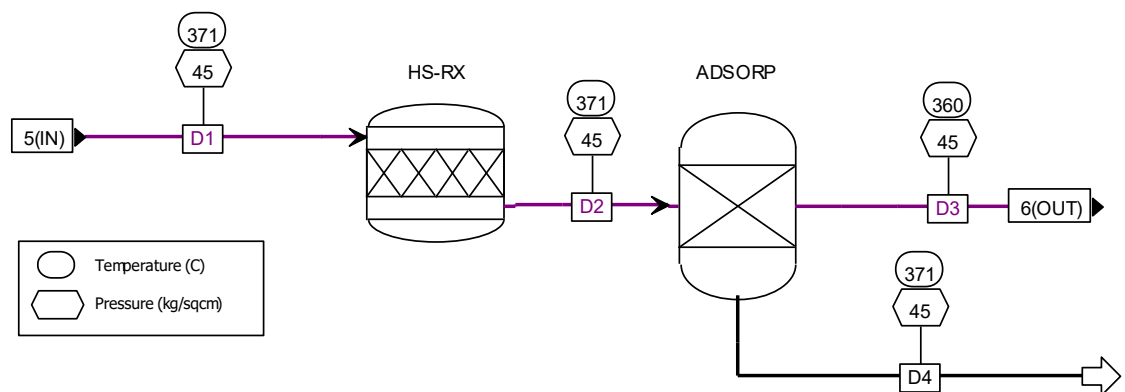
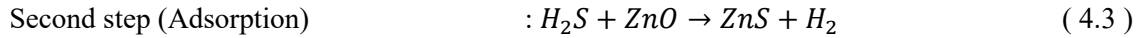
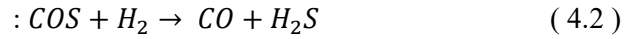


Figure 4.3 Desulfurization Section

As depicted in Figure 4.3, following hydrogenation in the “HS-RX” reactor, the H_2S is separated via zinc oxide (ZnO) adsorption (“ADSORP”) at temperatures between 340 – 390 °C (Reaction 4.3). The zinc within the reactor binds the sulfur, resulting in an effluent stream containing less than 0.1 ppm sulfur [44].



The desulfurization section plays a crucial role in safeguarding the catalysts used in downstream reactors, including the reformer, ammonia synthesis reactor, and methanation reactor. Eliminating sulfur impurities prevents catalyst poisoning, thereby ensuring the efficiency and longevity of these reactors. Following desulfurization, the purified natural gas is combined with medium-pressure steam at a specific ratio. This mixture is then introduced into the primary reformer, as depicted in Figure 4.1.

4.1.2 Reformer and Water Gas Shift (WGS) section

The reformer section comprises two distinct units: the primary and secondary reformers. In the primary reformer, the SMR reaction takes place, facilitated by an array of catalytic tubes. This reaction is characterized by its high endothermic nature and is sustained by multiple fire burners. Fueled by NG, these burners initiate and maintain the SMR process, with minor quantities of hydrogen products being recycled. Typically employing a nickel catalyst, the SMR reaction (Reaction 4.4) operates within a temperature range spanning from 800 to 1,000 °C. [5].

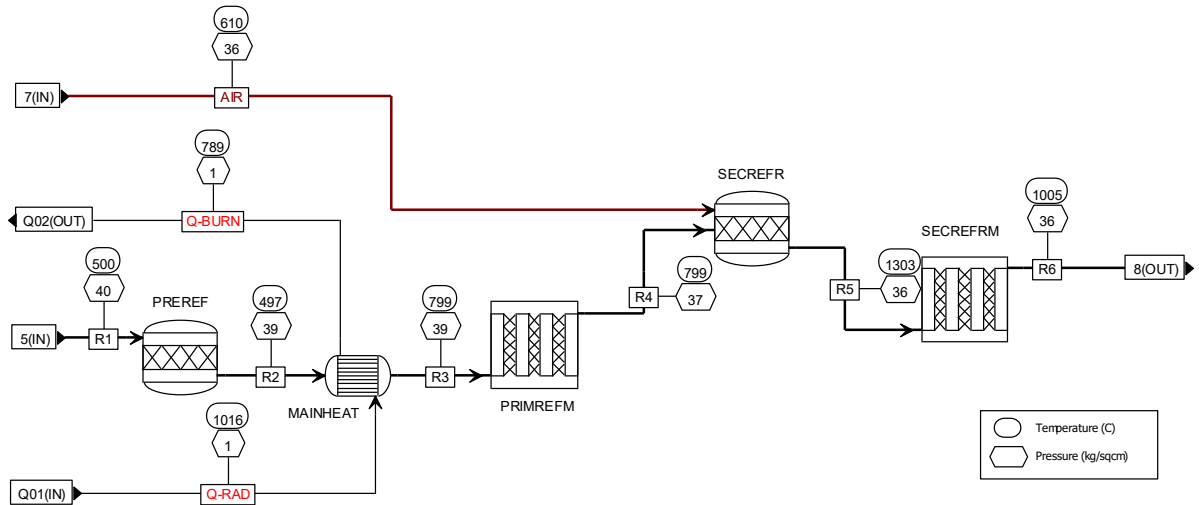
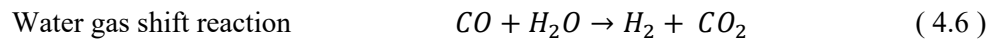
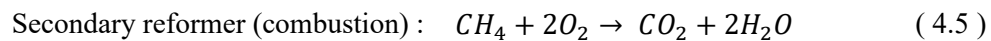
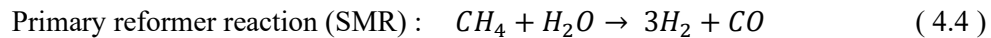


Figure 4.4 Process flow diagram of Reformer Section. SMR reaction happens in the Primary Reformer (“PRIMREFM”) and air injection in the secondary reformer (“SECREFR”).

Figure 4.4 shows the process flow diagram of the Reformer Section. The operating pressure of the reformers must align with that of the upstream process, specifically the pre-treatment section, which typically operates approximately 40 bar. This medium-pressure environment serves to extend the catalyst's lifespan by mitigating the risk of material deposition within the catalytic tubes. A critical parameter for the primary reformer is the maintenance of an optimal steam-to-carbon ratio (S/C) of approximately 4.04 by mass or 3.59 by molar ratio [99]. This ensures the efficient progression of the reforming reactions while optimizing hydrogen production.



The syngas and residual gases emanating from the primary reformer are subsequently directed to the secondary reformer to facilitate further conversion of CH_4 into H_2 . In this stage, air injection is employed to initiate a combustion reaction, utilizing the oxygen

content present. Notably, nitrogen serves as an inert component, destined for later use in the ammonia synthesis reactor. Given the intermediate pressure conditions, an air compressor is essential for supplying air to the secondary reformer.

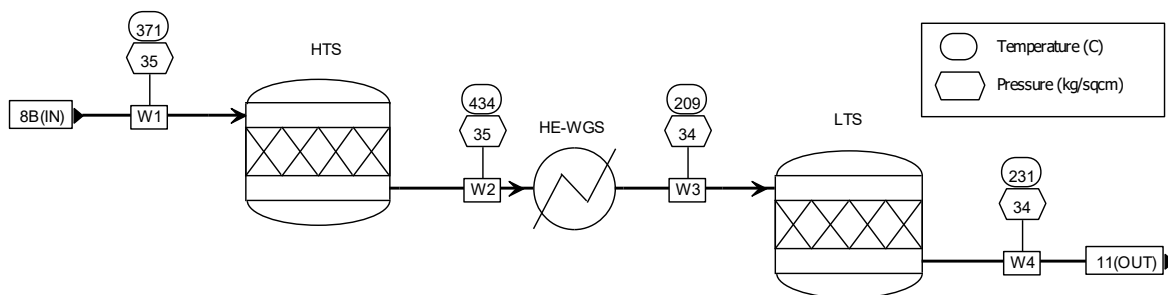


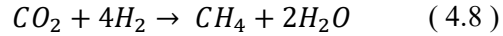
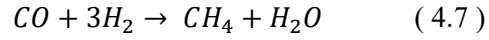
Figure 4.5 Flow diagram of Water Gas Shift Section

Within the water gas shift (WGS) section, the primary objective is to enhance hydrogen production by effecting the conversion of CO from the SMR product into CO₂ through the utilization of steam, as depicted in Reaction (4.6). As illustrated in Figure 4.5, the WGS section consists of two reactors, high-temperature shift (HTS) and low-temperature shift (LTS) reactors. The heat exchanger between the reactors is utilized to generate steam by flowing boiler feed water (BFW) in the tube section.

4.1.3 CO₂ Removal and Methanation Section

The final outputs from the reformers and WGS section primarily consist of H₂, CO, and CO₂, collectively referred to as synthesis gas or syngas. Initially, CO₂ is removed in the CO₂ removal section. Industrial plants commonly employ amine-based absorbers and strippers for CO₂ removal. The CO₂ outlet from the stripper, typically maintained at low pressure (around 1.5 bar), is directed as feed material to the urea plant. The remaining gas stream, predominantly composed of H₂ and inert gases, proceeds for ammonia synthesis.

Prior to entering the ammonia converter or ammonia synthesis reactor, most ammonia plants incorporate a methanation section to convert any residual carbon oxides (CO and CO₂) in the syngas stream into methane. The methanation reaction, depicted in Reactions (4.7) and (4.8), serves this purpose.



The overall methanation reactions are exothermic and typically occur within the temperature range of 300 – 400°C, facilitated by nickel-based catalysts, and are conducted at a comparable pressure level to that of the upstream process (approximately 30 bar). Methanation is essential due to the sensitivity of the iron catalyst utilized in the Haber-Bosch process for ammonia synthesis to the presence of carbon oxides. Carbon monoxide serves as a catalyst poison, impeding the activity of the iron catalyst within the ammonia synthesis reactor. Moreover, while carbon dioxide can also interact with the catalyst, its effect is comparatively less pronounced than that of CO.

4.1.4 Ammonia Synthesis

Hydrogen and nitrogen are utilized in the production of ammonia through the catalytic ammonia reactor or ammonia converter. The ammonia synthesis loop requires a high-pressure feed, typically between 100 and 150 bar. Hence, the output from the methanation section must undergo compression via a syngas compressor. Operating at high pressure facilitates increased ammonia yield per pass, as per Le Chatelier's principle [101].

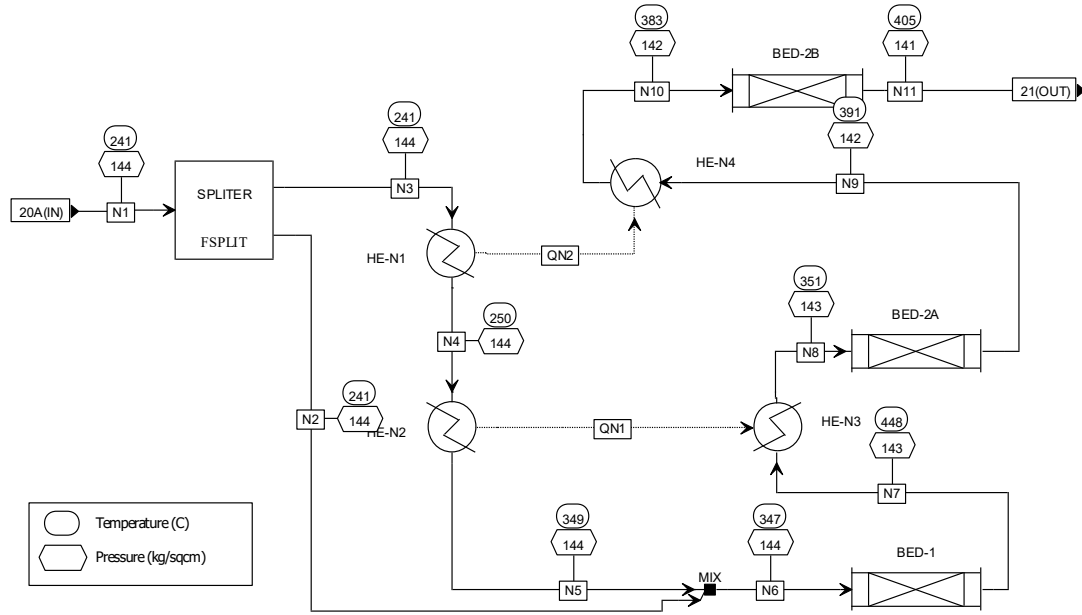
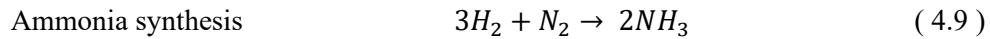


Figure 4.6 Ammonia synthesis reactor (NH_3 converter) configuration with 3 PFR bed model in series and intercoolers to control each bed inlet temperature

The ammonia synthesis reaction (Reaction 4.9) is exothermic. As depicted in Figure 4.6, careful temperature control by several intercoolers between the catalyst bed is imperative within the confines of the ammonia converter. While elevated temperatures can accelerate the reaction rate, they also elevate the likelihood of the reverse reaction transpiring, thereby diminishing the ammonia yield. In the Haber-Bosch process, the typical inlet temperature ranges from 238 to 390 °C when employing an iron-based catalyst [102].



4.1.5 Refrigerant Loop

Since the ammonia synthesis reactor has approximately 20 – 30% conversion, recycling nitrogen and hydrogen feed is necessary to optimize the yield of ammonia. The most practical pathway is through refrigeration system by condensing the ammonia

converter effluent so that ammonia will come as liquid, and the other gases will vaporize.

Figure 4.7 shows process flow diagram of the refrigerant loop unit in our model.

The ammonia converter effluent is cooled and then flashes through RF-F1. Condensed ammonia disengages from recycled gas through the flush drum. The recycled gas is reheated and sent to syngas compressor. A small fraction (approximately 2.5 – 3%) of the recycled gas is purged from the synthesis loop. This prevents methane and argon in the makeup gas from building up excessively in the loop. The flowrate of the purge is adjusted to maintain an inert gas content in the ammonia converter feed of approximately 8 %-volume.

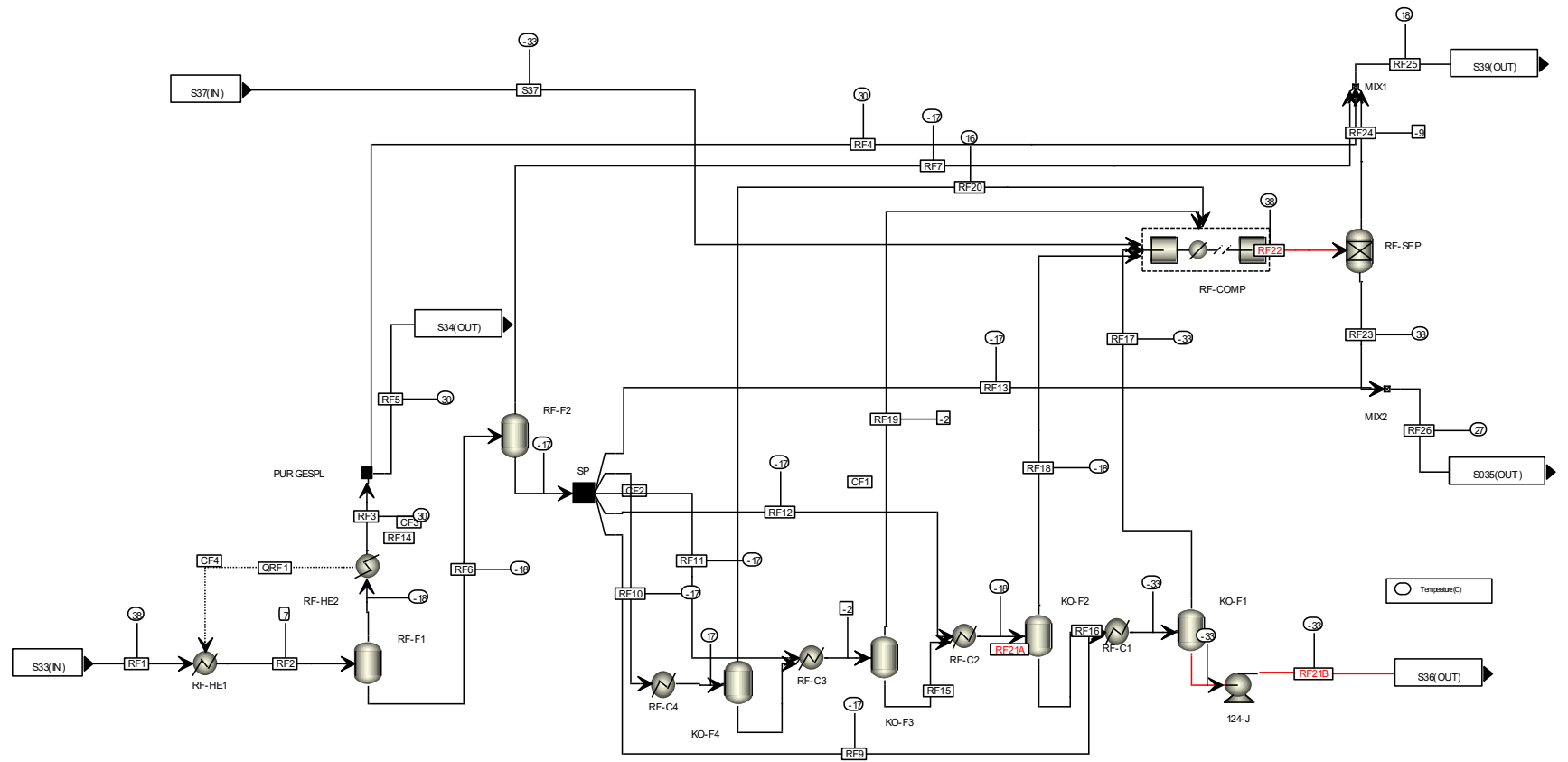


Figure 4.7 Refrigerant loop process flow diagram

The refrigeration system operates at four levels of pressure and temperature. Pressure ranging from 0 – 6.8 kg/cm²G and temperature from -33.3 to 16.6 °C. As shown in Figure 4.7, the refrigerant system is driven by an ammonia refrigerant compressor. The outputs of the refrigerant system are ammonia cold product and warm product. Cold ammonia product could be directly transferred and stored to the ammonia storage while the warm product is usually for nearby customer demand that transferred through pipeline.

4.2 Integration of MP-SMR-Ammonia (Proposed Model)

Various opportunities exist for integrating MP into the SMR process within ammonia plants. Pruvost et al. explored one such integration by combining SMR with a molten salt pyrolysis reactor arranged in a series configuration. In their study, the molten salt pyrolysis reactor was positioned upstream of the SMR reformer to convert higher hydrocarbons into hydrogen and solid carbon. The simulation model for the pyrolysis reactor assumed an equilibrium state without incorporating kinetic data [7].

In our study, we propose a fundamentally different and more detailed design approach. Following the pretreatment or desulfurization section, NG would be divided into a primary reformer and an MP reactor. Figure 4.8 schematically represents this proposed configuration.

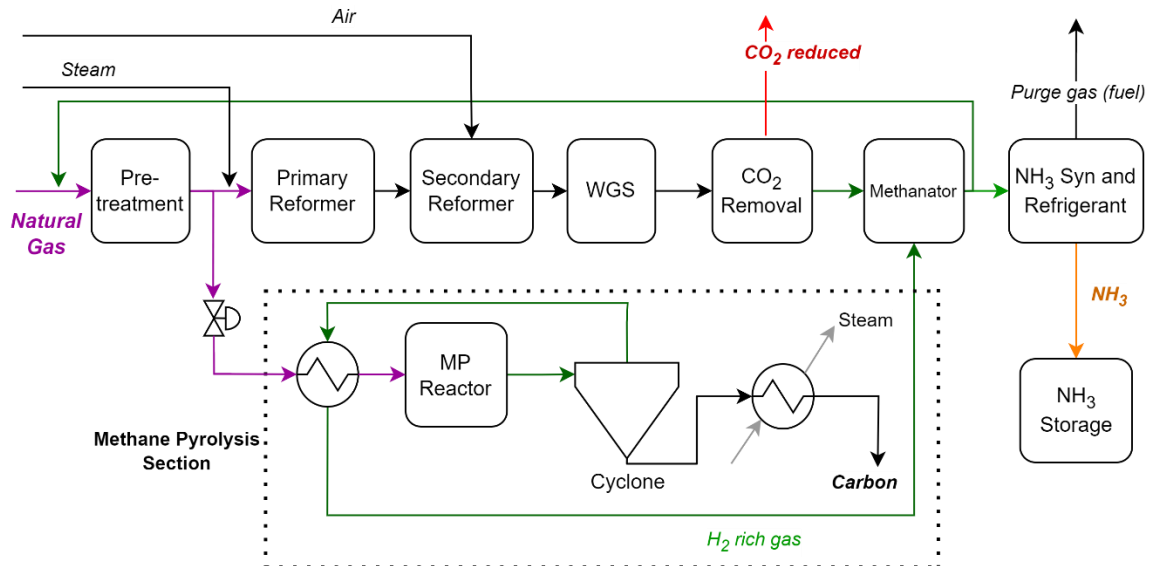


Figure 4.8 Proposed design of MP integration in SMR-ammonia-urea production plant.

Upon completion of the pretreatment phase, the NG feed is divided into two streams: one directed toward the reformer and the other toward the MP section. The division ratio can be adjusted from 0% to 100%, depend on several factors such as products yield or demand, CO₂ byproduct emission limit and reformer performance/maintenance. Both reformer and MP will produce syngas that will be combined in methanation section and further processed to ammonia synthesis.

However, the NG outlet from the pretreatment section operates at approximately 40 bar pressure, which presents a challenge for the MP process (reduced the methane conversion). Therefore, a pressure reduction control valve is necessary prior to feeding NG into the MP process to optimize the methane conversion. Moreover, methane recovery unit and recycle system are required to optimize the hydrogen and ammonia production.

Additionally, the product from the MP reactor consists of two phases: a mixed gas and solid carbon. As results, a gas-solid separator is required in the downstream of MP reactor. The solid carbon is withdrawn and can be further processed for cooling, purification, and packaging. The mixed gas, comprising hydrogen and unreacted NG, is passed through an economizer (heat exchanger) to exchange heat with the NG feed of MP reactor before transferred to the methanation reactor.

4.2.1 Methane Pyrolysis Kinetic

In the realm of ammonia process technology, the reaction mechanisms and kinetics of primary reactors, such as the SMR and the ammonia synthesis reactor, are well-established, agreed upon, and validated by researchers, as documented in the literature. However, the kinetic investigation of MP remains ongoing and continues to advance.

Among the various studies conducted, a comprehensive kinetic study was undertaken by Keipi et al., which evaluated a 37-step reaction mechanism. This study paired both experimental and modeling approaches within a temperature range of 795 – 1,180 °C under atmospheric pressure. Subsequently, the model was adapted by Catalan et al. for application in a higher-pressure reactor [85]. The final kinetic model proposed by Catalan et al., as shown in Equation (4.10), was based on the experimental model of Keipi.

$$r = \frac{dN_{CH_4}}{dt} = A \exp\left(-\frac{E_a}{8.314 T}\right) \cdot C_{CH_4}^n \left(1 - \frac{C_{H_2}^2}{C_{CH_4} \cdot K_c}\right) \quad (4.10)$$

With

$$\begin{aligned} A &= 4.4875 \times 10^{10} s^{-1} mol^{1-n} cm^{-3(1-n)} \\ E_a &= 284.95 \frac{kJ}{mol} \\ n &= 1.0809 \end{aligned}$$

$$K_c = K \left(\frac{P^0}{RT} \right)^{2-1} = \exp \left(13.2714 - \frac{91204.6}{8.314 T} \right) \left(\frac{10^5}{8.314 T} \right)$$

It is important to note that the experiment conducted by Keipi et al. was for a non-catalytic methane pyrolysis reactor, while the study by Catalan et al. utilized liquid metal bubble reactors (LMBRs) with a molten tin medium. An additional kinetic model was proposed in the Aspen Plus v14 example of methane pyrolysis simulation, as depicted by Equation (4.11).

$$r = A \exp \left(- \left(\frac{Ea}{R} \right) \left(\frac{1}{T} - \frac{1}{T_0} \right) \right) P_{CH_4}^n \quad (4.11)$$

$$A = 0.01 \frac{kmol}{m^3s}; T_0 = 1,000 \text{ } ^\circ C$$

$$Ea = 49.68 \frac{cal}{mol};$$

$$n = 1; P \text{ in bar}$$

All these kinetic models are subject to testing and validation under selected pressure and temperature conditions, using the experimental data from Keipi's study.

4.2.2 Operating Condition Selection

As discussed previously in the Thermodynamics of MP section, pressure and temperature are critical parameters for the MP reactor.

Pressure selection

As depicted in Figure 2.2, lower pressure leads to higher methane conversion. However, for integration with the base model, the pressure range should fall between 33 – 41 bar. This consideration arises from the fact that the NG feed outlet from the pretreatment

section operates at approximately 41 bar, while the lowest pressure for the downstream section (from methanation to syn gas compressor suction) is approximately 32 bar.

Opting for a pressure lower than 32 bar necessitates pressure reduction via a control valve, followed by the need for a compressor to elevate the pressure again for transferring the gas product into the downstream section. While this approach would indeed result in higher methane conversion, it is not the most efficient, as both capital and operational costs would significantly escalate with the addition of a compressor in the proposed model.

Therefore, to achieve a balance between conversion efficiency and economic considerations, a pressure of 33 bar is chosen for the MP reactor. This selection eliminates the need for a compressor in the MP section, requiring only a pressure reduction control valve in the upstream. This approach simplifies the process design and minimizes additional equipment costs.

Temperature selection

In determining the optimal temperature range, the primary consideration revolves around the desired coproduct, carbon black, which holds significant market potential compared to other solid carbon types. Therefore, the temperature range should exceed 1,150°C. While higher temperatures yield higher conversion rates, they also entail increased energy consumption and capital costs for material selection. Furthermore, as shown on Figure 2.9, to obtain carbon black as a coproduct in a non-catalytic reactor, the reaction temperature should ideally exceed 1,350°C. At temperatures between 1,100 and 1,200°C, the production of carbon black necessitates the use of an activated carbon or molten gallium catalyst [17,103].

Based on these considerations, the final operating conditions for the MP reactor in the proposed integration model are determined to be 33 bar and 1,400°C, employing a non-catalytic process.

4.2.3 MP Reactor Sizing Optimization

The MP reactor is the core equipment within the methane pyrolysis process. With the kinetic model and operating conditions established, optimizing the reactor design for the integrated process can offer significant energy and economic benefits. For large-scale MP processes employing a catalytic approach, plug flow reactors (PFRs) are generally not recommended due to rapid catalyst deactivation caused by solid carbon deposits. Fluidized bed reactors (FBRs) or moving bed reactors (MBRs) are typically preferred in such scenarios. However, considering the non-catalytic nature of the proposed MP process, a PFR model is deemed suitable.

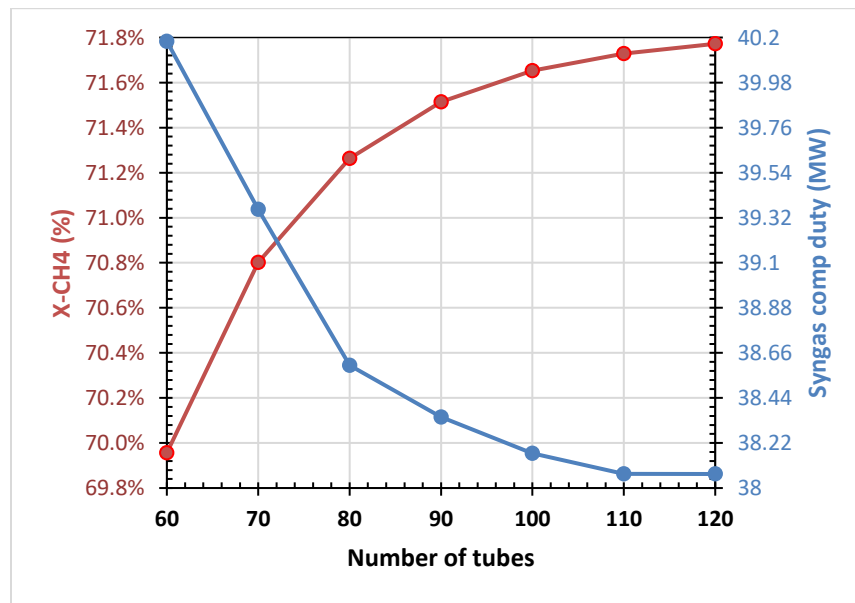


Figure 4.9 Sensitivity analysis to determine the optimal number of tubes in the MP reactor using existing dimensions of the SMR primary reformer tubes

During the integration design phase, it is crucial to consider the compatibility of new equipment with existing units. In this instance, Aspen Plus requires the specification of reactor length and diameter for the PFR model. Since the primary reformer in the existing plant is also modeled as a PFR with known dimensions obtained from plant data, a strategic decision was made. The MP reactor will utilize the same tube dimensions as the primary reformer, enabling the interchangeability of spare parts between the two units. The primary difference will lie in the number of tubes employed. The base case model indicates the primary reformer utilizes over 190 tubes. For the MP reactor, which is designed to also handle 100% of the NG feed, a reduced number of tubes is more likely due to the absence of steam. Figure 4.9 depicts the sensitivity analysis graph of the reactor's number of tubes in relation to methane conversion and syngas compressor duty at 100% NG Feed to MP.

As illustrated in Figure 4.9, increasing the number of tubes beyond 80 does not yield a significant enhancement in methane conversion and insignificant duty reduced for syngas compressor. Figure 4.10 illustrates the process flow diagram of the MP Section, reflecting the chosen operating conditions and optimized reactor sizing.

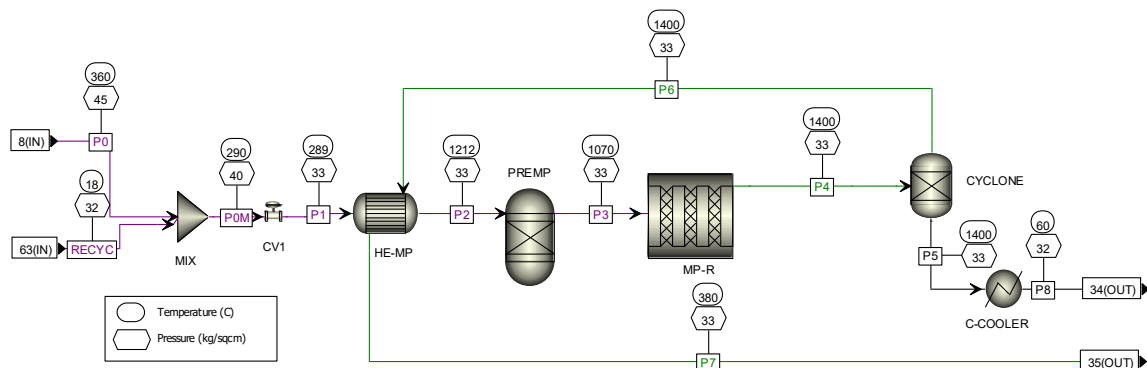


Figure 4.10 Methane pyrolysis section.

The carbon black cooler (C-COOLER) holds potential for steam generation from BFW due to its notable temperature differential. Finally, Figure 4.11 shows the complete flowsheet of our proposed integration model. Additionally, Table 4.1 outlines other essential equipment and their corresponding input specifications. The material balance for 50% split ratio of integration model is shown by Table 4.2.

Table 4.1 Major unit operation models and specification

Unit	Model	Specification
NG Compressor	Compr (Isentropic)	Disch. Press = 45.2 kg/sqcm Isentropic Efficiency: 0.72 (Aspen default)
Air Compressor	Mcompr (Isentropic)	No. of stages: 4 Disch. Press last stage = 36.4 kg/sqcm Interstage cooler: 3, outlet T = 38 °C
Desulfurizer	RStoic	P = 45 kg/sqcm; duty = 0 MW Fractional conv. = 1 of S (S+H ₂ became H ₂ S)
Primary Reformer	RPlug	T constant at 799 °C No. of tubes: 192 Tube length: 11.528 m (d: 0.1 m)
Secondary Reformer	Rplug	Jacketed reactor (Thermal fluid = 50 °C) Length: 3.056 m (d: 3.55 m)
WGS.HTS	RStoic	P = 35 kg/sqcm; T = 434 °C Fractional conv. = 0.715 of CO
WGS.LTS	RStoic	P = 34 kg/sqcm; T = 231 C Fractional conv. = 0.91 of CO
CO ₂ Removal	Sep	Flash temp. = 38 C, pressure = 1.9 kg/sqcm CO ₂ stream split fraction 0.99 CO ₂ , 0.0015 H ₂
Methanator	RGibbs	Specified T = 345 °C; P drop = -0.5 kg/sqcm
Syngas Compressor	Mcompr (Isentropic)	No. of stages: 2 Disch. Press last stage = 144.6 kg/sqcm Interstage cooler: 1, outlet T = 55 °C
NH ₃ Converter	RPlug (Adiabatic)	Configuration: 3 bed in series with intercooler inlet : P = 144 kg/sqcm, T = 241 °C Bed-1: l=2.1 m (d=2 m), out T = 448 °C Bed-2A: l=3.3 m (d=2 m), out T = 391 °C Bed-2B: l=3.3 m (d=2 m), out T = 405 °C
NH ₃ Refr.Comp.	Mcompr (Isentropic)	No. of stages: 2 Disch. Press last stage = 16.4 kg/sqcm Interstage cooler: 1, outlet T = 38 °C
NH ₃ Storage	Sep	Flash temp. = -33 °C, vapor frac. = 1
MP.Reactor	RPlug	T constant at 1,400 °C No. of tubes: 80 Tube length: 11.528 m (d: 0.1 m)
MP.Cyclone	Sep	CB stream split fraction 1 C (Carbon)

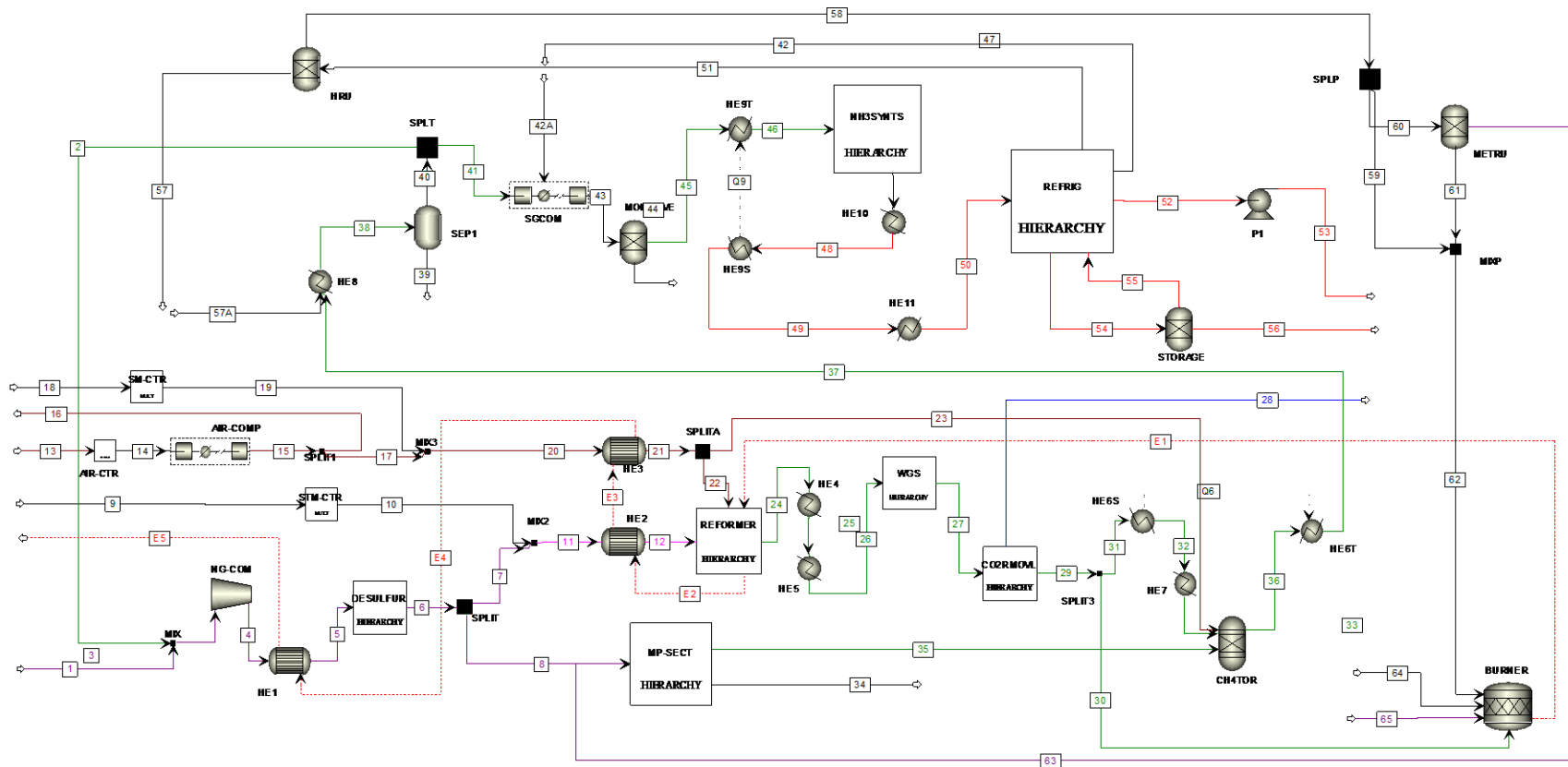


Figure 4.11 Proposed integration model flowsheet design through Aspen Plus

Table 4.2 Material balance of proposed integration model with 50% NG split ratio

	Units	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Temperature	C	31.9	38	31.942	174.82	371	360	360	360	347	347	348.07	500	37	37	163.3	163.3	163.3	347	347	175.08	610	610	
Pressure	kg/sqcm	11.2	31.55	11.2	45.2	45.2	45.2	45.2	45.2	42	42	42	40	1	1	36.4	36.4	36.4	42	42	36.4	36.4	36.4	
Vapor		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
Solid		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Mole Flows	kmol/hr	1207.3	27.571	1234.9	1234.9	1234.9	1234.8	617.39	617.39	3952.6	1978.3	2595.7	2595.7	1877	1434	1434	85	1349	171.85	85.927	1435	1435	1435	0
Mole Fractions																								
CO2		1.8%	0.0%	1.8%	1.8%	1.8%	1.8%	1.8%	1.8%	0.0%	0.0%	0.4%	0.4%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
CO		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
H2		0.0%	69.9%	1.6%	1.6%	1.6%	1.6%	1.6%	1.6%	0.0%	0.0%	0.4%	0.4%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
N2		2.5%	23.3%	3.0%	3.0%	3.0%	3.0%	3.0%	3.0%	0.0%	0.0%	0.7%	0.7%	78.0%	78.0%	78.0%	78.0%	78.0%	0.0%	0.0%	73.4%	73.4%	73.4%	
CH4		91.0%	5.8%	89.1%	89.1%	89.1%	89.1%	89.1%	89.1%	0.0%	0.0%	21.2%	21.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
AR		0.0%	0.3%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.9%	0.9%	0.9%	0.9%	0.9%	0.0%	0.0%	0.9%	0.9%	0.9%	
NH3		0.0%	0.5%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
H2O		0.0%	0.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	100.0%	76.2%	76.2%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	100.0%	6.0%	6.0%	6.0%	
O2		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	21.0%	21.0%	21.0%	21.0%	21.0%	0.0%	0.0%	19.7%	19.7%	19.7%	
C2H6		2.9%	0.0%	2.8%	2.8%	2.8%	2.8%	2.8%	2.8%	0.0%	0.0%	0.7%	0.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
C3H8		1.0%	0.0%	1.0%	1.0%	1.0%	1.0%	1.0%	1.0%	0.0%	0.0%	0.2%	0.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
N-BUTANE		0.4%	0.0%	0.3%	0.3%	0.3%	0.3%	0.3%	0.3%	0.0%	0.0%	0.1%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
I-BUTANE		0.4%	0.0%	0.3%	0.3%	0.3%	0.3%	0.3%	0.3%	0.0%	0.0%	0.1%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
S		0.003%	0.0%	0.003%	0.003%	0.003%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
H2S		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
C		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Mass Flows	kg/hr	21540	251.28	21791	21791	21791	21790	10895	10895	71207	35639	46534	46534	54371	41539	41539	2462.2	39077	3096	1548	40625	40625	40625	

Continued in the next page.

	Units	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	42A	43	44	45	46
Temperature	C	1174.9	700	371	230.7	230.7	47	47	47	310	316	60	380	345	174.58	38	38	38	38	30	30	55	55	55	241.6
Pressure	kg/sqcm	35.6	35.5	35.4	33.9	33.9	33.2	33.2	33.2	33	32.8	32	33	32.3	32.05	31.77	31.55	31.55	31.55	134.97	134.97	144.4	144.4	144.4	144.29
Vapor		1	1	1	1	1	1	1	1	1	1	0	1	1	1	0.99	0	1	1	1	1	1	0	1	1
Solid		0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
Mole Flows	kmol/hr	4987.4	4987.4	4987.4	4987.4	620.81	2974.1	139.78	2834.3	2834.3	2834.3	607.23	1423	4215.1	4215.1	4551.9	32.111	4519.8	4492.2	24637	24637	29129	8.4312	29121	29122
Mole Fractions																									
CO2		4.4%	4.4%	4.4%	12.4%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.8%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
CO		8.3%	8.3%	8.3%	0.2%	0.0%	0.4%	0.4%	0.4%	0.4%	0.4%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
H2		29.4%	29.4%	29.4%	37.5%	0.0%	62.9%	62.9%	62.9%	62.9%	62.9%	0.0%	83.1%	68.6%	68.6%	69.4%	0.0%	69.9%	69.9%	43.5%	43.5%	47.6%	0.0%	47.6%	47.6%
N2		21.5%	21.5%	21.5%	21.5%	0.0%	36.0%	36.0%	36.0%	36.0%	36.0%	0.0%	1.3%	24.7%	24.7%	23.1%	0.0%	23.3%	23.3%	14.7%	14.7%	16.0%	0.0%	16.0%	16.0%
CH4		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	14.9%	5.5%	5.5%	5.7%	0.0%	5.8%	5.8%	36.5%	36.5%	31.8%	0.0%	31.8%	31.8%
AR		0.3%	0.3%	0.3%	0.3%	0.0%	0.4%	0.4%	0.4%	0.4%	0.4%	0.0%	0.0%	0.3%	0.3%	0.3%	0.0%	0.3%	0.3%	2.2%	2.2%	1.9%	0.0%	1.9%	1.9%
NH3		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.5%	0.1%	0.5%	0.5%	3.1%	3.1%	2.7%	0.0%	2.7%	2.7%
H2O		36.2%	36.2%	36.2%	28.1%	0.0%	0.3%	0.3%	0.3%	0.3%	0.3%	0.0%	0.0%	1.0%	1.0%	0.9%	99.9%	0.2%	0.2%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%
O2		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C2H6		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C3H8		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
N-BUTANE		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
I-BUTANE		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
S		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
H2S		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Mass Flows	kg/hr	87159	87159	87159	87159	27322	34751	1633.3	33118	33118	33118	7293.5	6783.4	39901	39901	41772	578.45	41193	40942	301760	301760	342702	151.89	342550	342598

Continued in the next page

	Units	47	48	49	50	51	52	53	54	55	56	57	57A	58	59	60	61	62	63	64	65
Temperature	C	333.62	262	72	38	17.756	27.178	27.265	-32.774	-33	-33	17.756	17.756	17.756		17.756	17.756	17.756	17.76	30	31.9
Pressure	kg/sqcm	138.77	138.27	137.87	137.37	32	16.4	18	4	1.0127	1	32	32	32		32	32	32	32	1	11.2
Vapor		1	1	1	1	1	0	0	0	1	0	1	1	1		1	1	1	1	1	1
Solid		0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	0
Mole Flows	kmol/hr	27229	27229	27229	27229	698.86	1818.7	1818.7	82.433	8.2433	74.19	336.87	336.87	361.98	0	361.98	163.65	163.65	198.34	7000	448.39
Mole Fractions																					
CO2		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	0.0%	1.8%
CO		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
H2		40.5%	40.5%	40.5%	40.5%	43.0%	0.0%	0.0%	0.0%	0.0%	0.0%	80.2%	80.2%	8.3%		8.3%	18.3%	18.3%	0.0%	0.0%	0.0%
N2		13.7%	13.7%	13.7%	13.7%	14.5%	0.0%	0.0%	0.0%	0.0%	0.0%	3.9%	3.9%	24.4%		24.4%	53.9%	53.9%	0.0%	79.0%	2.5%
CH4		34.0%	34.0%	34.0%	34.0%	37.1%	0.0%	0.0%	0.0%	0.0%	0.0%	8.5%	8.5%	63.7%		63.7%	19.7%	19.7%	100%	0.0%	91.0%
AR		2.0%	2.0%	2.0%	2.0%	2.2%	0.0%	0.0%	0.0%	0.0%	0.0%	1.0%	1.0%	3.3%		3.3%	7.4%	7.4%	0.0%	0.0%	0.0%
NH3		9.8%	9.8%	9.8%	9.8%	3.3%	100.0%	100.0%	100.0%	100.0%	100.0%	6.5%	6.5%	0.3%		0.3%	0.7%	0.7%	0.0%	0.0%	0.0%
H2O		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
O2		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	21.0%	0.0%
C2H6		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	0.0%	2.9%
C3H8		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	0.0%	1.0%
N-BUTANE		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	0.0%	0.4%
I-BUTANE		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	0.0%	0.4%
S		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
H2S		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
C		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%		0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Mass Flows	kg/hr	342598	342598	342598	342598	8600.8	30973	30973	1403.9	140.39	1263.5	1870.5	1870.5	6730.4		6730.4	3548.5	3548.5	3181.87	201953	8000

CHAPTER 5

RESULTS AND DISCUSSIONS

This chapter presents key findings from the simulations. Base case model validation is discussed first, followed by details of the proposed integrated design, including reactor design, operating conditions, and configuration. A comparative analysis across both models explores product yield, CO₂ emissions, and energy consumption under various NG feed splitting ratios. Finally, the economic analysis assesses the proposed integration's economic viability.

5.1 Base Model Reactor Validation

The validation of the base case ammonia plant model primarily focused on key reactors, namely the primary reformer, secondary reformer, and ammonia converter, or ammonia synthesis reactor. These reactors were simulated using Aspen Plus software, employing a kinetic reactor type based on data sourced from various literature references. The simulation results were subsequently validated against plant design data.

Reformers

Figure 5.1 illustrates a comparison of primary and secondary reformer gas compositions between the simulation results and actual plant data, presented in dry mol basis percentage. The analysis reveals a close alignment between the simulation model and the plant design data for both the primary and secondary reformers. For instance, in the primary reformer model, the steam-to-carbon ratio (S/C) in the feed stream closely

approximated 3.595 mol/mol, which closely matched the design plant's value of 3.594 mol/mol. While steam components were omitted from the tables due to the presentation in dry basis percentages, noteworthy findings include the simulation model yielding a methane slip below the design data, measuring 13.4% in the primary reformer and 0.42% in the secondary reformer.

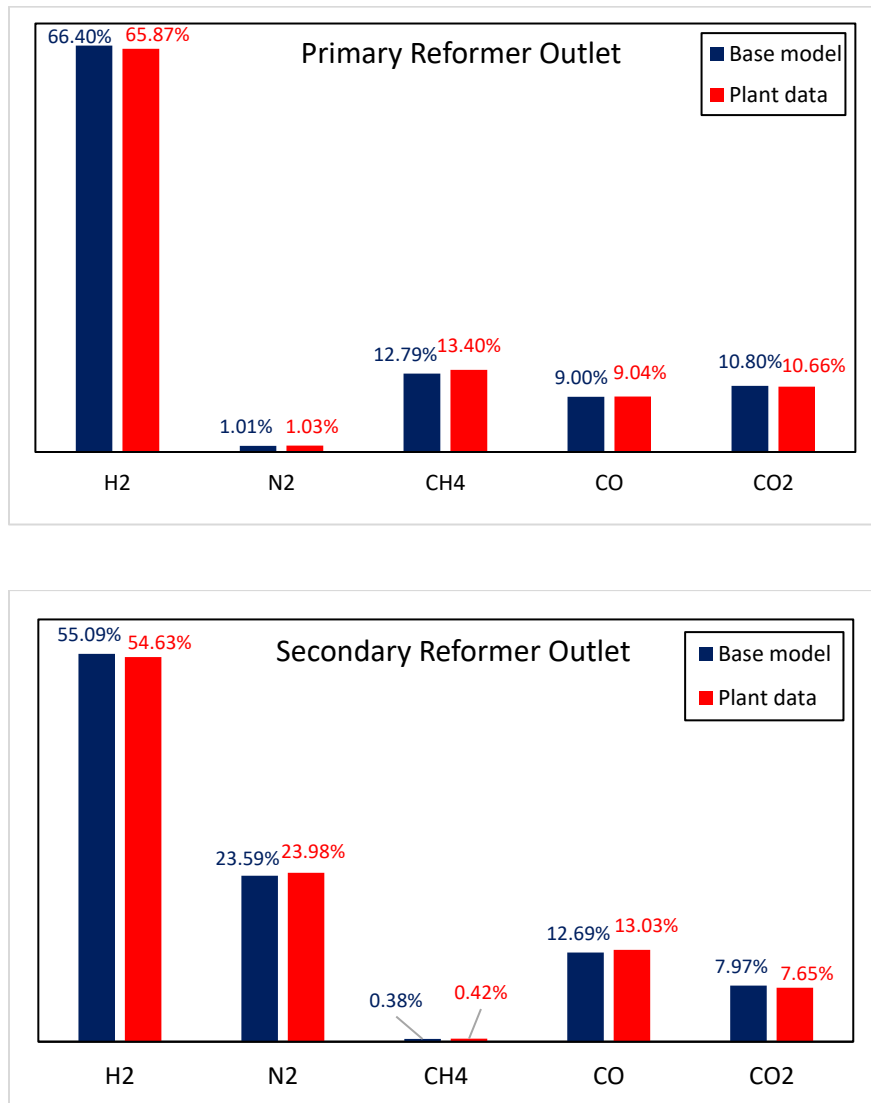


Figure 5.1 Validation of Primary and Secondary Reformer with actual plant data

Moreover, the simulation model demonstrated lower methane slip and higher methane conversion rates in both reformers compared to the design data. Specifically, the total methane conversion for the primary and secondary reformers reached 97.94% in the simulation, slightly surpassing the plant design's value of 97.72%.

Ammonia Converter

The primary reactor utilized in the production of ammonia from hydrogen and nitrogen is the ammonia synthesis reactor, also known as the ammonia converter. This reactor was modeled using a kinetic reactor approach, assuming a single bed as a plug flow reactor, with a total of four beds arranged in a series configuration, each interspersed with an intercooler. Table 5.1 presents a comparison of several key parameters in the NH_3 converter model with the plant's design data.

Table 5.1 Validation of key parameters of ammonia converter model with actual plant data

Parameter	H/N feed	Inert feed	$x\text{-H}_2$	$x\text{-N}_2$	ΔNH_3	Total NH_3 (tpd)
Base model	2.92	8.30%	30.37%	29.60%	15.98%	1001.15
Design data	3.00	8.00%	27.34%	27.33%	14.31%	1012.30

The hydrogen-to-nitrogen feed molar ratio is a crucial parameter in the operation of the ammonia converter, ideally maintained at approximately 3.00. In the model, this ratio was recorded at 2.92 mol/mol, slightly lower than the corresponding plant data. However, both hydrogen and nitrogen conversions exceeded the design data. Additionally, the fresh ammonia yield (ΔNH_3) was marginally higher, despite similar inert feed composition (argon and methane). Furthermore, the outlet gas composition of the simulated ammonia converter closely aligned with the design data, as illustrated in Figure 5.2.

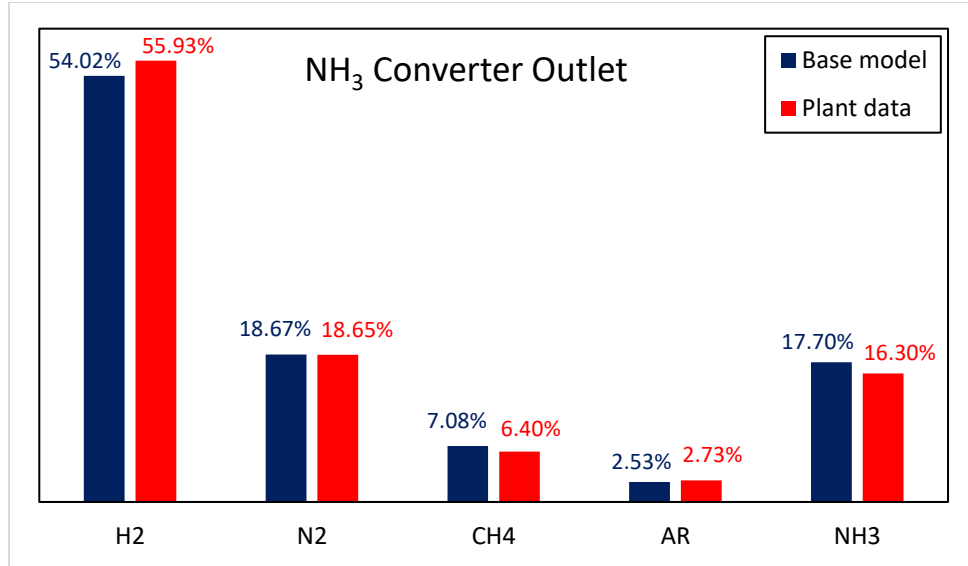


Figure 5.2 Ammonia converter outlet gas composition compared with the actual plant data

Operating at a capacity of 1,000 MTPD of ammonia production, this simulated ammonia converter exhibits consistent performance across key parameters. Hence, it is deemed ready for integration with the MP model.

5.2 MP Reactor Kinetic Validation

To ensure seamless integration with the existing SMR-ammonia plant, which operates at pressures of up to 41 bar at the SMR inlet feed, the MP reactor necessitates modeling and validation under high-pressure conditions. Sensitivity analysis was conducted on two kinetic models: the Catalan model (Equation 4.10) and the Aspen model (Equation 4.11), with comparison to the equilibrium condition. The resulting model profiles are depicted in Figures 5.3a and 5.3b, respectively.

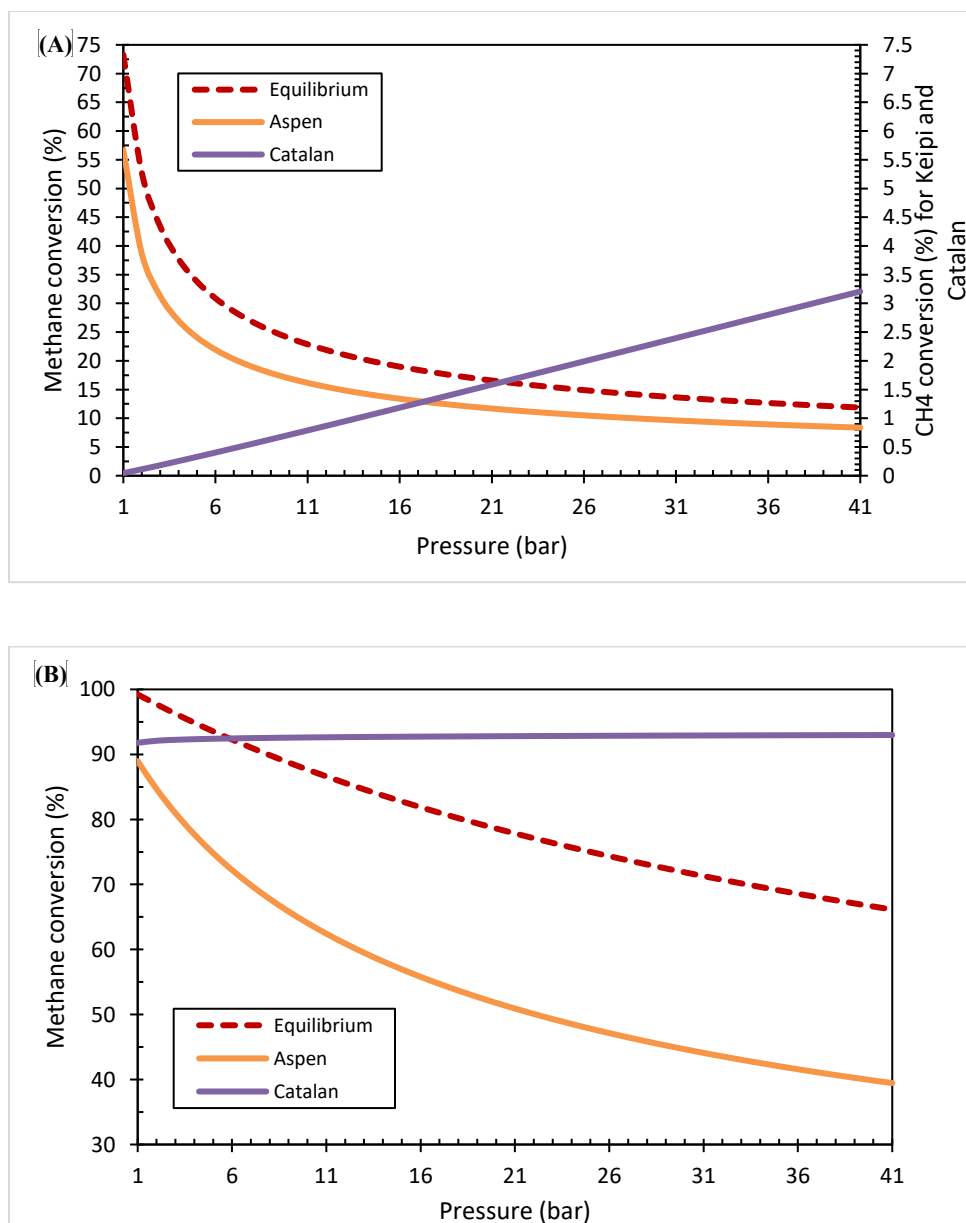


Figure 5.3 MP kinetic model under high-pressure conditions at a constant temperature of 600°C (Figure 5.3a) and 1,000°C (Figure 5.3b), compared with the equilibrium state

At 600°C (Figure 5.3a), the Catalan model exhibits significantly lower methane conversion rates (< 1% at 1 bar) compared to the Aspen model and the equilibrium conversion (55 – 75% at 1 bar) (Figure 12a). Furthermore, the model shows an unrealistic increase in conversion rate with pressure. At higher temperatures (1,000°C, Figure 5.3b),

the discrepancy between Catalan models and the equilibrium curve becomes more pronounced.

Therefore, the Aspen kinetic model with a kinetic reactor type is preferred for integration process simulation. While the Aspen model predicts approximately 26% lower methane conversion compared to equilibrium, it provides a more realistic representation for the integrated model, even if it necessitates additional energy or temperature adjustments for hydrogen/ammonia production compared to ideal reactors.

Upon selecting the kinetic model, further validation with experimental data was pursued. However, obtaining experimental data for methane pyrolysis reactors is challenging compared to ammonia and reformers. The most comprehensive and readily available experimental data stem from the work of Keipi et al. [98], which utilized a noncatalytic plug flow reactor with varying methane concentrations (diluted by nitrogen) and gas flow rates, spanning a wide temperature range (390 – 1,171°C) at atmospheric pressure. While Keipi's experiment yielded 47 data points, only data with temperatures exceeding 900°C (cases numbered 34 to 47) were considered, as these exhibited methane conversions exceeding 70%. Figure 5.4 depicts the experimental data plot from Keipi for each case alongside their corresponding methane conversion rates.

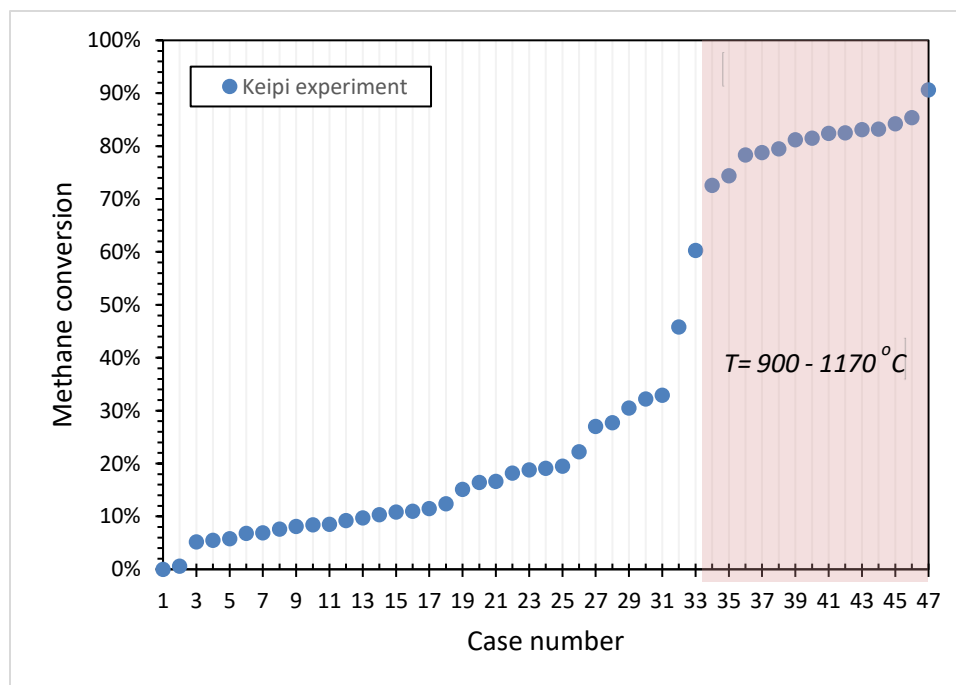


Figure 5.4 Keipi experimental data for non-catalytic MP process at atmospheric pressure and temperature range of 390 – 1,170 °C. The red box shows the highest methane conversion at the highest temperature range (900 – 1,170 °C)

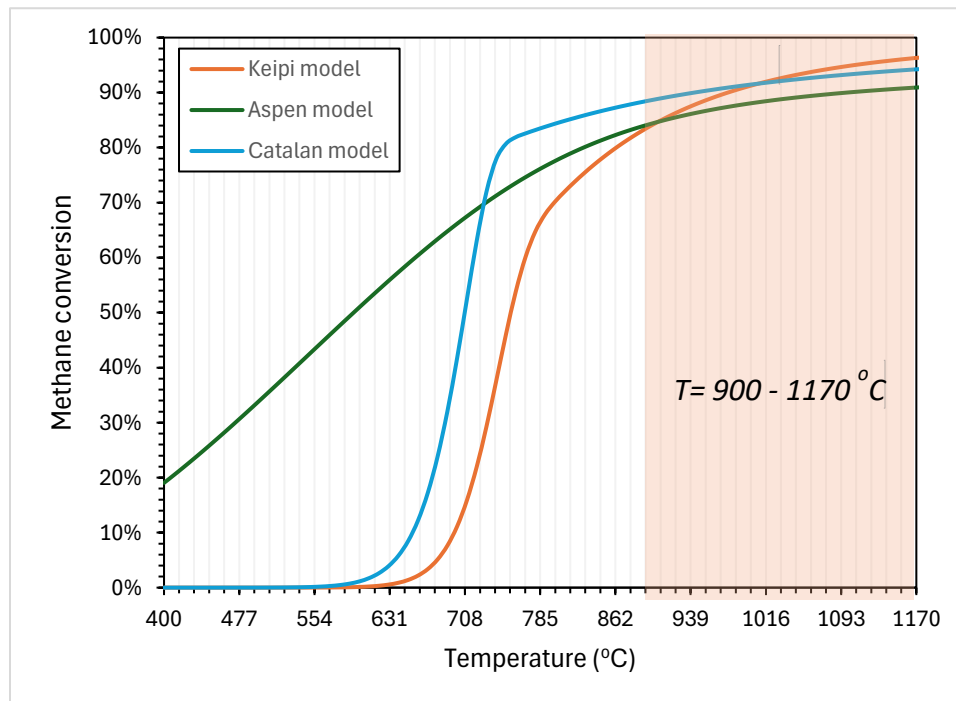


Figure 5.5 MP kinetic reactor models compared with the Catalan model with the same reactor type and thermodynamic properties (RKS-BM) in Aspen Plus v11

Keipi et al. developed a reaction rate model based on their experimental findings. Subsequently, Catalan et al. refined the reaction rate equation using the same experimental data, asserting that both models exhibited consistency with the experimental data. The Aspen model was then compared to these two models, revealing a similar profile, particularly in the high-temperature range (above 900°C), as depicted in Figure 5.4.

While displaying differing profiles at lower temperatures (below 700°C), the Aspen kinetic rate model for methane pyrolysis has demonstrated its efficacy in providing accurate estimates, particularly in the high-temperature range, notably beyond 900°C. The Aspen model exhibited only a 4–8% deviation in methane conversion compared to both the Keipi and Catalan models. Consequently, the Aspen kinetic model presented is deemed suitable for simulating MP kinetic reactors under high-pressure (1–40 bar) and high-temperature (above 900°C) conditions.

5.3 Product and CO₂ Emission

This section provides an analysis of the product yields and CO₂ emission profiles derived from simulations conducted on both the base case model and the integrated model using Aspen Plus v11. The analysis focuses on various split ratio integration within the plant. Figure 5.6 illustrates various gap load scenarios alongside the product profiles.

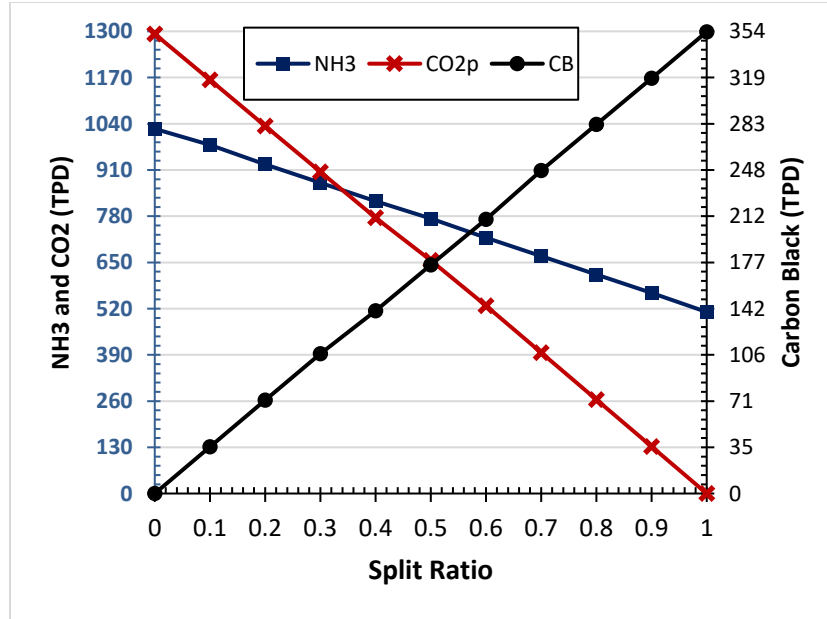


Figure 5.6 Products and CO₂ emission in different split ratio

More NG split portion to MP will reduce the CO₂, increase the CB but will also reduce the NH₃ product yield. In conventional SMR-ammonia plant (split ratio = 0), the CO₂ product (1300 tpd) is higher than the NH₃ product (1000 tpd). We can reduce 50% of CO₂ emission by splitting the NG feed 50% into MP section resulting in 650 tpd CO₂ emission and 780 tpd ammonia product. The proposed integration model design also possible to switch the SMR into MP completely so that the split ratio 100%. In the 100% split scenario, the hydrogen production will be completely from MP with no CO₂ byproduct from the process. The CO₂ emission from combustion or flue gas will still appear, but it will be lower or reduced since the amount of fuel or energy is less than SMR. The energy analysis would be discussed in the next section.

5.4 Energy Analysis

The simulation result showed that the total energy of overall integration plant is lower than original (base case) model. Figure 5.7 gives an overview of energy consumption comparison for base case (original plant) and proposed integration model in various split ratio.

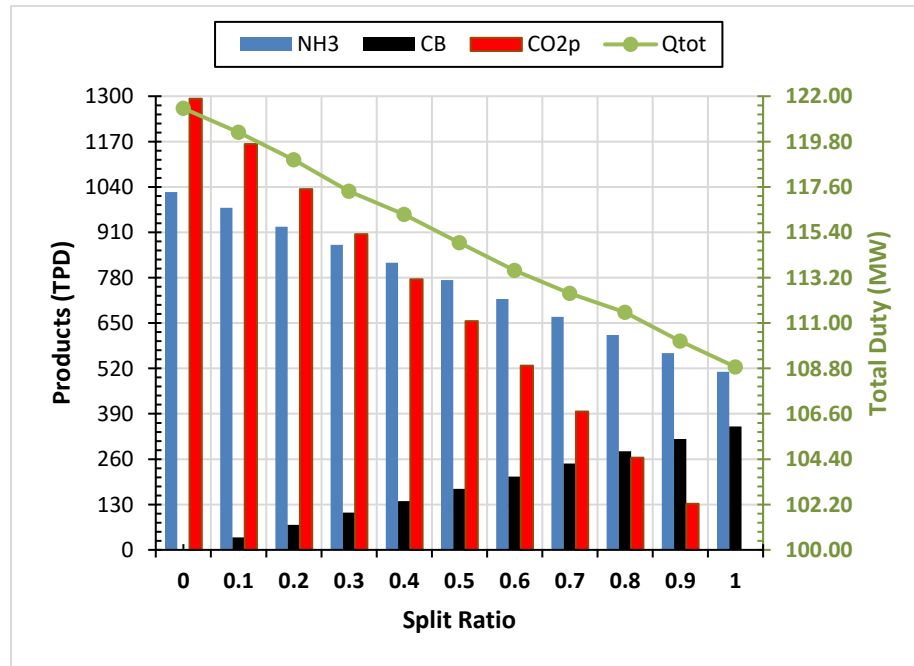


Figure 5.7 Energy and products profile for various split ratio

Furthermore, as depicted in Figure 5.8, the integration scheme positively impacts other auxiliary units. The syngas compressor, air compressor, and steam feed requirement for the SMR are all expected to decrease due to lower syngas production, leading to a further reduction in overall energy consumption.

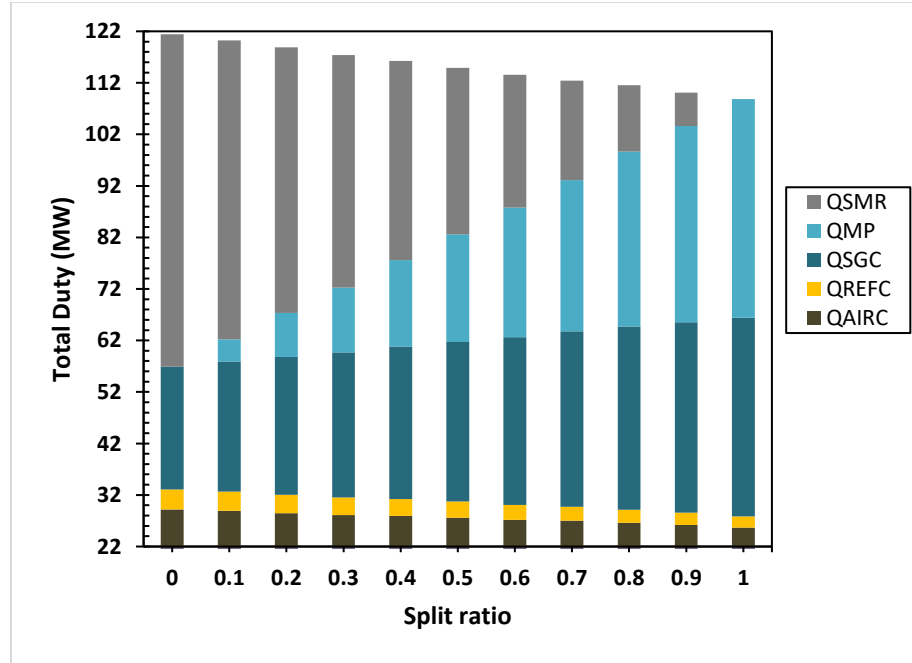


Figure 5.8 Energy distribution profile comparison of base case model (split ratio = 0) and integration model at different NG feed spit ratio

The base case model (0% split or gap) identifies the primary reformer (63 MW) and syngas compressor (24 MW) as the most significant energy consumers. In the integrated model, both these units demonstrate lower energy consumption compared to the base case. The primary reformer's energy is partially diverted to power the MP reactor, while the syngas compressor requires less energy due to the reduced syngas production from the MP process. The urea plant's energy consumption remains largely unchanged across all gap-load scenarios since it operates downstream from the integration point. The natural gas compressor maintains a constant energy demand due to the consistent NG feed rate. Air compressor energy exhibits a slight decrease due to adjustments made to maintain a N/H ratio of approximately 3.0 at the syngas compressor suction and the inlet NH_3 converter. Energy consumption in the refrigerant loop section, including the ammonia refrigerant

compressor, experiences a minor reduction due to lower ammonia yield. Other auxiliary units such as boiler feed water pumps, utility pumps, motor oil pumps, and induced fans were assumed to have constant energy consumption across both models.

5.5 Economic Analysis

This section analyzes the economic viability of the proposed integrated model compared to the base case model. While the integrated model incurs higher capital costs due to the additional equipment required for the MP section, it offers significant operational advantages that translate into economic benefits.

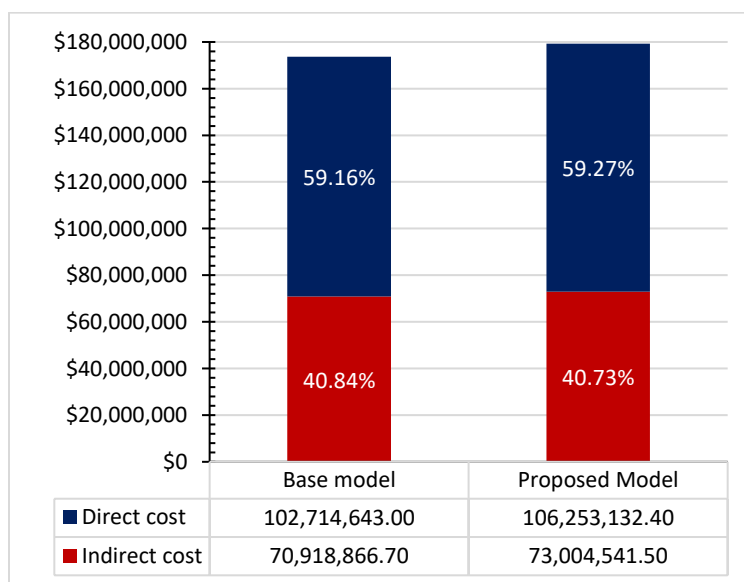
Investment analysis

Utilizing Aspen Plus Economic Analyzer (APEA) v11, investment analysis was performed for both base and proposed integration models under a 50% split ratio scenario. Key parameters included a project economic life of 25 years, a salvage value of 20%, a desired rate of return of 10% per year, and a start-up period of 2 weeks. Parameters such as depreciation method, overhead percentage, and raw materials and product escalation were set to APEA defaults. Comparisons were made based on net present value (NPV), payback period, internal rate of return (IRR), and profitability index. Under this analysis, a CO₂ tax of 8 USD/ton-CO₂ and a carbon black coproduct price of 1.5 USD/kg were assumed based on current policies and market conditions in the Middle East area. The results of the investment analysis are summarized in Table 5.2. The most notable difference between the two models lies in product sales. The proposed model with 50% integration yields an annual profit approximately 48 million USD higher than the base model.

Table 5.2 Key parameter summary for investment analysis comparison between base and proposed model

	BASE MODEL	PROPOSED MODEL	
Total Project Capital Cost	171,510,792	177,066,200	USD
Total Operating Cost	53,654,298	54,239,144	USD/Year
Total Raw Materials Cost	25,653,600	24,813,600	USD/Year
Total Utilities Cost	13,361,306	13,477,830	USD/Year
Total Product Sales	183,304,664	232,187,493	USD/Year
P.O. Period	4.34	3.77	Year
NPV (Net Present Value)	935,409,981.21	1,303,467,891.03	USD/Year
IRR (Internal Rate of Return)	48.9	60.33	Percent
PI (Profitability Index)	1.65	1.77	

The total capital cost for the base model is approximately 171 million USD, while for the proposed model, it is around 177 million USD. Figure 5.9 show the capital cost breakdown for both models. The proposed model incurs higher capital costs and slightly higher direct cost percentage due to additional equipment required for the MP section, with the most significant expense being the MP reactor, costing approximately 2.2 million USD.

**Figure 5.9** Total capital cost breakdown in direct and indirect cost

Direct cost such as equipment purchasing, installation, painting, insulation, dominated the percentage of capital cost with almost 60% component. The indirect cost including design, engineering, and general administrative approximately contribute 40% of total capital cost. While the capital cost of both model show slightly different value, the operating cost of both model with the breakdown component are similar as shown in Figure 5.10.

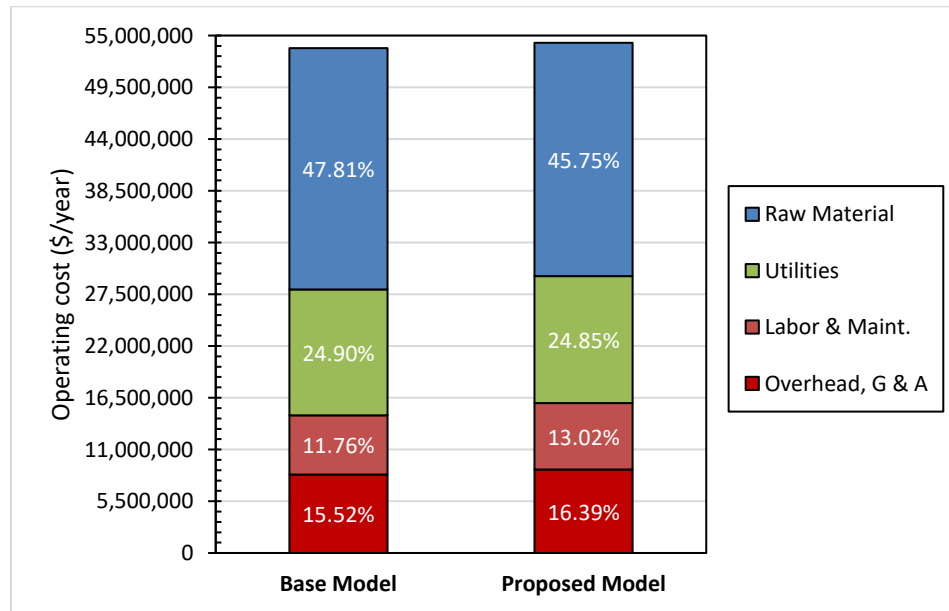


Figure 5.10 Operating cost breakdown comparison for each model

The operating costs are approximately 53.6 million USD/year and 54.2 million USD/year for the base and integrated models, respectively. As discussed in the energy analysis section, proposed model has lower total energy consumption. This will lead to a reduced NG fuel requirement. However, the additional equipment necessitates a slight increase in other operational cost components. NG constitutes the most significant cost component in the operating expenses of both models, typically ranging from 45% to 48%. This is primarily due to the assumed NG price of 2 USD/MMBTU in the Middle Eastern

context. A hypothetical scenario with a higher NG price, such as 6 USD/MMBTU, would elevate the NG cost contribution to over 70% of the operating expenses. Both models utilize NG as a feedstock and fuel source. While the feedstock NG quantity remains identical at 21,540 kg/hr for both models, the integrated model exhibits lower NG consumption for fuel purposes due to its overall improved energy efficiency.

The increase in the integrated model can be attributed to factors such as utilities cost, labor and maintenance costs, and even overhead and administrative costs. The utilities cost primarily encompasses expenses for electricity, cooling water, and boiler feed water (BFW). This aligns with the fact that both models generate steam to power their compressor turbines by leveraging waste heat from the reformer and, in the integrated model's case, the carbon cooler as well.

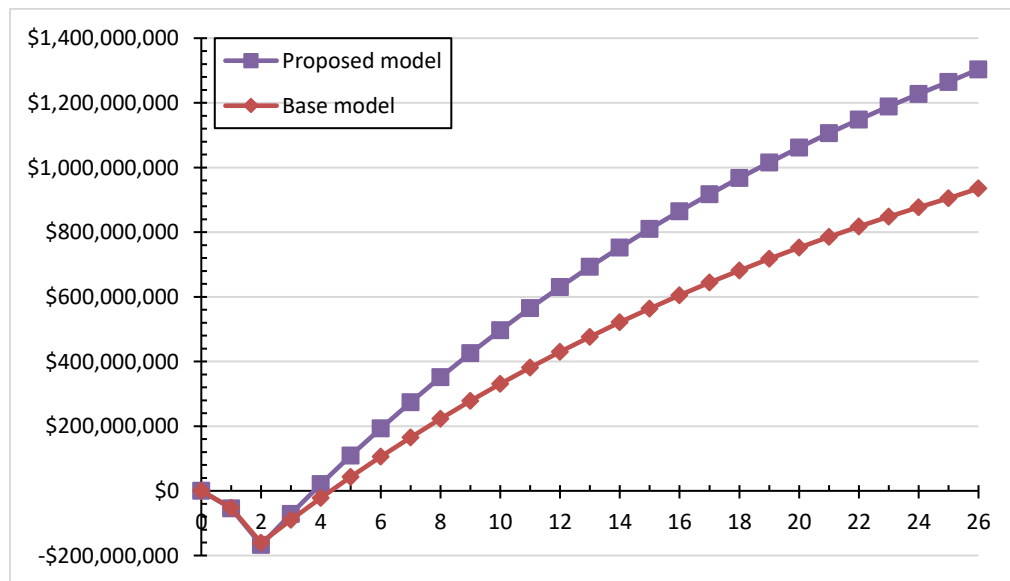


Figure 5.11 Cash flow comparison for base and proposed model when CO₂ tax USD 8/ton applied

Figure 5.11 show that both models exhibit profitability; however, the integrated model demonstrates a higher profitability index compared to the base model, along with 7

months faster payback period. This enhanced profitability is primarily driven by two key factors. Firstly, carbon black sales that proposed model generates as a co-product, contributing additional revenue. Secondly, CO₂ emission reduction from proposed model compared to the base model, potentially leading to cost savings under CO₂ tax policies.

Levelized Cost of Ammonia (LCOA)

The base model shows an annual operational cost of 60,514,730 USD/year with a production capacity of 330,000 metric tons per year (MT/yr), resulting in an LCOA of \$183.38 per metric ton (USD/MT). The proposed model, incorporating 50% integration, demonstrates a slightly higher annual operational cost of 61,321,792 USD/year and a reduced production capacity of 255,220 MT/yr. This adjustment leads to an increased LCOA of 240.27 USD/MT. However, when revenue from carbon black is considered, the LCOA is reduced to 187.42 USD/MT.

Gray ammonia, which is produced using traditional methods without carbon capture, has an LCOA ranging from 180 to 260 USD/MT. The proposed model's LCOA, considering the carbon black revenue, aligns closely with this range, making it a competitive alternative. Blue ammonia, which involves carbon capture and storage (CCS), has a higher LCOA of 320 to 330 USD/MT. The proposed model is significantly more economical than blue ammonia, even before accounting for the revenue from carbon black. Moreover, green ammonia, produced using renewable energy sources, has an LCOA between 600 and 800 USD/MT, which is considerably higher than both the base and proposed models.

Sensitivity analysis

To further assess the proposed model under different CO₂ tax and carbon black price scenarios, a sensitivity analysis was conducted. Table 5.3 illustrates the no-CO₂ tax scenario for both models at various carbon black prices. It indicates that in a no-CO₂ tax scenario, the proposed model would be more profitable than the base model if the carbon black price exceeds 0.89 USD/kg. Fortunately, current carbon black prices surpass this threshold in most areas.

Table 5.3 Annual revenue comparison of based and proposed model in no CO₂ tax scenario

CB price (\$/ton)	Based Rev. (\$/year)	Proposed Rev (\$/year)	Difference (\$/year)	B or P
893	221,370,270	221,376,322	6,052	Similar
1200 ^a	221,370,270	225,771,150	4,400,880	Proposed
1500 ^b	221,370,270	230,065,770	8,695,500	Proposed
2000 ^c	221,370,270	237,223,470	15,853,200	Proposed

*) Note: ^aPrice in NE Asia; ^bMiddle east, and ^cEurope & US based on [15]

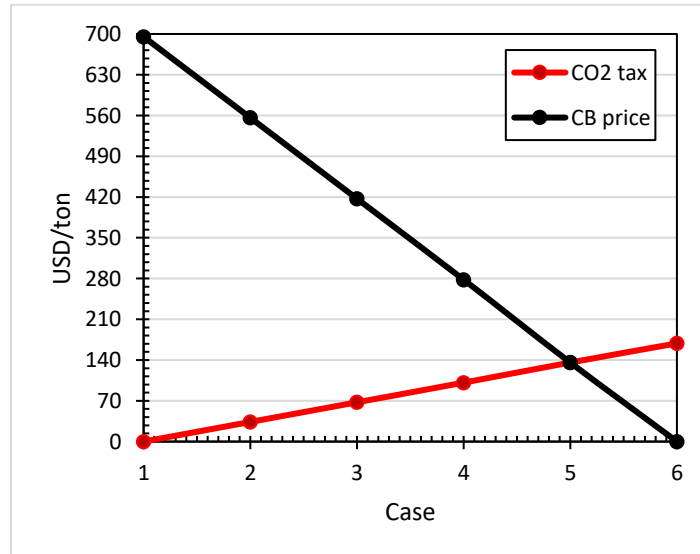


Figure 5.12 Sensitivity analysis of CO₂ tax and carbon black price for the similar profitability of proposed and based model

Figure 5.12 presents the sensitivity analysis of CO₂ tax and carbon black price for achieving similar profitability between the proposed and base models. It indicates that the proposed model would yield equal economic benefits than the base model when CO₂ tax, and carbon black coproduct prices align at each case. For instance, in case 1, with CO₂ tax at 0, carbon black should be sold at 0.695 USD/kg. As CO₂ tax increases, the minimum carbon black price required decreases. Notably, when CO₂ tax exceeds 169 USD/ton-CO₂, the proposed model becomes preferable, even if the carbon black price is zero.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The integration of methane pyrolysis (MP) into a conventional steam methane reforming (SMR)-ammonia plant has been shown to be technically feasible and economically advantageous. Operating the MP section at 33 bar and 1,400°C, with carbon black as a co-product, optimizes capital and operational costs. The MP reactor's design matches the primary reformer's tube dimensions, facilitating interchangeability and efficient operation with 80 optimized tubes and a 71.2% methane conversion rate.

Sensitivity analyses at a 50% natural gas (NG) feed split revealed a 35% reduction in CO₂ emissions and competitive energy consumption, producing 773 MTPD of ammonia. The 50% integrated model, despite higher initial capital expenditures, shows an annual profitability increase of \$48 million compared to the base model, considering Middle East prices and CO₂ tax policies. With an LCOA reduced to \$187.42 USD/MT due to carbon black revenue, this model is competitive with grey ammonia and more economical than blue and green ammonia. The proposed model remains profitable even without CO₂ tax if carbon black prices are at least \$0.695/kg, and significantly more so with a carbon black price of \$1.5/kg, underlining its economic viability.

6.2 Recommendations

The future work for developing the low carbon ammonia production include the pilot-scale experimental in methane pyrolysis reactor at medium-high pressure (30 – 45 bar). The solid carbon co-product analysis especially for the non-catalytic process at those range pressure with temperature of 1,400 °C need to be further examined and validated with current commercial carbon black standard. Material development and research for commercial use that able to handle 1,400 °C temperature in long lifetime period is also required.

REFERENCES

- [1] IRENA and AEA. Innovation Outlook: Renewable Ammonia. International Renewable Energy Agency 2022:144.
- [2] Executive Summary – Ammonia Technology Roadmap – Analysis - IEA n.d. <https://www.iea.org/reports/ammonia-technology-roadmap/executive-summary> (accessed November 25, 2023).
- [3] Ammonia’s Potential Role in a Low-Carbon Economy 2022.
- [4] International Energy Agency (IEA). Global Hydrogen Review 2023. Paris: 2023.
- [5] Katebah M, Al-Rawashdeh M, Linke P. Analysis of hydrogen production costs in Steam-Methane Reforming considering integration with electrolysis and CO2 capture. Clean Eng Technol 2022;10:100552. <https://doi.org/10.1016/J.CLET.2022.100552>.
- [6] Oni AO, Anaya K, Giwa T, Di Lullo G, Kumar A. Comparative assessment of blue hydrogen from steam methane reforming, autothermal reforming, and natural gas decomposition technologies for natural gas-producing regions. Energy Convers Manag 2022;254:115245. <https://doi.org/10.1016/J.ENCONMAN.2022.115245>.
- [7] Pruvost F, Cloete S, Arnaiz del Pozo C, Zaabout A. Blue, green, and turquoise pathways for minimizing hydrogen production costs from steam methane reforming with CO2 capture. Energy Convers Manag 2022;274:116458. <https://doi.org/10.1016/j.enconman.2022.116458>.
- [8] Chehade G, Dincer I. Progress in green ammonia production as potential carbon-free fuel. Fuel 2021;299:120845. <https://doi.org/10.1016/J.FUEL.2021.120845>.
- [9] Maxwell GR, editor. Uses of Ammonia. Synthetic Nitrogen Products: A Practical Guide to the Products and Processes, Boston, MA: Springer US; 2004, p. 199–203. https://doi.org/10.1007/0-306-48639-3_7.
- [10] Nitrogen demand by end use and scenario, 2020-2050 – Charts – Data & Statistics - IEA n.d. <https://www.iea.org/data-and-statistics/charts/nitrogen-demand-by-end-use-and-scenario-2020-2050> (accessed February 4, 2024).
- [11] Pupuk Kujang resmikan pabrik CO2 cair senilai 7,4 juta dolar - ANTARA News n.d. <https://www.antaranews.com/berita/1826888/pupuk-kujang-resmikan-pabrik-co2-cair-senilai-74-juta-dolar> (accessed November 15, 2023).
- [12] G&et C, Daroux+ M, Billaudi F. Methane pyrolysis: thermodynamics. vol. 52. 1997.

- [13] Korányi TI, Németh M, Beck A, Horváth A. Recent Advances in Methane Pyrolysis: Turquoise Hydrogen with Solid Carbon Production. *Energies* (Basel) 2022;15. <https://doi.org/10.3390/en15176342>.
- [14] Global carbon taxes by country 2023 | Statista n.d. <https://www.statista.com/statistics/483590/prices-of-implemented-carbon-pricing-instruments-worldwide-by-select-country/> (accessed March 31, 2024).
- [15] Anderson Gareth. A Low-Carbon Future for the Middle East and Central Asia : What are the Options? International Monetary Fund; 2022.
- [16] C-Zero Raises \$11.5M to Scale Up ‘Turquoise Hydrogen’ Technology | Greentech Media n.d. <https://www.greentechmedia.com/articles/read/c-zero-raises-11.5m-to-scale-up-turquoise-hydrogen-technology> (accessed October 24, 2023).
- [17] Prabowo J, Lai L, Chivers B, Burke D, Dinh AH, Ye L, et al. Solid carbon co-products from hydrogen production by methane pyrolysis: Current understandings and recent progress. *Carbon* N Y 2024;216:118507. <https://doi.org/10.1016/J.CARBON.2023.118507>.
- [18] Carbon black price index - businessanalytiq n.d. <https://businessanalytiq.com/procurementanalytics/index/carbon-black-price-index/> (accessed March 31, 2024).
- [19] Speight JG. The refinery of the future. 2nd ed. Gulf Professional Publishing; 2020.
- [20] Nikolaidis P, Poullikkas A. A comparative overview of hydrogen production processes. *Renewable and Sustainable Energy Reviews* 2017;67:597–611. <https://doi.org/10.1016/J.RSER.2016.09.044>.
- [21] 7.3. Technologies for Hydrogen Production | netl.doe.gov n.d. <https://www.netl.doe.gov/research/carbon-management/energy-systems/gasification/gasifipedia/technologies-hydrogen> (accessed August 31, 2023).
- [22] Comparison of the emissions intensity of different hydrogen production routes, 2021 – Charts – Data & Statistics - IEA n.d. <https://www.iea.org/data-and-statistics/charts/comparison-of-the-emissions-intensity-of-different-hydrogen-production-routes-2021> (accessed September 4, 2023).
- [23] Parkinson B, Tabatabaei M, Upham DC, Ballinger B, Greig C, Smart S, et al. Hydrogen production using methane: Techno-economics of decarbonizing fuels and chemicals. *Int J Hydrogen Energy* 2018;43:2540–55. <https://doi.org/10.1016/j.ijhydene.2017.12.081>.

- [24] Seyfaee A. HYDROGEN PRODUCTION VIA METHANE PYROLYSIS: MODELLING OF A SINGLE RISING AND PYROLYSING METHANE BUBBLE WITHIN A MOLTEN CATALYST BATH. 2022.
- [25] Wnukowski M. Methane Pyrolysis with the Use of Plasma: Review of Plasma Reactors and Process Products. *Energies* (Basel) 2023;16:6441. <https://doi.org/10.3390/en16186441>.
- [26] McConnachie M, Konarova M, Smart S. Literature review of the catalytic pyrolysis of methane for hydrogen and carbon production. *Int J Hydrogen Energy* 2023;48:25660–82. <https://doi.org/10.1016/j.ijhydene.2023.03.123>.
- [27] Lott P, Mokashi MB, Müller H, Heitlinger DJ, Lichtenberg S, Shirsath AB, et al. Hydrogen Production and Carbon Capture by Gas-Phase Methane Pyrolysis: A Feasibility Study. *ChemSusChem* 2023;16:e202201720. <https://doi.org/10.1002/cssc.202201720>.
- [28] Dadsetan M, Khan MF, Salakhi M, Bobicki ER, Thomson MJ. CO₂-free hydrogen production via microwave-driven methane pyrolysis. *Int J Hydrogen Energy* 2023;48:14565–76. <https://doi.org/10.1016/j.ijhydene.2022.12.353>.
- [29] Chen C-J, Back MH, Back RA. The Thermal Decomposition of Methane. I. Kinetics of the Primary Decomposition to C₂H₆ + H₂; Rate Constant for the Homogeneous Unimolecular Dissociation of Methane and its Pressure Dependence. *Can J Chem* 1975;53:3580–90. <https://doi.org/10.1139/v75-516>.
- [30] Sánchez-Bastardo N, Schlögl R, Ruland H. Methane Pyrolysis for Zero-Emission Hydrogen Production: A Potential Bridge Technology from Fossil Fuels to a Renewable and Sustainable Hydrogen Economy. *Industrial & Engineering Chemistry Research* 2021;60:11855–81. <https://doi.org/10.1021/acs.iecr.1c01679>.
- [31] Chen C-J, Back MH, Back RA. The thermal decomposition of methane. II. Secondary reactions, autocatalysis and carbon formation; non-Arrhenius behaviour in the reaction of CH₃ with ethane. *Can J Chem* 1976;54:3175–84. <https://doi.org/10.1139/v76-452>.
- [32] Peng S. Alkaline Water Electrolysis. In: Peng S, editor. *Electrochemical Hydrogen Production from Water Splitting: Basic, Materials and Progress*, Singapore: Springer Nature Singapore; 2023, p. 57–68. https://doi.org/10.1007/978-981-99-4468-2_3.
- [33] Methane n.d. <https://webbook.nist.gov/cgi/cbook.cgi?ID=C74828&Mask=1> (accessed September 25, 2023).

- [34] Fromm C. Hydrogen Production via Methane Pyrolysis: An Overview of “Turquoise” Hydrogen 2023.
- [35] Von Keitz M. Methane Pyrolysis for Hydrogen-Opportunities and Challenges Hydrogen Shot Summit Thermal Conversion with Carbon Capture & Storage. 2021.
- [36] Al-Fatesh AS, Fakeeha AH, Ibrahim AA, Khan WU, Atia H, Eckelt R, et al. Decomposition of methane over alumina supported Fe and Ni–Fe bimetallic catalyst: Effect of preparation procedure and calcination temperature. *Journal of Saudi Chemical Society* 2018;22:239–47. <https://doi.org/10.1016/J.JSCS.2016.05.001>.
- [37] Msheik M, Rodat S, Abanades S. Methane Cracking for Hydrogen Production: A Review of Catalytic and Molten Media Pyrolysis. *Energies (Basel)* 2021;14. <https://doi.org/10.3390/en14113107>.
- [38] Popov M V., Bannov AG, Brester AE, Kurmashov PB. Effect of Temperature and Pressure on Conversion of Methane and Lifetime of the Catalyst in the Catalytic Decomposition of Methane. *Russian Journal of Applied Chemistry* 2020;93:954–9. <https://doi.org/10.1134/S1070427220070022/FIGURES/6>.
- [39] Pruvost F, Cloete S, Hendrik Cloete J, Dhoke C, Zaabout A. Techno-Economic assessment of natural gas pyrolysis in molten salts. *Energy Convers Manag* 2022;253:115187. <https://doi.org/10.1016/J.ENCONMAN.2021.115187>.
- [40] Siriwardane R, Riley J, Atallah C. Production of carbon and hydrogen from natural gas via catalytic pyrolysis n.d.
- [41] Pangestu MRG, Jameel AGA. Predicting Conversion and Catalyst Performance of a De-hydrogen Catalytic Reactor in Urea Plant. *Arab J Sci Eng* 2023:1–15. <https://doi.org/10.1007/s13369-023-08288-5>.
- [42] Fan Z, Weng W, Zhou J, Gu D, Xiao W. Catalytic decomposition of methane to produce hydrogen: A review. *Journal of Energy Chemistry* 2021;58:415–30. <https://doi.org/10.1016/J.JECHEM.2020.10.049>.
- [43] Armor JN. The multiple roles for catalysis in the production of H₂. *Appl Catal A Gen* 1999;176:159–76. [https://doi.org/10.1016/S0926-860X\(98\)00244-0](https://doi.org/10.1016/S0926-860X(98)00244-0).
- [44] Ciambelli P, Palma V, Palo E, Iaquaniello G. Natural Gas Autothermal Reforming: an Effective Option for a Sustainable Distributed Production of Hydrogen. *Catalysis for Sustainable Energy Production*, 2009, p. 287–319. <https://doi.org/https://doi.org/10.1002/9783527625413.ch9>.

- [45] Huard M, Briens C, Berruti F, Gauthier TA. A Review of Rapid Gas-Solid Separation Techniques 2010;8. <https://doi.org/doi:10.2202/1542-6580.2069>.
- [46] Solid Gas separation methods overview - Industrial dust collectors - cyclone - scrubbers - filtration - PowderProcess.net n.d. https://www.powderprocess.net/Solid_gas_separation.html (accessed January 24, 2024).
- [47] Rahimi N, Kang D, Gelinas J, Menon A, Gordon MJ, Metiu H, et al. Solid carbon production and recovery from high temperature methane pyrolysis in bubble columns containing molten metals and molten salts. Carbon N Y 2019;151:181–91. <https://doi.org/10.1016/j.carbon.2019.05.041>.
- [48] Parkinson B, Tabatabaei M, Upham DC, Ballinger B, Greig C, Smart S, et al. Hydrogen production using methane: Techno-economics of decarbonizing fuels and chemicals. Int J Hydrogen Energy 2018;43:2540–55. <https://doi.org/https://doi.org/10.1016/j.ijhydene.2017.12.081>.
- [49] Muradov N. Low to near-zero CO₂ production of hydrogen from fossil fuels: Status and perspectives. Int J Hydrogen Energy 2017;42:14058–88. <https://doi.org/10.1016/j.ijhydene.2017.04.101>.
- [50] Muradov N, Smith F, Huang C, T-Raissi A. Autothermal catalytic pyrolysis of methane as a new route to hydrogen production with reduced CO₂ emissions. Catal Today 2006;116:281–8. <https://doi.org/10.1016/j.cattod.2006.05.070>.
- [51] Patlolla SR, Katsu K, Sharafian A, Wei K, Herrera OE, Mérida W. A review of methane pyrolysis technologies for hydrogen production. Renewable and Sustainable Energy Reviews 2023;181. <https://doi.org/10.1016/j.rser.2023.113323>.
- [52] Abánades A, Abánades A. Low Carbon Production of Hydrogen by Methane Decarbonization. Biofuels and Biorefineries 2015;5:149–77. https://doi.org/10.1007/978-94-017-7330-0_6.
- [53] Elnashaie SSEH, Elshishini SS. Modelling, Simulation and Optimization of Industrial Fixed Bed Catalytic Reactors. London: Routledge; 2022. <https://doi.org/10.1201/9780203746769>.
- [54] Berndt FM, Perez-Lopez OW. Catalytic decomposition of methane over Ni/SiO₂: influence of Cu addition. Reaction Kinetics, Mechanisms and Catalysis 2017;120:181–93. <https://doi.org/10.1007/S11144-016-1096-4/METRICS>.

- [55] Fan Z, Weng W, Zhou J, Gu D, Xiao W. Catalytic decomposition of methane to produce hydrogen: A review. *Journal of Energy Chemistry* 2021;58:415–30. <https://doi.org/10.1016/J.JECHM.2020.10.049>.
- [56] Sikander U, Samsudin MF, Sufian S, KuShaari KZ, Kait CF, Naqvi SR, et al. Tailored hydrotalcite-based Mg-Ni-Al catalyst for hydrogen production via methane decomposition: Effect of nickel concentration and spinel-like structures. *Int J Hydrogen Energy* 2019;44:14424–33. <https://doi.org/10.1016/J.IJHYDENE.2018.10.224>.
- [57] Tezel E, Figen HE, Baykara SZ. Hydrogen production by methane decomposition using bimetallic Ni-Fe catalysts. *Int J Hydrogen Energy* 2019;44:9930–40. <https://doi.org/10.1016/J.IJHYDENE.2018.12.151>.
- [58] Cunha AF, Órfão JJM, Figueiredo JL. Methane decomposition on Ni-Cu alloyed Raney-type catalysts. *Int J Hydrogen Energy* 2009;34:4763–72. <https://doi.org/https://doi.org/10.1016/j.ijhydene.2009.03.040>.
- [59] Matthey J. Steam reforming catalysts product brochure (c2019). 2019.
- [60] Neyestanaki AK, Klingstedt F, Salmi T, Murzin DY. Deactivation of postcombustion catalysts, a review. *Fuel* 2004;83:395–408. <https://doi.org/10.1016/j.fuel.2003.09.002>.
- [61] Avci AK, Önsan ZI. 2.16 Catalysts. *Comprehensive Energy Systems*, Elsevier; 2018, p. 475–523. <https://doi.org/10.1016/b978-0-12-809597-3.00235-2>.
- [62] Parfenov VE, Nikitchenko N V., Pimenov AA, Kuz'min AE, Kulikova M V., Chupichev OB, et al. Methane Pyrolysis for Hydrogen Production: Specific Features of Using Molten Metals. *Russian Journal of Applied Chemistry* 2020;93:625–32. <https://doi.org/10.1134/S1070427220050018>.
- [63] Wang K, Li WS, Zhou XP. Hydrogen generation by direct decomposition of hydrocarbons over molten magnesium. *J Mol Catal A Chem* 2008;283:153–7. <https://doi.org/https://doi.org/10.1016/j.molcata.2007.12.018>.
- [64] Wang G, Jin Y, Liu G, Li Y. Production of Hydrogen and Nanocarbon from Catalytic Decomposition of Methane over a Ni-Fe/Al₂O₃ Catalyst. *Energy & Fuels* 2013;27:4448–56. <https://doi.org/10.1021/ef3019707>.
- [65] Rastegarpanah A, Rezaei M, Meshkani F, Dai H, Arandiyan H. Thermocatalytic decomposition of methane over mesoporous Ni/xMgO·Al₂O₃ nanocatalysts. *Int J Hydrogen Energy* 2018;43:15112–23. <https://doi.org/10.1016/J.IJHYDENE.2018.06.057>.

- [66] Gao B, Wang I-W, Ren L, Hu J. Catalytic Methane Decomposition over Bimetallic Transition Metals Supported on Composite Aerogel. *Energy & Fuels* 2019;33:9099–106. <https://doi.org/10.1021/acs.energyfuels.9b01723>.
- [67] Zhang J, Qi M, Zhang G, Hu H, Xie L, Ma X. Co-production of hydrogen and fibrous carbons by methane decomposition using K₂CO₃/carbon hybrid as the catalyst. *Int J Hydrogen Energy* 2017;42:11047–52. <https://doi.org/10.1016/J.IJHYDENE.2017.03.113>.
- [68] Nishii H, Miyamoto D, Umeda Y, Hamaguchi H, Suzuki M, Tanimoto T, et al. Catalytic activity of several carbons with different structures for methane decomposition and by-produced carbons. *Appl Surf Sci* 2019;473:291–7. <https://doi.org/10.1016/J.APSUSC.2018.12.073>.
- [69] Upham DC, Agarwal V, Khechfe A, Snodgrass ZR, Gordon MJ, Metiu H, et al. Catalytic molten metals for the direct conversion of methane to hydrogen and separable carbon. *Science* (1979) 2017;358:917–21. <https://doi.org/10.1126/science.aao5023>.
- [70] Kang D, Rahimi N, Gordon MJ, Metiu H, McFarland EW. Catalytic methane pyrolysis in molten MnCl₂-KCl. *Appl Catal B* 2019;254:659–66. <https://doi.org/10.1016/J.APCATB.2019.05.026>.
- [71] Patzschke CF, Parkinson B, Willis JJ, Nandi P, Love AM, Raman S, et al. Co-Mn catalysts for H₂ production via methane pyrolysis in molten salts. *Chemical Engineering Journal* 2021;414:128730. <https://doi.org/10.1016/J.CEJ.2021.128730>.
- [72] Rahimi N, Kang D, Gelinas J, Menon A, Gordon MJ, Metiu H, et al. Solid carbon production and recovery from high temperature methane pyrolysis in bubble columns containing molten metals and molten salts. *Carbon N Y* 2019;151:181–91. <https://doi.org/https://doi.org/10.1016/j.carbon.2019.05.041>.
- [73] Zeng J, Tarazkar M, Pennebaker T, Gordon MJ, Metiu H, McFarland EW. Catalytic Methane Pyrolysis with Liquid and Vapor Phase Tellurium. *ACS Catal* 2020;10:8223–30. <https://doi.org/10.1021/ACSCATAL.0C00805>.
- [74] Patlolla SR, Katsu K, Sharafian A, Wei K, Herrera OE, Mérida W. A review of methane pyrolysis technologies for hydrogen production. *Renewable and Sustainable Energy Reviews* 2023;181. <https://doi.org/10.1016/j.rser.2023.113323>.
- [75] ETP Clean Energy Technology Guide – Data Tools - IEA n.d. <https://www.iea.org/data-and-statistics/data-tools/etp-clean-energy-technology-guide> (accessed September 19, 2023).

- [76] Schultz I, Agar DW. Decarbonisation of fossil energy via methane pyrolysis using two reactor concepts: Fluid wall flow reactor and molten metal capillary reactor. *Int J Hydrogen Energy*, vol. 40, Elsevier Ltd; 2015, p. 11422–7. <https://doi.org/10.1016/j.ijhydene.2015.03.126>.
- [77] Riley J, Atallah C, Siriwardane R, Stevens R. Technoeconomic analysis for hydrogen and carbon Co-Production via catalytic pyrolysis of methane. *Int J Hydrogen Energy* 2021;46:20338–58. <https://doi.org/10.1016/j.ijhydene.2021.03.151>.
- [78] Pohlenz JB, Scott NH. Method for hydrogen production by catalytic decomposition of a gaseous hydrocarbon stream 1966.
- [79] Shirzad M, Karimi M, Silva JAC, Rodrigues AE. Moving Bed Reactors: Challenges and Progress of Experimental and Theoretical Studies in a Century of Research. *Ind Eng Chem Res* 2019;58:9179–98. https://doi.org/10.1021/ACS.IECR.9B01136/ASSET/IMAGES/LARGE/IE-2019-011362_0015.JPEG.
- [80] Bode A. Methane Pyrolysis-a potential new process for hydrogen production without CO₂ emission. n.d.
- [81] Tyrer D. Production of hydrogen, 1931.
- [82] Farmer TC, McFarland EW, Doherty MF. Membrane bubble column reactor model for the production of hydrogen by methane pyrolysis. *Int J Hydrogen Energy* 2019;44:14721–31. <https://doi.org/10.1016/j.ijhydene.2019.03.023>.
- [83] Parkinson B, Patzschke CF, Nikolis D, Raman S, Hellgardt K. Molten salt bubble columns for low-carbon hydrogen from CH₄ pyrolysis: Mass transfer and carbon formation mechanisms. *Chemical Engineering Journal* 2021;417. <https://doi.org/10.1016/j.cej.2020.127407>.
- [84] NECOC-Negative Emissions Through Separation of Atmospheric CO₂ into Economically Usable Carbon Black and Oxygen 2022.
- [85] Catalan LJJ, Rezaei E. Coupled hydrodynamic and kinetic model of liquid metal bubble reactor for hydrogen production by noncatalytic thermal decomposition of methane. *Int J Hydrogen Energy* 2020;45:2486–503. <https://doi.org/10.1016/j.ijhydene.2019.11.143>.
- [86] 2020 Shell TechXplorer DIGEST | Shell Global n.d. <https://www.shell.com/energy-and-innovation/shell-techexplorer-digest/shell-techexplorer-digest-2020.html> (accessed January 30, 2024).

- [87] Lieberman MA, Lichtenberg AJ. Principles of Plasma Discharges and Materials Processing: Second Edition. Principles of Plasma Discharges and Materials Processing: Second Edition 2005:1–757. <https://doi.org/10.1002/0471724254>.
- [88] Magazova A, Bøddeker S, Bibinov N, Agar DW. Systematic Simulation Strategy of Plasma Methane Pyrolysis for CO₂-Free H₂. *Chemie Ingenieur Technik* 2022;94:690–700. <https://doi.org/10.1002/CITE.202100181>.
- [89] Fulcheri L, Rohani VJ, Wyse E, Hardman N, Dames E. An energy-efficient plasma methane pyrolysis process for high yields of carbon black and hydrogen. *Int J Hydrogen Energy* 2023;48:2920–8. <https://doi.org/10.1016/j.ijhydene.2022.10.144>.
- [90] Mesrobian C. Monolith ARPAE Methane Pyrolysis, 2021.
- [91] Jenkins S, Fromm C. Commercial Progress on Turquoise Hydrogen 2023.
- [92] Keipi T, Tolvanen KES, Tolvanen H, Kontinen J. Thermo-catalytic decomposition of methane: The effect of reaction parameters on process design and the utilization possibilities of the produced carbon. *Energy Convers Manag* 2016;126:923–34. <https://doi.org/10.1016/J.ENCONMAN.2016.08.060>.
- [93] Palmer C, Bunyan E, Gelinas J, J. Gordon M, Metiu H, W. McFarland E. CO₂-Free Hydrogen Production by Catalytic Pyrolysis of Hydrocarbon Feedstocks in Molten Ni–Bi. *Energy & Fuels* 2020;34:16073–80. <https://doi.org/10.1021/acs.energyfuels.0c03080>.
- [94] Leal Pérez BJ, Medrano Jiménez JA, Bhardwaj R, Goetheer E, van Sint Annaland M, Gallucci F. Methane pyrolysis in a molten gallium bubble column reactor for sustainable hydrogen production: Proof of concept & techno-economic assessment. *Int J Hydrogen Energy* 2021;46:4917–35. <https://doi.org/10.1016/J.IJHYDENE.2020.11.079>.
- [95] Kang D, Palmer C, Mannini D, Rahimi N, J. Gordon M, Metiu H, et al. Catalytic Methane Pyrolysis in Molten Alkali Chloride Salts Containing Iron. *ACS Catal* 2020;10:7032–42. <https://doi.org/10.1021/acscatal.0c01262>.
- [96] Dagle R, Dagle V, Bearden M, Holladay J, Krause T, Ahmed S. An Overview of Natural Gas Conversion Technologies for Co-Production of Hydrogen and Value-Added Solid Carbon Products. 2017.
- [97] Rupp B. High-Throughput Methane Pyrolysis for Low-Cost, Emissions-Free Hydrogen Project Vision. n.d.

- [98] Keipi T, Li T, Løvås T, Tolvanen H, Konttinen J. Methane thermal decomposition in regenerative heat exchanger reactor: Experimental and modeling study. *Energy* 2017;135:823–32. <https://doi.org/10.1016/j.energy.2017.06.176>.
- [99] Ghavam S, Vahdati M, Wilson IAG, Styring P. Sustainable Ammonia Production Processes. *Front Energy Res* 2021;9:580808. <https://doi.org/10.3389/FENRG.2021.580808/BIBTEX>.
- [100] Sánchez-Hervás J, Ortiz I, Martí V, Andray A. Removal of Organic Sulfur Pollutants from Gasification Gases at Intermediate Temperature by Means of a Zinc–Nickel-Oxide Sorbent for Integration in Biofuel Production. *Catalysts* 2023, Vol 13, Page 1089 2023;13:1089. <https://doi.org/10.3390/CATAL13071089>.
- [101] Qian J, An Q, Fortunelli A, J. Nielsen R, A. Goddard III W. Reaction Mechanism and Kinetics for Ammonia Synthesis on the Fe(111) Surface. *J Am Chem Soc* 2018;140:6288–97. <https://doi.org/10.1021/jacs.7b13409>.
- [102] Ojelade OA, Zaman SF, Ni BJ. Green ammonia production technologies: A review of practical progress. *J Environ Manage* 2023;342. <https://doi.org/10.1016/j.jenvman.2023.118348>.
- [103] Mašláni A, Hrabovský M, Křenek P, Hlína M, Raman S, Sikarwar VS, et al. Pyrolysis of methane via thermal steam plasma for the production of hydrogen and carbon black. *Int J Hydrogen Energy* 2021;46:1605–14. <https://doi.org/10.1016/j.ijhydene.2020.10.105>.

VITAE

Full Name : Muhamad Reda Galih Pangestu

Nationality : Indonesia

Email : redagalih@gmail.com

Address : Perumahan PT Pupuk Kujang Blok E-31, Jalan Jend. A. Yani, 37
Cikampek, Kab. Karawang, Jawa Barat, 41373.

Research Interests:

Process design and simulation, methane pyrolysis, ammonia, urea

Academic Background:

- *Master of Science in Chemical Engineering*

King Fahd University of Petroleum and Minerals, Dhahran, 31261, KSA

Year of Passing: 2024

CGPA: 3.679 (on a scale of 4)

- *Bachelor of Science in Chemical Engineering*

Institute Technology of Bandung (ITB), Bandung, 40132, Indonesia.

Year of Passing: 2014

CGPA: 3.04 (on a scale of 4)

Professional Experience:

- *Teaching Assistantship (TA)*
Term 221, 222, 231, 232
Chemical Engineering Department
King Fahd University of Petroleum and Minerals, Dhahran, 31261, KSA
- *Production Engineer of Ammonia-Urea Plant*
July 2014 to 2024
PT Pupuk Kujang Cikampek
Karawang, Jawa Barat, 41373, Indonesia

Publications:

- Pangestu, M.R.G., Jameel, A.G.A. Predicting Conversion and Catalyst Performance of a De-hydrogen Catalytic Reactor in Urea Plant. *Arab J Sci Eng* 48, 16403–16417 (2023). <https://doi.org/10.1007/s13369-023-08288-5> (**Published**)
- Pangestu, Muhamad R.G., Zahid Umer. Process Integration of Urea Production with Methane Pyrolysis for Reduced Carbon Emissions. *Computer Aided Chemical Engineering*, vol. 53, Elsevier; 2024 (**Accepted for publication**)
- Pangestu, Muhamad R.G., Malaibari Zuhair, Muhammad Ayyaz, Al-Rowaili, Fayeze Nasir, Zahid Umer. Comprehensive Review on Methane Pyrolysis for Sustainable Hydrogen Production. *Energy & Fuel*. American Chemical Society (ACS). 2024 (**Under journal review**)

- Pangestu, Muhamad R.G., Zahid Umer. Design Development of Integrated Methane Pyrolysis and Reforming Processes for Low-Carbon Urea Production. **(Ready for submission)**
- Pangestu, Muhamad R.G., Zahid Umer. Integrating Methane Pyrolysis and Reforming Processes for Sustainable Ammonia Production. **(Manuscript under preparation)**

Conferences:

- *Middle East Process Engineer Conference (MEPEC)*, 6 – 8 May 2024, Dhahran Expo, KSA. Methane Pyrolysis Integration for Low Carbon Ammonia & Urea Production. **Oral presentation.**
- *European Symposium on Computer Aided Process Engineering (ESCAPE-34)* and *International Symposium on Process Systems Engineering (PSE-24)*, 2 – 6 June 2024, Florence. **Oral presentation.**