Catalytic Dry Reforming of Methane: Paving the Road to a Carbon Neutral Industrial Scale Blue Hydrogen Production Process Technology via Monolithic Catalyst-Based Reformer Bolstered by a Techno-Economic Assessment

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Abstract

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Dry Reforming of Methane (DRM) is a relatively new process technology that provides economic and environmental incentives for several industries that rely heavily on Hydrogen (H₂) and syngas (H₂ and Carbon Monoxide (CO)) utilization. The process utilizes Carbon Dioxide (CO₂) and Natural Gas, containing mainly Methane (CH₄), as a feedstock to produce H₂ and CO. Hydrogen intensive applications and syngas processing facilities benefit mostly by generating new revenue streams as well as achieving a reduced overall carbon footprint of their operations, since CH₄ and CO₂ are both powerful greenhouse gases. This process can be considered on a reactive basis to treat flue gases and emitted streams rich in CO₂, and it also can be a proactive approach to eliminating CO₂ emissions before they occur. The focus in this work is on the latter approach, where DRM, deposited on a low-pressure monolith, is being studied as a relatively new process to produce a pure H₂ gas stream (+99.9% purity) while maintaining carbon neutrality and prove its superiority to the dominating technology today; Steam Methane Reforming (SMR) which utilizes steam (H₂O) as a reactant instead of CO₂, and reacts with Natural Gas to produce H₂ and CO, however, they are accompanied by a large generation of CO₂ emissions.

A comprehensive life cycle assessment (LCA) analysis was conducted to compare both technologies, DRM and SMR, and has demonstrated the feasibility of DRM in almost all environmental impact categories with a significant reduction in CO₂ equivalent emissions. This
study assessed the performance of SMR and DRM in various indicators, including energy consumption, air emissions, global warming potential, water consumption, wastewater production, solid catalyst utilization and solid waste production. Although DRM requires higher energy in the reformer, its overall energy consumption is lower than SMR since steam generation needed is only roughly one third that of SMR. Harmful components released by DRM in air emissions are lower in all categories which reduces global warming potential to a large extent and in particular, CO\textsubscript{2} is reduced by approximately 61% when compared with SMR. Since SMR relies heavily on steam input and cooling purposes, water consumption and wastewater generation indicators are more adverse compared to DRM. This outcome acts as a strong driver to invest more in this research field and accelerate commercialization of this process technology.

The research focus around DRM has been studied for over 20 years focusing on landfill gas (CO\textsubscript{2}:CH\textsubscript{4} with a ratio of 0.8) and only few commercial testing facilities exist as of today due to major catalyst stability drawback, due to excess CH\textsubscript{4} causing coking issues. While most of the research body is considering DRM to process landfill gas, this research work has found out that by moving to a coke-free regime, the catalyst retains excellent initial stability properties. Thermodynamic analysis demonstrated that ratios of CO\textsubscript{2}:CH\textsubscript{4} equal to and greater than 1.5, solid carbon no longer thermodynamically forms, and indeed, the experimental studies have confirmed the same conclusion evident by stable catalyst performance. Both Nickle (Ni) and Rhodium (Rh) in powder forms exhibited excellent activity and stability levels under a CO\textsubscript{2}:CH\textsubscript{4} ratio of 1.5. This was the first and most important stepping stone in constructing a solid argument supporting DRM as a stable process with great potential for commercialization. This ratio is possible when separate sources of CO\textsubscript{2} and CH\textsubscript{4} are available and thus ratios can be adjusted unlike in landfills where CH\textsubscript{4} is always in excess. The work continued in performing several parametric experiments and
screening multiple catalysts with different metal loadings. Three active metals were tested, Ni, Rh, and Ruthenium (Ru), and the results concluded that the most promising formulations are 10% Ni on Alumina (Al₂O₃) and 1% Rh on Al₂O₃. Those were further investigated in details for artificially aging by intentionally forming coke and successfully regenerated by steam gasification. The catalysts were coked and regenerated to essentially fresh activity.

Commercial SMR is operated with a packed-bed reactor design and utilizing catalysts (most commonly Ni on alpha Al₂O₃) in the form of pellets and rings, which lead to large pressure drops and ultimately large reactor design and increased energy requirements. To help overcome the design challenges, this research work has considered monolithic catalysts for testing and scale-up purposes. Monoliths, with their high open frontal areas and large geometric surface areas, overcome the challenges of high pressure drop, experienced in pellets, exhibit solid mechanical strength and provide large geometric surface areas of catalysts (washcoat) contact for reactions to take place, and hence, significantly reduce reactor sizes and eventually, overall capital and operating costs. The monolithic catalysts were prepared by washcoating 10% Ni and separately 1% Rh, both on gamma Al₂O₃ on their walls. The same parametric studies conducted for powders were tested for monolithic catalysts, and the results were positively surprising. Monolithic catalysts possessed extremely high activities, far better than all powders tested even at higher loadings. Moreover, their excellent stability results provide a possible road to a more compact reactor design. One conclusion; monolithic catalysts, or washcoated structured reactors as known in industry, are strong competitors that have the potential to deliver superior results when compared to packed-bed reactors. Therefore, this research is proposing the use of monolithic catalysts working under the favorable thermodynamic environment, as a potential solution to accelerate DRM advanced testing for H₂ production.
To further support the thesis argument, a basic process design of the DRM was carried out to understand the various compositions of streams and the material and energy requirements for a feasible commercial plant. The design resembled very closely that of an SMR plant with the major difference in the main reactor, known as the “Reformer”. With this data on hand, a financial modelling was constructed to preliminarily prove the feasibility of this technology when compared to competitors in the market. Consequently, when compared to SMR with and without carbon capture (CC), DRM achieved relatively low H₂ prices in the range of 1.07-1.32 $/kg in the case of a Methanator design case and up to 1.91 $/kg for the CC design case, while SMR exceeded 2.1 $/kg for sustainable H₂ production; indicating that DRM, on preliminary basis, is a very profitable process technology. In conclusion, the laboratory research work combined with process design and financial feasibility, strongly supports the grounds of recommending DRM as a viable H₂ production technology for a future pilot plant testing and advancement for commercialization. A more detailed engineering design and financial assessment would provide more accurate results after the successful pilot plant testing.
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To my Father, my number one fan, my caring Mother and my loving family members
Chapter 1: Introduction

1.1 Motivation

The first and foremost important motivating factor to conduct research in the field of catalytically upgrading CO$_2$ to a useful product is the noble desire to positively contribute to the solution in the face of the ever-growing climate change challenge; the toughest risk threatening the existence of human beings. Because the solution requires the collective efforts of every person, entity, institution, and nation on the planet, it is quite crucial to understand what can be done and how it is done. Hence, capitalizing on this platform, this research work aims at pointing the attention towards one step that helps in formulating a workable global solution.

As a professional experienced in crude oil refining, the horizon of knowledge and thinking was vastly expanded after the in-depth knowledge in this research project and the courses attended at the Earth and Environmental Engineering department. Understanding how different ecological systems work has opened up an angle of thinking pointing towards a practical interpretation of “sustainability”. Unlike common understanding, sustainability does not mean shutting down all fossil fuels operations and replacing them with green technologies. Several green technologies do not have the capability of industrial scale production, and hence, are somewhat limited. Therefore, sustainability points towards converting today’s operations to more environmentally friendly ones, while in parallel developing new technologies. Producing H$_2$ and CO, referred to as synthesis gas, from CO$_2$ and CH$_4$ via DRM, is such a sustainable technology for ultimately producing useful chemicals from greenhouse gas contributors.

From the above context, a focus on transforming current fossil fuels operations to become environmentally sustainable has emerged as a driver in the pursuit of prolonging the beneficial
utilization of crude oil and natural gas, considering the vast range of useful products that can be derived. Therefore, the mindset has shifted into how Refining, Petrochemical and Chemical process plants can be revamped to close the gap between an unsustainable present, and an evergreen future. Moreover, since Hydrogen is an essential intermediate stream vital in the conversion of black oil to white products, this research focus is on blue H₂ production which is of essential importance to the crude oil industry and its derivatives, in the sense that H₂ can be produced sustainably at a mass rate while potentially replacing SMR and gray H₂. As of today, over 90% of the world’s H₂ is being produced from fossil fuels via technologies without carbon capture [1, 2, 3], and the most dominating is SMR, while emitting harmful emissions in the process. Therefore, the driver to find an alternative solution is stronger than ever.

This may be the first step in the direction of sustainable operations, but the journey will encompass exciting areas to be considered, as the world transitions into a new form that serves humanity in a much better format. The ultimate goal is to live and prosper in a responsible manner, while preserving the right of future generations to continue building responsibly.

From a personal perspective, the goal is to grow in the Research and Development leadership track at Saudi Aramco, PhD program sponsor, to positively change and create new horizons for value creation that would enable the company and the country of Saudi Arabia to continuously advance its economic infrastructure and sustain its contribution to the world energy markets. Furthermore, this research work, once materialized, would support the kingdom’s strategic plans to reach carbon neutral levels by 2060 [4, 5]. The circular carbon economy framework is now a main focus of the kingdom and Saudi Aramco, in order to manage and reduce carbon related emissions. This approach is relying on the 4Rs: Reduce, Reuse, Recycle, and Remove. [6]
In view of the advantageous position of working in an industrial R&D center for an energy and chemical corporation, this technology has the potential to be considered for future commercial applications. Upon graduation from the PhD program, the work in this thesis can be further evaluated to be tested at pilot plant scale at Aramco’s facilities, after passing the project funding and approval requirements. Due to the large demand for pure Hydrogen gas in several operating facilities, there is a clear motivation to pursue such emerging technology for deployment in the company’s Refineries, petrochemical and chemical complexes, Natural Gas Liquids Fractionation plants, and more. Furthermore, upon successful testing, DRM can be considered for patents and licensing and eventually turn into a trademark for sustainable Hydrogen production technology.

1.2 Thesis Structure

The overall goal of this thesis is to present a laboratory feasibility research and economic study that supports the utilization of DRM as a sustainable and viable process technology for blue hydrogen production, and recommend it for pilot plant testing to accelerate its commercialization aspects. The thesis begins with the literature review and background information that summarizes prior art work conducted by the research community, and what aspects are being proposed that differentiates the body of this research from literature. In order to support the initial proposal, a life cycle assessment was conducted to compare DRM and SMR, and the main results were emphasized to act as a motivation to support this process technology.

The detailed laboratory work is then laid down in chapter 4 in the order it was performed, which was built on stepwise basis to derive new experiments. The work started with powdered catalyst testing to gauge the activity and aging performance of several catalysts with different metal types and loadings. From there, 10% Ni and 1% Rh catalysts were selected as the optimal
choices for this application and further testing was carried out. Impact of space velocity on activity level, catalyst characterization as well as a kinetic study were conducted to strengthen the understanding of initial catalyst performance. The work continued to test the operating envelopes to perform artificial aging followed by regeneration of coke (known deactivating species) via steam gasification. Once powder parametric experiments were shown to be satisfactory, monolithic catalyst testing was performed as a new structure for an advanced design with an improved carbon footprint.

Chapter 5 introduced an aspect of scale-up that addresses the pressure drop experienced in packed-bed reactors, utilizing monolithic substrates and coating them with catalytic material. First, the coating procedure is described in detail and the results were presented. The catalytic activities of 1% Rh and 10% Ni were plotted along with product yields and distributions. The stability of those catalysts were examined and demonstrated to possess very stable levels of performance compared to environments mimicking landfill gas compositions. Finally, the catalysts were artificially aged, for coking, and regenerated, and the promising results added another layer of feasibility to the proposed concept.

The thesis continues supporting the use of monolithic supported catalysts under the favorable thermodynamic environment by proposing a process design configuration in chapter 6, while chapter 7 includes a comprehensive financial model suggested to finance this process technology. The results concluded that DRM is a viable technology with excellent financial metrics, ready to be tested in pilot plant scale to accelerate its commercialization.
Chapter 2: Literature Review

2.1 Global Energy Market

The world is transitioning into a greener and more sustainable mix of energy supply to combat the adverse consequences of climate change. Governments have come to a wide spread common conclusion: a sustainable energy mix that serves its nation and the world, is the only way moving forward. The misconceptions of having only selected sources of energy to fuel the future are no longer viable and a quick transition to green technologies will disrupt the ecological system of the world’s energy infrastructure. Rather, the world will continue relying on the most available sources of energy including fossil fuels, renewable sources, and nuclear energy however, the ultimate resulting mix is of a sustainable nature. Non-renewable energy source will comprise around 35% of the energy mix by 2050 in the ambitious transformation sustainable scenario [7, 8]. According to the 2050 Net Zero Emissions (NZE) report by IEA (2021) [9], 20% of the direct total energy consumption will be comprised of fossil fuels, while H₂ will have a significant increase in contribution to the energy mix.

The above fact solidifies the notion that the world needs a sustainable mix of all energy sources, even at the extreme case of achieving zero emissions by 2050. Therefore, nations worldwide are announcing strategic plans to reach carbon neutrality within the period 2030 to 2060 under the Paris agreement, including countries that depend heavily on fossil fuels and major exporters of this abundant commodity [9, 10]. This is being done by deploying green technologies derived from renewable energies, converting fossil fuel operations to a more sustainable form by investing in new process technologies and carbon capture techniques, as well as investing in upgrading current systems to more efficient levels. One commodity that is gaining great deal of
focus is Hydrogen. Hydrogen is being regarded as the fuel of the future, simply because the combustion of H\textsubscript{2} yields energy and steam (H\textsubscript{2}O) as a by-product \cite{11, 12}. Hence, if this commodity can be produced in an environmentally and economically viable form, then it may be a key player in transitioning into a clean fuel for the future \cite{13}.

In both cases, announced pledges scenario and net zero emissions by 2050 by IEA, the Hydrogen production is dramatically increased \cite{1}. In the former case, H\textsubscript{2} production will grow from around 90 Million Tons in 2020 up to around 250 Million Tons by 2050. Moreover, since H\textsubscript{2} will play a major role in combatting climate change, the net zero emissions by 2050 case requires H\textsubscript{2} production levels to exceed 500 Million Tons by 2050 \cite{1}. This can only emphasize the importance of H\textsubscript{2} in the future and the associated sustainable production technologies.

### 2.2 Hydrogen Production Technologies

Hydrogen gas is an essential component in many industries including Oil refining (Hydrotreating and Hydrocracking), Petrochemicals and Chemicals, such as CH\textsubscript{3}OH, NH\textsubscript{3}…etc, while syngas (combinations of H\textsubscript{2} and CO) is the main feedstock for the Fischer-Tropsch processes where valuable products such as diesel, olefins, gasoline, and other hydrocarbons are produced. The process technologies commercially available today for H\textsubscript{2} production include SMR and Partial Oxidation of Natural gas. While both processes are mature, a new environmentally friendly process, DRM, is evolving. Unlike SMR and Partial Oxidation, DRM process consumes CO\textsubscript{2} in the process while the former processes generate it. This relatively new process reacts CH\textsubscript{4} with CO\textsubscript{2} catalytically to produce H\textsubscript{2} and CO at favored ratios.

SMR is the dominating process technology used worldwide due to its maturity, catalyst availability, favored H\textsubscript{2}/CO ratios and lower capital cost compared to partial oxidation and Auto-
Thermal Reforming (ATR). However, SMR requires a large energy input and incurs high CO₂ emissions [22]. It has the following main chemical reaction:

\[ CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_{rx} = +206 \text{ (kJ/mol)} \]

Partial oxidation, and ATR, utilize partial amount of O₂ in the feedstock composition to overcome the external energy requirements. While commercially available, both technologies face the challenges of having large capital costs associated with O₂ generation, as well as lower H₂/CO ratios; making them less favorable [22]. The reactions proceed as follows:

\[ CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \quad \Delta H_{rx} = -36 \text{ (kJ/mol)} \]

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H_{rx} = -803 \text{ (kJ/mol)} \]

DRM, on the other hand, is growing as an appealing technology for sustainable H₂ production. It has the main advantage of consuming CO₂ in the process, nevertheless, catalyst deactivation, especially Ni based, and high energy requirements are still major obstacles in the road to commercialization [22]. Similar to SMR, it is a highly endothermic reaction and proceeds as follows:

\[ CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H_{rx} = +247 \text{ (kJ/mol)} \]

Another emerging technology for hydrogen production is Chemical Looping Reforming (CLR). This technology utilizes the new concept of chemical looping to generate O₂ and which is incorporated into the fuel to be combusted without the negative impact of N₂ dilution and NOx emissions. This is done via two reactors, Air reactor and Fuel reactor, as well as a solid oxygen carrier that continuously generates O₂ for combustion via an oxidation/reduction reaction. The controlled combustion in the fuel reaction yields syngas product, i.e. H₂ and CO, with CO₂ and H₂O as byproducts. This process acts as a more efficient system for partial oxidation without the negative impact of N₂ dilution [14]. The challenges of this technology lie in the fact that it is
relatively new and requires research and development [15] as well as the fact that the chemical 
looping system adds a significant amount to the capital cost; reducing its competitiveness with 
other technologies [16].

Electrolysis for H\2 production is a technology that attracts significant attention. It has the 
potential to produce green hydrogen, which is produced by means of renewables, and it builds on 
the mature technology of splitting water molecules into H\2 and O\2 via applied electric current. The 
reaction proceeds in the following set of reactions [17, 18]:

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad \text{Anode}
\]

\[
4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2 \quad \text{Cathode}
\]

Although the technology is available, it faces several challenges; source of clean constant 
and cheap supply of electricity is not yet available and the scalability is another concern. 
Electrolysis requires constant supply of electricity, which means that it has to rely on the grid. And 
since a majority of electricity production in the world is carried out from fossil fuels sources, the 
carbon footprint is large and the levelized cost is high. Electricity from renewables is potentially a 
good option, however, it is intermittent and requires power storage systems to be supplied on 
constant basis; this dramatically increases the cost of supply. In fact, according to the IEA [1], 
electrolysis from renewables will only start becoming a competitor to natural gas reforming with 
carbon capture and utilization/storage (CCUS) by 2030 in some regions of the world.

2.3 DRM for H\2 Production

The research focus around DRM has been in place for over 20 years and only few 
commercial testing facilities exist as of today. Most of the research body is considering DRM to 
process landfill gas (LFG), which is composed primarily of 55% CH\4 (favors coking and catalyst
deactivation) and 45% CO₂, according to US EPA. In 2019, around 15% of the US methane emissions were generated from Municipal Solid Waste in the form of landfill gas, and since methane is roughly 30 times more powerful than CO₂ in terms of greenhouse gas effect, efforts are being deployed to tackle its adverse effects. Because it is rich in CH₄, landfill gas can replace some of the feedstock and fuel streams after it is treated, however, CO₂ is still separated and emitted as a harmful emission. Hence, DRM seems as a potential solution since it converts both components, CH₄ and CO₂, into a valuable product [19]. Despite its advantages, high energy demand and catalyst stability issues, Nickel (Ni) based in particular, are still major obstacles to be overcome for commercial applications. Although Ni exhibits low cost compared to noble metals and has been demonstrated with good activity in the form of powders and pellets under DRM conditions, it deactivates rapidly due to carbon formation [20, 21] especially in CO₂:CH₄ ratios less than 1:1, which is most common for landfill gas.

Several noble metals (Rh, Ru, Ir, Pd, Pt) and transition metals (Ni, Co) were found to provide adequate levels of activity under the DRM reaction with landfill composition. However, the stability of transition metals-based catalysts turned out to be a concern; mainly due to excessive coke formation. Since the reaction proceeds with CH₄ dissociation on the active metal site and CO₂ decomposition on the carrier, the emphasis has been on the role of the support. The most common choices for a carrier material are Alumina (Al₂O₃) and Silica (SiO₂) in view of their high internal surface area and basicity. The effort to drive catalyst development forward relied on improving the basicity of the support in order to enhance the adsorption of CO₂ on the surface of the carrier and subsequent decomposition to provide oxygen atoms for gasification of carbon atoms. Moreover, the support material is further enhanced with promoters such as TiO₂, CeO₂, and ZrO₂. Those promoters provide the capability of oxygen storage via their redox properties, which
increases the rate of carbon gasification. The below table 2.1 [15] includes some of the recent catalysts developed for the DRM process that demonstrated improved performance:

**Table 2.1**: Recent advancements in catalyst development for DRM in continuous flow reactors.

Data Source: Abdulrasheed et al. [15]

<table>
<thead>
<tr>
<th>Recent DRM Catalysts</th>
<th>Ni(Ru)/La₂O₃</th>
<th>La₂Zr₁.₈₈₈Rh₀.₁₁₂O₇</th>
<th>Fibrous Ni/Al₂O₃</th>
<th>Ni/porous γ-Al₂O₃ via ALD</th>
<th>Ni/ALSBA-15</th>
<th>Ni-Sn/CeO₂-Al₂O₃</th>
</tr>
</thead>
</table>

Hyun Seo [55] summarized recent progress on Ni catalyst development for DRM. The review showed that increasing the basicity of the catalyst surface improves the stability by promoting the CO₂ dissociation reaction to avail more Oxygen (O₂) atoms. In this context, an alkali support such as Magnesium Oxide (MgO) and Lanthanum Oxide (La₂O₃) are good examples of such materials. Additionally, better dispersion of Ni atoms and achieving particle sizes smaller than 8 nm demonstrated stronger tolerance towards solid carbon formation. This was accomplished by proposing alternative catalyst preparation methods, including a modified impregnation technique utilizing ligands and Atomic Layer Deposition (ALD) technique for enhanced Ni atoms dispersion inside the pores of the support. The results illustrated improvements of catalyst activity and stability under DRM conditions.

While some of the above catalysts had enhanced stability levels for feedstock compositions of CO₂:CH₄ ratios closer to 1:1 and lower, this research work has explored another angle of thermodynamic operating conditions that had little attention by the research community. It was found out that by moving to a no-carbon formation regime, the catalyst retains initially excellent stability properties. Thermodynamic analysis demonstrated that ratios above CO₂:CH₄ of 1.4, solid
carbon is no longer formed, and indeed, the experimental studies in this thesis have reached the same conclusion. Both Ni and Rhodium (Rh) delivered excellent activity and stability levels under a \( \text{CO}_2:\text{CH}_4 \) ratio of 1.5. The ratio of \( \text{CO}_2 \) to \( \text{CH}_4 \) has a strong impact on thermodynamic coke formation and deactivation since excess \( \text{CO}_2 \) produces more oxygen atoms that react with carbon atoms and significantly reduces the deactivation rate of the catalyst. For petroleum refineries and petrochemical applications, sources of \( \text{CH}_4 \) and \( \text{CO}_2 \) are independent and therefore, can be varied to desired ratios that overcome the disadvantages of landfill gases. The scientific publications in “ScienceDirect” and “Scopus” revolving around DRM only started early 2000’s, indicating the recent interest in this process technology [22].

The main focus of the research community remains to be catalytic materials that will overcome the challenges mentioned earlier. However, the target of this thesis work is to address the stability issues of the catalyst, propose a more compact Reformer design using monolithic catalysts, and prove the environmental and financial viability of the DRM process technology.

### 2.4 Monolithic Catalysts

Monoliths, Ceramic or Metal, are structures made with a large number of parallel channels and equally sized; similar to a honeycomb shape. The channels, being square, triangular, hexagonal…etc, provide large open frontal areas (80-90%) for high flow rates and with low pressure drops. They are common in environmental applications, especially for the catalytic converter installed in vehicles to control toxic emissions. Additionally, bulk mass transfer limitations are overcome by the high cell densities and high linear velocities (\( u \)). This is in view of the increased Reynolds number (\( \text{Re} \)) and ultimately turbulent flow:
Where $\rho$ is the density of the fluid, $u$ is the linear velocity, $L$ is the distance travelled, $\mu$ is the viscosity and $\nu$ is the kinematic viscosity. Although the structures themselves have low internal surface area (around 0.3 m$^2$/g), they have large geometrical surface areas (GSA) (3-3.5 m$^2$/L) suitable for coating with a high surface area catalyzed washcoat. Structures with 400-600 cells per square inch (cpsi), enhance gas/surface contact and are readily available commercially. The walls are washcoated with a high internal surface area support material, such as $\gamma$-Alumina (150-200 m$^2$/g), containing the active catalytic material impregnated from solution and fixed onto the walls [23]. The monolith is immersed for some time in a washcoating slurry and then dried [24].

The most widely used ceramic monolith is synthetic cordierite consisting mainly of the following chemical formula: 2MgO.2Al$_2$O$_3$.5SiO$_2$. Compact reactors and flexibility in orientation, solid thermal and mechanical shock abilities as well as attrition resistance are significant advantages monolithic structures offer compared to particulate materials [23]. Despite the fact that metal monoliths have better heat transfer rates, less expensive ceramic monoliths were utilized in this research since they provide ease of noble metals recovery; which is crucial in the economic viability in industrial applications.

This research work builds on the premise of having a sustainable process technology as a proactive approach to reducing harmful emissions with the main focus of achieving ultra-low levels of CO$_2$ generation. Moreover, the economic assessment is essential in laying the foundation for this technology to find pathways to commercialization when compared to carbon capture technologies (CC). This is in view of the fact that coupling CC technologies with today’s mature technologies, result in substantial swell of the capital investment, which in turn impacts the
project’s financial indicators. Therefore, the anticipated outcome has to combine a strong basis of scientific reasoning proven by experimental work with the financial modeling results targeting nominal and worst-case scenarios.

2.5 U.S. Patent Review

In order to shed light on the patentability aspect of technologies in the field of DRM, a brief patent review was conducted in the US patent office database. The search for “dry reforming” resulted in 537 patents, while a search for “steam reforming” yielded 8,648 patents; indicating a clear gap in the advancement of both technologies. Narrowing the search further, adding the “monolith” term alongside “dry reforming” reduced the number of granted patents down to 119. However, by replacing the “monolith” term with “structured reactor”, the results revealed 2 patents with generic referencing to dry reforming and structured catalysts and reactors, despite the fact that the terms “structured reactors” and “monolith reactor” resulted in 51 and 122 patents, respectively. This could point towards the fact that scaling up dry reforming utilizing structured reactors with specific operating conditions and catalytic formulations could potentially be a patentable focus area.

A random selection of relevant patents under the above search terms has shown that the focus is mainly developing new catalytic materials for DRM process covering a wide range of noble and transition metals, with special attention given to Ni as the active metal. Feed compositions and operating conditions were generally stated in patents and the ratio of CO\textsubscript{2} and CH\textsubscript{4} in the feedstock was expanded to cover wide ranges. Furthermore, the use of “monolith” has also been stated as an option for the support material in some patents. The very early patents introduced the process of DRM with very basic catalytic compositions and operating conditions.
An example is the earliest US patent **5,431,855**, found under “dry reforming” search, produced in 1995 by Green et al. [68] from the British Gas plc introduced DRM along with partial oxidation processes and covered a wide range of active metals as well as a generic reference to metal oxides as a suitable support material. With time, the knowledge in this field expanded and more specific catalytic formulations, support material, promoters, doping elements and so on, were further proposed. For instance, Ide et al. from Exxon Mobil Research and Engineering Company proposed catalytic formulations for steam and dry reforming reactions under US patent **10,577,243** [69] utilizing transition and noble metals on a lanthanum-stabilized alumina support which possessed higher surface area, even at higher temperatures, than conventional supports, as well as proposing a monolith as a support material. Additionally, Fadhel et al. from Saudi Arabian Oil Company (Aramco) demonstrated the use of red mud, material containing metal oxides at different ratios such as aluminum oxide, titanium oxide, calcium oxide, iron oxide…etc., catalyst formulations supported with group 3-12 active metals for the dry reforming process under US patent **11,059,720** [70]. The evolution of the scientific knowledge in this field reflects the growing importance of DRM in playing a major role in future sustainable production of clean Hydrogen and syngas.
Chapter 3: LCA Analysis

3.1 Material and Energy Flow Analysis

A life cycle assessment was conducted to compare DRM vs a conventional SMR process configuration while targeting various indicators. The study showed that the results favored DRM in almost all categories including: CO₂ emissions, global warming potential (GWP), clean water consumption, waste water generation, and solid waste generation [38].

In order to estimate the environmental sustainability indices for both processes, it is first essential to perform a basic material and energy balance within the established LCA boundary. In both, SMR and DRM, the main reactions taking place are the reforming reactions along with the water gas shift (WGS) reaction which transform the reactants, followed by the downstream physical separation unit; the pressure swing adsorber (PSA) to pure H₂. The basic process flow diagrams with material and flow analysis for both processes are illustrated below [25-28]:

Figure 3.1: Material and Energy balances for SMR and DRM as well as the LCA boundaries
The main parameters that affect energy consumption in both processes are heats of reactions as well as steam consumption. The former is represented as heat input required in the furnaces and the latter as fuel required to produce the steam consumed in the reforming and water gas shift (WGS) reactions. Figure 3.2 illustrates the overall fuel consumption along with the breakdown between furnace, steam contributions and energy required to recycle CO\textsubscript{2} to the reformer inlet stream:

![Diagram](image)

**Figure 3.2:** Fuel consumptions of SMR and DRM processes

At initial comparison, DRM is assumed to consume more energy since the endothermic heat of reaction (247 kJ/mol) is higher than that of SMR (206 kJ/mol). However, due to the necessary requirements of maintaining a steam ratio of 3:1, the overall energy consumption in SMR is in fact larger than DRM. Despite the fact that the DRM process requires additional energy to recycle the CO\textsubscript{2} stream to the inlet of the reformer, the above chart shows that on an overall basis, SMR process consumes 2200 m\textsuperscript{3} of fuel versus 2130 m\textsuperscript{3} in DRM for every MMSCF H\textsubscript{2} produced. Hence, DRM is a less energy intensive process than SMR.
3.2 Global Warming Potential

The global warming potential estimation requires a series of material and energy calculations coupled with reference emissions data and fuel composition from literature. Hence, the methodology adopted to estimate CO₂ and air emissions from both processes is demonstrated below:

By examining the process configurations of SMR and DRM, it can be observed that the main sources of air emissions result from the reformer stack flue gas as well as pressure swing adsorption (PSA) tail gas stream. While the tail gas is mainly comprised of CO₂, the fuel combustion in the furnace results in CO₂ as well as other pollutant emissions including NOₓ, SOₓ, and CO. According to EIA of the US Department of Energy [29], Typical emission levels of combusting Natural Gas in the US generate 117,000 lb/BBTU of CO₂, 40 lb/BBTU of CO, 92
lb/BBTU of NOx and 1 lb/BBTU of SO2. Utilizing this data combined with the material and energy flow analysis conducted earlier, the following CO2 and other air emissions [30-36] were estimated for both processes on the basis of combusting Natural Gas as a fuel source:

**Figure 3.4:** Estimated CO2 emissions of SMR and DRM processes

**Figure 3.5:** Air emissions of SMR and DRM processes
It can be clearly observed that the DRM process emits less harmful emissions than SMR. CO$_2$ emissions from DRM are 10,968 kg/MMSCF H$_2$ compared to 17,491 kg/MMSCF H$_2$ from SMR. NOx emissions, producing acid rains, are 3.29 compared to 3.04 kg/MMSCF H$_2$ from SMR and DRM, respectively. SO$_x$ emissions are both low due to stringent sulfur regulations in the US; yet slightly higher in SMR as well. Moreover, the emissions of poisonous CO are 1.43 kg in SMR and 1.32 kg in DRM, respectively. Although those levels per MMSCF H$_2$ may not seem so significant, extrapolating this data to the annual US production of hydrogen will have dramatic impact. Hydrogen production in the US amounts to 10 Million MTons per year [37]; which is almost 4 trillion SCF of H$_2$ gas. Consequently, CO$_2$ emissions from DRM are almost 26.3 megatons less than SMR process on an annual basis. Moreover, almost one kiloton of NO$_x$ and 0.5 kiloton of CO are estimated as differential between SMR and DRM.

3.3 Overall Environmental Indices

Looking at all indices considered, the study resulted in significant reductions from DRM as can be observed in the following chart [38-49]:

19
It can be clearly observed that DRM has outperformed SMR in all environmental impacts by producing less harmful emissions and waste streams. In the case of Global Warming Potential, DRM resulted in nearly 60% reduction in harmful emission levels. Similarly, water consumption is significantly lower in DRM by almost 40% overall reduction. Those results are solid indicators that DRM is a far better technology from a sustainability standpoint. Therefore, the driver to pursue this technology is very clear, and this outcome has played a significant role in motivating the work performed in this thesis.

Figure 3.6: Overall LCA comparison between DRM and SMR. Source: Alkhani et al. [38], shared with permission from co-authors.
Chapter 4: Powder Parametric Testing

4.1 Thermodynamic Analysis

A deep dive into the Gibbs Free Energy of reactions illustrates the development of the equilibrium constant (K) at different temperatures, which directly provides insight of the preferred operating conditions. The equilibrium constants (K) of DRM and SMR reactions exhibit similar behavior thermodynamically, where products are exponentially maximized above temperatures around 720-730°C [22].

Since equilibrium conditions govern the extent of reactions, thermodynamic analysis was carried out to determine the operating regions that favor DRM products; Hydrogen and Carbon Monoxide. Figure 4.1, produced by HSC Chemistry 5.1 Thermodynamic Software [50], highlights the regions where reactants, products and by-products occur. It can be clearly observed that temperatures closer to 700°C (green brackets) and above, favor the existence of DRM products (H₂ in the turquoise and CO in the black color) as well as low formation of solid carbon (light green).

![Equilibrium Amounts](image)

**Figure 4.1:** Thermodynamic equilibrium amounts produced by HSC Chemistry 5.1 Software
Coke, being solid carbon deposited on the catalyst surface, can significantly decrease the stability and activity of the catalytic reaction while increasing pressure drop. Hence, in order to adequately evaluate different catalytic metals for their performance with respect to activity and selectivity, it is essential to operate away from a solid carbon-formation condition. Therefore, by utilizing HSC 5.1 Chemistry software [50], the following chart, figure 4.2, demonstrates the effect of varying CO$_2$:CH$_4$ ratios on the formation of coke at various temperatures:

![Coke Formation Regions](image)

**Figure 4.2:** Impact of varying CO$_2$:CH$_4$ ratio on solid carbon formation at equilibrium

The first intuition of 1:1 CO$_2$:CH$_4$ ratio is inappropriate, since coke formation continues to occur at temperatures at 800°C. However, a ratio of 1.4 (shown in yellow) and above, provides a working condition for carrying out activity screening of different catalysts as coke formation is thermodynamically unfavorable at temperatures over 700°C. Those results are inline with thermodynamic analysis obtained from literature and produced by Aspen Plus [51].

It is imperative to identify the levels of equilibrium conversions of reactants in order to determine optimal parametrics for the experimental runs. Additionally, kinetic controlled regimes
require operating at conversions far removed from equilibrium which distinguishes the respective inherent activities for different catalysts. Hence, ChemReax software [52] was utilized to simulate the conditions of the experimental runs with the objective of determining equilibrium reaction constants from Gibbs energy of reaction. Consequently, the extent of reactions containing all components involved in this process, DRM and reverse water gas shift (RWGS), were estimated and thus, equilibrium conversions of CH$_4$ and CO$_2$, in a feed containing CO$_2$:CH$_4$ ratio of 1.5, were plotted versus temperature as seen in figure 4.3 below:

![Equilibrium Conversions of Methane & CO2](image)

**Figure 4.3**: Estimation of equilibrium conversions of CH$_4$ and CO$_2$ in a feed containing CO$_2$:CH$_4$ ratio of 1.5 at various temperatures

Those limits will be referenced when comparing activity levels of different catalysts. CH$_4$ approaches 100% conversions at temperatures around 700°C and above, while CO$_2$ approaches 80% and plateaus at around 750°C.
It is again worth mentioning that petrochemical sources of CH₄ and CO₂ are independent and thus, ratios of each can be adjusted to eliminate the coking tendency that plagues landfill gas with catalyst deactivation.

4.2 1st Experimental Setup

This project’s initial experimental activities were carried out utilizing a vertically installed packed-bed flow reactor and furnace, loaded with powdered catalytic material supported on inert quartz wool, with analysis provided by a Gas Chromatography (GC) instrument. The reactor shape and size will change once monoliths are to be tested. The accompanying image (Fig 4.4) illustrates the configuration of laboratory equipment and the steps for catalyst preparation:

![Experimental Setup and catalyst preparation procedure](image)

**Figure 4.4:** Experimental Setup and catalyst preparation procedure
Catalyst preparation was performed using the conventional technique of Incipient Wetness Impregnation (IWI) to ensure proper and uniform distribution of the metal on top of the carrier surface area. Rhodium Chlorides, Ruthenium Nitrates and Nickel Nitrates were used as the salts to impregnate γ-Alumina support having a pore volume of 1.06 ml/g. The samples were dried and calcined at 500°C, under an air-exposed environment, to ensure complete decomposition and evolution of all nitrates and chlorides from the catalysts’ surface.

Initially it is essential to determine the activities of the active metals of interest under the desired DRM reaction conditions. Therefore, the project was initiated by conducting an activity comparison of Rh vs Ni and Ru. The reaction, initially, started with a pretreatment reduction step where each catalyst was exposed to a Hydrogen rich environment (20% H₂ and balance N₂) in order for its reduction to their active metallic state form. The corresponding reaction is as follows:

\[ M-O + H_2 \rightarrow M + H_2O \]

M: Rh, Ni...etc

The reduction step proceeds in a slow temperature-controlled increase to 500°C and with a hold for 1-2 hours. When the reduction is complete, evident by lack of consumption of Hydrogen, DRM reaction begins by introduction of CH₄ and CO₂. These are fed at a controlled ratio of CO₂:CH₄ of 1.5 while flowing at a Weight Hourly Space Velocity (WHSV) of 240,000 mL/hr.g. The temperature is then increased in step-wise intervals of 50°C, from 500 to 750°C, while stabilizing and analyzing products at every step. This procedure generated a set of conversion verses temperature profiles that differentiate the performance of each active catalytic metal.

**4.3 Catalyst Screening**

The metals of interest are Rh, Ni, and Ru and their performance with respect to the DRM reaction is the area of focus. Hence, a set of experiments were conducted to gauge their activities
and selectivities towards desired products. The charts below represent the impact of increasing metal loadings on catalyst performance with a feed stream containing 6 mol% CO₂, 4 mol% CH₄, and 90 mol% N₂, operated at WHSV 240,000 mL/hr.g and CO₂:CH₄ ratio of 1.5 for both Rh and Ni. As can be observed, increasing metal loading is not proportional to conversion. This can be explained by the fact that dispersion efficiency of metal atoms decreases with increased loading, this is because metal atoms tend to bind together or agglomerate forming larger crystal sizes and lower external catalytic surface area. For Rh, 1% is the optimal loading as it increased significantly from 0.5%, but 2 and 3% did not exceed its performance. Similarly, 10% Ni is the optimal choice since it substantially increased conversion over 3% and matched 1% Rh in performance.

![Figure 4.5: Impact of varying metal loadings on catalyst activity for both Ni and Rh powder catalysts with a feed stream containing 6 mol% CO₂, 4 mol% CH₄, and 90 mol% N₂, operated at WHSV 240,000 mL/hr.g and CO₂:CH₄ ratio of 1.5](image-url)
The figure below compares the activity of all catalysts tested at several metal loadings operated at WHSV 240,000 mL/hr.g and CO\textsubscript{2}:CH\textsubscript{4} ratio of 1.5. The equilibrium limit (black color) is also included for reference:

![Rh, Ni, Ru Activity Screening](image)

**Figure 4.6:** Activity screening for all catalyst powders with a feed stream containing 6 mol% CO\textsubscript{2}, 4 mol% CH\textsubscript{4}, and 90 mol% N\textsubscript{2}, operated at WHSV 240,000 mL/hr.g and CO\textsubscript{2}:CH\textsubscript{4} ratio of 1.5.

It is clear that Rh is the most active metal with respect to the DRM reaction, since the conversions are higher at identical temperatures and lower weight contents. It was observed that 3% Rh matches 14.5% Ni at 500°C and then Ni exceeds it at higher temperature. Also, 2% Rh matches 10% Ni at 500°C and then it outperforms Ni. Moreover, 1% Rh starts lower but then slightly outperforms 10% Ni. Furthermore, 0.5% Rh clearly outperforms 3% Ni by roughly 5% conversion at almost every temperature point. Additionally, 1% Ru has a performance comparable to 0.5% Rh at low temperatures but then increases in performance to a level a bit lower than 10% Ni. The black solid line is the equilibrium conversion level at corresponding temperatures.
The above results showed that the metals with highest intrinsic activity are in the order of Rh > Ru > Ni. From figure 11 below, it can be noted that 1% Rh showed comparative performance levels to 10% Ni catalyst while 1% Ru is of relatively lower activity level:

![Graph showing activity comparison for 1% Rh, 10% Ni, and 1% Ru catalysts, with temperatures ranging from 450 to 800°C.](image)

**Figure 4.7:** Activity comparison for 1% Rh, 10% Ni, and 1% Ru catalysts with a feed stream containing 6 mol% CO₂, 4 mol% CH₄, and 90 mol% N₂, operated at WHSV 240,000 mL/hr.g and CO₂:CH₄ ratio of 1.5

Consequently, it can be concluded that Rh has a higher activity density than either Ni and Ru in the range up to 10:1 and 2:1 ratios, respectively, based on the preliminary screening results of 1% Rh, 10% Ni, and 1%Ru. Based on the above results, 10% Ni and 1% Rh are the recommended catalysts of choice for the subject application.

### 4.4 Impact of Space Velocity

In order to quantify the activity ratio of Rh to Ni, 3% wt Ni catalyst was tested at lower WHSV to match the conversion levels of 3%wt Rh, as shown in Table 4.1 below. Therefore, an
experiment was designed with a feed stream containing 6 mol% CO₂, 4 mol% CH₄, and 90 mol% N₂, to operate Ni catalyst at lower space velocities and compare its activity to Rh catalyst.

**Table 4.1:** Ni catalyst operated at lower space velocities

<table>
<thead>
<tr>
<th>T (C)</th>
<th>WHSV mL/hr.g</th>
<th>CH₄ Conversion</th>
<th>WHSV mL/hr.g</th>
<th>CH₄ Conversion</th>
<th>T (C)</th>
<th>WHSV mL/hr.g</th>
<th>CH₄ Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>240,000</td>
<td>20%</td>
<td>240,000</td>
<td>5%</td>
<td>500</td>
<td>57,000</td>
<td>20%</td>
</tr>
<tr>
<td>550</td>
<td>240,000</td>
<td>34%</td>
<td>240,000</td>
<td>15%</td>
<td>550</td>
<td>81,000</td>
<td>34%</td>
</tr>
<tr>
<td>650</td>
<td>240,000</td>
<td>69%</td>
<td>240,000</td>
<td>49%</td>
<td>650</td>
<td>114,000</td>
<td>69%</td>
</tr>
<tr>
<td>750</td>
<td>240,000</td>
<td>95%</td>
<td>240,000</td>
<td>81%</td>
<td>750</td>
<td>126,000</td>
<td>95%</td>
</tr>
</tbody>
</table>

The results below demonstrate the degree of WHSV reduction (longer residence time) needed for Ni to achieve similar conversions of Rh catalyst at different temperatures:

**Table 4.2:** Activity ratios of Rh/Ni based on Relative WHSV

<table>
<thead>
<tr>
<th>T, °C</th>
<th>WHSV needed for Ni to achieve Rh Conversion</th>
<th>Activity Ratio Rh / Ni at 3%wt Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>57,000</td>
<td>240,000 / WHSV = 4.21</td>
</tr>
<tr>
<td>550</td>
<td>81,000</td>
<td>240,000 / WHSV = 2.96</td>
</tr>
<tr>
<td>650</td>
<td>114,000</td>
<td>240,000 / WHSV = 2.11</td>
</tr>
<tr>
<td>750</td>
<td>126,000</td>
<td>240,000 / WHSV = 1.90</td>
</tr>
</tbody>
</table>

Where, the weight hourly space velocity (WHSV) is given by:

\[
W_{\text{HSV}} = \frac{\text{Total Flow Rate}}{\text{Mass of Catalyst}} = \frac{240 \text{ ml/min}(10\% \text{ CO}_2) + 160 \text{ ml/min}(10\% \text{ CH}_4)}{0.1 \text{ grams (Rh + Alumina)}} \times 60 \frac{\text{min}}{h} = 240,000 \text{ ml/h.g}
\]

From the above experiments, it was determined that reducing WHSV by 4.21 times is necessary for Ni to achieve the same conversion of Rh at 500°C. In other words, WHSV was
reduced from 240,000 to 57,000 mL/hr.g in order for Ni to be able to achieve the same conversion of Rh at 500°C.

### 4.5 Catalyst Characterization

While testing activity of catalysts enables screening the performance in an operating environment, it is very beneficial to understand the molecular behavior that attributes to better or worse performance. For this reason, 3% Ni and 3% Rh were tested initially under temperature-programmed reduction (TPR) to obtain a preliminary gauge of the efficiency of dispersion of active metal distribution within the carrier’s porous structure. The chart below illustrates the difference between both catalysts in terms of consumption of Hydrogen during the reduction phase:

![Figure 4.8: Experimental temperature programmed reduction for 3% Rh and 3% Ni powder catalysts performed with a 150 mL/min inlet stream of 20 mol% H₂ and 80 mol% N₂ under a fixed 10°C/min temperature increase and contact with 0.1 grams of catalyst. The y-axis represents the H₂ concentration in the outlet stream.](chart.png)
The above results immediately indicate that at the same metal loading, there are more Rh atoms available to carry out the reaction compared to Ni, as evident by the lower H$_2$ concentrations in the case of Rh. To better understand the monolayer properties of each catalyst, a Quantachrome instrument [53] was utilized to accurately measure the dispersion effectiveness via pulse titration of 3% Rh and 3% Ni. The following table 4.3 summarizes the results:

**Table 4.3**: H$_2$ chemisorption test results by a Quantachrome Pulsar TPR instrument

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>3% Rh / Al$_2$O$_3$</th>
<th>3% Ni / Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total volume adsorbed, µL</td>
<td>224.07</td>
<td>46.55</td>
</tr>
<tr>
<td>Monolayer uptake volume, µmole/g</td>
<td>73.21</td>
<td>15.21</td>
</tr>
<tr>
<td>Crystallite Size, nm</td>
<td>7.3</td>
<td>56.66</td>
</tr>
<tr>
<td>Metal Surface Area, m$^2$/g</td>
<td>6.63</td>
<td>1.19</td>
</tr>
<tr>
<td>Dispersion %</td>
<td>50.22</td>
<td>5.95</td>
</tr>
</tbody>
</table>

The results of the tests clearly show that Rh atoms have a greater dispersion than the Ni atoms. The larger volume adsorbed in titration tests and the smaller crystallite size, indicated by diameter of the resulting cluster, are direct indicators of active metal distribution effectiveness. Thus, the metal surface area available for reaction in Rh is about 6 times greater than that of Ni, and this plays a major role in activity performance. Therefore, combining the superior electronic properties and dispersion effectiveness of Rh as an active metal, the difference in performance between Rh and Ni can be scientifically justified.

### 4.6 Kinetic Study

The main goal of a kinetic study is to experimentally identify the elements of a rate law specific to a certain reaction. Those elements include reaction orders of reactants, activation energy $E_a$, as well as the rate constant and pre-exponential factor $A$. Experimentally measuring the
mentioned parameters provides insightful details on the effect of varying reactant concentrations, the effect of temperature, and the values of constants on the overall rate of reaction. Consequently, an empirical rate law model can be developed which will act as a basis for fundamental understanding of the parameters impacting the kinetically controlled rate of the overall reaction. This information is also essential for future reactor design and scaling up studies for commercial applications.

The kinetic study entails operating the catalyst in the kinetically controlled regime, conversions between 10-20%, and then varying one concentration at a time while maintaining the other parameters constant. The variables of the subject study are depicted from the following empirical rate law expression:

\[ r = k [CH_4]^x[CO_2]^y \]

\[ r = A e^{\left(-\frac{E_a}{RT}\right)} [CH_4]^x[CO_2]^y \]

where x and y are the reactant orders and k is the rate constant, given by the Arrhenius principle as \( k = A \exp(-E_a/RT) \); A being the pre-exponential factor and \( E_a \) is the activation energy for the reaction pathway.

The first step of the study is to take the natural logarithm of the rate expression and hence:

\[ \ln(r) = \ln(k) + x \ln([CH_4]) + y \ln([CO_2]) \]

Also, expanding on k yields the following:

\[ \ln(r) = \ln(A) - \frac{E_a}{RT} + x \ln([CH_4]) + y \ln([CO_2]) \]

It is necessary to vary one reactant concentration while maintaining the other in a large excess so the rate is only impacted by the reactant with the lower concentration. Therefore, once the reaction rate is measured experimentally against each variable varied solely at a time, the set of
data will enable generating several plots to determine the subject kinetic parameters. The plots include the following:

1. Plot of ln(r) vs ln [CH₄] generates a straight line with a slope being the reactant order x
2. Plot of ln(r) vs ln [CO₂] generates a straight line with a slope being the reactant order y
3. Plot of ln(k) vs 1/T generates a straight line with a slope leading to the determination of activation energy Ea and the intercept leading to pre-exponential factor A.

The experiment commenced by reducing the Ni catalyst with 20% H₂ (balance nitrogen N₂) for one hour at 500°C followed by introducing the gaseous reactants, CH₄ and CO₂, and stabilizing the reaction condition at the same temperature with the following base case parameters:

Table 4.4: Base case conditions for the kinetic study experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>10% Ni/Al₂O₃</td>
</tr>
<tr>
<td>Catalyst weight</td>
<td>0.1 grams</td>
</tr>
<tr>
<td>Feed Composition CO₂:CH₄:N₂</td>
<td>6%:4%:90%</td>
</tr>
<tr>
<td>CO₂/CH₄ ratio</td>
<td>1.5</td>
</tr>
<tr>
<td>Total Flow</td>
<td>400 mL/min</td>
</tr>
<tr>
<td>WHSV</td>
<td>240,000 mL/hr.g</td>
</tr>
<tr>
<td>Temperature</td>
<td>510°C</td>
</tr>
<tr>
<td>Conversion</td>
<td>20.0%</td>
</tr>
</tbody>
</table>

First, in order to determine the reaction order (x) of CH₄, all of the above parameters were held constant at an excess value, while the concentration of CH₄ was varied by adjusting the flowrate of CH₄ gas; while maintaining the space velocity constant. This was done by introducing N₂ to maintain an overall flowrate of 400 mL/min for every step change. At each different reactants’ mixture, the system was stabilized and multiple samples were taken. The below table 4.5 represents the results obtained for this step:
Table 4.5: Experimental methane reaction order data

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Total Inlet Flowrate mL/min</th>
<th>In (mol %)</th>
<th>Out (mol %)</th>
<th>CH₄ Conversion</th>
<th>ln(R) vs. ln[CH₄]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH₄</td>
<td>CO₂</td>
<td>N₂</td>
<td>CH₄%</td>
</tr>
<tr>
<td>510</td>
<td>400</td>
<td>4.0</td>
<td>6.0</td>
<td>90.00</td>
<td>3.15</td>
</tr>
<tr>
<td>510</td>
<td>400</td>
<td>2.75</td>
<td>6.0</td>
<td>91.25</td>
<td>2.03</td>
</tr>
<tr>
<td>510</td>
<td>400</td>
<td>1.50</td>
<td>6.0</td>
<td>92.50</td>
<td>0.99</td>
</tr>
</tbody>
</table>

The above data was used to plot the rate vs CH₄ concentration to yield the following plot:

![Graph showing lnR vs ln[CH₄]](image)

**Figure 4.9:** Logarithmic plot of rate of reaction vs CH₄ concentration

The fitted straight line yields a slope equivalent to the reaction order (x), hence:

**Reaction order (x) = 0.5253**

Similarly, the concentration of CO₂ was varied while maintaining all other parameters constant in order to determine the reaction order (y). Below table 4.6 illustrates the results:
Table 4.6: Experimental carbon dioxide reaction order data

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Total Inlet Flowrate mL/min</th>
<th>ln (mol %)</th>
<th>Out (mol %)</th>
<th>Conversion</th>
<th>ln(R) vs. ln[CO₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH₄</td>
<td>CO₂</td>
<td>N₂</td>
<td>CH₄%</td>
</tr>
<tr>
<td>510</td>
<td>400</td>
<td>4.0</td>
<td>6.00</td>
<td>90.00</td>
<td>3.1513</td>
</tr>
<tr>
<td>510</td>
<td>400</td>
<td>4.0</td>
<td>3.50</td>
<td>92.50</td>
<td>3.3658</td>
</tr>
<tr>
<td>510</td>
<td>400</td>
<td>4.0</td>
<td>1.75</td>
<td>94.25</td>
<td>3.5012</td>
</tr>
</tbody>
</table>

The above data was used to plot the rate vs CO₂ concentration to yield the following plot:

![Logarithmic plot of rate of reaction vs CO₂ concentration](image)

**Figure 4.10: Logarithmic plot of rate of reaction vs CO₂ concentration**

The fitted straight line yields a slope equivalent to the reaction order (y), hence:

**Reaction order (y) = 0.537**

The third important kinetic parameter is the Activation Energy (Ea) which is highly dependent on reaction temperature. Therefore, the reaction was carried out at several temperatures while maintaining the other parameters in the base case constant (low conversions). This experiment yields values for three crucial parameters: rate constant k, pre-exponential factor A,
and activation energy \(E_a\). This is done by expanding on the rate constant \(k\) via the Arrhenius principle. This experimental step resulted in the following outcome:

**Table 4.7**: Experimental reaction constant (\(k\)) data

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Average (R) (mol/min)</th>
<th>([\text{CH}_4]^{\times})</th>
<th>([\text{CO}_2]^{\times})</th>
<th>(K) (1/min*mol^0.0623)</th>
<th>(\ln(k)) (1/min*mol^0.0623)</th>
<th>1/T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.0001259</td>
<td>4.29</td>
<td>5.51</td>
<td>0.00000533</td>
<td>-12.143</td>
<td>0.0012937</td>
</tr>
<tr>
<td>550</td>
<td>0.0002221</td>
<td>4.29</td>
<td>5.51</td>
<td>0.00000939</td>
<td>-11.576</td>
<td>0.0012151</td>
</tr>
<tr>
<td>650</td>
<td>0.0004928</td>
<td>4.29</td>
<td>5.51</td>
<td>0.00002084</td>
<td>-10.778</td>
<td>0.0010834</td>
</tr>
<tr>
<td>750</td>
<td>0.0006871</td>
<td>4.29</td>
<td>5.51</td>
<td>0.00002906</td>
<td>-10.446</td>
<td>0.0009775</td>
</tr>
</tbody>
</table>

The above data was used to plot the reaction constant vs the inverse of temperature to yield the following plot:

![Figure 4.11: Logarithmic plot of reaction constant \(k\) vs 1/T](image)

The fitted straight line yields a slope equivalent to \(-E_a/R\) and an intercept of \(\ln(A)\), hence:

**Activation Energy \(E_a\) (KJ/mol) = 43.683**

**Pre-exponential Factor \(A\) (1/min*mol^0.0623) = 0.005425**
This experimental study enabled determining the kinetic parameters pertaining to the Ni catalyst used for the dry reforming reaction conditions. The overall rate expression obtained from the study has the following forms:

\[ r = k [CH_4]^{0.52} [CO_2]^{0.53} \]

\[ r = 0.005425 e^{\left(-\frac{43.683}{RT}\right)} [CH_4]^{0.52} [CO_2]^{0.53} \]

Or for gaseous form:

\[ r = k P_{CH_4}^{0.52} P_{CO_2}^{0.53} \]

Those forms of the rate expressions can play a major role in process design and scaling up studies to support the commercialization of this process technology. The above results are inline with the kinetic studies results obtained from literature [54].

4.7 Aging

Now that the activity screening was performed, coupled with understanding of molecular behaviour of the catalyst monolayer and obtaining a kinetic rate model, both Ni and Rh catalysts were subjected to a carbon formation environment to induce deactivation of the catalyst and gauge its resistance to it for the sake of comparison. The charts below represent the decline in activity of both catalysts when exposed to two environments, CH\textsubscript{4}:CO\textsubscript{2} ratios of 1.75 and 2.0:
Figure 4.12: Artificial aging of Ni and Rh catalysts exposed to different CH$_4$:CO$_2$ ratios of 1.75 and 2.0, and operated at WHSV 240,000 mL/hr.g and constant temperature of 750°C
In both cases, the slopes of Rh catalyst were lower than Ni catalyst, as depicted from the trendline equations. This observation indicates slower rates of deactivation and greater tolerance of Rh catalyst over Ni, when exposed to a carbon-formation environment. The table 4.8 below summarizes the aging data gathered for Ni and Rh catalysts under both conditions:

**Table 4.8:** Conversion levels of fresh and aged Ni and Rh catalysts at different CH₄:CO₂ ratios

<table>
<thead>
<tr>
<th>Ratio</th>
<th>CH₄:CO₂ Ratio 1.75</th>
<th>CH₄:CO₂ Ratio 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Ni</td>
<td>Rh</td>
</tr>
<tr>
<td>Fresh Conversion</td>
<td>95.3%</td>
<td>92.7%</td>
</tr>
<tr>
<td>Aged Conversion</td>
<td>70.8%</td>
<td>88.4%</td>
</tr>
<tr>
<td>Deactivation Period, hrs</td>
<td>2.5</td>
<td>5</td>
</tr>
<tr>
<td>Deactivation Rate %/hr</td>
<td>9.8%</td>
<td>0.86%</td>
</tr>
</tbody>
</table>

It can be evidently determined from the above table that Rh has greater tolerance to deactivation compared to Ni. At a ratio of 1.75, Ni deactivated at 9.8% per hour while Rh mainatined only 0.86% per hour deactivation rate. At a ratio of 2, deactivation rates were 15.5% and 6.1% per hour for Ni and Rh, respectively. In all charts, H₂ % product is directly proportional to conversion and it drops as deactivation proceeds.

**4.8 Regeneration**

In industry, operating facilities tend to prefer having an option of regenerating the catalyst instead of purchasing a fresh batch for replacement. Based on the application, this option can be economically viable and would act as an appealing feature. Therefore, an experimental effort was deployed using a Ni catalyst to understand which environment is optimal for regeneration. The regeneration expriments were conducted via Steam Gasification according to the following reaction:
\[2\text{H}_2\text{O} + \text{C} \rightarrow 2\text{H}_2 + \text{CO}_2\]

After aging the catalyst to a 55% conversion, the regeneration was conducted at 750°C with a stream of 40-60% Steam in Nitrogen for 2 hours. The catalyst reversibly restored almost all of its activity after the regeneration process. Summary of the results are shown in the charts below. The knowledge gained will be the basis for aging and regeneration experiments of monolithic catalysts for those conditions where coke is formed.
Figure 4.13: Aging and Regeneration of a 10% Ni powder catalyst. Aging conducted with a feed ratio CH$_4$:CO$_2$ of 2.0 and constant temperature at 750°C. Regeneration conducted with a feed stream containing 50 mol% steam and 50 mol% N$_2$ at 750°C.
Chapter 5: Scale-up and Monolithic Catalyst Testing

5.1 2nd Experimental Setup

Amid the pandemic situation in April of 2020, the work was transitioned to a new laboratory at the sponsor’s research facility and hence, a new system apparatus was installed to continue this project’s milestones.

The new setup utilized a PID Engineering reactor which is a sophisticated device that enables the user to conduct a wide range of experimental research projects for catalytic and non-catalytic reaction systems. The device contains tubular reactors supported by automated gas mass flowmeters (MFC), furnaces and thermocouples, liquid injection manifold as well as a smart software that enables manual and programmed sequences to be carried out. The PID is also connected to an Agilent GC 7890B through an outlet line that transfers the products to the sampling section followed by the vent line to the exhaust canopy.

5.2 Washcoating Procedure

Transitioning from powders to monolithic catalysts requires a delicate preparation procedure. The washcoating is conducted by first preparing the catalytic powder via the conventional IWI impregnation procedure. Once the catalyst is dried and calcined, a slurry is prepared by combining 30-40% vol. of catalyst with 60% vol. of distilled water as well 1-2 mL of Acetic acid to achieve a pH of 3-4. The addition of the acid ensures proper suspension of the catalyst particles in the slurry; however, it adversely impacts the viscosity which could lead to the solids separating during the coating step. To overcome this challenge, the slurry is milled in a ball milling jar containing 10-12 ceramic milling balls (1 cm diameter) for 2-3 hours to <5 microns.
The milling process mainly enhances the adhesion of the catalyst particles on the walls of the monolith as well as reduces the separation from the liquid media. After milling, the monolith is dipped in the slurry for few minutes and then blown with low pressure air to clear the channels followed by drying and calcining in air at 500°C for 4 hours. The weight of the monolith is determined at every step to obtain the washcoat loading (WCL). Finally, the monolith is loaded in a tubular reactor in preparation for an experiment. It is adequately reduced to convert the catalytic component to its active metallic state. The procedure is illustrated in the below figure 5.1:

![Figure 5.1: Stepwise procedure for monolith washcoating](image)

Based on the initial activity comparison results, a decision was made to begin the monolithic experiments with Ni as the active metal. Therefore, a slurry was prepared according to the above procedure and 2 monolithic substrates were coated. The results are represented in the below table 5.1:

**Table 5.1: Slurry preparation parameters and coating results**

<table>
<thead>
<tr>
<th>Slurry Preparation</th>
<th>Coating Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% Ni Catalyst</td>
<td>Monolith initial weight/Volume</td>
</tr>
<tr>
<td>DI Water</td>
<td>Substrates</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>Number of Dips</td>
</tr>
<tr>
<td>pH</td>
<td>Final weight, g</td>
</tr>
<tr>
<td>Milling time at 70 rpm</td>
<td>WCL, g/in³</td>
</tr>
</tbody>
</table>
The results of the coating experiments demonstrate the effective adhesion of the particles on the walls of the monolith substrates evident from the low number of dips. Those substrates are now ready to be tested in a flow reactor.

5.3 Activity Testing

In preparation for testing, Ni and Rh monolithic catalysts of equal WCL of 1.0 g/in³ were prepared using the above-mentioned procedure. Those monolithic catalysts were loaded in 1” stainless steel reactors and were tested at WHSV 80,000 mL/hr.g and CO₂:CH₄ ratio of 1.5. WHSV for monoliths is defined as the total inlet flowrate divided by the weight of the catalyst coated on the walls, which is the difference between clean and coated monolith. The following charts represent the main results of comparison between both catalysts:
Figure 5.2: Comparison of 10% Ni and 1% Rh monolithic catalysts for activity levels and product distribution, with a feed stream containing 6 mol% CO$_2$, 4 mol% CH$_4$, and 90 mol% N$_2$, operated at WHSV 80,000 mL/hr.g and CO$_2$:CH$_4$ ratio of 1.5.

Both catalysts demonstrated excellent activity levels while Rh produced higher conversions at temperatures between 500 and 650°C. Similarly, the H$_2$ product evolution trends exhibit same performance. H$_2$/CO ratio was almost identical for both catalysts and reached high
levels close to 1.0 at temperatures around 650-700°C. This finding almost resembles stoichiometric ratios which simplifies the process design calculations for downstream equipment. Additionally, H₂ yield in both cases were high exceeding 43% maintaining a reasonable selectivity to this valuable product.

In order to provide a holistic view on activity screening, the monolithic catalysts performance were gauged against the previously tested powder catalysts. It can be clearly observed from figure 5.3 below that monolithic Rh (1% Rh M) and Ni (10% Ni M) have exceeded the activity levels of all powder catalysts, and this is mainly due to the lower space velocity 80,000 vs 240,000 in powders.

**Figure 5.3:** Activity screening of Monolithic catalysts compared to powder catalysts with different metal loadings, with a feed stream containing 6 mol% CO₂, 4 mol% CH₄, and 90 mol% N₂, operated at WHSV 240,000 mL/hr.g for powders and 80,000 mL/hr.g for monolithic catalysts, and CO₂:CH₄ ratio of 1.5
Moreover, one observation made during the activity screening is that the monolithic catalysts performed better than powders with higher metal loadings. For instance, 1% Rh M tested at WHSV 80,000 was far better than 3% Rh powder tested at WHSV 240,000. Similarly, 10% Ni M at WHSV 80,000 outperformed 14.5% Ni powder catalyst at WHSV 240,000. Below charts summarize this observation:

![Figure 5.4: Washcoating effectiveness for Ni and Rh monolithic catalysts, with a feed stream containing 6 mol% CO₂, 4 mol% CH₄, and 90 mol% N₂, operated at WHSV 240,000 mL/hr.g for powders and 80,000 mL/hr.g for monolithic catalysts, and CO₂:CH₄ ratio of 1.5](image)

It can be concluded that the excellent activity is a good reflection of the washcoating effectiveness as well as the ability of the turbulent flow to overcome bulk mass transfer limitations.

### 5.4 Stability Testing

One crucial property to be examined is the catalyst stability. Both monolithic catalysts were tested at long periods at normal operating conditions, WHSV 80,000 mL/hr.g and CO₂:CH₄ ratio
of 1.5, and fixed at 750°C to gauge the degree of nominal deactivation. This reflects how stable a catalyst can perform in a commercial application. The results are included in the below chart:

![Stability Test Chart](image)

**Figure 5.5:** Stability tests comparing Ni and Rh monolithic catalysts with a feed stream containing 6 mol% CO₂, 4 mol% CH₄, and 90 mol% N₂, performed at WHSV 80,000 mL/hr.g, CO₂:CH₄ ratio of 1.5 and constant temperature of 750°C

Both Catalysts resulted in excellent stability performance even after running for 1000 minutes. The Rh catalyst exhibited extremely high stability at the normal operating conditions and with no drop in conversion. Ni, on the other hand, deactivated at a slow rate of 0.23% per hour and still maintained conversions around 92% after 1100 minutes; which is considered a stable system. In order to further understand Ni stability, it was operated in a condition closer to landfill gas composition, and the results demonstrated a dramatic difference in stability. The chart below shows that Ni catalyst deactivated at a rate of 8.6% per hour under landfill composition compared to the 0.23% per hour deactivation under favorable conditions:
Figure 5.6: Stability tests demonstrating Ni monolithic catalyst at different conditions, performed at WHSV 80,000 mL/hr.g and constant temperature of 750°C

The stability testing conducted above represents a crucial outcome in the tolerance of the subject catalysts to the exposed environment containing the mixture of the main model components CH₄ and CO₂. This observation strongly supports the approach taken in this research project, which revolves around producing a stable catalyst system for the DRM process.

Natural Gas contains several types of impurities and hence, further stability testing to mimic real-life situation is needed. This is typically conducted in the laboratory by including impurities to the feedstock in the testing protocols while conducting the experiments, or by utilizing a sample of Natural Gas for testing. This type of testing is best performed in pilot plant setups, where the configuration of the plant is equipped with all tools to handle a real-life sample. Typical natural gas impurities include moisture, solid particulates, and sulfur compounds, such as Hydrogen Sulfide and Mercaptans [56], which could impact the catalyst performance and life cycle.
For instance, sulfur compounds exhibit adverse effects on the catalyst performance and can permanently poison the active sites. For this reason, hydrocarbon processing facilities install sulfur treating units such as, Hydrotreating, Amine treating or Sulfur guard-beds to reduce the sulfur to acceptable levels. Pilot plant scale tests can somehow accurately measure the loss of catalyst life due to traces of impurities and can also estimate the level of treating required for the removal of impurities. Having separate sources of CH₄ and CO₂ in a petroleum or petrochemical facility, allow for specialized purification for DRM. Additionally, when recycling the CO₂ stream from the downstream separation unit in a DRM plant, the additional needs for purification are reduced, as it is already impurities-free, produced from the PSA.

5.5 Aging & Regeneration

Since the monolithic catalysts are being proposed as a potential solution for industrial applications, both Rh and Ni were subjected to aging and regeneration experiments to determine how well they would perform. Both experiments were conducted under the same operating conditions performed for the powder catalysts presented earlier. The Results for both catalysts are available in the charts below:
Figure 5.7: Monolithic 10% Ni/Al$_2$O$_3$ catalyst performance in terms of aging and regeneration.

Aging conducted with a feed ratio CH$_4$:CO$_2$ of 2.0 and constant temperature at 650°C.

Regeneration conducted with a feed stream containing 40 mol% steam and 60 mol% N$_2$ at 750°C constant temperature.
Figure 5.8: Monolithic 1% Rh/Al₂O₃ catalyst performance in terms of aging and regeneration.

Aging conducted with a feed ratio CH₄:CO₂ of 2.0 and constant temperature at 650°C.

Regeneration conducted with a feed stream containing 40 mol% steam and 60 mol% N₂ at 750°C constant temperature.
The charts above illustrate the capabilities of both catalysts to restore almost full activities after regeneration and hence, can be recommended for regeneration for industrial applications. In the case of Ni, the catalyst activity was reduced from 97% to 75.8% by artificial aging over 2 hours and then restored to 93.6% over an 80-minute regeneration period. Similarly, Rh catalyst, while having greater tolerance to deactivation, was regenerated for 80 minutes from an aged activity level of 80.2% up to 92.3%, after having a fresh conversion level of 95.7% at the very start. Those results point towards the fact that carbon formation on the surface of the catalyst is temporary and can hinder its activity after a significant amount has deposited. Fortunately, this phenomenon is reversible and the activity can be almost fully restored with regeneration; placing this technology at an advantageous position. Having separate sources of CO$_2$ and CH$_4$ as well as the internal CO$_2$ recycle stream, as proposed in this feasibility study, the ratio can be preadjusted to minimize deactivating phenomena.
Chapter 6: Process Design

6.1 Process Flow Diagram

A major part of the novelty in this proposed PhD research lies in the use of monolithic structured reactors in chemical plants as well as a unique process design. In this design, the emphasis is given to the merit of a CO₂ recycle stream to the feed stream as well as a methanation step, both leading to an overall net zero CO₂ generation from the process side. The following process flow diagram illustrates the proposed design configuration of the monolithic Dry Reforming process:

Figure 6.1: Proposed Dry Reforming process flow diagram utilizing structured reactor design for the Reformer and combined with a Methanator system

Natural gas is combined with CO₂, from the recycle stream or an external source, at a ratio of CO₂:CH₄ of 1.5 and enters the reformer, which contains catalyzed washcoats on its walls, at a
temperature between 750-800°C after passing through a feed-effluent heat exchanger (FEHE) followed by a fired heater. The reformer outlet stream, containing mainly H₂ and CO, is cooled in a heat exchanger before it enters the high temperature shift converter (HTSC) after combining with injected steam. The effluent is further cooled and enters the low temperature shift converter (LTSC) to achieve close to 100% conversion of CO to CO₂. The resultant stream now being H₂ and CO₂ with traces of unreacted CO and steam is separated in a Pressure Swing Adsorber (PSA) to produce a 99.9% pure H₂ product and off gas containing mainly CO₂ and any unconverted constituents; i.e. CH₄, CO, H₂O and small amounts of H₂. The off gas stream (tail gas) splits into 2 streams: 80% CO₂ recycle stream back to the feed and another 20% waste stream. In order to have a carbon neutral process, zero carbon generation from the process side, a methanator system is added to convert all CO₂ in the waste stream to CH₄ via the following catalytic reaction:

\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \]

The CH₄ is recycled to the feedstock to be converted again to products. During startup operation, an external pure source of CO₂ is utilized until a sufficient amount is produced in the downstream process and is recycled back to the feed. This proposed process design resembles that of a typical SMR plant operating today, with the exception of the Reformer and CO₂ recycle, and hence, DRM has a strong potential to replace it in future projects.

The rationale for using a Methanator system in the above process design, which poses a significant penalty on H₂ consumption (4 moles for each mole of CO₂), lies in the fact that today, almost all methane reforming process plants do not have a practical utilization of the CO₂-rich waste stream produced from the PSA. Although there are tremendous research and development efforts taking place to find practical utilizations for CO₂ streams generated from process plants, current designs have to be tailored to a real-life application where most CO₂ streams are safely
vented to atmosphere; leading to a large carbon footprint. In the case of SMR and DRM, carbon capture technologies alongside a Methanator design are the two main routes for CO₂ conversion and reduction, in the case where pure H₂ gas product is the desired configuration. However, if syngas stream is the product of focus, then the design basis for carbon management will have options other than the above.

In the case where a CC technology is proposed to be utilized for CO₂ reduction in the DRM, then the overall design will have the following configuration:

![Figure 6.2: Proposed Dry Reforming process flow diagram utilizing structured reactor design for the Reformer and combined with a carbon capture & utilization technology](image)

The above figure illustrates the replacement of the Methanator system with a carbon capture technology that enables the production of “blue” H₂. The choice of technology depends on several variables including capital cost limitations, access to resources, scale of production and economy of scale. Although the choice of CC eliminates the penalty imposed on H₂ utilization for
the Methanation reaction, CC technologies are usually associated with a large capital cost. A financial assessment and an outlet for the CO₂ stream are typically the determining factors in the choice of carbon management design for the subject process plants.

6.2 Washcoated Structured Reactors

The concept of washcoating monolithic reactors has been enormously successful since they were first introduced in 1980 for the controlling of toxic emissions from the gasoline internal combustion engines i.e the catalytic converter. Since then, the application of monoliths dominates environmental applications in emission control from diesel and stationary sources world wide.

In view of the fact that monolithic or structured reactors have lower pressure drop, the design of the Reformer will have a more compact nature compared to the packed-bed reactor design. This entails a significant reduction in heat input and losses during normal operation. The heat generation and transfer will most probably be in the form of a fired heater design encapsulating the catalytically coated structured reactor. Should the void space in the channels pose a slower rate to heat transfer, the reactor can be divided into multiple segments for more efficient heat distribution. Moreover, a study conducted by Carlo et al [57] has shown that monolithic reactors constructed with high thermal conductivity metals, such as Aluminum and Copper, have relatively higher heat transfer rates by heat conduction, effectively enabling the management of heat transfer profiles within structured reactors. This approach can increase the rate of heat input to the catalytic walls to carry out the dry reforming reaction. A typical schematic design of a monolithic structured reactor is composed of multiple segments, each representing a monolith, coupled with multiple temperature sensing points to monitor temperature profile along
the reactor length [58]. Additional heat input can be embedded in between monolithic segments to maintain desired conversion levels.

Alternatively, Auto-thermal Reforming (ATR), the process of adding oxygen (O₂) with the feedstock components, can prove very efficient in this configuration. Generating the heat internally within the channels of the reactor will eliminate the need for external heat sources and significantly reducing harmful emissions from fuel combustion. A paper from literature studying dry reforming at landfill gas conditions [59] demonstrates that partial amounts of O₂ in the feed was sufficient to generate the heat input needed for the reaction to proceed without external source. Nevertheless, the cost of producing pure O₂ is relatively high and having an air separation unit as part of the design substantially increases the capital investment for a process plant.

According to Maria et al [60], who studied the activity of Fischer-Tropsch synthesis reaction over multiple forms of catalysts, washcoated structured reactors were found to have a higher activity per mass of catalyst compared to packed-bed reactors in the range of 1.4-2.9 times depending on particle size, while their activity per unit volume reached up to 3.6 times that of packed-bed reactors. One reason for the better performance is the significantly lower pressure drop in catalytic washcoated reactors, reducing the resistance to fluid flow and access to catalytic sites [61].
Chapter 7: Financial Modeling

7.1 Financial Modeling Basis

The previous sections have strongly demonstrated that dry reforming of methane is a technically viable process technology that has significant environmental and economic advantages over steam reforming of methane, which is the dominant process technology today for Hydrogen production. In order to accelerate the road to commercialization, it is essential to address the economic and financial aspects to support its competitiveness for future syngas and hydrogen production industrial projects.

Since DRM does not require steam as a feed component for the reforming process and it consumes CO$_2$ in the reaction, it may potentially have a reduced overall operating cost compared to SMR; reduced energy needed for steam generation, overall cost and a reduced carbon tax once applied in the future. For instance, Mondal et al. [62] has shown that DRM has an advantageous overall economic viability at around 33% Return on Investment (ROI) when compared to SMR at an ROI of 25% for the production of methanol.

An overall economic evaluation is a good estimation however, proving that the project will have a net positive financial return over the course of its lifetime will lead to a solid buy-in from investors. Therefore, a comprehensive and detailed financial model was constructed to demonstrate the financial viability of DRM for H$_2$ production and it was compared to a similar assessment for SMR from literature to boost the argument. A study by Salkuyeh et al [63] was conducted to compare the most promising hydrogen production technologies with and without carbon capture options, and the following tables summarize the main parameters considered and the resultant costs for SMR with and without CC:
Table 7.1: Main techno-economic assessment parameters and basis of financial comparison.

Data Source: Salkuyeh et al [63]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas Price</td>
<td>2.65 $/MJ</td>
</tr>
<tr>
<td>Plant Capacity</td>
<td>18.9 Tons H₂/hr</td>
</tr>
<tr>
<td>Project Lifetime</td>
<td>30 years</td>
</tr>
<tr>
<td>Capacity Factor</td>
<td>85%</td>
</tr>
<tr>
<td>Loan lifetime</td>
<td>15 years</td>
</tr>
<tr>
<td>Interest Rate</td>
<td>9.5%</td>
</tr>
<tr>
<td>Loan Percentage</td>
<td>40% of capital cost</td>
</tr>
<tr>
<td>Inflation rate</td>
<td>2.8%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SMR w/o CC</th>
<th>SMR with CC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas Consumption, Ton/Ton H₂</td>
<td>3.8</td>
<td>5.2</td>
</tr>
<tr>
<td>CO₂ Captured, Ton/Ton H₂</td>
<td>0</td>
<td>13.2</td>
</tr>
<tr>
<td>Total Capital Cost, $ Million</td>
<td>241</td>
<td>831</td>
</tr>
</tbody>
</table>

The newly constructed financial model for DRM has incorporated an identical project basis and assumptions; i.e. capacity, prices, lifetime, loan structure...etc, in order to conduct a fair comparison between the above-mentioned technologies and the DRM process. The resultant capital, operating and feedstock costs for DRM are as follows:

Table 7.2: Capital cost, O&M cost, and feedstock cost estimations for DRM

<table>
<thead>
<tr>
<th>Capital Cost Estimation</th>
<th>$ Million</th>
<th>O&amp;M Estimation</th>
<th>$ Million</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reformer</td>
<td>63.8</td>
<td>Labor Cost</td>
<td>22.08</td>
</tr>
<tr>
<td>WGS</td>
<td>14.0</td>
<td>Supervisory labor</td>
<td>2.21</td>
</tr>
<tr>
<td>PSA</td>
<td>81.0</td>
<td>Utilities</td>
<td>24.29</td>
</tr>
<tr>
<td>Boilers and Turbines</td>
<td>48.0</td>
<td>Operating Supplies</td>
<td>1.10</td>
</tr>
<tr>
<td>Methanator (only for Blue Hydrogen Case)</td>
<td>14.0</td>
<td>Lab charges</td>
<td>2.21</td>
</tr>
<tr>
<td>Total</td>
<td>220.8</td>
<td>Overhead</td>
<td>12.14</td>
</tr>
<tr>
<td>Natural Gas (NG) Feedstock Cost Estimation</td>
<td>Value</td>
<td>Administrative</td>
<td>3.64</td>
</tr>
<tr>
<td>NG feed Kg/hr</td>
<td>71820</td>
<td>Distribution and selling</td>
<td>4.42</td>
</tr>
<tr>
<td>NG LHV MJ/kg</td>
<td>47.1</td>
<td>R&amp;D</td>
<td>4.42</td>
</tr>
<tr>
<td>NG MJ/yr</td>
<td>2.5 x10¹⁰</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NG Cost Million $/yr</td>
<td>33.37</td>
<td>Total</td>
<td>76.51</td>
</tr>
</tbody>
</table>
The above capital costs have been performed on an approximate estimation basis, and hence, a more detailed engineering design estimation would provide more accurate results.

7.2 Base Case Results

After constructing the cashflow model along with respective debt structure and internal rates of return (IRR), the H₂ price, also known as the levelized cost of H₂, estimation was conducted at varying inflation rates and zero net present value (NPV) to determine the carbon credit needed if any, to justify its feasibility. The figure below represents the outcome:

![Figure 7.1: H₂ prices and carbon credit for the Zero NPV and 10% IRR case](image)

It is very clear that at low inflation rate of 1%, compared to conventional 1.9% according to the Hydrogen program at US DOE [64], the project achieved a low H₂ price of $1.07 /Kg and financially performed equally to today’s mature SMR technology without CC on breakeven basis. Additionally, at the DOE recommended inflation rate of 1.9%, the price of H₂ achieves lower levels at 98.3 cents/Kg and zero carbon credit. This indicates that carbon credit or government
subsidy would not be needed to advance this technology to market. In fact, low marginal H$_2$ price increments resulted in substantial profit indicated by positive NPV values. The following chart demonstrates the appealing financial indicators of DRM:

![Impact of Varying H$_2$ price at an annual inflator 1% case](chart.png)

**Figure 7.2:** NPV and IRR at multiple H$_2$ prices for the 1% annual inflation case

As evident from the above chart, a small increase in H$_2$ price of roughly 0.1$/kg, the project excelled in terms of profit generation and the NPV reached around $140 Million over the course of the project lifetime. This estimation remains on the conservative side, where inflation rates did not exceed 1% annually. The above results are even more impressive considering the CO$_2$ generated is roughly 60% less than SMR. Moreover, applying the inflation rate indicated by the DOE at 1.9% yields the following results:
The above chart indicates that the DRM project would be very profitable once the indicated inflation rates are applied. In fact, at $1.07/Kg H\textsubscript{2} price, which is the breakeven of SMR in the study, DRM has achieved 22.4% IRR and $126.5 Million net profits over the lifetime of the project. This outcome strengthens the argument that DRM technology is an economically viable technology with no carbon credit or governmental support needed.

7.2 Blue Hydrogen Case Results

Expanding this estimation to a DRM plant with a Methanator system, the resulting process is a carbon-neutral DRM process that generates zero CO\textsubscript{2} from the process side, and reduces overall CO\textsubscript{2} emissions to almost “blue” hydrogen classification; H\textsubscript{2} produced from fossil fuel sources with an overall CO\textsubscript{2} equivalent emission levels of 36.4 g CO\textsubscript{2}/MJ H\textsubscript{2} or lower, according to the European CertifHy label [65]. After incorporating the costs associated with the Methanator
(approximate estimation) and additional H₂ consumption, the results appear very promising as demonstrated by the following chart:

Figure 7.4: Impact of varying H₂ price at 1% inflation rate for the blue Hydrogen case with a Methanator

Similarly, once the indicated inflation rate of 1.9% is applied, the results yield the following chart:

Figure 7.5: Impact of varying H₂ price at 1.9% inflation rate for the blue Hydrogen case with a Methanator
The above results show that a breakeven price of blue H$_2$ with a Methanator is $1.21$/Kg compared to around $2.15$/Kg for SMR with CC, while at prices in the range of 1.27-1.32 $$/kg, this carbon-neutral (from the process side) blue hydrogen project becomes very profitable for the case where the annual price inflation rate of 1% is applied. Additionally, at 1.9% price inflation rate, the breakeven price of the project is reduced to $1.11$/Kg while substantial positive NPV is achieved at prices in the range $1.16-1.21$/Kg. This preliminary outcome positively supports DRM, and a more detailed process design would lead to more accurate results.

When compared to the study outcome [63], the cases of SMR without and with CC resulted in minimum H$_2$ prices at 1.07 $$/Kg H_2$ and 2.15 $$/Kg H_2$, respectively, with the assumption of zero price on carbon. Should there be a mandatory cost of carbon imposed, those minimum prices will increase. Therefore, with or without a carbon tax, DRM achieved comparable H$_2$ prices when compared to SMR without carbon capture (CC), and dramatically lower prices compared to SMR with CC [63]. While H$_2$ prices in a DRM project achieved low values of 1.07-1.32 $$/Kg, SMR H$_2$ prices ranged between 1.07 and 2+ $$/kg, and much higher if a price on carbon is enforced.

In the case where a CC technology is a preferred choice of design for carbon management, the project will incur an associated cost. This approach produces “blue” H$_2$, and to continue the equal comparison to the study basis and results, the Methanator system will be replaced with a CC technology composed of the amine absorption/regeneration unit followed by a CO$_2$ liquefaction system identical to the one selected in the study. This approach includes a crucial assumption that liquid CO$_2$ produced has a practical use; which is not always the case. This choice of CC has resulted in a significant increase in the project capital and operating costs as follows:
Table 7.3: Capital cost, O&M cost, and feedstock cost estimations comparison between a Methanator and a CC design, based on the cost factors considered in the study

<table>
<thead>
<tr>
<th></th>
<th>DRM</th>
<th>Methanator Design</th>
<th>CC Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital Cost, $ Million</td>
<td>220.8</td>
<td>76.5</td>
<td>168.7</td>
</tr>
<tr>
<td>Operation and Maintenance Cost, $ Million</td>
<td>76.5</td>
<td>168.7</td>
<td></td>
</tr>
<tr>
<td>Feedstock cost, $ Million</td>
<td>33.4</td>
<td>39.5</td>
<td></td>
</tr>
</tbody>
</table>

By applying the corresponding project cost and carrying out the same analysis conducted previously, the resulting project financial performance is as follows:

**Figure 7.6**: Impact of varying H₂ price at 1% (upper chart) and 1.9% (lower chart) inflation rates for the CC design hydrogen production case on IRR and NPV
It is evident from the above charts that a CC technology incurs a significant increase in capital and operating costs which led to an increase in H₂ breakeven prices. While the minimum H₂ price resulted in the Methanator case at 1.9% inflation rate was 1.11 $/kg, the incorporation of a CC design has increased the minimum price to a 1.91 $/kg; compared to SMR with CC at 2.15 $/kg. This is a clear indication that CC technologies require significant investments in R&D to reduce the associated costs and make them more viable. A more detailed engineering design estimation would be required to compare the Methanator system to CC technologies, and provide more accurate results.

7.3 Impact of Structured Reformer Design

Since structured reactors washcoated with catalytic material typically performs better than conventional packed-bed reactors in the range of 1.4-2.9 times in terms of activity, the main benefit would be a more compact design for industrial applications and hence, a lower capital cost. Therefore, a sensitivity analysis was performed to measure the impact of reducing the capital cost of the Reformer on the breakeven H₂ price (Zero NPV) for the blue hydrogen case. The analysis was carried out at both, 1% and 1.9% inflation rates, with Reformer cost reduction of 10%, 30% and 50%. The below figure 7.7 summarizes the results:
Figure 7.7: Impact of reducing Reformer cost on breakeven H₂ price at 1% and 1.9% inflation rates for the blue Hydrogen case with a Methanator design

The above chart demonstrates that for the 1% price inflation rate case, the breakeven H₂ price decreases from $1.21/Kg at base case (no reduction in Reformer cost) down to $1.19/Kg at 10% capital cost reduction, $1.14/Kg at 30% capital cost reduction and $1.10/Kg at 50% capital cost reduction. While on the other hand, at a price inflation rate of 1.9%, the breakeven price drops from $1.11/Kg at base case to $1.09/Kg, $1.05/Kg, and $1.00/Kg at 10%, 30% and 50% Reformer cost reductions.

Those collective results suggest that DRM outperforms SMR financially, and it is a viable candidate for a sustainable technology waiting to be advanced commercially in industrial applications. Moreover, the premise of proposing washcoated structured reactors for the DRM applications has been further supported by its positive impact on a project’s financial assessment.
Conclusion and Future Work

**Conclusion**

The work presented in this thesis supports DRM/monolith process as an emerging technology worthy of consideration for further development and commercialization. In view of its close relevance to SMR, the mature technology of today for H\(_2\) production, DRM has the potential to gain a lot of momentum of becoming an industrial mature technology for large scale production of pure H\(_2\) gas while utilizing CO\(_2\) as a reagent. Its advantages revolve around the unique low carbon footprint compared to SMR, and its scalability for large industrial processes. After performing a comprehensive LCA analysis, DRM was found to have overall better environmental indicators. Therefore, the motivation in developing this technology further is well supported.

The experimental research conducted in this project has demonstrated that DRM is a scientifically sound process under the right thermodynamic conditions. The test results showed that catalysts, Ni and Rh, performed well in terms of activity, stability, aging and regeneration. This is supported by the fact that the ratio of these reactants, CH\(_4\) and CO\(_2\), can be adjusted outside of the favorable non-coking regimes. The activity testing of monolithic catalysts has revealed astonishing results supporting the use of catalytically washcoated structured reactors. This is in view of the fact that they exceeded the performance of equivalent powder catalysts as well as catalysts with higher metal loadings. The stability testing, under favorable thermodynamic conditions, concluded that the catalysts performed exceptionally well and phased out the perception that DRM is associated with stability issues. This was confirmed by comparing the stability of the catalyst under higher CO\(_2\) compositions, around 1.5, compared to a typical landfill gas condition. The successful aging and regeneration of the monolithic catalysts paved the way for
understanding the main reasons behind declining activity over time due to coking. It also added to the main features of those catalysts, the ability to be regenerated after a significant reduction in conversion levels. This enables commercial units to be regenerated in-situ and avoids the costs associated with typical turnarounds.

The above results were enhanced by a basic process design and a financial modeling evaluation. The preliminary financial indicators suggest a very profitable process technology. Several variables were considered part of the assessment and when compared to literature, it was concluded that DRM resulted in lower H\(_2\) prices than conventional SMR producing grey H\(_2\). The assessment was extended and the sensitivity analysis of multiple cases of blue hydrogen production were considered; which in turn performed better than SMR with CC. Furthermore, DRM with a CC design was considered and it was found that the breakeven price of “blue” H\(_2\) has dramatically increased in view of the significant capital and operating costs incurred by deploying a CC technology. Until there is a practical and viable use of captured CO\(_2\) that can be widely available, the choice of carbon capture and reduction will still face major challenges. Moreover, since structured reactors are being proposed, a sensitivity analysis was carried out around a reduced capital cost of the Reformer by several folds, yielding even more positive results. This outcome acts as a strong basis for recommending DRM as a viable technology compared to SMR, and it is ready for advancement to the next phase of scale up testing. A more detailed engineering design and financial assessment would be required to produce more accurate results, which can be performed after successful pilot plant testing.
**Future Work**

While activity and short-term stability issues of the catalyst were addressed, it is recommended to explore the Auto-thermal dry reforming (ATDR) operation in the future to eliminate the need for an external energy source for processing the reactants. This step would be advantageous in two folds: first, it tackles the high energy requirement for the DRM reaction to be generated internally while overcoming any radial heat transfer limitations, and second, combustion products, i.e. CO and CO$_2$, can be converted in the shift converters and then methanated in the downstream operation units; this would drastically reduce the overall CO$_2$ equivalent emissions from the process plant. A disadvantage is the cost of O$_2$-N$_2$ separation for pure O$_2$ production, as indicated by the relatively large capital cost of ATR in the financial analysis presented earlier.

In view of the success of bench-scale testing, this research outcome is proposing DRM, and potentially ATDR, to be tested in a pilot plant scale along with real-life Natural Gas feedstock. This level of testing would bring the performance closer to commercial levels and a successful outcome would be very appealing to operators and investors worldwide. In this scheme, the structured reactor would be between 10-100 times larger than the magnitude tested in this research and would have amounts of catalytic material roughly 3-30 grams coated on the walls; this would enable higher throughputs to be tested. Additionally, a real-life sample of Natural Gas would be beneficial in estimating a closer to accurate life cycle of the catalyst under the subject conditions and the impurities present in the feed. Three industrial pilot plants for DRM under CO$_2$:CH$_4$ ratio of 1 have been reported, namely: Linde Pilot Reformer, a collaboration between Linde and BASF, as well as SPARG and CALGOR plants [15]. The recommended pilot plant testing in this thesis would add a significant advancement to the DRM technology.
A full extensive patent review will play a major role in the success of dry reforming as an emerging commercial technology. Since the preliminary patent review revealed that the extensive focus is on catalytic formulations, including active metals, support material, and promoters, there is great potential in aligning the effort towards patenting novel process designs and potential licensing capabilities. This can be done by capitalizing on the expired patents, greater than 20 years of age, and proposing more specific formulations and operating conditions. Consequently, a patentable area could arise if the focus is given to developing a specific process design, with CO$_2$ recycle for instance, and with narrow ranges of operating conditions based on experimental results, catalytic material compositions, structured reactors designs and installations.

Once the pilot plant scale tests prove effective, this work can be further expanded by collaborating with an engineering design company to provide a practical design for the structured Reformer with an accurate estimate of the capital and operating costs. This would close the loop on the technical and economic viability of this process technology, and a demonstration plant can then be pursued by companies interested in blue Hydrogen production.

Finally, policy reforms; once the engineering design and demonstration plants turn out to be successful, DRM, and ATDR, would be proposed as viable replacement for SMR and ATR in future projects. Central environmental protection agencies can then lay down carbon credit requirements and incentives as motivation to drive sustainable technologies forward. In this case, DRM would be advertised as the optimal choice of process technology needed to produce blue Hydrogen at industrial large scale. Several countries have established Hydrogen strategies with committed investment funds to drive it forward. For instance, Germany announced its national hydrogen strategy in 2020 with around 10.3 billion USD of committed investment. Similarly, France and Japan announced their hydrogen strategic roadmaps in 2019-2020 with 8.2 billion USD
and 6.5 billion USD of dedicated investment funds, respectively [1]. Furthermore, Saudi Arabia is currently constructing a $5 billion project of green Hydrogen in NEOM planned to be commissioned in 2026 [66]. Additionally, the country is planning to become the largest Hydrogen producer in the world [67], considering its great resources and potential for green and blue Hydrogen production at low costs [1].

In the above context, DRM can positively impact those strategic plans once it is proven commercially. It can be considered as a replacement for SMR with CC projects, and take the lead on all blue Hydrogen projects constructed worldwide. An outlook at the future can picture a global Hydrogen market divided by blue Hydrogen from DRM and green Hydrogen by Electrolysis; depending on the geographical location and available resources.
References


4357 (2008).


60. María Ibáñez a, Oihane Sanz a, Ane Egan a, Inés Reyero, Fernando Bimbela, Luis M. Gandía, Mario Montes, “Performance comparison between washcoated and packed-bed monolithic reactors for the low-temperature Fischer-Tropsch synthesis”, Chemical Engineering Journal 425 (2021) 130424


