

INTEGRATION OF SOLAR PHOTOVOLTAICS AND WATER ELECTROLYSIS
FOR TUNABLE AND SUSTAINABLE SYNGAS PRODUCTION

A Thesis

by

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ABSTRACT

Synthesis gas is chemical intermediate used to produce liquid fuels, methanol, ammonia, and other chemical products. This work assesses a novel design that incorporates solar energy and water electrolysis in the production of synthesis gas. To assess this design, two case studies are performed: one which uses economic benchmarking to justify the use of solar energy and water electrolysis, and one which performs a techno-economic analysis of the proposed design in synthesis gas and methanol production. These case studies conclude that the proposed design is capable of producing 3336 tonnes per day of methanol with an annual return on investment (ROI) of 29.90. This work concludes with the recommendation that the proposed design has potential to be an economically viable option for synthesis gas production, and further studies on marketing, safety, and applications with other alternative energies should be pursued.

DEDICATION

This thesis is dedicated to my sister, Nicolette Campbell, for her unwavering support in me and constant example of how to hold strong and persevere through tough times with beauty and grace. While I might be the older sister, I am so fortunate to have a younger sister that I can look up to.

I would also like to thank my parents, Midori and Oliver Campbell for their guidance, encouragement, and support of my goals and dreams. I would like to thank my brother, Mitchell Campbell, for never failing to make me laugh and smile. And I would like to thank Travis for his constant encouragement, love, and support.

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CONTRIBUTORS AND FUNDING SOURCES

Contributors

This work was supervised by a thesis committee consisting of Dr. El-Halwagi and Dr. Hasan of the Department of Chemical Engineering and Dr. Mannan of the Department of Petroleum Engineering.

All work conducted for this thesis was completed the student independently. There are no outside funding contributions to acknowledge related to the research and compilation of this document.

NOMENCLATURE

ATR	Autothermal Reforming of Methane
C_p	Specific Heat Capacity
CF	Cubic Feet
CR	Combined Reforming
DMR	Dry Reforming of Methane
EGP	Economic Gross Potential
FCI	Fixed Capital Investment
FOB	Free On Board
GAMS	General Algebraic Modeling System
ΔH	Change in Enthalpy
LCOE	Levelized Cost of Electricity
IROI	Incremental Return on Investment
\dot{m}	Molar Flow Rate
MISR	Metric for Inspection Sales and Reactants
NP	Net Profit
P	Pressure
POX	Partial Oxidation of Methane
PV	Photovoltaic
ROI	Return on Investment
S	Entropy
SMR	Steam Reforming of Methane

T	Temperature
TES	Thermal Energy Storage
TCI	Total Capital Investment
USD	United States Dollars
WES	Water Electrolysis
WCI	Working Capital Investment

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1. BACKGROUND

There is a constant global drive to seek improvements in any given process; there is a pressing question of how that something can be re-worked to be made better. In everyday life, this desire for improvement can be seen with the increase in smart technologies connections and utilization. On the industrial scale, the desire for improvement can be seen in the drive for improved energy efficiencies.

Going hand-in-hand with improvement, sustainability is a growing theme across the globe. Sustainability is multidimensional concept, encompassing a balance of environmental, social and economic factors ¹. Sustainability is significant because it allows people and industry across the globe to meet their present-day quantity and quality demands without compromising the quantity and quality of the future.

This work encompasses the theme of sustainability to assess alternative methods of producing synthesis gas. Here, a novel and alternative design of producing synthesis gas, and applicable downstream products, is presented by combining solar energy with abundant shale gas resources. To objectively assess the potential of this design, two case studies assessing the economic implications of the design are performed. This work demonstrates that other methods of producing synthesis gas are not only possible, but can be superior over traditional practices. The following subsections provide a comprehensive overview of the history, concepts, and details involved within this work.

1.1 Solar Energy

Solar energy is the fastest growing method of energy production across the globe². Since 2013, there has been a significant trend of solar infrastructure growing and prices falling. In 2016, solar energy was the renewable energy source with the most growth due to significant development and installations of solar farms in the United States and China³.

The interest in pursuing the utilization of solar energy stems from the magnitude of energy that it can provide. Solar energy has the largest potential for energy on earth with a maximum theoretical potential of 89,300 TW of energy. Putting this in perspective, theoretically the sun could provide the entire worldwide energy consumption (430 EJ) in 2011 in just ninety minutes⁴. Thus, due to large energy supply and potential of solar energy, it is critical to assess and consider solar energy in all present and future discussions on how to meet the world's growing energy demands.

Historically, electricity produced using solar photovoltaics has not had a high economical potential. However, through developments through the Department of Energy and the National Renewable Energy Lab, affordable electricity via photovoltaics is becoming a reality. One particular program series, the *SunShot2020* and *SunShot2030* series, has been working to bring the unsubsidized and levelized cost of energy (LCOE) for utility-scale electricity produced by photovoltaics (PV) down to \$0.06 per kWh by 2020 and \$0.03 per kWh by 2030⁵. These prices would be competitive with electricity prices from the grid.

In addition to photovoltaics, using solar energy with thermal energy storage (TES) has also been a developing area in renewable energy. With TES, solar energy is collected and stored in some heat transfer medium—often molten salts. That medium is then sent to a heat exchanger where it can generate steam, which in turn can be used to produce electricity ⁶. While TES has a relatively low energy efficiency, improvements in the TES two-tank and thermocline systems, as well as advancements in the properties of the thermal salts, are being made with recent projections of achieving an LCOE of \$0.05-\$0.07 per kWh (\$USD) ⁷.

The recent interest and advancements in both PV and TES, and global rapid growth of solar fields, it is critical to assess how solar energy will be integrated into existing processes and everyday life moving forward.

1.2 Shale Gas Growth and Monetization

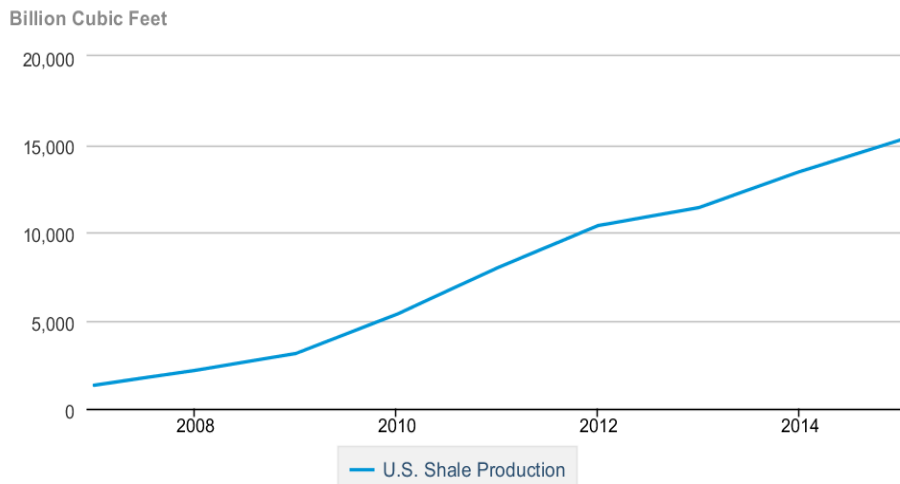
Shale gas is natural gas trapped within shale formations. Like all natural gas, shale gas is primarily comprised of methane, though heavier components such as ethane, propane, butane, and inorganic gasses, such as nitrogen, carbon dioxide (CO₂) and hydrogen sulfide (H₂S) are present as well ⁸.

The presence of shale gas has been known for centuries, with the first shale well constructed in 1821 in Frederick, New York ⁹⁻¹⁰. However, limitations in technology prohibited shale gas extraction and utilization from being economical ¹⁰. It was not until advancements made in horizontal drilling and hydraulic fracturing by Mitchell Energy & Development (now Mitchell Energy) in the early 2000s, and the development of the

Barnett Shale Play, that shale gas production was able to grow and become a key player in the energy industry ¹¹.

Since the advancements in hydraulic fracturing and horizontal drilling, shale gas has been growing in production and utilization over the past decade. From 2010 to 2015, shale gas flows nearly tripled, increasing from five to fifteen billion cubic feet. An illustration of the rapid growth of shale gas can be seen in Figure 1. The rapid growth of shale gas is significant because it provides an abundant resource of feedstock for many different chemical processes, including synthesis gas ^{8, 12}.

U.S. Shale Production



 Source: U.S. Energy Information Administration

Figure 1: Shale Gas Growth in the United States Since 2007 (Reprinted from ¹³)

While many shale plays are found throughout the United States, they are also found globally, with significant shale gas resources in China and Argentina ¹⁴. As a prominent, relatively new, and rapidly growing global resource, it is important to assess the potential applications and chemical pathways that utilize components of shale gas, and how shale gas contributes to industry.

1.3 Synthesis Gas

Synthesis gas, often referred to as syngas, is a gaseous mixture comprising of hydrogen (H_2) and carbon monoxide (CO) gasses. Syngas is a valuable chemical product because it can be used in the synthesis of liquid fuels and a variety of chemicals, including methanol and acetic acid. This is because the CHO (Carbon-Hydrogen-Oxygen) present within syngas can provide the backbones to these numerous other demanded chemicals.

The ratio of $H_2:CO$ in the syngas product is variable and dependent on the desired downstream chemical product. For example, syngas can be used to create methanol, which contains CHO in a 1:4:1 ratio. Thus, for methanol production a syngas $H_2:CO$ ratio of 2 is appropriate. Ammonia, on the other hand is comprised largely of hydrogen, so a higher syngas $H_2:CO$ ratio is appropriate when using it to create ammonia. Table 1 summarizes some of the common downstream chemicals that can be produced using syngas.

Table 1: Synthesis Gas Products.

H₂:CO Ratio	Product
1	Formic Acid
1	Acetic Acid
2	Methanol
2	Liquid Fuels (Fischer-Tropsch)
3	Hydrogen
3	Ammonia

1.4 Methane Reforming

In this work, methane reforming reactions combine methane with other chemicals to produce syngas. The most common methane reforming reactions are the Steam Reforming of Methane (SMR), Dry Reforming of Methane (DMR) Partial Oxidation of Methane (POX), and Autothermal Reforming (ATR), which is a combination of SMR and POX. The reactions for SMR, POX, and DMR are summarized respectively shown in Eq. 1, Eq. 2 and Eq. 3 ¹⁵.





Challiwalla et al. introduced an extensive analysis on the combination of the three methane reformers—SMR, POX, and DMR—in a fashion known as Combined Reforming ('CR'). Combined reforming combines the exothermic property of POX with the endothermic properties of DRM and SRM to reduce heating utilities, and has additional environmental benefits such as CO₂ utilization¹⁶. With combined reforming, extra care needs to be taken to ensure carbon formation (coke) does not form on the catalyst and inhibit the reactions. While catalyst developments have prohibited CR and DMR from commercialization and utilization, active catalyst research is being performed so these technologies can be implemented.

The Enthalpy of Reaction (ΔH_{rxn}) for SMR, DMR, and POX are shown in Table 2. Here it can be seen that both SMR and DMR are endothermic reactions, while POX is mildly exothermic. This is significant because the exothermic properties of POX can be used to drive the endothermic SMR and DMR reactions, such as is often seen in ATR and CR.

Table 2: Heat of Reaction for Methane Reformers

Methane Reformer	ΔH_{rxn} (kJ/mol)
SMR	206
DMR	247
POX	-36

Like all reactions, the extent of reaction with the methane reformers can vary under different temperature and pressure conditions. Understanding the extent of reaction is significant because the syngas $\text{H}_2:\text{CO}$ ratio of the syngas product is an important detail with downstream chemical processing. A thermodynamic approach can be taken to estimate the extent of reaction for the methane reformers under various operating conditions using the method of Gibbs Free Energy Minimization.

1.5 Water Electrolysis

Water Electrolysis is an established source for hydrogen production and is responsible for 4% of the global hydrogen production¹⁷⁻¹⁸. The water electrolysis process operates by providing energy to water, resulting in the water molecule splitting into hydrogen and oxygen gasses. This reaction is shown in Eq. 4.



While the setup of each electrolyzer is variable, all electrolyzers consist of an anode, where the water is oxidized to produce hydrogen gasses, a cathode, where water is reduced to produce oxygen gas, and a source of a high voltage, which drives the oxidation and reduction reactions. These half reactions are summarized in Eq. 5 and Eq. 6.



The theoretical minimum amount of energy required to produce 1kg of hydrogen from water electrolysis is 285.8 kJ, which is equivalent to 39.4 kWh. Compared to current technology which requires approximately 52 kWh to produce 1kg of hydrogen, there is clearly room for improvement for electrolyzer efficiency improvements. This efficiency issue is being actively researched and there is a demonstrated downward trend in the energy requirements for electrolysis for both Polymer Electrolyte Membrane/Proton Exchange Membrane (PEM) and Alkaline electrolyzers ¹⁹.

Water electrolysis' significant energy requirements and electricity expenses have traditionally been the cost prohibitive factors from making water electrolysis a more prominent process. The average cost of electricity, produced by coal consuming turbines, holds around \$0.10 per kWh ²⁰. At this price, and the electrolyzer requiring 50kWh to produce 1 kg of hydrogen, it costs \$5.00 alone in electricity expenses to

produce 1 kilogram of hydrogen. If pure hydrogen is selling at a price of \$2/kg, this is not economically sustainable. Lowering electricity prices is essential if water electrolysis practices are to ever grow.

Water electrolysis is known as a potential source for hydrogen, but the oxygen product is often ignored. While oxygen has fewer direct energy applications than water electrolysis, it still has does have a value as it can be used as a product in the medical field and as a feed for the POX reaction, which is further discussed below. In this design, using the oxygen product from water electrolysis as a feed for the POX reaction has the benefit of being able to be produced on site and on demand and reduce raw material costs.

Furthermore, oxygen separation from air is expensive. Traditionally, oxygen is separated from air through cryogenic separations or a pressure swing adsorption setup, both of which have their own affiliated equipment and operation costs ²¹. Thus it is reasonable to assume that the oxygen product be considered as a valued product in assessing the economic viability of water electrolysis.

2. PROBLEM STATEMENT

Global energy demands are rapidly increasing. With the global population expected to exceed 9 billion by 2040, the demands and requirements for energy production, storage, and distribution are predicted to only increase. To meet these demands, new and optimized processes will need to be developed and implemented. This work presents a novel design incorporating solar energy and water electrolysis in conjunction with established methane reforming processes to produce synthesis gas and applicable downstream chemicals, demonstrating how solar energy can be captured and used to store energy in the form of chemicals.

This work shows that with a known feed availability, feed purchase cost, downstream product selling cost, heating, cooling, and electricity costs, and determined amount of downstream product produced, an annual Return on Investment can be calculated. To demonstrate this, two case studies are provided to justify the incorporation of water electrolysis in this design and demonstrate how the presented design can be an economically viable method for chemical production and solar energy storage.

3. PROPOSED DESIGN

The methane reforming reactions, water electrolysis, and solar energy are known technologies that have been, and still are, researched both individually and coupled together. An example of this coupling is the integration of POX with SMR and DMR. However, a collaborative design incorporating all of the following components has yet to be implemented in both research and in industry. This design addresses the concern of how to incorporate abundant resources of shale gas and solar energy, use them in a sustainable way to produce syngas, and then use the syngas in downstream chemical processing. In this way, energy from two abundant resources, shale gas and solar energy, is being stored in the form of chemicals. This work proposes a design, which is referenced as “proposed design” hereafter, that incorporates the following key components:

- Solar energy collection and utilization in forms such as, but not limited to, solar photovoltaics and thermal energy collection
- Shale gas feed and utilization
- Water electrolysis used to produce separate oxygen and hydrogen streams; the hydrogen stream is directly added to syngas and the oxygen stream is used for the POX reaction
- Storage and dispatch for electricity, oxygen and hydrogen products
- Methane Reforming (SMR, DMR, POX)

- Combining products of water electrolysis and methane reforming to create a tunable H₂:CO ratio to suit the desired chemical product
- Mass and Heat Integration with downstream chemical processing
- Skid mounting and mobility of the proposed design

These key components are illustrated in Figure 2.

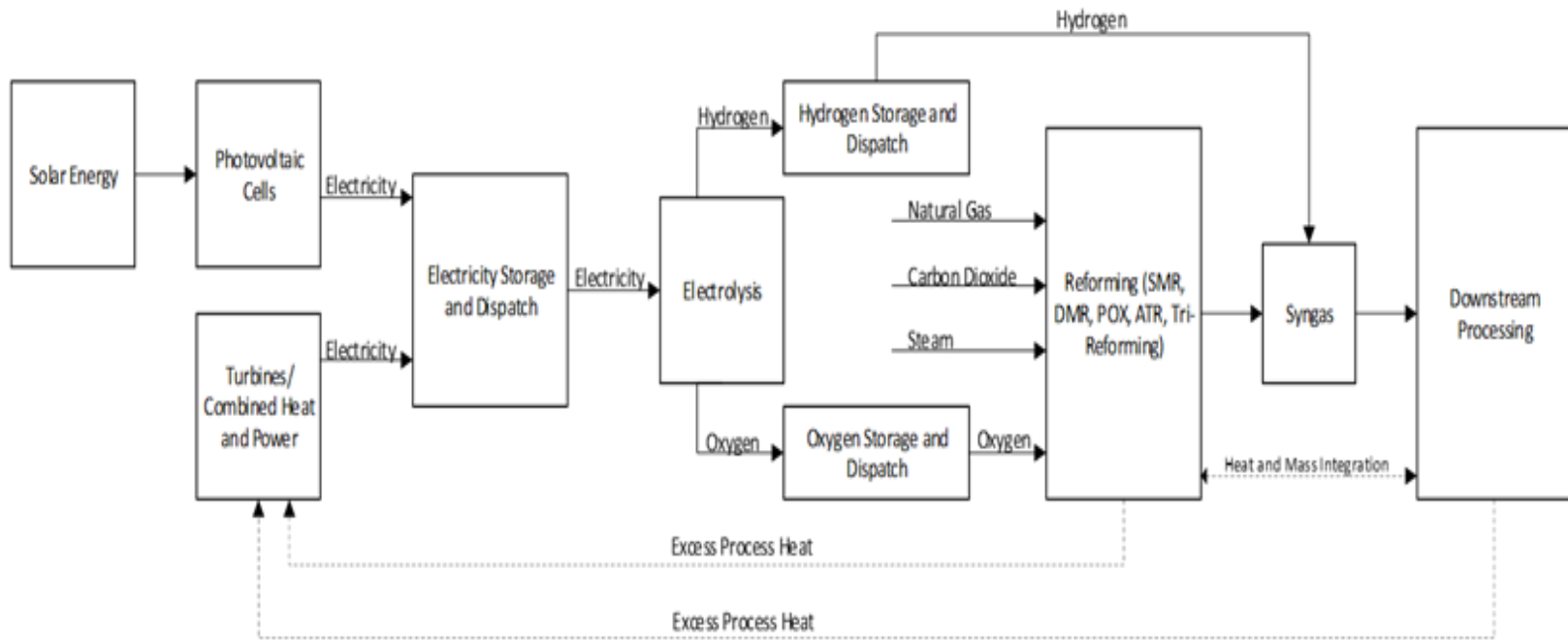


Figure 2: Proposed Design Diagram (reprinted from ²²)

In this figure, solar energy is collected and transferred to electricity. Methods of solar energy collection storage are inclusive of both photovoltaic cells and thermal collectors, as well as any other forms of solar energy collection and storage. In the event of inadequate solar coverage, cogeneration units can also be used to produce electricity and transfer it to electricity storage and dispatch. Next, electricity is used to power water electrolysis, using either a solid oxide, PEM, or any other form of electrolyzer, to separate water into separate, gaseous oxygen and hydrogen components. Both the oxygen and hydrogen products are stored separately and dispatched appropriately. The oxygen gas is distributed to the methane reforming for POX, and the hydrogen gas is distributed directly to the syngas product.

Using the product gasses from water electrolysis, the feed for the methane reformers are used to produce syngas in a determined $H_2:CO$ ratio. In this case, the hydrogen gas component from water electrolysis is particularly significant because it is used to fine-tune and adjust the $H_2:CO$ syngas ratio. Syngas is then used in downstream processing for chemical or liquid fuel production as applicable.

This design also allows for heat and mass integration throughout the design where appropriate. An example of potential heat integration is if the proposed design is incorporated into methanol production, and excess process heat from the highly exothermic methanol reaction is used to satisfy some of the heating requirements of the methane reformers. An example of potential mass integration is use of wastewater from shale gas horizontal fracturing being treated and used to satisfy feed requirements.

In addition to the points listed above, the design is able to be skid-mounted and mobile in order to access shale gas resources that are detached from the power grid and pipeline. This feature is critical in the ability to access and utilize all potential shale gas resources, including stranded shale gas, that would otherwise go unused. However, while it can be skid mounted and mobile, it is also able to be incorporated to existing syngas producing processes to fine-tune the H₂:CO syngas ratio.

The collection and collaboration of all of the points above are what make the proposed design unique. To this date, no patents have addressed all of the aforementioned points. Research publications have assessed portions of all aforementioned points, but have yet to encompass all of the points together.

4. METHODOLOGY

4.1 Methodology Overview

A comprehensive approach was taken to assess the economic benefits and disadvantages to the design proposed in Section 4. Figure 3 illustrates the steps taken within this work.

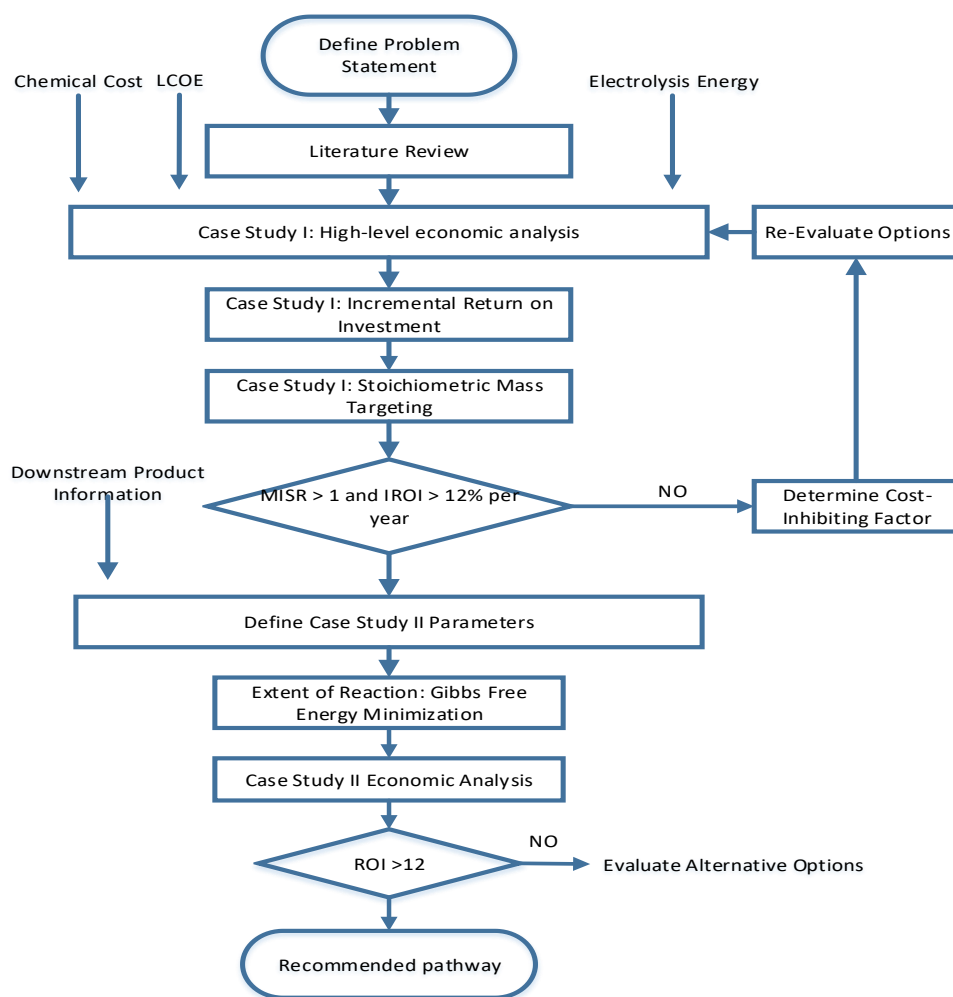


Figure 3: Methodology Process Flow Diagram

First, the problem statement was defined followed by a comprehensive literature search and review on components relevant to the problem statement. Using this information, a case study was performed to justify the use of water electrolysis from an economic standpoint with emphasis on a favorable annual incremental return on investment (IROI), of over 12%, and stoichiometric mass targeting, with a Metric Inspecting Sales and Reactants (MISR) of over 1. Conditions and assumptions about the LCOE, cost of chemicals, and electrolyzer energy requirements were re-evaluated and redefined until both conditions were satisfied.

Using the results from Case Study I, a second case study was performed implementing the proposed design to produce a downstream chemical. For this work, methanol was selected to be the assessed downstream chemical. To better understand the incomplete methane reforming reactions, a thermodynamic approach—Gibbs Free Energy of Minimization—was taken to determine the optimal operating parameters and product formation for the methane reforming reactions. This information was applied to a General Algebraic Modeling System (GAMS) script to determine the optimal feed to each of the methane reforming reactions to maximize the annual Return on Investment (ROI). This information was further applied to conduct a comprehensive economic analysis to determine if this design could satisfy the set hurdle rate requirements. Further sensitivity analyses on the effects of economies of scale, LCOE, and methanol selling price was performed to determine their influences on the annual ROI. The results from

Case Study I and Case Study II were then collectively used to conclude if this proposed design was favorable from an economic perspective.

4.2 Case Study I: Economic Benchmarking

To subjectively assess the proposed design, economic benchmarking tools were used and a case study was conducted. First, calculations of the Metric Inspecting Sales and Reactants (MISR), Economic Gross Potential (EGP), and Incremental Return on Investment (IROI) were performed for water electrolysis alone and then for stoichiometric benchmarking to demonstrate economic potential of the proposed design.

Initial economic benchmarking was performed on the water electrolysis component of the design, and the general overall design to demonstrate that this design showed potential to be economically sustainable. As a high-level analysis of the proposed design, the MISR, EGP, and IROI calculations were performed^{1, 23}. After these economic benchmarking calculations, general stoichiometric mass targeting was performed to predict which methane reformers would likely be utilized for various H₂:CO syngas ratios and justify the use of water electrolysis in this design.

4.2.1 Metric Inspecting Sales and Reactants

The MISR, shown in Eq. 7, measures the ratio of the value of the products against the cost of feed. If the MISR is greater than 1, it indicates that there is potential for the process to be economically sustainable. If the MISR is less than 1, it indicates that the process is not profitable and, consequently should not be pursued. When using the MISR to evaluate the economic prospect of multiple designs, the design resulting in the highest MISR should be investigated first¹.

$$\text{MISR} = \frac{\sum_{p=1}^{N_{\text{products}}} \text{Annual Production Rate of } p \times \text{Selling Price of } p}{\sum_{r=1}^{N_{\text{reactants}}} \text{Annual Feed Rate of } r \times \text{Purchase Price of } r} \quad \text{Eq. 7}$$

4.2.2 Economic Gross Potential

The Economic Gross Potential (EGP), like the MISR is another high-level benchmarking tool to evaluate the economic potential of a reaction or design. The EGP, shown in Eq. 8, measures the difference between the selling price of the product and the purchased cost of the reactants. If the EGP is greater than 0 it indicates that products are worth more than the reactants, and therefore potentially profitable from a material basis, and the reaction is worth further investigation. Like the MISR, when comparing several potential reactions or designs, the EGP with the greatest value is the one to be assessed first for further investigation.

$$\text{EGP} = \sum_{p=1}^{N_{\text{products}}} \text{Annual Production } p \times \text{Selling Price of } p - \sum_{r=1}^{N_{\text{reactants}}} \text{Annual Feed } r \times \text{Purchase Price of } r \quad \text{Eq. 8}$$

4.2.3 Incremental Return on Investment

Syngas, methane reforming, and methanol production are not new technologies or processes. The proposed design in this work uniquely assesses water electrolysis as a component in shale gas to syngas and shale gas to methanol production. However, to ensure the water electrolysis “enhancement” is appropriate and profitable, an

Incremental Return on Investment (IROI) is performed on the water electrolysis unit alone. The IROI is defined in Eq. 9.

$$\text{IROI} = \frac{\text{Incremental Annual Net (after-tax) profit of add-on project}}{\text{Incremental TCI of add-on project}} \quad \text{Eq. 9}$$

The IROI on water electrolysis is assessed with only hydrogen as a product, and with both hydrogen and oxygen as a product. While the value of hydrogen is several times that of oxygen on a per weight basis, oxygen is actually the main product of water electrolysis, comprising of approximately 90% of the product stream on a per weight basis. Because of this, it is important to consider the value of the oxygen stream in water electrolysis.

4.2.4 Stoichiometric Mass Targeting

To preliminary assess the proposed design, the EGP, MISR, and selection of feed for water electrolysis and methane reformers was determined for three separate H₂:CO ratios of 1, 2 and 3. To assist with the optimal feed selection, a software, GAMS, with the *Antigone* solver, was used²⁴. The purchase and selling prices of the chemicals are provided in Table 3 and Table 4, respectively²⁵. The following assumptions were also made:

- All reactions go to completion
- The reactions assessed here are DMR, SMR, POX, and WES

- H₂ and CO are the only products in each reaction (elementary stoichiometry only)
- Electricity is available at an LCOE of \$0.03/kWh. This is the target LCOE using solar photovoltaics as set forth by the United States Department of Energy for 2030.
- The electrolyzer is operating at the theoretical minimum (285.8 kJ) to split one mole of water.
- Feed is available at 5000 kmol/hour for water, carbon dioxide, and methane

Table 3: Purchased Price of Chemicals for Stoichiometric MISR Benchmarking

Purchased Prices (\$/tonne)	
Methane	156.48
Carbon Dioxide	0.00
Water	1.50

Table 4: Selling Price of Chemicals for Stoichiometric MISR Benchmarking

Selling Prices (\$/tonne)	
Carbon Monoxide	75.00
Oxygen	110.00
Hydrogen	1500.00

The purpose of this benchmarking exercise is to evaluate if using multiple reaction pathways should be considered with this design.

4.3 Case Study II: Methanol Production

4.3.1 Case Study II Overview

To provide a more comprehensive evaluation of the economic potential of the proposed design than the EGP or MISR can provide, a case study was performed. The case study uses solar energy, water electrolysis, and the methane reformers, to produce syngas, which is then used to produce methanol as the final product. An economic analysis was performed to determine the Return on Investment (ROI) as a measure of success for the proposed design. Furthermore, sensitivity analysis' on the scale of production, selling price of methanol, and LCOE were performed to demonstrate their impacts on the ROI. The ROI and respective variables are defined in Eq. 10 and Eq. 11. The ROI hurdle rate in this case study is 12%.

$$\text{ROI} = \frac{\text{Annual Profit}}{\text{TCI}} \times 100\%$$

Eq. 10

$$\text{Annual Profit} = (\text{Annual Income} - \text{Annual Op Ex} - \text{Dep}) \times (1 - \text{Tax rate}) + \text{Dep} \quad \text{Eq. 11}$$

An overview of the assumptions were made to conduct the economic analysis are provided below:

- The FCI was calculated using the six-tenths factor rule for a methanol production plant reported from literature, and addition of water electrolysis equipment.
- Lang Factors for a fluid facility were assumed to estimate the equipment costs and their portion of the FCI.
- The working capital investment (WCI) was assumed to be 15% of the Total Capital Investment.
- A ten-year linear depreciation scheme was used with zero salvage value.
- A 30% tax rate was used.
- Annual operation hours were assumed to be 8000 hours (On-stream efficiency of 91.2%).
- The electrolyzer requires 50 kWh to produce 1 kg of hydrogen.
- Feed is available at 5000 kmol/hour for water, carbon dioxide, and methane
- Gibbs Free Energy Minimization was used to predict the conversions for the methane reforming reactions
- All oxygen product produced from water electrolysis is sent to the POX reformer.

Additional information regarding these assessments are provided in the following subsections.

4.3.2 Methanol Overview

Case Study II used the proposed design with methanol production used as downstream processing. Methanol is a valuable petrochemical used as a feed for production of various chemicals, including liquid fuels, antifreeze, and dimethyl ether. Syngas can be used as a feedstock to produce methanol. Eq. 12, Eq. 13, and Eq. 14 shows the reactions involved in the synthesis of methanol. The third reaction (Eq. 14) is a net overall combination of the previous two reactions (Eq. 12 and Eq. 13) and is highly exothermic. A summary of the heat of reactions for Eq. 12, Eq. 13, and Eq. 14 are shown in Table 5.



Table 5: Methanol Synthesis Enthalpy

Equation	ΔH_{rxn} (kJ/mol)
Eq. 12	-41
Eq. 13	-50
Eq. 14	-91

Methanol has low feedstock conversion as a single pass reaction on its own. To ameliorate this issue, multiple passed loops are often implemented where the initial crude methanol product is cooled, flashed, and degassed before the components are recycled back to the methanol reactor, and increase overall conversion, and the methanol product is redirected to further downstream processing. While single pass methanol conversion is typically between 5-10%, using multiple passes significantly increase conversion²⁶⁻²⁷. This case study assumes with multiple passes are used and the overall methanol conversion is 74%, which is the value Ehlinger et al. had found in their assessment of a natural gas to methanol processes¹².

The selection of methanol as the end product in this case study is appropriate due to the prevalence of research in using methane reforming reactions in methanol production¹². This provides context when interpreting the economic results from the proposed design as the product is in demand.

4.3.3 Water Electrolysis Limitations

To account for reasonable production capacities a limit was placed on how much hydrogen and oxygen could be produced from water electrolysis in the proposed design. It is anticipated that water electrolysis plants will be built to be responsible for producing up to 50 tonnes per day of hydrogen gas, which is equivalent to 400 tonnes per day of oxygen gas, and requires 450 tonnes per day of water ²⁸. Because of this, 50 tonnes per day of hydrogen gas was selected to be the upper limit of hydrogen produced by water electrolysis in this case study.

The water electrolysis unit was assumed to be operating at an efficiency of 78.9%, requiring 50 kWh to produce 1 kg of hydrogen. While it is not realistic that electrolyzer units will ever be operating at 100% efficiency, it is reasonable to assume that electrolyzers will be able to make improvements over their current efficiency of 73%. Assuming a modest efficiency increase of 7% is a realistic projection of what efficiencies water electrolyzers may be operating at in the upcoming years ¹⁹.

It was assumed that the electricity cost (LCOE) was \$0.03 per kWh, reflecting the target of the SunShot 2030 program, and a modest decrease off of the price of the current utility scale price of electricity. As previously mentioned, to assess the how electricity costs influence profitability and the ROI, a sensitivity analysis assessing on the LCOE's impact on the ROI was assessed.

4.3.4 Feed Selection

Feed selection for the case study was built upon the GAMS script and governing equations that been previously used in the economic benchmarking (section 5.2).

However, the script was updated to reflect the true extent of reaction for all of the methane reformers and utility costs affiliated with each of the methane reformers.

4.3.5 Raw Materials and Profit

Beyond the efficiency adjustments made for the water electrolysis unit, the purchase prices for the raw materials were assumed to be the same as those used on the economic benchmarking assessment in Section 5.2.4. The selling price of methanol was assumed to be \$600/tonne¹². A sensitivity analysis was performed to assess the impacts of methanol price on the ROI.

A ‘buy vs make’ approach is also applied to the products from water electrolysis to determine if using water electrolysis, at capacity, to produce hydrogen and oxygen in this scenario is the most cost-effective strategy. Here, the ROI is recalculated two ways: (1) including the electrolyzer equipment, but purchasing the oxygen and hydrogen that would have been produced using water electrolysis, to represent the potential ROI if the water electrolysis equipment is unable to function due to lack of solar energy availability, and (2) without the electrolyzer equipment, and purchasing the hydrogen and oxygen that would have been produced using water electrolysis, to compare it to the base case.

4.3.6 Equipment Size and Cost

To estimate the equipment costs, a broad literature review was performed to find studies and results of methanol production from syngas. The six-tenths rule was applied to economic data from these reports to estimate the FCI scaled to the size of the proposed design. The six-tenths rule is described Eq. 15.

$$FCI_B = FCI_A \left(\frac{\text{Capacity}_B}{\text{Capacity}_A} \right)^{0.6} \quad \text{Eq. 15}$$

While the literature review providing a starting basis to estimate the FCI, because this design is unique, no design was found with all the components presented in the proposed design. To ensure all equipment was estimated, it was assumed that the Lang Factors for a fluid facility could be applied to the FCI, the purchased equipment cost was estimated, and the purchased equipment cost for the remaining equipment (DMR reactor, oxygen and hydrogen storage tanks, water electrolysis units) were added, and the FCI was recalculated.

4.3.7 Operating Expenses

While the water electrolysis energy requirements have been addressed, operating expenses and utilities affiliated with the rest of the proposed design are not an insignificant expense. Unlike the initial economic benchmarking assessment, operating expenses, including heating and cooling utilities, and their impact on economic potential and reformer selection were included in this case study assessment.

To estimate the overall utility requirements, the duties for processing the methane, steam, carbon dioxide, oxygen, syngas, and methanol were determined. It was assumed cooling was available at a cost of \$2.00/MMBTU and heat was available at a cost of \$5.00/MMBTU. Heating and cooling was assumed to have an efficiency of 70% with no heat integration. This was combined with the energy expenses contributed to by water electrolysis, which is explained below, to provide an initial estimation of the

expected utility costs. While this has its limitations, it is justified here as the case studies are evaluating the economic potential from a high-level analysis.

Energy expenses contributed by water electrolysis were separately calculated. The total utility costs were calculated by adding together the electricity costs and requirements for water electrolysis and utility costs for the methane reforming reactions, methanol reactors, and applicable product purification and separation processes.

5. CASE STUDY I: ECONOMIC BENCHMARKING RESULTS

5.1 Initial Economic Benchmarking- Water Electrolysis

Energy requirements affiliated with water electrolysis have traditionally made it a cost-prohibitive technology. Current water electrolysis technologies require approximately 52 kWh to produce 1 kg of hydrogen ¹⁹. With an electricity cost of \$0.06 per kWh, this translates to an additional cost of \$0.35 of electricity per kg water (or equivalently \$3.12 per kg of hydrogen). With a selling price of \$2/kg of hydrogen, this is unprofitable as the electricity price exceeds the value of the product. While cost-prohibitive now, the cost of water electrolysis can be ameliorated through several ways, including:

- using cheaper electricity
- using more efficient water electrolysis technologies
- addressing applications of the gaseous oxygen product produced during water electrolysis

An MISR assessing the economic potential and break even point of the water electrolysis products has been performed using the hydrogen, oxygen selling prices of \$2/kg and \$0.11/kg, respectively ²⁹. Furthermore, for the MISR, it is assumed that the electrolyzer is operating at maximum efficiency and requires 286 kJ per mole of electrolyzed water, and electricity is available at a cost of \$0.03 per kWh.

A sensitivity analysis, shown in Figure 4, of the impact of the LCOE on the MISR for water electrolysis has been calculated to demonstrate the break even point for water electrolysis. Due to the significant expense of energy (electricity) necessary for water electrolysis to occur, the LCOE of electricity is considered a reactant in this assessment.

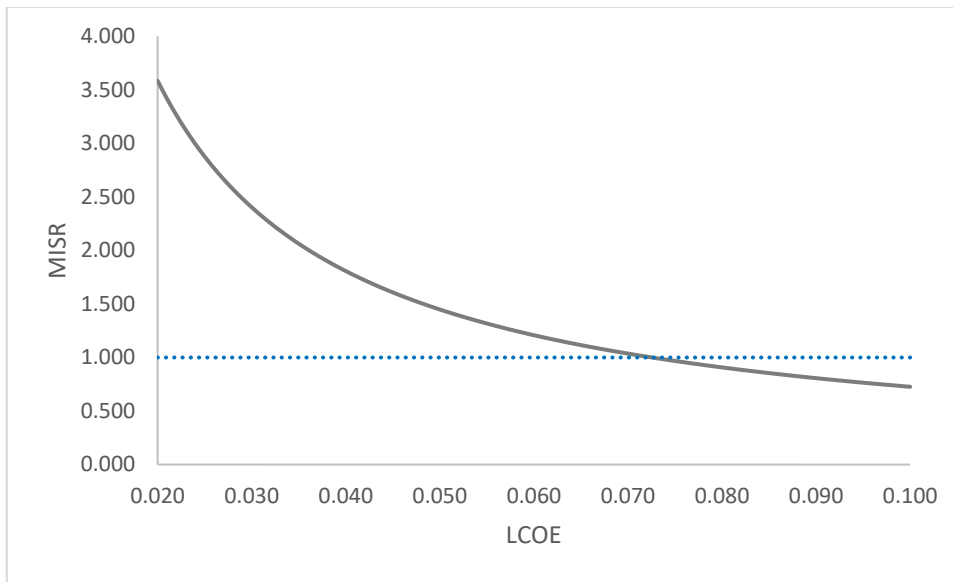


Figure 4: Sensitivity Analysis of Electricity Prices on MISR

As shown in Figure 4, the MISR is equal to 1 at an LCOE of approximately \$0.07/kWh. This means that, at an LCOE of \$0.07/kWh the selling value of the hydrogen and oxygen product is equal to the cost of water and electricity; it is the break even point. The sensitivity analysis also shows that at LCOE prices projected by the *SunShot 2020* and *2030* initiatives, \$0.06 and \$0.03 per kWh, respectively, the MISR indicates that there is potential for water electrolysis to be profitable.

Under the same chemical prices and assumptions as the MISR calculations, a sensitivity analysis on the EGP for water electrolysis was calculated and is shown in Figure 5. Like the MISR, the EGP indicates that the break even point for electricity is approximately \$0.07 per kWh.

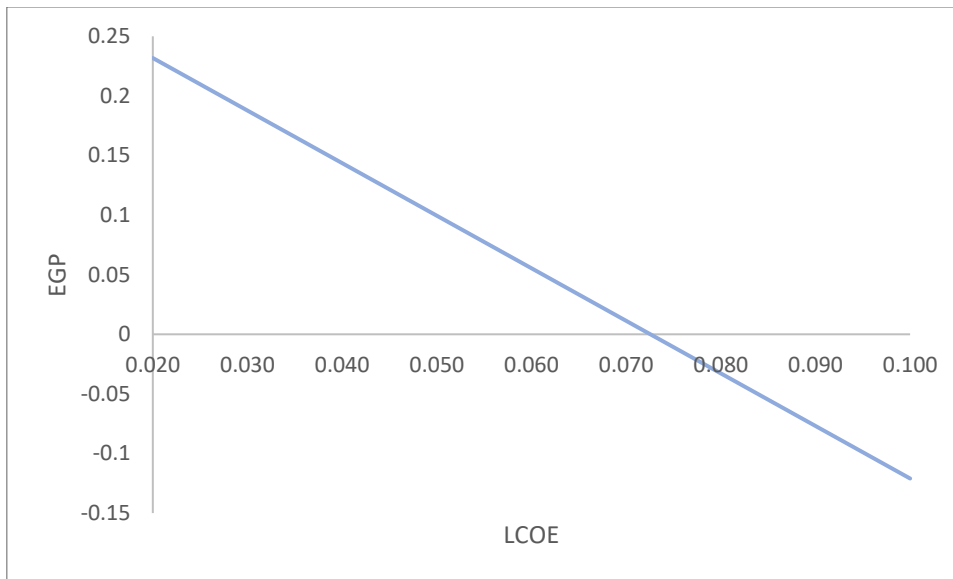


Figure 5: Sensitivity Analysis of Electricity Prices on Water Electrolysis EGP

To further support the idea of incorporating water electrolysis into the design, the IROI was performed on the water electrolysis unit itself using cost estimations reported by the United States National Renewable Energy Laboratory²⁸. The same assumptions for the MISR and EGP (chemical prices, electricity price, electrolyzer efficiency) are also assumed for the IROI calculation, and this base case assumes that five water electrolysis cell stacks are used to produce 50 tonnes of H₂ per day. A seven year depreciation scheme with no salvage value, and tax rate of 30% are assumed. An on-

stream efficiency of 91.2%, and hurdle rate of 12% are assumed. The FCI, TCI, Annual Net After-Tax Profit, and IROI are summarized in Table 6. All prices as \$ USD.

Table 6: Water Electrolysis IROI

	Calculations with Oxygen Product	Calculations without Oxygen Product
FCI (M\$)	60,000,000	60,000,000
WCI (\$M)	150,000	150,000
TCI	60,000,000	60,000,000
Raw Materials	22,300	22,300
Utilities	1,950,000	1,950,000
After Tax Net Annual Profit	11,760,000	1,590,000
IROI (%/year)	19.56%	2.66%

As shown by Table 6, when oxygen is considered as a product, the IROI value increases by nearly six-fold. While the value of hydrogen gas is almost ten times as valuable as the value of oxygen gas on a per-weight basis, on a per mass basis water electrolysis produces much more oxygen than hydrogen, with 112 kg of hydrogen and 888kg of oxygen gas per metric ton of water; the quantity of oxygen produced is not insignificant. Therefore when assessing the economic applications of water electrolysis,

it is critical to consider the value of the oxygen product, which is what the proposed design in this work does.

5.2 Stoichiometric Mass Targeting

To determine what feed was needed and which of the methane reformers to use to produce the desired H₂:CO ratio of 2, a model in GAMS was created. The model operated by specifying the following constraints for chemical species *i* and reaction *j*: available feed, the H₂:CO ratio, heat duties, and water electrolysis limitations. The following constraints were applied:

$$\sum_j f_{in}(i,j) \leq \text{initial}(i) \quad \text{Eq. 15}$$

$$r \times \sum_j f_{outCO,j} = \sum_j f_{outH_2,j} \quad \text{Eq. 16}$$

$$\sum_i (f_{in}(i,j) \times \text{mw}(i)) = \sum_i (f_{out}(i,j) \times \text{mw}(i)) \quad \text{Eq. 17}$$

$$\text{NP} = \sum_j f_{outCO,j} \times \text{cost}_{CO} + \sum_j f_{outH_2,j} \times \text{cost}_{H_2} - \sum_j \sum_i f_{in,i,j} \times \text{cost}_i - f_{inH_2,WES} \times \text{el} \quad \text{Eq. 18}$$

Where Eq. 15 says the sum of molar flows for chemical *i* into process *j*, over all processes *j*, can not exceed the initial availability for chemical *i*. The exception to this the oxygen feed, where the availability of oxygen is the initial availability, zero in this

exercise, plus the oxygen product from water electrolysis. In Eq. 16, the syngas H₂:CO ratio is specified to be fixed to ratio r.

Atomic mass balancing for each atomic species a over each process j was performed under the constraint presented in Eq. 17, where mw(i) is the molecular weight of each chemical species i. The net profit (NP) of the materials was calculated with Eq. 18, where electricity cost affiliated with splitting one mole of water in water electrolysis (WES) was also considered to be a material expense in the MISR and EGP equations.

The MISR and EGP were calculated for syngas H₂:CO ratios of 1, 2, and 3. Both the MISR and EGP were calculated with a base case providing a feed of 5000 kmol/hour of methane, carbon dioxide, and water to be distributed among the reformers, as previously described. It is assumed there are 8000 annual operating hours. Table 7 compares the MISR and EGP values for H₂:CO ratios of 1, 2, and 3. Table 8 compares the reformer selected to be used for these syngas ratios.

Table 7: Economic Benchmarking MISR and EGP Values

H₂:CO	MISR	EGP (\$MM USD)
1	4.09	31.00
2	4.17	33.57
3	4.22	34.13

Table 8: Methane Reformers Selected for MISR and EGP

H₂:CO	MISR	EGP
1	DMR	DMR
2	DMR, SMR	DMR, SMR, WES
3	SMR	SMR

For all syngas ratios, the MISR is greater than 1 and the EGP is greater than 0, indicating that the proposed design has potential for economic success. Table 8 demonstrates there is a difference in the reformers selected when the H₂:CO ratio is 2. The results of this screening suggest that SMR, DMR, and WES be further assessed as part of the design.

While POX was selected, heating utilities and requirements were also not incorporated into this benchmark assessment. POX has exothermic components and benefits, as there is potential for them to be a heat source, so they will still be included in the case study and economic evaluation.

6. CASE STUDY II: METHANOL PRODUCTION RESULTS

6.1 Gibbs Free Energy Minimization

Temperature, pressure, and simultaneous side reactions can alter the extent of reaction for the methane reformers and the expected syngas product composition.

Pressure and temperature also affect additional thermodynamic properties such as the heat of reaction (ΔH_{rxn}), the change in Entropy (ΔS), and specific heat (C_p) of a chemical.

The Shomate Equations, Eq. 20, Eq. 21, and Eq. 22, can be used to recalculate ΔH_{rxn} , ΔS , and C_p over a range of temperatures and for the individual methane reforming reactions. In the Shomate Equations, constants A, B, C, D, E, F, G and H are specific to each chemical species. The parameters used are provided in the Appendix. T is the temperature in Kelvin divided by 1000.

$$H^\circ = H^\circ_{298.15} + AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} - \frac{E}{T} + F - H \quad \text{Eq. 20}$$

$$S^\circ = A \ln(T) + BT + C \frac{T^2}{2} + D \frac{T^3}{3} - \frac{E}{2T^2} + G \quad \text{Eq. 21}$$

$$C_p^\circ = A + BT + CT^2 + DT^3 + \frac{E}{T^2} \quad \text{Eq. 22}$$

With the Shomate Equations calculating the ΔH_{rxn} , ΔS values at a given temperature, the minimum Gibbs Free Energy for each of the methane reformers reactions was performed to determine the extent of reaction and syngas product composition for a range of temperatures and pressures. For all reactions, it was assumed that the feed— $\text{CH}_4/\text{H}_2\text{O}$ for SMR, CH_4/CO_2 for DMR, CH_4/O_2 was introduced in a 1:1 mole ratio—for all of the reactions. It was found that a pressure of 1 atm was ideal for all of the reforming reactions from this thermodynamic perspective. Figure 6 illustrates the effect of temperature on extent of reaction for each of the methane reforming reactions. Figure 7 illustrates the effect of temperature on the $\text{H}_2:\text{CO}$ ratio for each of the reformers.

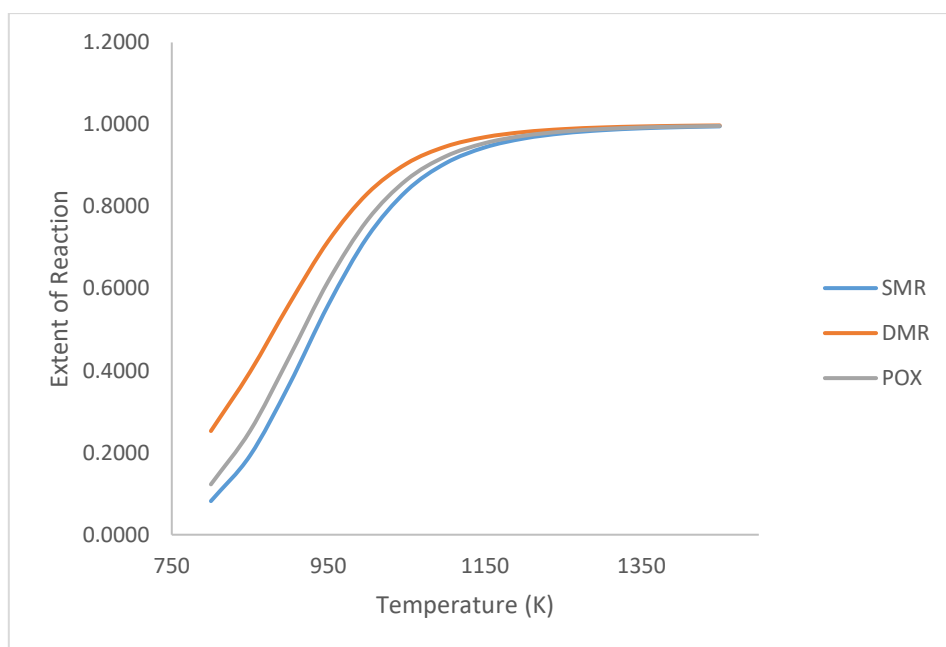


Figure 6: Effect of Temperature on Extent of Reaction

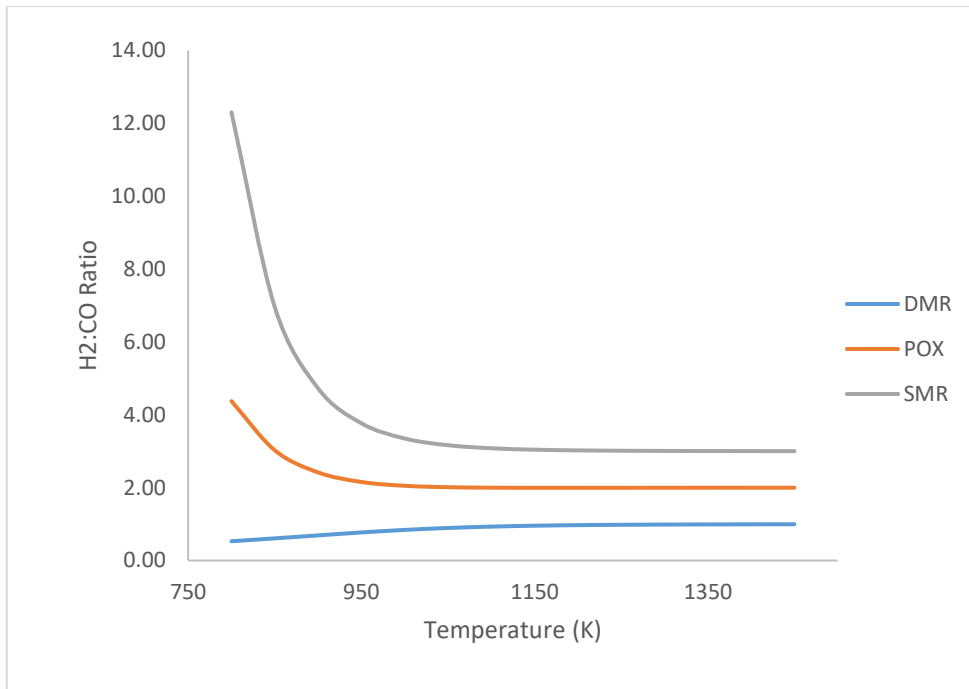


Figure 7: Effect of Temperature on H₂:CO Ratio

Using this information, the optimal pressure and temperature conditions, and resulting syngas product compositions, for each of the methane reformers are summarized in Table 9. The temperature and pressure conditions were chosen to be the lowest temperature and pressure where the H₂:CO ratio was within 1% of the expected H₂:CO ratio.

Table 9: Optimal Temperature, Pressure, Extent of Reaction, and H₂:CO ratio

Methane Reformer	Temperature (K)	Pressure (atm)	Extent of reaction	Actual H₂:CO ratio
SMR	1200	1	0.9442	3.02
DMR	1300	1	0.9928	0.99
POX	1050	1	0.9224	2.00

It should be noted that while utilizing the method of minimizing Gibbs Free Energy to determine conversion and operating conditions is appropriate for SMR and POX, in DMR carbon formations on the catalyst are also a significant product. However, for the purposes of this case study, it is assumed that the catalyst is engineered to inhibit carbon formation. Challiwala et al provides a more in depth discussion on the thermodynamic and kinetic parameters that come into play with modeling carbon deposition on the catalyst in DMR ¹⁶.

6.2 Economic Analysis- Base Case

An economic analysis was performed on the case study after the equipment cost and material cost estimates, and heating utility estimates were made. The assumptions and conditions going into the base case were previously summarized in Section 7. A comprehensive summary of the economic results for this case study are provided in Table 10.

Table 10: Case Study Results

Number of Electrolyzers	50
Total Equipment Cost (\$MM)	223.73
FCI (\$MM)	1275.99
WCI (\$MM)	198.99
TCI (\$MM)	1474.98
Annual Utilities (\$MM)	119.24
Annual Electricity (\$MM)	25.00
Annual Raw Materials (\$MM)	101.12
Annual Net After Tax Profit (\$MM)	401.03
Annual ROI (%/year)	29.90

The calculated ROI (29.90%) for this case study surpasses the hurdle rate (12%), indicating that this proposed system has potential to be profitable with an annual production rate of 738.6 MM tonnes per year of methanol. While overall profitable and surpassing the hurdle rate, the ROI indicates that it will still take 3.35 years for the proposed design to make up the initial investment. Furthermore, the reported ROI for this design is still low in comparison to other similar reported methanol production ROI's that are in excess of 30% and 40% ¹².

However, while this case study presents a slightly lower, but still acceptable, ROI than other syngas or methanol producing plants, this proposed design offers other

benefits that other designs do not, such as providing easy tunability of the H₂:CO ratio for the syngas product, incorporation of a renewable energy, non-reliance of grid-electricity, and utilization of carbon dioxide as a feed source. These benefits should also be considered when determining which design should be implemented in syngas production and relevant downstream processing.

Figure 8 illustrates how the materials, electricity, and utilities compare in their contribution to the variable operating expenses. In this figure, it can be seen that while electricity for water electrolysis is a significant expense to the overall utility costs, accounting for 13% of all variable operating expenses, it is not a dominating expense. In comparison, materials were the dominating variable operating expense, accounting for 52% of the variable operating costs.

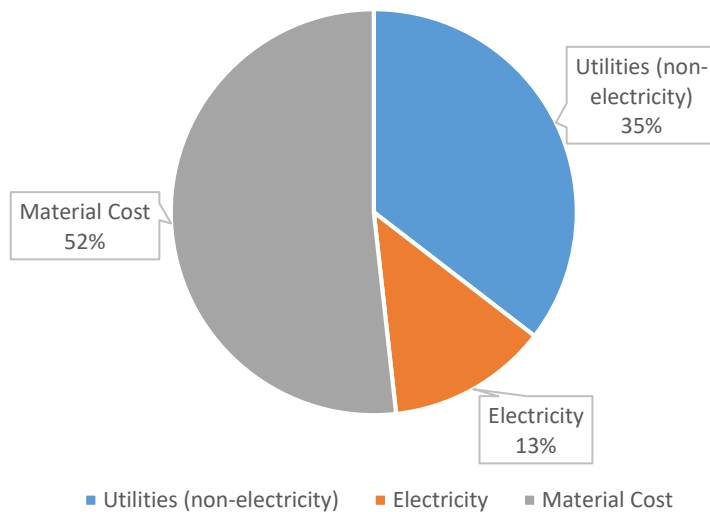


Figure 8: Case Study Variable Operating Expenditures

The contribution of the 50 water electrolysis cell stacks on the overall equipment cost can be seen in Figure 9. While the electricity contributions for water electrolysis are reasonable, the cost of the electrolysis cell stack units are significant. Each electrolysis cell stack has an equipment cost of \$1.2MM and is capable of producing 1 kg of hydrogen per day. This case study used 50 cell stacks—accounting for \$60MM and 27% of equipment cost—making it a considerable portion of the equipment cost. A decrease in the cost of the electrolysis cell stack units can make a significant impact in the decreasing the equipment cost, and therefore the FCI and TCI, and increasing the ROI.

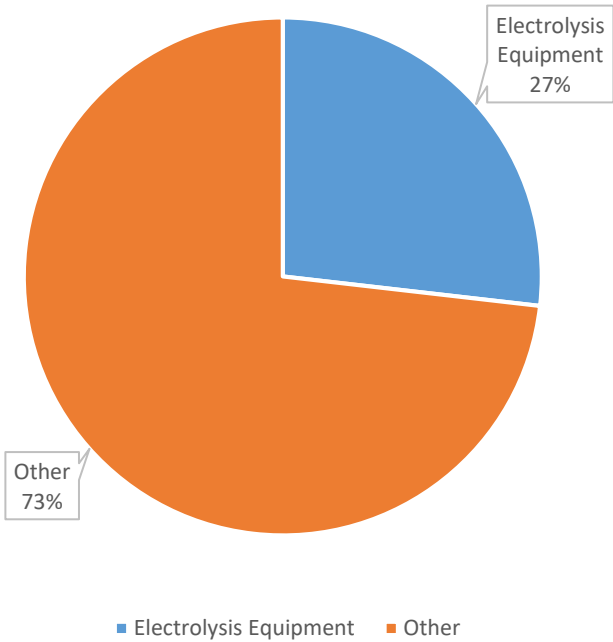


Figure 9: Case Study Electrolysis Equipment Comparison

The GAMS software was used to determine an appropriate feed to the methane reforming reactions to make up the desired 2:1 H₂:CO ratio used to produce methanol for this case study. The resulting feed selection to each of the methane reformers is shown as both kmol/hr and kg/hr in Table 11. This feed was found to be optimal using the methane reforming conversions as dictated by Gibbs Free Energy of Minimization, heating and cooling utilities affiliated with the methane reformer feed and reactions, water electrolysis limitations, and the oxygen feed of the water electrolysis unit being used as a feed for POX. The outlet streams for each of the reformers is shown in Table 12.

Table 11: Case Inlet Streams

	SMR	DMR	POX	WES
CH₄ (kmol/hr)	2309	1660	1031	
CH₄ (kg/hr)	37031	26626	16543	
CO₂ (kmol/hr)		1660		
CO₂ (kg/hr)		73039		
H₂O (kmol/hr)	2309			1031
H₂O (kg/hr)	41602			18585
O₂ (kmol/hr)			516	
O₂ (kg/hr)			16502	

Table 12: Case Study Outlet Streams

	SMR	DMR	POX	WES
CH₄ (kmol/hr)	59	15	57	
CO₂ (kmol/hr)	12	6	19	
H₂O (kmol/hr)	47	9	38	
H₂ (kmol/hr)	6759	3273	1910	1031
CO (kmol/hr)	2237	3298	955	
O₂ (kmol/hr)				516

It is notable that on a per-mass basis, DMR consumes the most feed, including 73039 kg/hr (1660 kmol/hr) of CO₂. This is equivalent to 584,320 tonnes of CO₂ consumed annually. With this significant CO₂ consumption, this design has potential to provide a solution of ameliorating CO₂ emissions, benefiting the environment and surround communities. Further divisions of the feed amongst the methane reforming reactions and water electrolysis on a per-mass basis can be seen in Figure 10.

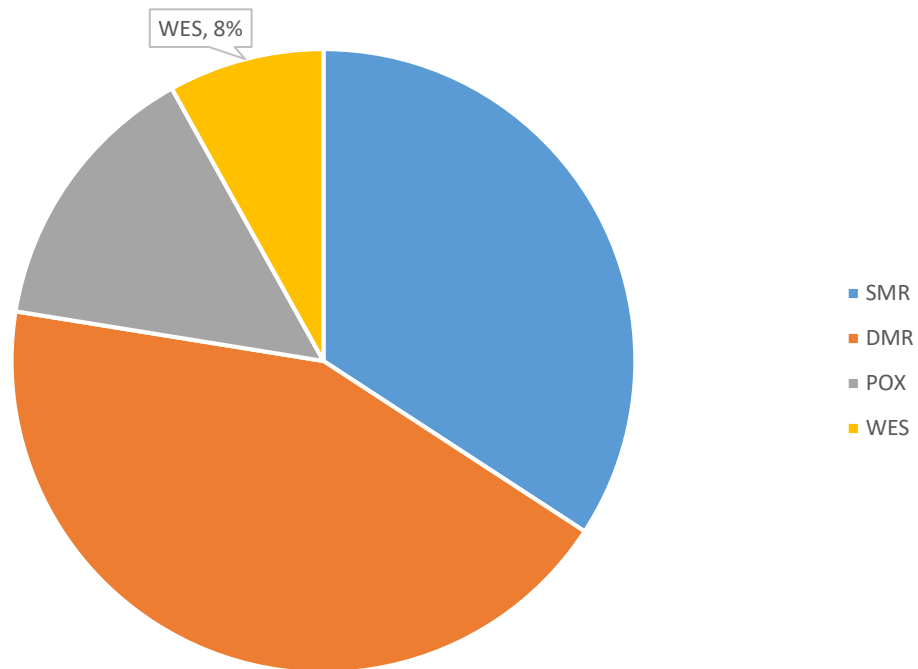


Figure 10: Case Study Feed Mass Fractions

With this configuration, water electrolysis is not the main consumer of water or producer of hydrogen gas component, but it does consume 8% of the total feed on a mass basis, produce all of the O_2 utilized for the POX reformer, produces 8% of the hydrogen gas product by weight, as shown in Figure 11, that is later utilized in the methanol reformer for methanol production. This demonstrates that water electrolysis, while not dominating the syngas and consequent methanol production, does have a significant impact in the processing and synthesis of these products.

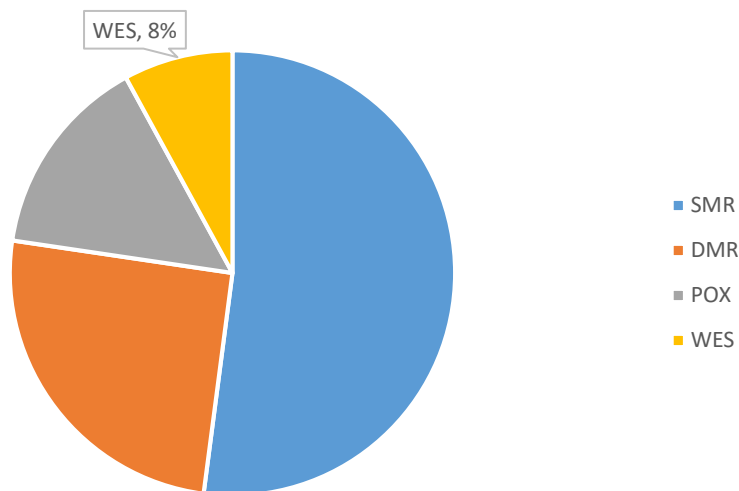


Figure 11: Water Electrolysis Hydrogen Percentage

The annual ROI was also recalculated purchasing the oxygen and hydrogen that would have been produced using water electrolysis, with and without the including the cost of the water electrolysis equipment, to demonstrate the impact on ROI. Under these conditions it was found, including the cost of water electrolysis equipment, the annual ROI would be 29.14, and without the water electrolysis equipment, the annual ROI would be 38.89. This demonstrates that the cost of the electrolysis unit does significantly impact the annual ROI, and, in this design, could be cost prohibitive to pursue in comparison to other design arrangements. Further work assessing sustainability weighted ROI, and safety considerations of not transporting hydrogen, should be assessed to justify the extra expense of the water electrolysis equipment.

6.3 Sensitivity Analysis: ROI and Economies of Scale

The base case assessed the ROI and production scale assuming 50 electrolyzer cell stacks were available. Feed availability for each production scale was based on the assumption that 500 kmol/hr of CH₄, H₂O, and CO₂ was available for every 5 electrolyzer cell stacks. These feeds were chosen so the proportion of water sent to each electrolyzer stack remained fixed throughout the sensitivity analysis. For this sensitivity analysis, cell stacks of 50, 35, 25, and 10 units were selected to demonstrate the effect of plant size on The ROI (%/year) and daily methanol production. Figure 12 shows the effect of the production scale on the annual ROI.

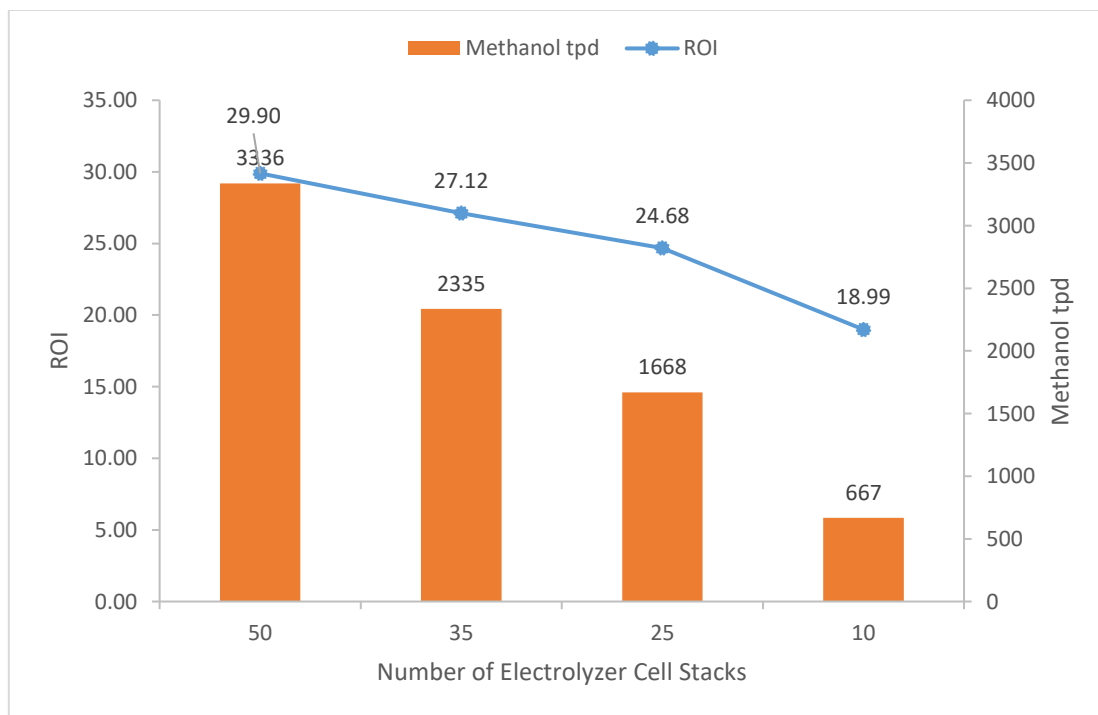


Figure 12: ROI and Economies of Scale

From this figure, it can be seen that the ROI surpasses the hurdle rate of 12% at all capacities, producing 3336, 2335, 1668, and 667 tpd of methanol. This demonstrates the potential profitability at production scales less than the up and coming 5000-1000 tpd methanol plants^{12, 19}. From an economic perspective the economies of scale appear profitable, and leave room for more research regarding the other two pillars of sustainability—environmental and social effects—on the proposed design to determine if it is truly the best pathway. Incorporating environmental and social effects with the design evaluation could further improve the potential ROI.

6.4 Sensitivity Analysis: Electricity Prices

Operational costs affiliated with electricity requirements for water electrolysis are also a significant expense. The case study utilized the *SunShot 2020* project of \$0.03 per kWh target as a goal. With LCOE prices ranging from \$0.03 per kWh, the goal of *SunShot 2060*, to \$0.07 per kWh, the break even point for water electrolysis with water and oxygen both considered as pure product streams, and the electrolyzer requiring 50kWh to produce 1kg of hydrogen, it was found that the ROI maintained above the 12% threshold. This is shown in Figure 13.

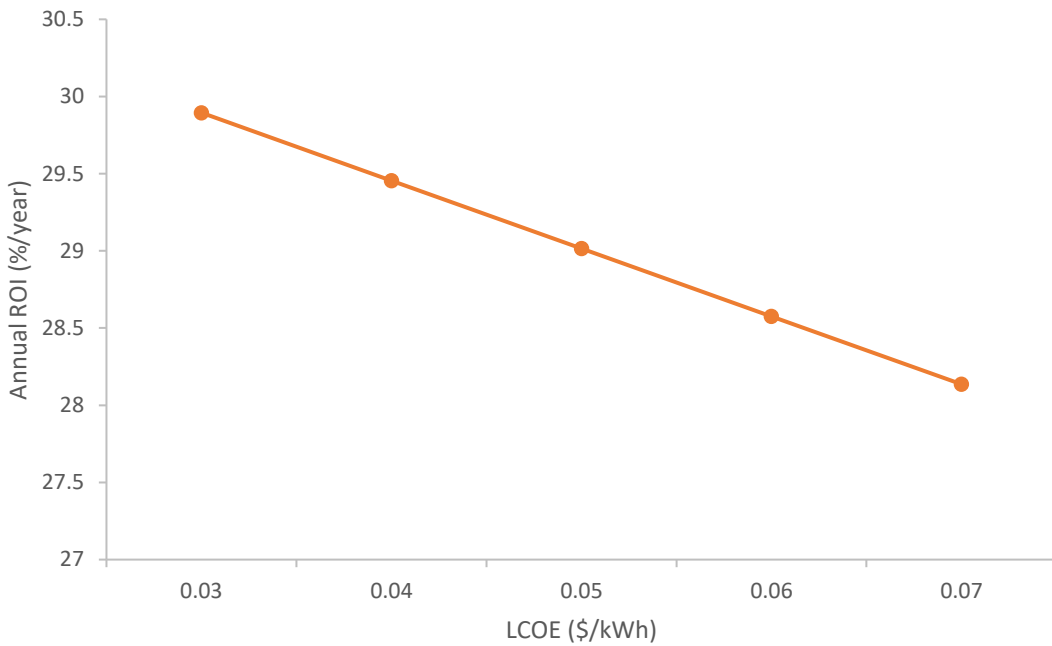


Figure 13: Electricity Price on ROI

At the most expensive LCOE assessed, \$0.07/kWh, the ROI was found to be above 12% with a value of 28.14. This is significant because it shows that the proposed design satisfies the hurdle rate requirement even if the LCOE falls short of the *SunShot 2030* goal. The ROI assessments above an LCOE of \$0.07/kWh were not assessed because \$0.07 per kWh was determined to be the break-even point for using water electrolysis.

6.5 Sensitivity Analysis: Methanol Price

The selling price of methanol used in the base case is \$600 per tonne. A sensitivity analysis assessing the impact of methanol price on the net after-tax profit, and consequently the ROI, was performed. The methanol prices were varied from \$300 to

\$900 per tonne. An illustration of the methanol price effects on the net after-tax profit and ROI are shown in Figure 14.

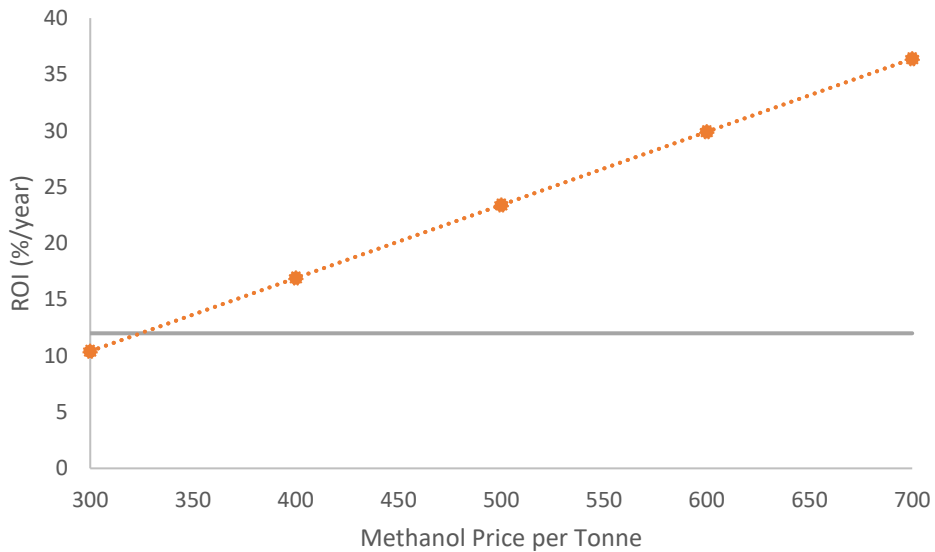


Figure 14: Methanol Price on ROI

The assessment of price variability is important because it shows what price methanol needs to be sold at to maintain an ROI at or above 12%. As seen in Figure 14, with all else equal in the case study, the proposed design will maintain an ROI at 12% as long as the selling price of methanol is at least \$324/tonne, a 46% decrease than the base case price (\$600/tonne). This is significant because it demonstrates that the methanol price can considerably vary and the ROI will still maintain at or above the 12% threshold.

Increases in methanol price will also significantly affect the annual ROI. If the price of methanol increases by \$100 (16.7%), from \$600 to \$700 per tonne, the annual

ROI increases by almost one-fifth (21.7%), going from 29.90 to 36.39. This demonstrates that increasing the selling price of methanol can significantly increase the annual ROI and profitability of this case study

7. FUTURE WORK

7.1 Industry Needs and Market Applications

Steam reforming, syngas production, and methanol production are already well-established processes with a prominent impact and presence in industry. While the case study demonstrated that the proposed design has potential from an economic perspective, and has favorable components such as utilizing renewable energy resources and carbon dioxide consuming processes, this design will only be successful if industry decides to adapt and use it. For this to happen, industry needs to see the proposed design as something to be desired, and as a solution to some problem they are facing and cannot solve.

To gauge a more comprehensive and holistic understanding of industry applications, future work will include conducting interviews with industry representatives. These will be used to gauge a better idea on what their needs are, what kinds of solutions will catch their attention, and what kind of results they want to see from these solutions. Furthermore, these interviews will allow for direct understanding and perspective on how they see renewable technologies, such as water electrolysis, photovoltaics, and thermal energy storage, being incorporated into, or even replacing, traditional methods of energy and chemical production. With this information, the proposed design presented in this work can be fine-tuned and better detailed to fit the demands and needs of industry.

7.2 Hydrogen Storage and Safety

Future work will also include a more comprehensive understanding and assessments with safety concerns and considerations. In particular, hydrogen storage and dispatch is a key component of this proposed design. Hydrogen is highly flammable, and its use in any application poses a valid and serious safety risk. For any ignition, all three components of the fire triangle must be present: fuel, oxygen, and heat ³⁰. In this proposed design, two out of the three components are within close vicinity to each other as both hydrogen (fuel) and oxygen are products simultaneously being emitted out of water electrolysis. While oxygen and hydrogen are emitted from separate ends of the electrolyzer unit, should they become mixed, and an ignition source added, it could create potential for explosion disaster to occur. These safety concerns will be addressed in future research.

7.3 Renewable Energy Advancements

Investment in renewable energy research, growth, and development has been on the rise for many years. While shale gas and natural gas are prominent in the energy industry, their renewable energy counterparts can not be forgotten, as this work as shown. Even within this past decade, massive growth has been made in not only solar energy utilization, but also renewable energy resources such as wind, geothermal, and biomass sources. Applications of the proposed design alongside other sources of solar energy collection and utilization, such as thermal energy storage, or even other renewable energy sources, such as wind energy, will need to be assessed in future

research. Along with this case study, this will provide a better understanding of the potential applications of the proposed design.

Furthermore, the base case in Case Study II used water electrolysis to produce 50 tonnes of hydrogen per day. If the electrolyzer requires 50 kWh to produce 1 kg of hydrogen, requiring 2.50 MM kWh daily. If photovoltaics can provide an average daily rate of 5.5 kWh/m², then this design would require photovoltaics spanning an area of 455,000 m²³¹. This would be a significant area dedicated to photovoltaics, and future work should assess if, considering the area requirements, photovoltaics are the appropriate renewable energy source for this design.

8. CONCLUSION

This work addressed the rising issue of how upcoming renewable energy technologies, such as solar energy, might be incorporated with traditional chemical processes. Here, a novel design to create syngas has been proposed. This design incorporated solar energy collection and dispatch, water electrolysis, hydrogen and oxygen storage and dispatch, methane reforming technologies, including but not limited to the steam reforming of methane, dry reforming of methane, partial oxidation of methane, to produce syngas in a predetermined, but tunable H₂:CO ratio. This design is subject to heat and mass integration within itself or with downstream processes, such as methanol production.

Two case studies were performed. The first measured the Economic Gross Potential, Metric Inspecting Sales and Reactants, and Stoichiometric Mass Targeting, to indicate the proposed design had potential to be profitable. The second case study was conducted to calculate the annual ROI using methanol as the downstream product. With this arrangement, it was found that the ROI was 29.90%. Sensitivity analysis on production of scale, selling price of methanol, and the LCOE all showed how these variables impacted the annual ROI, and what values they needed to be in order to meet the 12% hurdle rate requirement. This work demonstrated that the proposed design has potential to be profitable in industry and that future steps, such as a more detailed conversations to determine industry needs and market applications, safety considerations

with hydrogen storage, and implications of continuing renewable energy advancements, should be pursued.

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APPENDIX

Calculations:

Conversion from kg to kmol:

$$\frac{\$}{\text{kmol}} = \frac{mw(\text{kg})}{1 \text{ kmol}} \times \frac{\$}{\text{kg}}$$

Conversion from \$/kWh to \$/kmol when determining cost of electrolyzing 1 kmol of water:

$$\frac{\$}{\text{kmol } H_2O} = \frac{\$}{\text{kWh}} \times \frac{50 \text{ kWh}}{1 \text{ kg } H_2} \times \frac{2.02 \text{ kg } H_2}{\text{kmol } H_2} \times \frac{\text{kmol } H_2}{\text{kmol } H_2O}$$

Table 13: Chemical Price Conversion

Chemical	Price per kg	Molecular weight (kg)	Price per mol	Price per kmol
H2O	0.0015	0.0180	0.0000	0.027
H2	1.500	0.0020	0.0030	3.030
CH4	0.1565	0.0160	0.0025	2.510
CO2	0.0000	0.0440	0.0000	0.00
CO	0.0750	0.0280	0.0021	2.10
O2	0.1100	0.0320	0.0035	3.52