

TECHNO-ECONOMIC AND SUSTAINABILITY ANALYSIS OF THE
PRODUCTION OF ACETIC ACID FROM METHANE AND CARBON DIOXIDE

A Thesis

by

MARCO ESTEBAN AVENDANO LOPEZ

Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee,	Mahmoud El-Halwagi
Committee Members,	René Elms
	Ahmad Hilaly
Head of Department,	Arul Jayaraman

May 2020

Major Subject: Chemical Engineering

Copyright 2020 Marco Esteban Avendano Lopez

ABSTRACT

Methane and carbon dioxide together represent 90% of greenhouse gases, and one way of diminishing their emissions is by converting them into added value chemicals. Acetic acid is one of such chemicals, and efforts at the laboratory scale have been carried out to prove it can be directly and indirectly synthesized from CH₄ and CO₂. However, there are very few studies that evaluate the possibility of implementing any of these processes at a larger scale. In this thesis, techno-economic and sustainability analyses were used to assess the feasibility of upscaling two pathways to produce acetic acid: (1) by direct conversion of methane and carbon dioxide using a plasma-assisted reactor and (2) by indirect catalytic conversion, using syngas (obtained from dry methane reforming) as an intermediate. ASPEN Plus was used for simulation, and with literature values and plant cost estimation techniques, the capital and operational expenses were estimated and compared to those of the commercial route. The indirect and direct pathways attained return on investment (ROI) values of 1.5% and 5.5%, respectively, and unless credit is given to the reduction in the carbon footprint, neither process can economically compete with the commercial route, which attained an ROI of 19%. In terms of sustainability, the indirect and direct processes captured 0.7 and 2.5 times more carbon dioxide compared to the emitted amount by the commercial pathway. For the direct pathway it was found through a sensitivity analysis the carbon credit value can be reduce down to a value of \$50/tonne to render the process economically viable.

Keywords: plasma-assisted; sustainability; process upscaling; carbon capture; greenhouse gases

DEDICATION

I will like to dedicate this thesis to my mom and dad who have supported me at every point of life. Without them none of this could be possible.

ACKNOWLEDGEMENTS

I will like to thank Dr. Mahmoud M. El-Halwagi for his advice and support throughout this past year and a half and for his eagerness and patience in guiding and supervising my thesis. More than an excellent scholar, he is a remarkable human being. He has contributed immensely to the development of my career and I can safely say I could have not asked for a better advisor. I will also like to thanks Dr. René Elms and Dr. Ahmad Hilaly for serving in my committee.

I will like to also thank my officemates Ahmad, Kedar, Lidia, Shaik and Soham for their support and companionship throughout my degree. Especially, I will like to thank Abdulrahman Alsuhaibani, who from day one offered me his help and who most importantly is a great person and friend.

Also, I am very grateful for all the great people I met at Texas A&M. I will like to thank Ashley and Terah for always helping me out. I also want to thank my friends: Aravind, Chika, David, Diego, George, Ian, Jarad, Kevin, Rachit Sourav, Steven and Suveesh, for making these two years an incredible experience.

Finally, and most importantly, I want to thank my family. First, my parents, Marco Tulio Avendano and Natividad Lopez, who have been a constant source of support at every stage of my life. Also my sister and aunts, Sara Avendano, Gloria Avendano, Nila Lopez and Karen Lopez who have shaped me into who I am. I also want to thank my aunt, uncle and cousins: Miriam Lozano, Leonidas Soto, Mariana Soto and Jessica Soto-Imm. It has been more than eight years now since we moved to the United States and they have given me and the rest of family unwavering support and companionship.

CONTRIBUTORS AND FUNDING SOURCES

Contributors

This work was supervised by a thesis committee consisting of Professors Mahmoud M. El-Halwagi and Ahmad Hilaly of the Department of Chemical Engineering and Professor René Elms of the Department of Engineering

All other work conducted for the thesis (or) dissertation was completed by the student independently.

Funding Sources

Graduate study was supported in part by a scholarship from Texas A&M University.

NOMENCLATURE

AA	Acetic Acid
AATP	Annual After-Tax Profit
AOC	Annual Operating Cost
CEPCI	Chemical Engineering Plant Cost Index
CO _{2e}	Carbon Dioxide Equivalent
DMR	Dry Methane Reforming
EC	Energy Consumption
EIA	Energy Information Administration
EPA	Environmental Protection Agency
EtOH	Ethanol
f_x	Flow Rate of Species X
FCI	Fixed Capital Investment
G°_{298K}	Standard Free Energy at 298 K
GHG	Greenhouse Gas
GWP	Global Warming Potential
H°_{298K}	Standard Enthalpy at 298 K
HPS	High Pressure Steam
IEA	International Energy Agency
ISBL	Inside Battery Limits
kJ	Kilojoule
kSCF	Thousand standard cubic feet

kWh	Kilowatt-hour
LPS	Low Pressure Steam
MeOH	Methanol
MISR	Metric for Inspecting Sales and Reactants
MM	Million
MPS	Medium Pressure Steam
MW	Megawatts
MWh	Megawatt-hour
NRTL	Non-random Two-liquid
OSBL	Outside Battery Limits
PSA	Pressure Swing Adsorption
ROI	Return on Investment
RSTOIC	Stoichiometric Reactor
RYIELD	Yield reactor
SEI	Specific Energy Input
SMR	Steam Methane Reforming
SWROIM	Sustainable Weighted Return on Investment Metric
TAC	Total Annualized Cost
TCI	Total Capital Investment
WCI	Working Capital Investment

TABLE OF CONTENTS

	Page
ABSTRACT.....	ii
DEDICATION.....	iii
ACKNOWLEDGEMENTS.....	iv
CONTRIBUTORS AND FUNDING SOURCES	v
NOMENCLATURE	vi
TABLE OF CONTENTS.....	viii
LIST OF FIGURES	xi
1. INTRODUCTION	1
1.1. Natural Gas	1
1.1.1. Shale Gas Revolution.....	1
1.1.2. Uses of Natural Gas	2
1.2. Carbon Dioxide.....	3
1.2.1. Carbon Dioxide Emissions	3
1.2.2. Use of Carbon Dioxide as a Feedstock and Carbon Capture	4
1.3. Acetic Acid	4
1.3.1. Acetic Acid Market.....	4
1.3.2. Production of Acetic Acid	5
2. PROBLEM STATEMENT AND OBJECTIVES.....	8
2.1. Motivation.....	8
2.1.1. Atomic Efficiency.....	8
2.1.2. Current State of Technology.....	8
2.2. Problem Description	9
2.3. Objectives	9
2.3.1. Main Objective.....	9
2.3.2. Specific Objectives	10
3. METHODOLOGY	11
3.1. General Approach	11
3.2. Targeting.....	12

3.2.1. Theoretical Stoichiometric Targeting	12
3.2.2. Actual Stoichiometric Targeting	12
3.3. Simulation Assumptions	13
3.4. Process Description.....	13
3.4.1. Commercial Pathway Process Description	13
3.4.2. Indirect Pathway Process Description	15
3.4.3. Direct Pathway Process Description.....	19
3.5. Economic Model Assumptions.....	21
3.5.1. Total Capital Investment and Return on Investment	21
3.5.2. Annual Operating Cost.....	23
3.5.3. Cost Estimation for Reactors	25
3.5.4. Plasma Calculations	25
3.6. Sustainability model	28
3.6.1. Net CO ₂ emissions	28
3.6.2. CO ₂ e Emission	28
3.6.3. Sustainable Weighted Return on Investment Metric (SWROIM)	31
3.7. Sensitivity Analysis	33
3.7.1. Minimum Acetic Acid Selling Price.....	33
3.7.2. Subsidies	33
3.7.3. Sensitivity Analysis Model	34
4. RESULTS AND DISCUSSION.....	35
4.1. Targeting Results	35
4.1.1. Theoretical Stoichiometric MISR Results	35
4.1.2. MISR Results with Actual Stoichiometry and Reactant and Product Recovery	35
4.2. Simulation Results	36
4.2.1. Mass and Energy Balance	36
4.2.2. Equipment Size	39
4.3. Economic Model Results	39
4.4. Sustainability Model Results	41
4.4.1. CO ₂ e Emissions Results.....	41
4.4.2. SWROIM Results	42
4.5. Sensitivity analysis	43
5. CONCLUSIONS.....	47
5.1. Main Conclusions	47
5.2. Final Recommendation	47
5.3. Future Work.....	48
REFERENCES	49
APPENDIX A MONTE CARLO SIMULATION CODE	56
APPENDIX B ASPEN PLUS FLOWSHEETS.....	57

APPENDIX C MINIMUM FRESHWATER DETERMINATION	59
APPENDIX D MODIFIED COMMERCIAL PATHWAY CALCULATIONS.....	61
APPENDIX E SUSTAINABILITY CALCULATIONS.....	65

LIST OF FIGURES

	Page
Figure 1. Projection of Shale Reserves in the U.S. Reprinted from EIA (Source: U.S. Energy Information Administration, March 2019 ¹).	1
Figure 2. Trend of Carbon Dioxide Emissions. Reprinted from EIA (Source: U.S. Energy Information Administration, March 2019 ¹).	3
Figure 3. Current and Future State of Technology for Plasma-Assisted Chemical Manufacturing Processes (Adapted from de la Fuente et al., 2017 ⁷⁷).....	9
Figure 4. General Approach Flowsheet	11
Figure 5. Supply Chain Flowsheet for the Production of Acetic Acid	14
Figure 6. Carbonylation of Methanol Process Flowsheet (Adapted from Hydrocarbon Processing [®] , 2014 ⁶³).....	15
Figure 7. Syngas-to-Acetic Acid Product Distribution.....	16
Figure 8. Syngas-to-Acetic Acid Process Flowsheet.....	18
Figure 9. Direct Pathway Process Flowsheet.....	20
Figure 10. Product Distribution of the Direct Pathway	21
Figure 11. Unit Cost of Plasma-Assisted Reactors (Adapted from de la Fuente et al., 2017 ⁷⁷)...	27
Figure 12. Expected MISR vs. Reactant Recovery for a fixed Product Recovery of 80%	36
Figure 13. TCI and ROI Comparisons of the Three Pathways	41
Figure 14. Tornado Plot for the Direct Pathway.....	44
Figure 15. Achieving a \$50/tonne Carbon Subsidy through Process Improvement.....	45
Figure 16. Effect of Plant Capacity on TCI and ROI	46
Figure 17. Indirect Pathway ASPEN Plus Flowsheet.....	57
Figure 18. Direct Pathway ASPEN Plus Flowsheet	58
Figure 19. Minimum Freshwater Stream for Indirect Pathway Contactor	59
Figure 20. Minimum Freshwater Stream for Indirect Pathway Distillation Column	60

LIST OF TABLES

	Page
Table 1. Economic Model Assumptions.....	23
Table 2. Feedstock Purchasing Price Assumptions	23
Table 3. Summary of Utility Costs	24
Table 4. 100-Year Global Warming Potential for different Green House Gases	29
Table 5. Energy Factor for Each Utility.....	32
Table 6. SWROIM Indicator Values	32
Table 7. Sensitivity Analysis Model Lower and Upper Boundaries	34
Table 8. Theoretical Stoichiometric MISR Results	35
Table 9. Mass Balance Results in tonne/tonne AA.....	37
Table 10. Energy Balance Results (Units in MWh/ tonne AA).....	38
Table 11. TCI Results	39
Table 12. TAC Results.....	40
Table 13. CO ₂ and CO _{2e} Emissions Breakdown (tonne CO ₂ /tonne AA).....	42
Table 14. SWROIM Results	43
Table 15. Minimum Acetic Acid Selling Prices and Carbon and Electricity Subsidy	44
Table 16. Modified Commercial Pathway Mass Balance Calculations.....	61
Table 17. Modified Commercial Pathway SMR/DMR Values	62
Table 18. Equipment Cost Estimation Base Case Syngas Production and H ₂ PSA Unit	63
Table 19. Equipment Cost for Syngas to Methanol	64
Table 20. CO _{2e} Emissions	65

1. INTRODUCTION

1.1. Natural Gas

1.1.1. Shale Gas Revolution

The shale gas revolution has drastically increased the supply of natural gas in the United States and new discoveries as well as advances in hydraulic fracturing and directional drilling are expected to continue this trend. Figure 1 shows that over the past ten years, shale gas has become one of the most important sources of natural gas and is projected to keep growing in the upcoming decades¹⁻³.

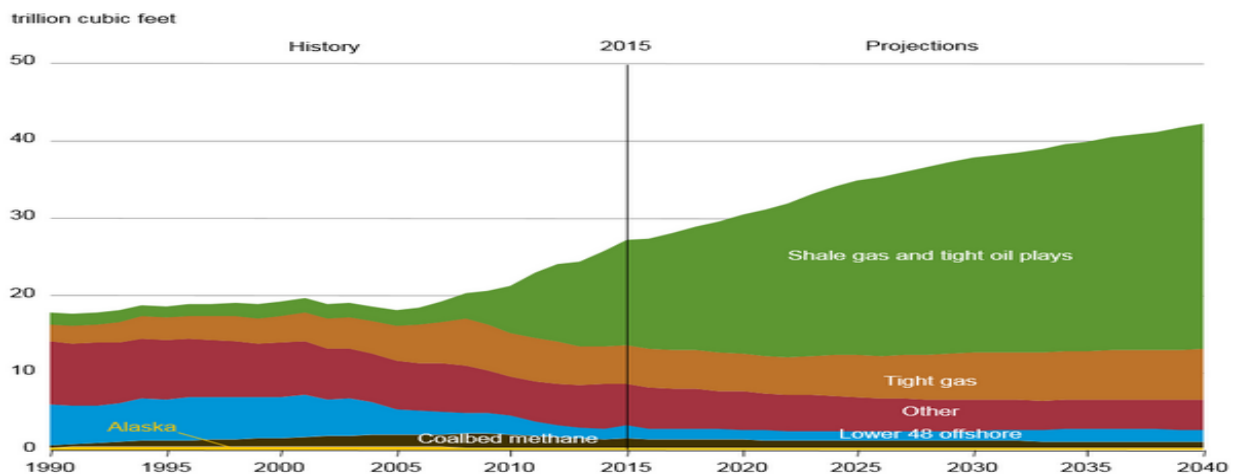


Figure 1. Projection of Shale Reserves in the U.S. Reprinted from EIA (Source: U.S. Energy Information Administration, March 2019¹).

This increase in supply and demand, as well as the relative cleanliness of natural gas, is expected to position it above more conventional sources of energy. According to Elbashir et al. it will be the second most used form of energy in the world by 2025 (surpassing coal) and the first

most used by 2040 (surpassing oil)^{4,5}. Therefore, knowing how and where to use the surpluses of natural gas is a key task for the United States energy sector.

1.1.2. Uses of Natural Gas

1.1.2.1. Use of Natural Gas for Non-conversion Ends

While natural gas is considered one of the cleanest form of fossil-fuels, it is comprised mostly of methane, which has a supply chain network closely tied to carbon dioxide⁶⁻⁸. This represents an environmental complication since methane and carbon dioxide together comprise over 92% of the greenhouse gases⁹. One way to diminish the emissions of these gases is through their conversion into added value products¹⁰. Currently, however, the majority of natural gas is utilized for industrial, power and residential applications and less than 15% is being used for chemical conversion^{11,12}.

1.1.2.2. Use of Natural Gas as a Feedstock

Usage of methane as a feedstock is very limited due to its stability and difficulty to convert into other products¹³. At mild temperature and pressure conditions (less than 500 K and less than 20 bar), non-catalytic conversion of methane is very impractical and requires a large energy input, as well as a potential safety hazard. Substantial progress, however, has been achieved in the area of heterogeneous catalysis, which has opened the possibility of directly converting methane into higher hydrocarbons, oxygenates and even fuels¹⁴⁻¹⁷. Nevertheless, the usage of natural gas as a reactant is still dominated by the production of syngas through steam methane reforming (SMR), partial oxidation (POx) and to a lesser extent dry methane reforming (DMR)¹⁸⁻²⁰. Then the composition of the syngas is adjusted via water gas shift (WGS) and reverse water gas shift (RWGS) reactions and the resulting mixture is fed to the Fischer-Tropsch (FT) process for conversion into chemicals and fuels^{21,22}. Nevertheless, syngas production needs a high energy

input and has a limited sustainability potential due to the small number of carbon dioxide sinks throughout the process²³. Developing alternative routes that convert methane into added value products could represent not only savings in energy but also a direct pathway to capture methane.

1.2. Carbon Dioxide

1.2.1. Carbon Dioxide Emissions

Carbon dioxide is exceedingly the largest source of greenhouse gases exceeding methane, NO_x's and fluorinated gases. It is known as the most influential agent in global warming and therefore most of the efforts to prevent climate change are concentrated towards the reduction in CO₂ emissions into the atmosphere²⁴. In the United States, and in many of the industrialized countries, emissions have been steadily decreasing since 2005, with ambitious targets for 2025 and 2030^{25,26}. Figure 2 shows that this trend is expected to continue in the upcoming decades, with a rapid decrease expected to happen in the near future¹.

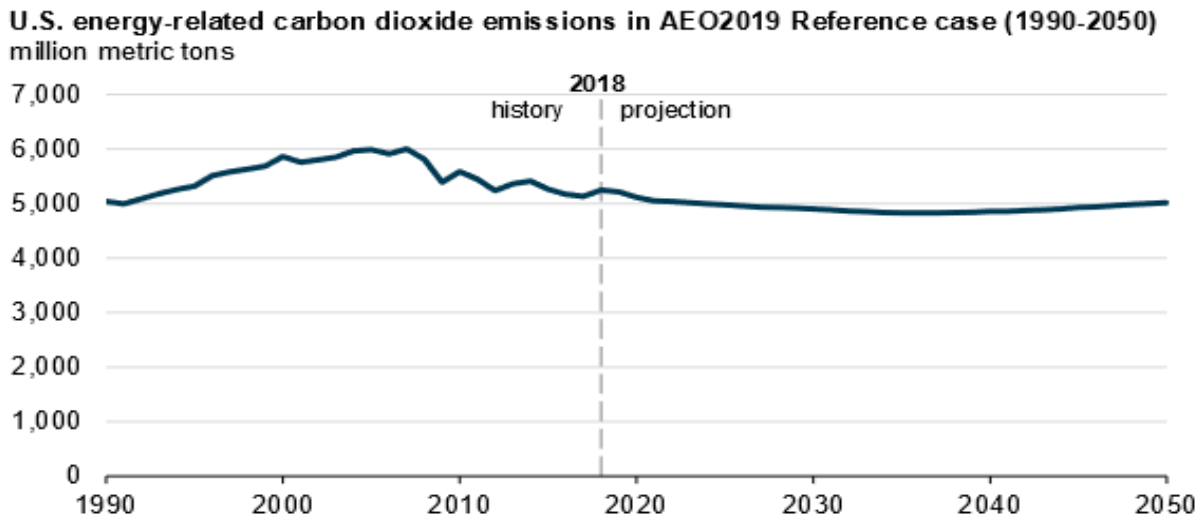


Figure 2. Trend of Carbon Dioxide Emissions. Reprinted from EIA (Source: U.S. Energy Information Administration, March 2019¹).

1.2.2. Use of Carbon Dioxide as a Feedstock and Carbon Capture

Similarly, carbon dioxide is also a highly stable molecule and is not commonly used in chemical conversion processes. Furthermore, noncatalytical reaction pathways to activate the C=O bond require large inputs of energy^{27, 28}. Capture of carbon dioxide is, therefore, mostly physical and is mainly carried out through the use of pressure swing adsorption (PSA) systems, molecular sieves, electrochemical and photochemical reduction, membranes, amine-based solvents and molecular organic frameworks (MOFs)^{29, 30}. Then the captured stream is stored underground in geological formation or used in the food and carbonated drinks industry^{31, 32}. The cost to capture carbon dioxide through these methods can be as low as \$30-40/tonne³³. Developing and assessing the feasibility of chemical sequestration of carbon dioxide can open the possibility to reduce the current carbon capture prices³⁴. Coupling this sequestration process with methane could close the emission cycle of the two most abundant greenhouse gases³⁵.

1.3. Acetic Acid

1.3.1. Acetic Acid Market

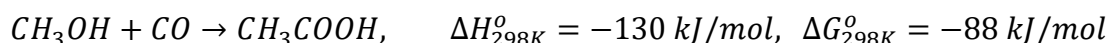
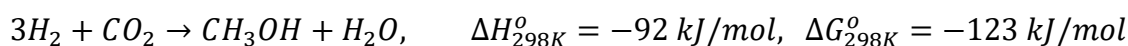
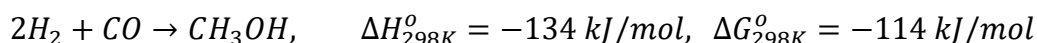
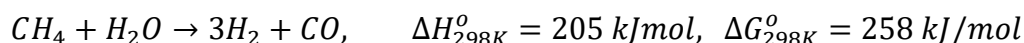
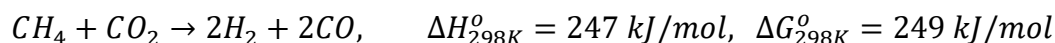
In order to produce an added value chemical from the highly stable methane and carbon dioxide molecules, a large energy input and capital investment has to be incurred³⁶. Such an added value chemical, must therefore have a strong market position in order to make the project financially feasible. Acetic acid is one of such added value chemicals, it is the second simplest form of carboxylic acids and is one of the fastest growing commodities in the chemicals industry. It has a global demand of 15 MMT and an annual revenue of more than \$11B³⁷. It is mostly used as an intermediate for other added value products such as vinyl acetate monomer (VAM), purified terephthalic acid (PTA) and acetic anhydride³⁸. It is mainly produced through the carbonylation of methanol, but other methods of production include oxidation of butane, and fermentation of

ethanol³⁹. However, despite its growing market and relevance, very few studies have deeply investigated the techno-economics of acetic acid and our work will be one of the first to do so.

1.3.2. Production of Acetic Acid

1.3.2.1. Commercial Pathway

As mentioned, the catalytical conversion of methane and carbon dioxide often requires large amounts of energy and capital investment⁴⁰. If acetic acid was to be produced from methane and carbon dioxide using only commercial methods it will follow the following three steps: (1) first syngas will be produced from a DMR reaction coupled with either SMR or POX and then the composition will be adjusted accordingly. (2) Then methanol will be obtained from syngas and finally (3) it will be reacted with carbon dioxide to produce acetic acid. This supply chain is not only very costly and intricate but it also lacks sufficient carbon dioxide sinks to make it a sustainable process. Therefore, other alternatives for the chemical utilization of methane and carbon dioxide that eschew any intermediate step should be explored.

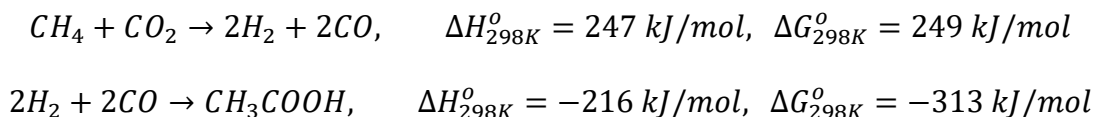


1.3.2.2. Indirect Pathway

The most common reaction that involves methane and carbon dioxide is DMR, which employs nickel and cobalt based catalysts and has been garnering substantial attention in academia for the past decade^{41, 42}. However, it is seldom used in industry due to its highly endothermic

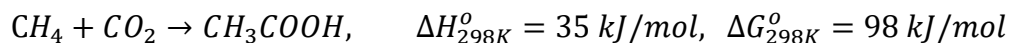
enthalpy of reaction and low syngas quality (i.e. H₂/CO ratio of 1). While the high enthalpy hurdle cannot easily be overcome, the low H₂/CO ratio can be advantageous if the syngas product is used for applications other than the FT process (where the ratio must be ≥2). One example is the production of acetic acid from an equimolar H₂/CO feedstock.

This is a 100% efficient reaction from an atomic point of view since theoretically acetic acid could be produced from methane and carbon dioxide without any side products or the need of an additional reaction or syngas composition adjustment unit. Furthermore, the enthalpy and Gibb's free energy of the reaction are also favorable. This process can be divided in two steps: (1) syngas production from DMR and (2) acetic acid production from syngas. It will be referred to as the "indirect pathway" throughout the paper and the following are the main reactions:



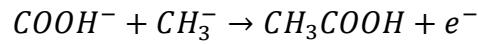
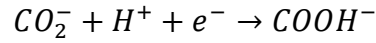
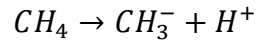
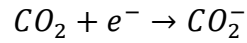
1.3.2.3. Direct Pathway

If the directness of the process is further exploited, then theoretically acetic acid could also be produced from a feedstock of methane and carbon dioxide with a 100% atomic efficiency and without the need of the syngas production intermediate step. This process, however, is not thermodynamically favored and its positive Gibb's free energy makes it non-spontaneous under any combination of pressure and temperature conditions. Many researchers have attempted to produce acetic acid from methane and carbon dioxide, but none with sufficiently high conversion and selectivity rates or without the need of additional reactants⁴³⁻⁴⁵.



To overcome this limitation, various researchers have proposed the utilization of plasma-assisted reactions to produce added value chemicals from relatively inert molecules⁴⁶. More

specifically, Wang et al. proved that acetic acid can be obtained at a reasonable conversion and selectivity rate through the use of a discharge dielectric barrier reactor⁴⁷. Throughout this paper this alternative process will be referred to as the “direct pathway”. While the kinetics of plasma-assisted processes are still not completely understood, the following process is a theoretical representation of the steps undertaken by methane and carbon dioxide to overcome the seemingly impassable thermodynamic barrier:



In this thesis, first the motivation and problem statement will be laid out. Then the methodology will be described. The technical, economic and sustainability assumptions will be listed and finally, the results, discussions, conclusion and closing remarks will be presented.

2. PROBLEM STATEMENT AND OBJECTIVES

2.1. Motivation

2.1.1. Atomic Efficiency

Atomic efficiency or atom economy in a chemical reaction refers to the efficiency of a certain process to convert reactants into desired products. It is one of the most important measures of sustainability, since it can determine the environmental potential for a given process. It is defined by the following equation^{48, 49}:

$$\text{Atom Efficiency} = \frac{\text{mass of atoms in desired product}}{\text{mass of atoms in reactants}}$$

The fact that acetic acid can be produced from the two main greenhouse gases at a maximum atomic efficiency represents an excellent opportunity to develop an economic and sustainable model that can be used in any other commodity chemical. Therefore, the chemical processes considered were those that convert methane and carbon dioxide to acetic acid without the need of another reactant.

2.1.2. Current State of Technology

Excellent efforts at the laboratory scale have been carried out to prove the technical feasibility of indirect and direct production of acetic acid from methane and carbon dioxide. However, very few papers evaluate the possibility of upscaling any of these experiments and any further progress is dissuaded due to the inherent uncertainty of the technology used⁵⁰⁻⁵⁴. Figure 3 shows the current state of technology, as well as the future timeline for the chemical manufacturing processes that are assisted by plasma. It shows that this thesis is at the onset of the “transition stage” and is one of the pioneer works in this area.

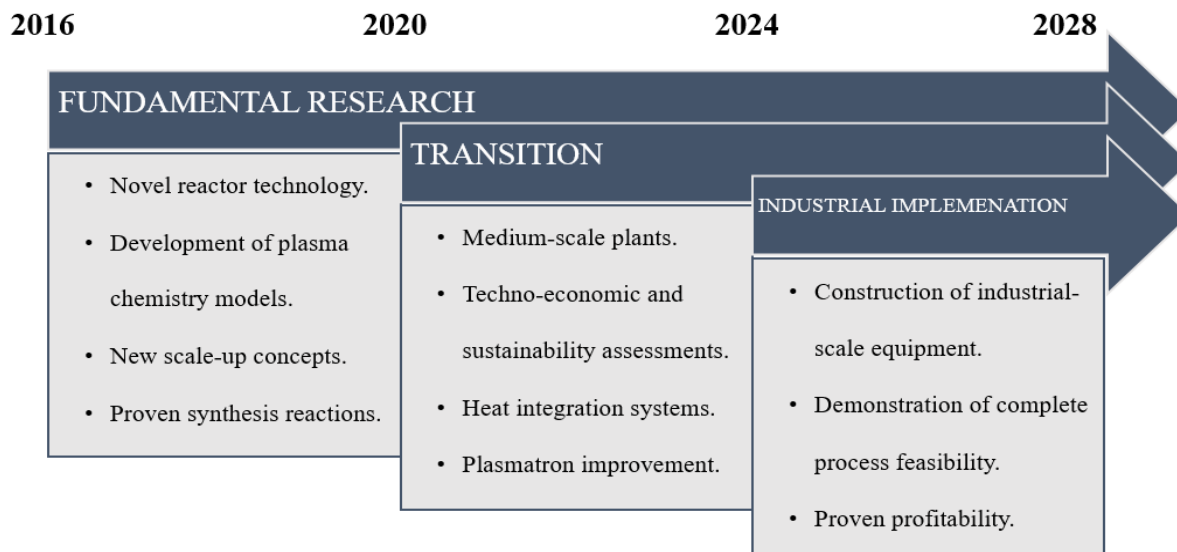


Figure 3. Current and Future State of Technology for Plasma-Assisted Chemical Manufacturing Processes (Adapted from de la Fuente et al., 2017⁷⁷)

2.2. Problem Description

In this thesis, we will determine whether or not the indirect and direct pathways can compete with the commercial route. This will require application of chemistry, kinetics, thermodynamics, economics and process engineering to assess the technologies in question, as well as basic optimization of chemical plant flowsheets.

2.3. Objectives

2.3.1. Main Objective

The main objective of this paper is to exploit the concept of atomic efficiency to determine whether or not the proposed alternative and sustainable pathways for the production of acetic acid are economically feasible.

2.3.2. Specific Objectives

The main objective of this paper can further be broken down into its simulation, economics and sustainability aspects. The specific objectives of this thesis then can be summarized as follow:

- 1) Determine if the production of acetic acid from syngas, produced from methane and carbon dioxide, can economically compete with the commercial route.
- 2) Determine if the production of acetic acid from methane and carbon dioxide can economically compete with the commercial route.
- 3) Determine if the sustainability potential of the indirect and direct pathways can compensate, if necessary, for the shortcomings in economic profit.
- 4) Develop a design recommendation based on all studied metrics.

3. METHODOLOGY

3.1. General Approach

To evaluate all three pathways, the general procedure shown in Figure 4 was followed. First, any inviable alternative was ruled out based on theoretical and stoichiometric targeting. Then each process was simulated in ASPEN Plus and key technical data was extracted to produce economic and sustainability assessments. Finally, a sensitivity analysis was employed and any process with positive results was considered for re-design and optimization.

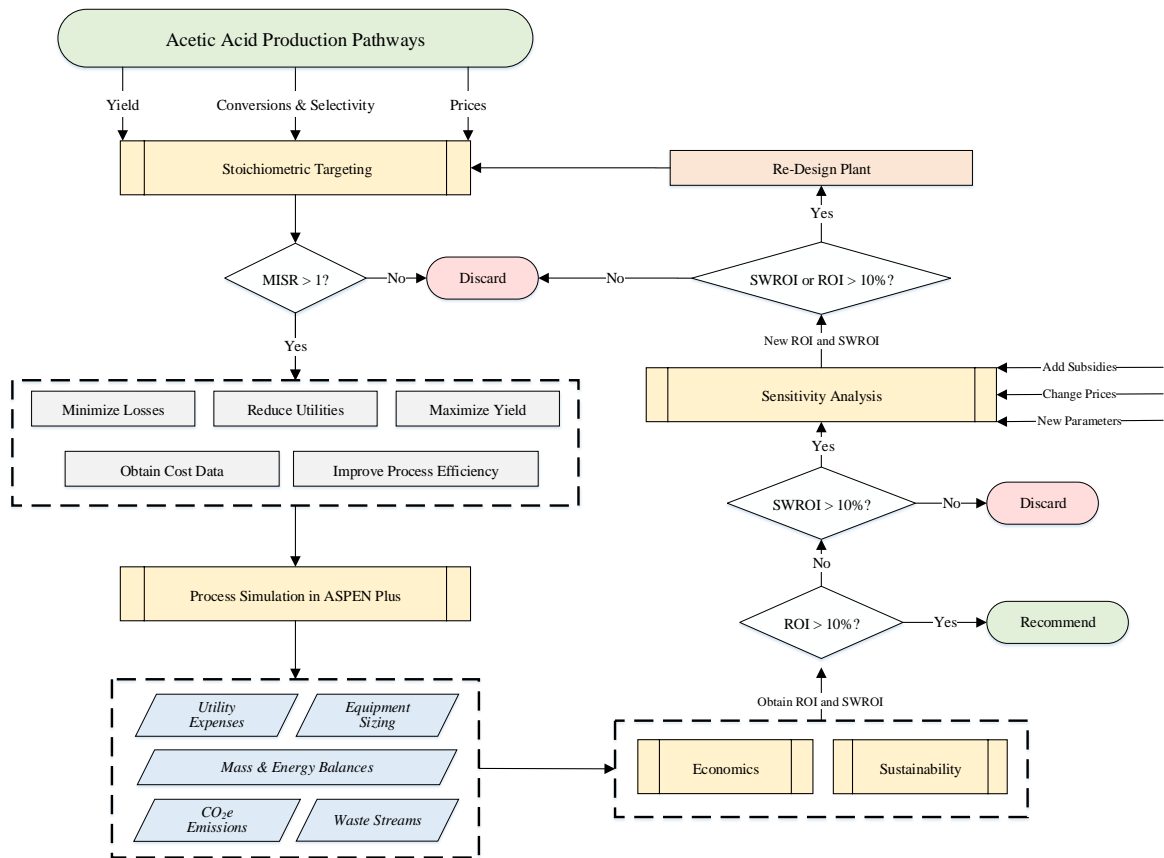


Figure 4. General Approach Flowsheet

3.2. Targeting

3.2.1. Theoretical Stoichiometric Targeting

In order to obtain a preliminary screening of each process, the Metric for Inspecting Sales and Reactants (MISR) was used. It quantifies the ratio between revenue and expenses for a 100% conversion process with full product recovery. In order for a specific process to be viable, its MISR must be greater than 1. MISR can be calculated according to the following equation⁵⁵:

$$MISR = \frac{\sum (\text{Annual Production of product } p \times \text{Selling price of product } p)}{\sum (\text{Annual Feed of reactant } r \times \text{Purchase price of reactant } r)}$$

As can be seen from the equation, the MISR is very sensitive to fluctuations in prices and a deterministic approach might not be enough to provide a complete picture of a certain process. To account for uncertainty we ran a Monte Carlo simulation with uniform price distributions. Finally, the results from a Monte Carlo distribution are often expressed in terms of low, expected and high outcomes.

Low (or P90): Conservative estimate, 90% of the values in the distribution are greater than or equal to this outcome.

Expected (or P50): Median estimate, 50% of the values in the distribution are greater than or equal to the expected outcome. For this paper an expected (P50) MISR value greater than 1 will be enough to consider the process viable.

High (or P10): Optimistic estimate, 10% of the values in the distribution are greater than or equal to the high outcome.

3.2.2. Actual Stoichiometric Targeting

In industrial applications, however, even for maximum of atomic efficiency processes, complete conversion is far from reality and mass balances need to be performed. Furthermore,

reactants are often lost throughout the system and products are usually not completely recovered. To more reliably screen pathways, a Monte Carlo simulation was re-run and a new set of expected (P50) MISR values was obtained. To re-calculate annual production of products and annual purchase of reactants the following formulas were used (f refers to the flow rate of a given species):

$$\text{Conversion of reactant } r = \frac{f_{r,in} - f_{r,out}}{f_{r,in}}$$

$$f_{r,recovered} = f_{r,out} \times \text{reactant } r \text{ recovery rate}$$

$$\text{Annual feed of reactant } r = f_{r,in} - f_{r,recovered}$$

$$\text{Selectivity of product } p = \frac{f_{p,out}}{\sum f_{p,out}}$$

$$\text{Annual production of product } p = f_{p,out} \times \text{product } p \text{ recovery rate}$$

3.3. Simulation Assumptions

] Aspen Tech recommends a liquid activity coefficients property method for carboxylic acids. More specifically the non-random two-liquid model (NRTL) for acetic acid⁵⁶.

3.4. Process Description

3.4.1. Commercial Pathway Process Description

As seen in Figure 5 the supply chain for this process begins with the production of syngas from methane, carbon dioxide and steam from an SMR/DMR process. It then is followed by the syngas-to methanol process and it finishes with the production of acetic acid as seen in Figure 5.

3.4.1.1. Production of Syngas through DMR

Technical and economic data was extracted from Baltrusaitis et al⁵⁷. The DMR process was selected because it begins with a feedstock of methane and carbon dioxide instead of the SMR/DMR process because it enhances sustainability and aligns with the objective of this thesis.

Also, if a COSORB unit is included and CO₂ is added to yield the appropriate syngas composition for the production of methanol, there is no need of any other reactant.

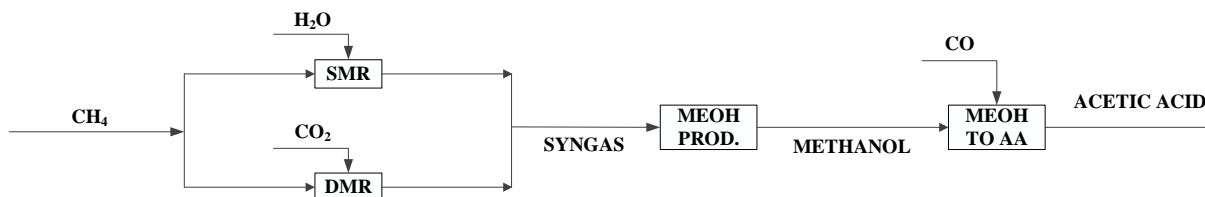


Figure 5. Supply Chain Flowsheet for the Production of Acetic Acid

3.4.1.2. Syngas-to-Methanol Process

The key data for the syngas-to-methanol process was obtained from Wang^{58, 59}, who evaluated the production of methanol from a biomass feed rather than methane and carbon dioxide. However, syngas is still the intermediate product and enough information was provided to obtain the key data of the syngas-to-methanol process. Any missing parameters were obtained from Alsuhaibani who reported expenses for the production of methanol from syngas⁶⁰.

3.4.1.3. Carbonylation of Methanol

Finally, the carbonylation of methanol or methanol-to-acetic acid step was based on the CT-ACETICA® process from Chiyoda Corporation⁶¹, as shown in Figure 6, and the process description was adapted from Hydrocarbon Processing® 2014 Petrochemical Handbook. This process reacts methanol and carbon monoxide in a bubble column reactor (1). This process achieves a 99% conversion and 99% liquid selectivity towards acetic acid. The product stream is then flashed in a separator tank (2); the off-gases are split with one stream recycled back into the reactor and the other stream sent to the high pressure absorber (4). The less volatile products from the flash tank are sent into a dehydration column (3). The distillate gases from this column are

used in the low pressure absorber (5) to be contacted with methanol. The liquid bottoms from the dehydration column is sent to a purification column (7) where acetic acid at a 99.5% purity rate is obtained. The distillate is sent for waste treatment or mixed with the off-gases from the two-stage absorber unit to be mixed in the furnace (6) for combustion with air and fuel. The overall acetic acid product recovery rate for this process is above 99%⁶²⁻⁶⁴.

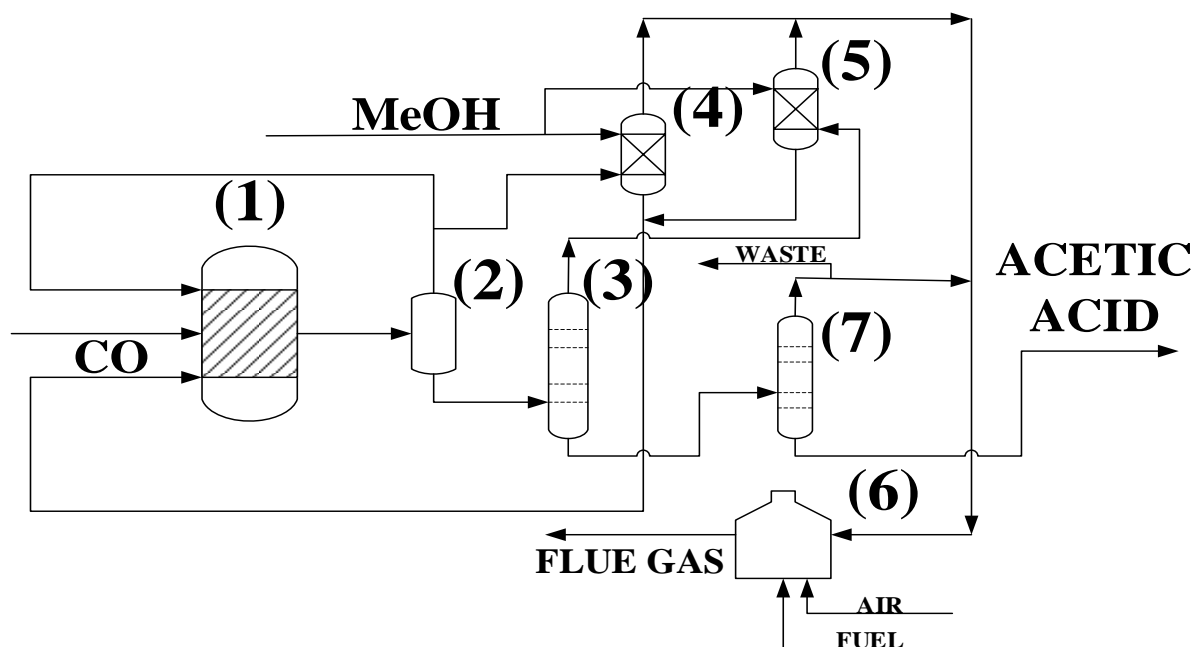


Figure 6. Carbonylation of Methanol Process Flowsheet (Adapted from Hydrocarbon Processing®, 2014⁶³)

3.4.2. Indirect Pathway Process Description

As mentioned previously, the production of acetic acid through the indirect pathway requires first the production of syngas. Syngas is obtained exclusively through DMR since it yields the appropriate H_2/CO ratio and has a large carbon dioxide sink. Finally, this mixture is converted into the desired product through the syngas-to-acetic acid step.

3.4.2.1. Syngas Production from DMR

For the production of syngas, we used data obtained from Luyben⁶⁵. We selected the flowsheet that attained 99% conversion and no recycle. This maintains the atomic efficiency and avoids the need to adjust the syngas ratio for the subsequent production of acetic acid.

3.4.2.2. Syngas-to-Acetic Acid Step

For the syngas-to-acetic acid step the entire flowsheet system was modelled using ASPEN Plus, using a 22.5% conversion for H₂ and CO and a 30% selectivity towards acetic acid. Figure 7 shows the product distribution of the process flowsheet as well as the main sections of the process.

3.4.2.2.1. Process Conversion and Selectivity

The conversion and selectivity values were obtained from Lopez et al.^{66, 67}. This is the highest conversion and selectivity reported for an experimentally reliable syngas-to-acetic acid process found in literature and therefore was considered the most suitable candidate for upscaling.

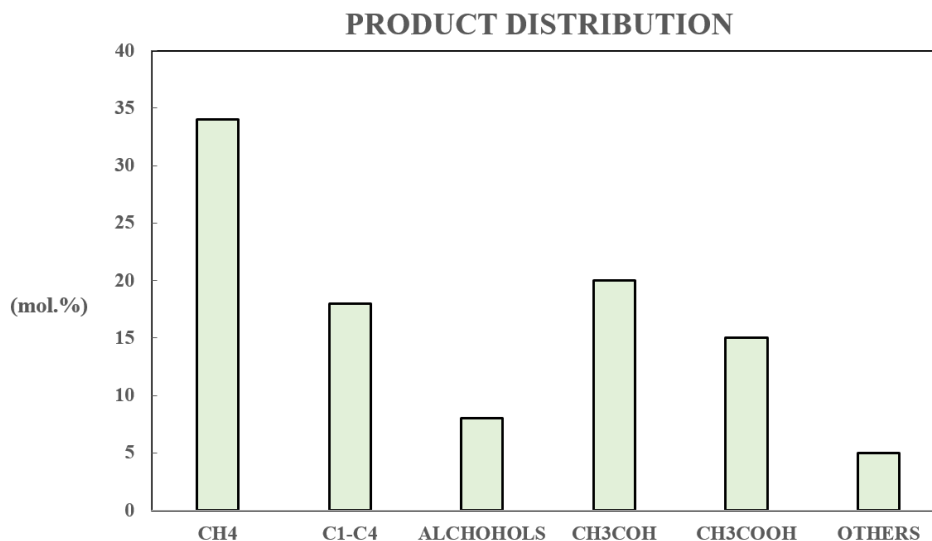


Figure 7. Syngas-to-Acetic Acid Product Distribution

3.4.2.2.2. *Process Specifications*

Figure 8 shows the process flowsheet for the indirect pathway. The reactor of this process operates at a temperature of 280 °C and a pressure of 20 bar, which yields a vapor-liquid product mix. These products are flashed in a separator tank with the liquid stream containing around 10% of the total acetic acid and the gaseous stream sent to the product recovery unit. This stream is quenched with 80,000 tonne/yr of freshwater and the mixture is cooled and then sent to a contactor to recover around 85% of the acetic acid. The off-gases from this column are then sent to the recycling unit. To recover H₂ from the reactants, we considered a swing adsorption (PSA) unit with 99.5% recovery and to recover CO we considered the COSORB process with 99% recovery⁶⁸.⁶⁹ The off-gases from the contactor are mixed with the unrecovered reactant and residue from this unit and then sent to the combustion chamber for heat recovery. The aqueous solution from the contactor is re-quenched with 100,000 tonne/yr of water and sent to a distillation column with seven theoretical stages. The acetic acid/water solution is then sent to an extraction column with 15 stages, where it is suggested to use an isopropyl acetate based solvent⁷⁰⁻⁷². The stream from the bottom of the extractor (consisting of isopropyl acetate and water) is sent to a two-distillation column unit for solvent recovery, with the bottoms water considered a waste stream. The stream withdrawn from the top of the extractor is cooled and sent to a dehydration column with 25 stages, where the solution is readily separated, the water distillate is considered a waste stream and from the bottoms a 99.5% acetic acid product is obtained. This process achieves an approximate reactant recovery rate of 95% and a product recovery of 93%.

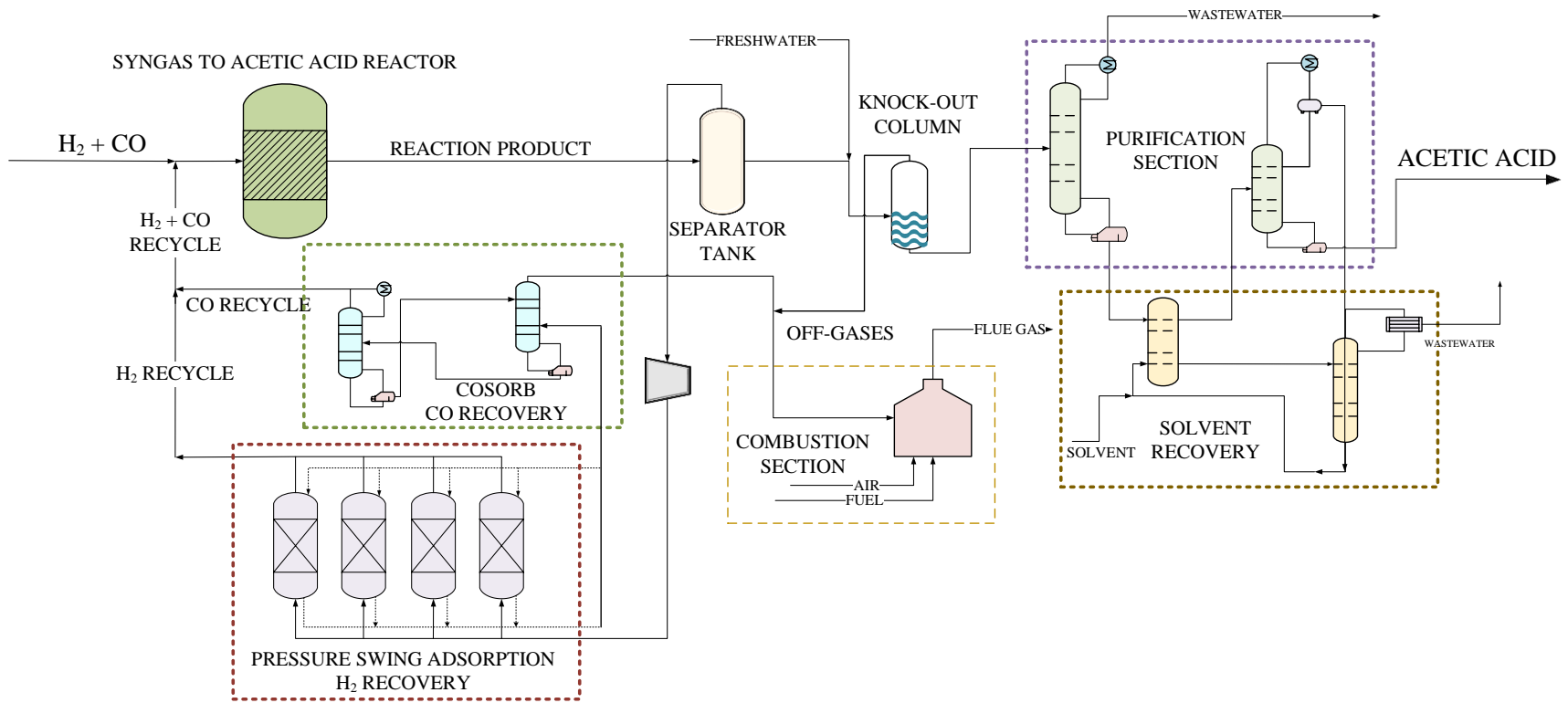


Figure 8. Syngas-to-Acetic Acid Process Flowsheet

3.4.3. Direct Pathway Process Description

For the production of acetic acid from methane and carbon dioxide the entire process was simulated in ASPEN Plus, since this only required one step, using a conversion of 18.4% and a carbon selectivity towards carbon of 30%. Figure 9 shows the process flowsheet for this process as well as the main sections. The reactor operates at a temperature of 30 °C and a pressure of 1 bar and yields a 98% vapor product that is cooled down and flashed in a tank. The rest of the flowsheet follows a similar structure as the syngas-to-acetic acid process. To recover the methane from the unreacted species, a three-stage membrane was utilized based on Haider et al., who suggested a unit that recovers 99% biomethane from biogas⁷³. The biomethane from this unit, however, was very sensitive to the presence of nitrogen, which has a comparable size to that of carbon monoxide. Therefore for this thesis, the purity of methane wasn't assumed to reach the reported 99% value. The methane, instead, is assumed to be recovered alongside the carbon monoxide based on the kinetic diameter and diffusivity through a membrane^{74, 75}. To separate methane and carbon monoxide, the COSORB process is suggested⁴⁰. To recover carbon dioxide, an amine scrubbing system was used, with 99% CO₂ recovery⁵⁷. In comparison to the syngas-to-acetic acid process, only 35,000 tonne/yr of freshwater were needed for quenching, based on the sensitivity analysis. The process then follows a similar route, with re-quenching and a subsequent distillation. In contrast to the syngas-to-acetic acid process, however, the purification section didn't require a solvent. This could be explained given the high acetic purity obtained after quenching. Only an additional dehydration column with a higher duty was needed to obtain 99.5% acetic acid.

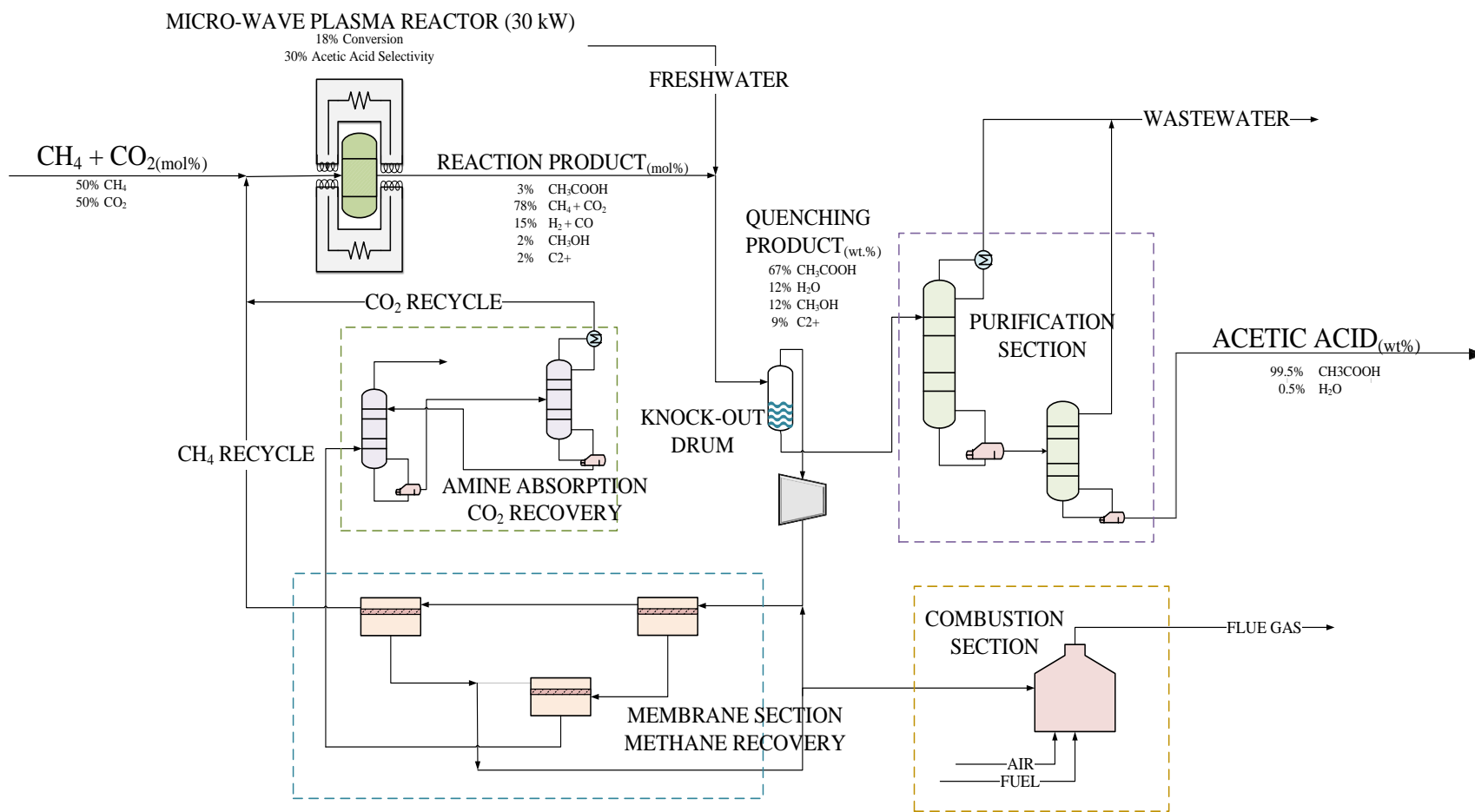


Figure 9. Direct Pathway Process Flowsheet

3.4.3.1. Process Conversion and Selectivity and Reactor Modelling

The conversion and selectivity values were obtained from Wang et al⁴⁷, and were used to obtain the product distribution shown in Figure 10. As mentioned previously, this process does not entail the use of catalyst but requires a plasma-assisted reactor, given the thermodynamic barrier that impedes direct conversion. Despite the complexities associated with plasma reactors, the simulation tools from ASPEN Plus were deemed sufficient and the conversion and selectivity were assumed to remain the same despite the upscaling of the process. Similar to the syngas-to-acetic acid flowsheet, we modelled the product distribution using the component mapping option from the RYIELD reactor.

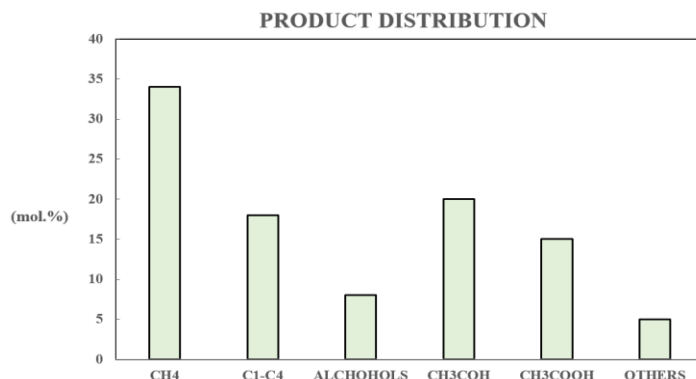


Figure 10. Product Distribution of the Direct Pathway

3.5. Economic Model Assumptions

3.5.1. Total Capital Investment and Return on Investment

To measure economic performance, two key metrics were evaluated: (1) total capital investment (TCI) and (2) return on investment (ROI). When possible, all equipment was sized in ASPEN Plus and direct costs were estimated using Aspen Process Economic Analyzer (APEA).

When either ASPEN Plus or APEA were not sufficient or reliable enough, literature values and rules of thumb were utilized. To account for inflation and discrepancies in plant size, the six-tenths factor rule and chemical engineering plant cost index (CEPCI) were used, respectively.

$$FCI_a = FCI_b \left(\frac{Capacity_{plant\ a}}{Capacity_{plant\ b}} \right)^{0.6}$$

$$FCI_{t1} = FCI_{t2} \left(\frac{CEPCI\ at\ time\ t1}{CEPCI\ at\ time\ t2} \right)$$

To estimate FCI from direct equipment cost, a revised Lang Factor of 4.7 was used and a 1.4 multiplying factor was applied when the costs were reported in terms of inside batter limits (ISBL). The working capital investment (WCI) was taken to be as 20% of the FCI, and the TCI was assumed to be the sum of the FCI and WCI.

$$TCI = FCI + WCI$$

$$AATP = (revenue - annual\ operating\ cost - depreciation) \times (1 - tax) + depreciation$$

$$revenue = production\ rate \times selling\ price$$

$$depreciation = \frac{TCI - Salvage\ Value}{Life\ Period}$$

$$ROI = \frac{Annual\ after\ tax\ profit\ (AATP)}{TCI}$$

To obtain depreciation, a 10-year linear scheme was used with a salvage value of 0. The only source of revenue was assumed to be acetic acid. With an acetic acid selling price of \$500/tonne, an on-stream efficiency of 91.32% (8000 hrs/yr) and a plant capacity of 300,000 tonne/yr (annual production of 273,000 tonnes), the total revenue for all three pathways is fixed and has an approximate value of \$150 MM/yr. Table 1 summarizes the main economic assumptions used to develop our model.

Table 1. Economic Model Assumptions

Item	Unit	Value
Acetic Acid Selling Price	\$/tonne	550
Plant Capacity	tonne/yr	300,000
Tax Rate	%	21
On-stream Efficiency	%	91
Salvage Value	\$	0
Depreciation Period	yrs	10

3.5.2. Annual Operating Cost

The annual operating cost (AOC) varied for each case given the intricacies and uniqueness of each pathway. However, the same feedstock, natural gas (with 98.5% methane quality) and carbon dioxide, is used for all processes. Table 2 shows the cost assumptions for the other reactants. Cost for air was not considered to be part of the feedstock expenses.

Table 2. Feedstock Purchasing Price Assumptions

Product	Unit	Value
Natural Gas	\$/kSCF	3.00
	\$/tonne	157
Carbon dioxide	\$/tonne	30
Process Water	\$/tonne	0.5

For most heating utilities, the heating duty was assumed to come from fuel (inlet of 50 °C and outlet of 700 °C). For all others, low (5 barg and 150 °C), medium (10 barg and 100 °C) and high (30 barg and 250 °C) pressure steams were used. Cooling duties were mostly satisfied using cooling water (inlet 20 °C and outlet 25 °C). Additionally, where much lower temperatures were needed, a low temperature refrigerant (inlet –40 °C and outlet –30 °C) was used. Finally, electricity at a 5 cents per kilowatt-hour rate was used for power needs. It should be noted that all utility price values are approximately scaled based on the cost of natural gas, which is assumed to be the ultimate source of fuel. Thus, for instance, if the price of natural gas is rated at \$3.00/MMBTU and assuming a fired heater efficiency of 87%, steam could be obtained at a price of around \$3.45/MMBTU. Thus, a high natural gas price would lead to a high steam price, which would lead to higher electricity and refrigeration prices. Conversely, low natural gas prices will lower down the cost for the remaining utilities, Table 3 summarizes the utility costs.

Table 3. Summary of Utility Costs

Item	Unit	Value	Equivalent (\$/MMBTU)
Fuel (Natural Gas)	\$/kSCF	3.0	2.9
Electricity	\$/kWh	0.05	14.7
Low Pressure Steam	\$/tonne	8.0	3.5
Medium Pressure Steam	\$/tonne	8.0	3.8
High Pressure Steam	\$/tonne	8.0	4.4
Cooling Water	\$/m ³	0.03	1.5
Refrigerant	\$/GJ	15	15.8

The remaining of the AOC includes process specific expenses such as catalyst for the commercial and indirect pathways and plasma generation for the direct pathway. Finally, a charge of 4 cents per tonne of waste water treatment was applied.

3.5.3. Cost Estimation for Reactors

To estimate reactor section costs, ASPEN simulation tools weren't employed, we instead used data obtained from literature and corrected for size and inflation. ASPEN Plus treats any reactor system as an empty vessel. While these assumptions might be acceptable for other unit operations in the flowsheet, the reactor is the most important one and often involves complex parts that carry additional costs not considered in the ASPEN Plus economic toolbox. Furthermore, the expenses associated with the reactor section usually take more than 80% of the FCI, and more accurate metrics are needed to provide a reliable estimate. For the syngas-to-acetic acid process, we used a report from Pacific Northwest National Labs (PNNL) that evaluates the production of methanol and other distillates directly from syngas⁷⁶. For the plasma reactor, we used the values reported by de la Fuente et al. for various chemical manufacturing processes⁷⁷. While the evaluated processes do not produce acetic acid, it is the closest economic in literature, and in this case, estimation by analogy is considered sufficient.

3.5.4. Plasma Calculations

As mentioned, for the plasma-assisted process Wang et al. used a dielectric discharge barrier reactor. However, there is no data available in literature that estimates the cost for dielectric discharge barrier, so instead we assumed the process used a microwave plasma reactor in the reaction system⁷⁷. Furthermore, dielectric discharge barrier reactors are known to be among the least efficient plasma-assisted processes involving methane and carbon dioxide, and using a microwave plasma to produce liquid products has been proven⁷⁸.

3.5.4.1. Plasma Duty Requirements

To estimate the plasma requirements in the form of energy, we used the equations given by Snoecks⁷⁹. The specific energy input (SEI) can be calculated from power input and enthalpy of reaction and then the molar energy consumption (EC) can be calculated. We assumed an EC value of 100 kJ/mol for the plasma model and moles converted were obtained from the simulation⁸⁰.

$$\text{Plasma Electricity Requirement} = EC \times \text{moles converted}$$

Finally, it is also assumed that not all the energy from plasma in the form of electric power is not going towards the enthalpy of the reaction. Instead it is dissipated as heat and it raises the temperature of the species in the reactor mix. Thus, in order to preserve the same exit temperature there must be an extra cooling utility that removes the additional heat. The enthalpy of the reaction was obtained from the ASPEN Plus results, the cooling utility was satisfied using cooling water and the efficiency was assumed to have a value of 0.8.

$$\text{Additional heat from plasma} = \Delta H \times \left(\frac{1}{\text{Efficiency}} - 1 \right)$$

3.5.4.2. Plasma Reactor Upscaling

To upscale this experiment, we assumed that plasma was provided to the reactor through plasmatrons or generators. In microwave assisted processes, a plasmatron is a device that generates jets of plasma through high current streams of energy, in the form of electricity. Each individual plasmatron follows an economy of scale pattern, where unit prices (measured in \$/kW) decrease with increasing production quantity. However, a single plasmatron is not sufficient to provide the required energy for a large scale system and hundreds (or even thousands) of units would need to be purchased. We assumed that the acquisition of all necessary plasmatron modules does not follow the six-tenths factor rules that chemical plants normally follow, and instead it follows a

linear pattern (no reduction in cost per unit for increase in capacity). While this assumption will considerably increase the capital expenses, there is no evidence in literature that suggests an economy of scale for these type of systems. We also decided to keep this conservative estimate given the importance and sensitivity of the reactor costing in our economic model. Figure 11 shows that the unit price quickly reduces as the capacity of each individual plasmatron increases, reducing costs from around \$10,000/kW for a 15 kW/2450 MHz generation unit down to around \$1500/kW for a 100kW/915 MHz unit.

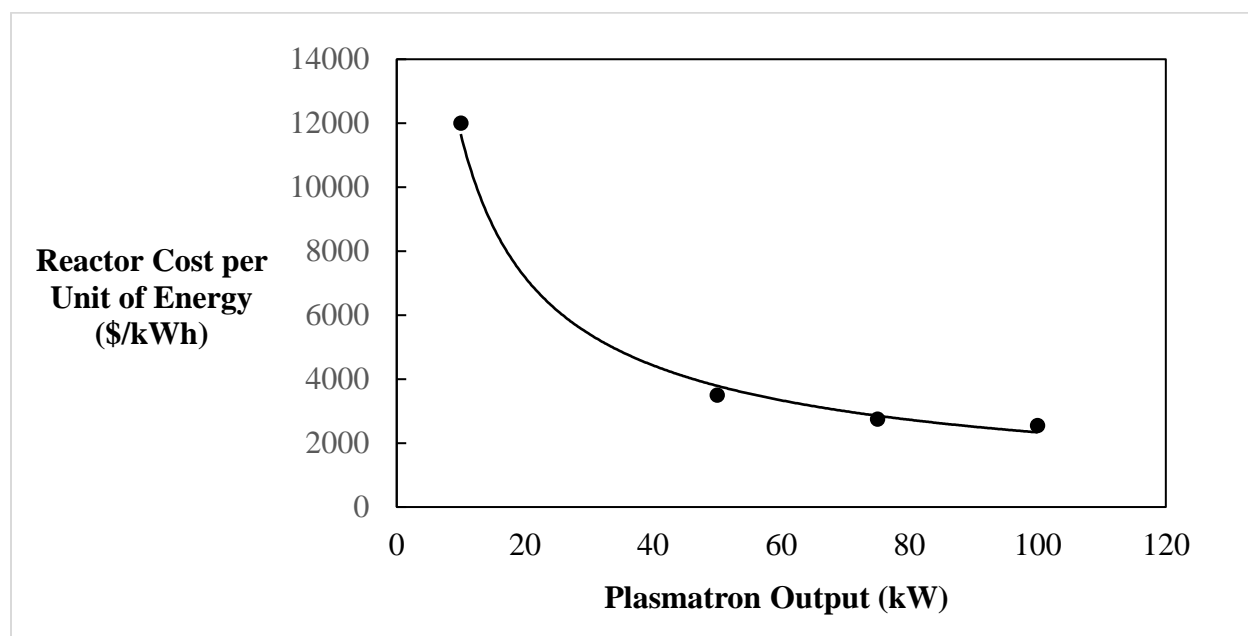


Figure 11. Unit Cost of Plasma-Assisted Reactors (Adapted from de la Fuente et al., 2017⁷⁷)

However, all processes that have been successful at input powers greater than 90 kW are designated for applications other than chemical manufacturing processes. Such high output power units require very low frequencies (<1000 MHz) and at these conditions a stable state is generally difficult to maintain for processes involving chemical applications. The process with the largest

capacity of such applications was reported by Sanchez et al⁸¹. The authors began operation in a medium scale plant that produced 1,500 tonne/yr of ethanol and 250 tonne/yr of fuel diesel, using 30 kW microwave units and a reactor pressure of 1 bar. This pilot plant ran for four years. This project is not only closely aligned with the objective of our work, but it also resembles the operating conditions and product distribution of our process. Therefore, for the direct pathway we also assumed a plasmatron input power of 30 kW (\$ 5000/kW) for a total cost of \$150,000 per unit.

3.6. Sustainability model

To estimate sustainability, three metrics were evaluated: (1) net CO₂ emissions, net CO₂ equivalent (CO₂e) emissions and (3) sustainability weighted return on investment (SWROI). Any required assumption was taken from the Environmental Protection Agency (EPA).

3.6.1. Net CO₂ emissions

The net CO₂ emission refer to the physical amount of carbon dioxide released into the atmosphere. Its rate can be readily calculated as the net sum of sinks and sources that capture and release carbon dioxide streams. Positive values indicate net emissions and a negative capture.

$$CO_2 = \sum (f_{CO_2,out} - f_{CO_2,in})$$

3.6.2. CO₂e Emission

The CO₂e emissions metric is a sustainability concept in which the effect of various greenhouse gases (GHG's) can be expressed in terms of the net amount of carbon dioxide released to the environment⁸². The CO₂e emissions of each pathway were calculated as the sum of CO₂e direct emissions and CO₂e utility emissions.

$$CO_2e = CO_2e \text{ direct} + CO_2e \text{ utility}$$

3.6.2.1. CO₂e Direct Emissions

The CO₂e direct emissions relate to the physical amount of carbon in the gaseous phase coming in and out of the system. To convert the emissions from each GHG, the United States government uses the 100-year global warming potential (100-year GWP), which is defined as the relative heat a GHG will absorb with respect to 1 kilogram of carbon dioxide over a 100-year period. Table 4 shows the 100-year GWP for various GHG's based on EPA's rule E9-5711⁸².

Table 4. 100-Year Global Warming Potential for different Green House Gases

GHG	100-Year GWP
Carbon Dioxide	1
Methane	25
Nitrous Oxide	298
Hydrofluorocarbon	1550
Chlorofluorocarbon	7350

3.6.2.1.1. CO₂e Direct Emissions, Case I

Since only two GHG's are involved in all three pathways, the CO₂e emission rate can be calculated from a mass balance of methane and carbon dioxide streams. If methane is purchased from a source whose main purpose is natural gas extraction for sales (which is the case of most non-associated and shale gas reserves), then the inlet stream of CH₄ in our model cannot be assumed to be captured. This stream instead carries a carbon footprint that needs to be included in the CO₂e emission model. In this model, we assumed that approximately 0.3 tonne of CO₂ is

emitted for every tonne of natural gas flowing into the system ($\sim 5 \text{g CO}_2/\text{MJ}$)¹⁰. Then if all sinks and sources are added the following expression can then be obtained:

$$CO_2e \text{ direct} = \sum (f_{CO_2,out} - f_{CO_2,in}) + 25 \times \sum f_{CH_4,out} + 0.3 \times f_{CH_4,in}$$

3.6.2.1.2. CO₂e Direct Emissions, Case II

If instead natural gas comes from a source where methane would have otherwise been vented or flared (associated and stranded gas reserves), then it could be assumed that the system is indeed capturing of methane. The following assumption would then be obtained:

$$CO_2e \text{ direct} = \sum (f_{CO_2,out} - f_{CO_2,in}) + 25 \times \sum (f_{CH_4,out} - f_{CH_4,in}) + 0.3 \times f_{CH_4,in}$$

To develop the sustainability model, we will use the expression obtained in Case I. Given the large capacity for the plant (300,000 tonne/yr), it would be unreasonable to assume that the necessary amount of associated or stranded gas would be collected for capture, and it will be more realistic instead to assume that it comes from purchases.

3.6.2.2. CO₂e Utility Emissions

The CO₂e utility emissions relate to the equivalent carbon dioxide that results from the usage of a specific utility. The quantity was calculated based on the following equation:

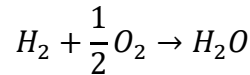
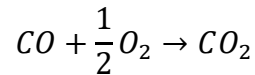
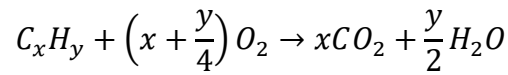
$$CO_2e \text{ utility} = \frac{\text{Duty} \times \text{Emission Factor}}{\text{Energy Factor}}$$

The emission factor relates to the amount of CO₂ released for each utility. For simplicity the ultimate fuel source was natural gas, with an emission factor of 5.8898×10^{-8} tonne CO₂/kJ according to EPA's rule E9-5711²⁴. It is also assumed that this factor considers the footprint from extracting, processing and delivering natural gas. The energy factor of each utility ranges between

-1 and 1 as shown in Table 5. Note that the cooling energy factor is negative because the associated duty is also negative and all CO_{2e} utility values must be greater than or equal to 0.

3.6.2.3. CO_{2e} Emissions and Heat Recovery

As mentioned previously, the off-gases in this process are sent to a combustion chamber that generates heat, which can be used instead of natural gas. To account for the CO₂ emitted, the stream containing the off-gases was sent to an RSTOIC reactor in ASPEN Plus. The following are the reactions for the main reagents in the off-gases:



Then we obtained the emission factor of our fuel. The net emissions were then estimated by comparing the CO_{2e} that would have resulted if natural gas or steam would have been used. The costs are assumed to be part of the recovery network that is already accounted for when we multiplied direct costs by 1.4 to obtain FCI and when we multiplied FCI by 1.2 to obtain TCI.

3.6.3. Sustainable Weighted Return on Investment Metric (SWROIM)

The sustainable weighted return on investment metric extends the concept of ROI and measures the sustainability performance of a project. It is calculated using the following formula:

$$SWROIM = \frac{AATP \left[1 + \sum w_i \left(\frac{Indicator_i}{Indicator_i^{target}} \right) \right]}{TCI}$$

The indicators refer to any sustainability metric that enhances the environmental potential of a pathway. The target indicator in our model is assumed to be equal to that obtained from the

commercial case and the indicator denotes an increase or decrease with respect to the target indicator. The only exception being the solvent category, where the target indicator was not the one from the commercial pathway since this would lead to zero in the denominator. Instead, the value from the direct pathway was entered. Note that the ROI and SWROIM for the commercial case would be the same and if for an alternative pathway the SWROIM is higher than ROI, then it could be said it outperforms the commercial route in sustainability. Finally, weights were assigned based on the guidelines given by El-Halwagi⁵⁵. Table 6 summarizes the main inputs of our model.

Table 5. Energy Factor for Each Utility

Utility	Energy Factor
Cooling	-1
Low Pressure Steam	0.87
Medium Pressure Steam	0.85
High Pressure Steam	0.83
Electricity	0.54

Table 6. SWROIM Indicator Values

Indicator	Target Indicator Value	Unit	Relative Weight
CO ₂ e Emissions	2.13	tonne/yr	0.25
Waste Stream	48854	tonne/yr	0.1
Usage of Water	36830	tonne/yr	0.1
Solvent Circulation	3.05	Million tonne/yr	0.1
Fuel Savings	5.5	MW	0.07

3.7. Sensitivity Analysis

3.7.1. Minimum Acetic Acid Selling Price

To determine if an alternative pathway can be competitive, we determined the minimum acetic acid that will give an ROI of 10%. In North America the selling price of acetic acid is around \$500-\$600 per tonne. However, in other markets the selling price can be as high as \$800. Any pathway that attains a value around this range is deemed suitable for further examination.

3.7.2. Subsidies

3.7.2.1. Carbon Subsidy/Credit

To estimate the minimum carbon subsidy/credit needed to attain economic viability, a threshold of 10% ROI was also used. A common carbon subsidy value in European countries is within a range of \$30-\$50 per tonne. However, values around \$70/tonne are also acceptable and competitive with respect to other carbon capture technologies.

3.7.2.1.1. Carbon Subsidy/Credit from Heat Recovery

To account for the carbon emissions from the combustion of off-gases, we assumed that credit could also be obtained from the heat recovery system. All heating utilities in each process were initially assumed to have purchased methane as the ultimate fuel source and a respective carbon foot print associated with it. However, any heat that is recovered from this fuel is not considered to add to the carbon footprint since this fuel is produced by system itself. Instead, the use of this fuel is preventing CO₂e emission that would have come from natural gas burning, and the emissions would then count towards carbon credit.

3.7.2.2. Electricity Subsidy

The increased use of wind and solar power can cause major fluctuations in grid systems due to their non-dispatchable technology. Thus, is not unreasonable to assume that government

subsidies can also be included in our model, especially considering the high intake of electricity of some of the processes we simulated such as separation units (PSA, membranes and COSORB) and plasma reactors. For wind electricity, government supports range from \$15-\$75 per MWh and for solar this range can be as high as \$80-\$250. Therefore, any alternative pathway that uses an electricity subsidy at the higher end of wind or the lower end of solar would be acceptable.

3.7.3. Sensitivity Analysis Model

For our sensitivity analysis model we considered four changing parameters: (1) acetic acid price, (2) carbon subsidies, (3) natural gas price and (4) renewable electricity subsidies. Table 7 summarizes the lower and upper boundaries for the changing parameters.

Table 7. Sensitivity Analysis Model Lower and Upper Boundaries

Parameter	Unit	Lower Boundary	Upper Boundary
Acetic Acid Selling Price	\$/tonne	400	700
Carbon Subsidy	\$/tonne	30	50
Natural Gas Purchasing Price	\$/kSCF	1.5	4.5
Electricity Subsidy	\$/MWh	10	50
Plasma Efficiency (SEI)	kJ/mol	100	450
Cost per Plasmatron	\$/kW	2000	10000
Plant Capacity	tonne/yr	1.5	4.5

4. RESULTS AND DISCUSSION

4.1. Targeting Results

4.1.1. Theoretical Stoichiometric MISR Results

The results from the Monte Carlo simulation in Table 8 show that all pathways have an expected (P50) MISR value greater than 1 and therefore were considered economically viable. The only pathway with a low (P10) MISR value less than 1 is the commercial, but since it was used as the base case flowsheet, it wasn't screened out.

Table 8. Theoretical Stoichiometric MISR Results

Pathway	Reaction	Low MISR	Exp. MISR	High MISR
Commercial	$CH_3OH + CO \rightarrow CH_3COOH$	0.89	1.15	1.49
Indirect	$2H_2 + 2CO \rightarrow CH_3COOH$	3.09	4.28	6.04
Direct	$CH_4 + CO_2 \rightarrow CH_3COOH$	6.20	8.38	11.15

4.1.2. MISR Results with Actual Stoichiometry and Reactant and Product Recovery

The next step was re-running the Monte Carlo simulation for the more realistic case, where conversion and reactant and product recovery were taken into account. As mentioned previously, the conversion values obtained from literature were used to perform a mass balance and calculate the required purchase quantity of reactants as well as the produced product. A fixed 80% product recovery was used and reactant recovery was variable. If a reactant recovery rate range of values between 85 and 95% is considered, then as Figure 12 shows the expected (P50) MISR value for

all three pathways remains greater than 1 and therefore we still consider them economically viable and proceeded to the simulation.

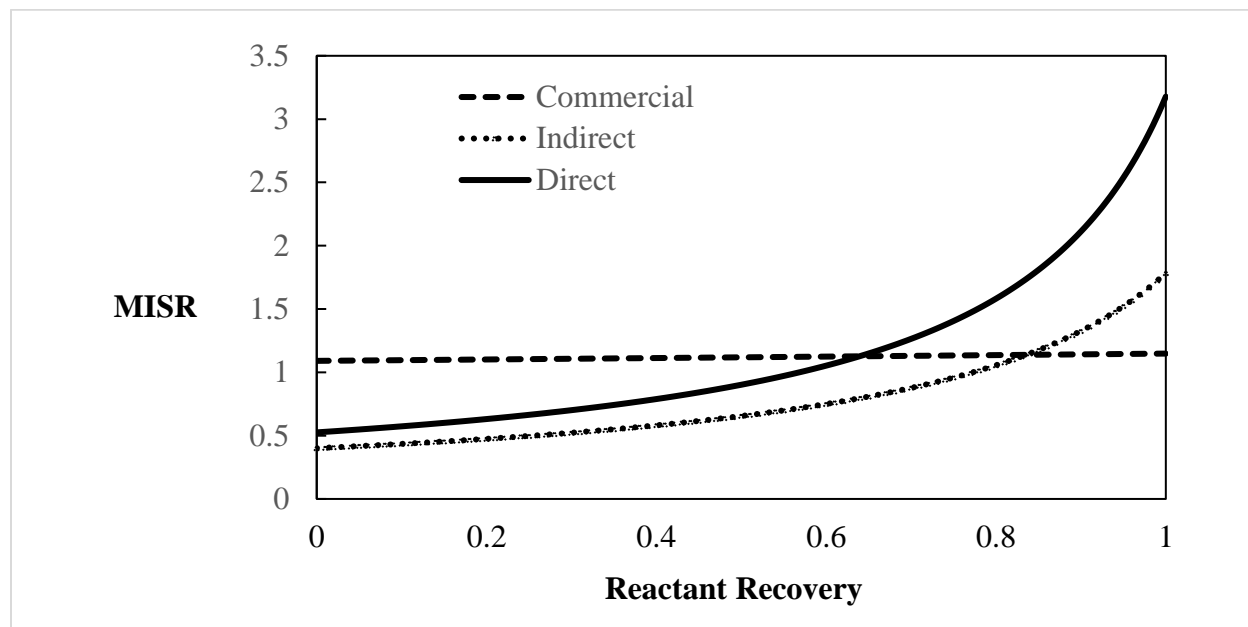


Figure 12. Expected MISR vs. Reactant Recovery for a fixed Product Recovery of 80%

4.2. Simulation Results

4.2.1. Mass and Energy Balance

The results of the ASPEN Plus simulations and the literature parameter extraction indicate that the commercial pathway is the best performing process based on its reduced consumption of both mass and energy. Table 9 shows that the commercial pathway is the least intensive on all categories, which could be attributed to the fact that all processes have very high conversions and selectivity towards acetic acid, and therefore not that much input or output mass is experienced (note that this is the only process that requires water as a reactant and it was added with the process water streams). Also an important observation is that the indirect pathway is the most material

intensive process in all categories. For methane and carbon monoxide, this is an expected result since the syngas-to-acetic acid process requires a high input of syngas, which in turn requires from the DMR a high input of methane and carbon dioxide. For the water and waste streams, this entirely comes from the syngas-to-acetic acid step. As mentioned in the process description, the product distribution for this process has a very challenging distillation curve. Finally, it should also be noted that despite the low conversion and selectivity, the direct pathway shows a low mass usage, aligning with the initial hypothesis that directness could indeed reduce raw material intensiveness.

Table 9. Mass Balance Results in tonne/tonne AA

Pathway	CH₄	CO₂	Water	Waste
Commercial	0.29	0.69	0.13	0.41
Indirect	1.37	3.76	0.72	4.16
Direct	0.99	2.26	0.36	1.37

Table 10 shows that the commercial pathway is the least energy intensive process, with the finishing step (the methanol-to-acetic acid process) being the one with the most consumption. This is an expected result considering that all data for the commercial pathway was retrieved from industrial reports, where the process flowsheets are optimized and intensified very close to its maximum level. Also, the mass rate is the lowest for this pathway, which translates into a lower duty value for most units. The indirect pathway is again the most intensive process, which is due mostly to the syngas-to-methanol process, which has very high temperature and pressure conditions and exhibits a rather challenging reactant recovery. Unlike methane and carbon dioxide, syngas has a very energy expensive separation and recovery process, and this is reflected in its

high electricity consumption. This coupled with the high pressure help explain the relative high energy consumption of this pathway with respect to the other two. Finally, the direct pathway has the lowest heating utilities given its low temperature and pressure conditions and the plasma requirements take a significant portion of the entire energy consumption of the process. It should be noted that the reported material and energy balances results are without any heat or mass in, and therefore do not include the values from the heat exchange network.

Table 10. Energy Balance Results (Units in MWh/ tonne AA)

Pathway	Cooling	Heating	Electricity	Plasma
Commercial				
Syngas Production (SMR/DMR)	0.23	0.47	0.17	0.00
Syngas-to-methanol	0.57	0.45	0.13	0.00
Methanol-to-acetic acid	0.70	0.85	0.14	0.00
<u>Total</u>	1.50	1.77	0.44	0.00
Indirect				
Syngas Production (DMR)	0.01	1.64	3.07	0.00
Syngas-to-acetic acid	5.98	7.41	1.82	0.00
<u>Total</u>	5.99	9.05	4.89	0.00
Direct				
Acetic acid from CH ₄ and CO ₂	2.73	3.21	1.66	2.09
<u>Total</u>	2.73	3.21	1.66	2.09

4.2.2. Equipment Size

Simulation results regarding the size of the equipment were done using ASPEN Plus. It should be noted that only equipment modelled in ASPEN Plus was considered for sizing.

4.3. Economic Model Results

Table 11 shows the calculated FCI values for each step, then the TCI was calculated assuming it is 1.2 times the FCI (i.e. the WCI is 20% of the FCI). It shows that the commercial pathway has the lowest TCI of all pathways and the indirect pathway the highest one, a result that follows the trend observed in the previous material and energy balances. Similarly, Table 12 shows the total annualized cost (TAC) breakdown. It shows the same result with the commercial pathway being the most economically attractive and the indirect pathway the least. This again can be explained based on the material and energy intensiveness of the processes. A noteworthy act however, is the relatively low non-plasma utility cost of the direct pathway, despite the large material usage. This again aligns with the hypothesis that suggests a reduced cost if the directness of a process is increased.

Table 11. TCI Results

Pathway/Process	(\$MM)
Commercial	
Syngas Production (SMR/DMR)	57
Syngas-to-methanol	79
Methanol-to-acetic acid	179
<u>FCI</u>	315
<u>TCI</u>	378

Table 11 Continued.

Pathway/Process	(\$MM)
Indirect	
Syngas Production (DMR)	375
Syngas-to-acetic acid	1440
<u>FCI</u>	1815
<u>TCI</u>	2177
Direct	
<u>FCI</u>	1247
<u>TCI</u>	1496

Table 12. TAC Results

Pathway	Commercial	Indirect	Direct
Fixed Annual Cost (FAC) (\$MM/yr)	37.8	217.7	149.6
Annual Operating Cost (AOC) (\$MM/yr)	35.5	176.7	100.5
Feedstock	18.2	93.5	53.8
Utilities (Non-plasma)	14.4	55.9	18.2
Waste Water Treatment	0.02	0.32	0.11
Catalyst	2.9	27.0	0.0
Plasma Utilities	0.0	0.0	28.4
<u>Total TAC (\$MM/yr)</u>	73.3	394.4	250.1

Finally, Figure 13 summarizes the economics of the three pathways. As previously mentioned, revenue is fixed for all three pathways and has a value of \$150 MM/yr. As was expected, the commercial pathway has the largest ROI of all three pathways. Furthermore, it is the only pathway with an ROI greater than or equal to 10%, making it the only economically attractive route. The indirect pathway shows again the lowest performance, with a very low AATP and ROI and very small room for improvement. This pathway is most likely not going to be considered for re-design. The AATP for the direct pathway, however, is almost the same as the one for the commercial pathway. The ROI for the direct pathway, however, is almost the same as the one for the commercial pathway. This is due mostly to its high TCI and therefore TAC. The direct pathway has an ROI of little less than 5%, but in contrast to the indirect one, it has a lot of room for improvement and is most likely going to be considered for re-design.

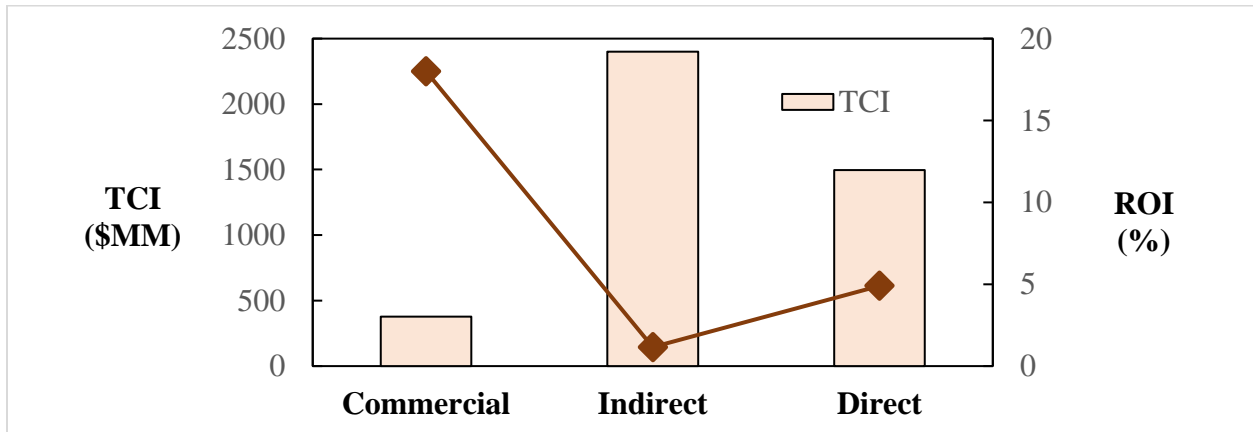


Figure 13. TCI and ROI Comparisons of the Three Pathways

4.4. Sustainability Model Results

4.4.1. CO₂e Emissions Results

As was theorized, both alternative pathways were not competitive enough against the commercial route, given the shortcomings in technology and of the process itself. However, as

Table 13 shows, these two alternatives have a much higher sustainability potential than the commercial pathway. Even though the commercial route emits the lowest quantity in terms of utility CO₂e values, it does not capture as much CO₂e, given its low material intensity. Thus, the factor that made the alternative pathways less economically favorable, now makes it more sustainable and the question becomes whether or not the environmental potential of either alternative can compensate for the technical and economic shortcomings.

Table 13. CO₂ and CO₂e Emissions Breakdown (tonne CO₂/tonne AA)

Pathway	Commercial	Indirect	Direct
Direct CO₂e emissions	-0.53	-3.34	-1.96
Carbon Dioxide	-0.62	-3.76	-2.26
Methane Footprint	0.09	0.42	0.30
Utility CO₂e emissions	0.91	3.08	1.00
Heating	0.43	0.06	0.05
Cooling	0.32	1.01	0.04
Electric	0.16	2.01	0.91
<u>Total</u>	<u>0.38</u>	<u>-0.26</u>	<u>-0.96</u>
<u>Total Emissions (tonne CO₂/yr)</u>	114,163	-70,692	-261,984

4.4.2. SWROIM Results

The results obtained from both alternative pathways were compared to the commercial route. An improvement in any sustainability metric would then contribute positively to SWROI and a downgrade in any of such metrics will decrease it. For the water footprint, it was assumed

that for both alternative pathways the fresh stream was 0, since a purity greater than 99% was obtained without further additions. Table 14 shows either pathway still does not manage to attain a combined economic and sustainable performance that could make it competitive against the commercial route. The indirect pathway, despite its net capture of CO_{2e}, has large waste and solvent streams, which reduces its SWROIM and holds it still as the least attractive alternative. Nevertheless, its SWROIM is higher, which denotes it is more sustainable than the commercial route. The direct pathway, also increases its SWROIM but not to the level of the commercial route.

Table 14. SWROIM Results

Indicator	Unit	Commercial	Indirect	Direct
CO _{2e} emissions	1×10 ⁵ tonne/yr	0.00	1.73	3.65
Waste Stream	tonne/yr	0.00	-1,024,331	-262,491
Water Footprint	tonne/yr	0.00	36,830	36,830
Solvent Usage	Million tonne/yr	0.00	-0.25	-3.05
Fuel Savings	MW	0.00	380.82	104.03
SWROI	%	19.2	7.83	11.70

4.5. Sensitivity analysis

To determine whether or not to proceed with a more detailed sensitivity analysis, first we implemented a model with three variables: minimum (1) acetic acid selling price, (2) carbon subsidy and (3) electricity subsidy. Table 15 shows the minimum values needed to attain an ROI of 10%. It can be seen that the indirect pathway has largely unrealistic values for all variables and thus it wasn't considered for re-design or further inspection. Furthermore, Alsuhaibani reported

minimal improvements in ROI for an increase in conversion per pass, reassuring the notion that the indirect pathway had very little room for enhancement⁸³. The direct pathway however, has values for the variables within a more realistic range, and therefore was considered for re-design.

Table 15. Minimum Acetic Acid Selling Prices and Carbon and Electricity Subsidy

Sensitivity Analysis Variables	Unit	Indirect	Direct
Minimum Acetic Acid Selling Price	\$/tonne	1440	870
Minimum Carbon Subsidy	\$/tonne	230	140
Minimum Electricity Subsidy	\$/MWh	640	109

Figure 14 shows the effect of various parameters on the direct pathway's ROI. As can be seen, there must be major technological improvements for it to become economically attractive.

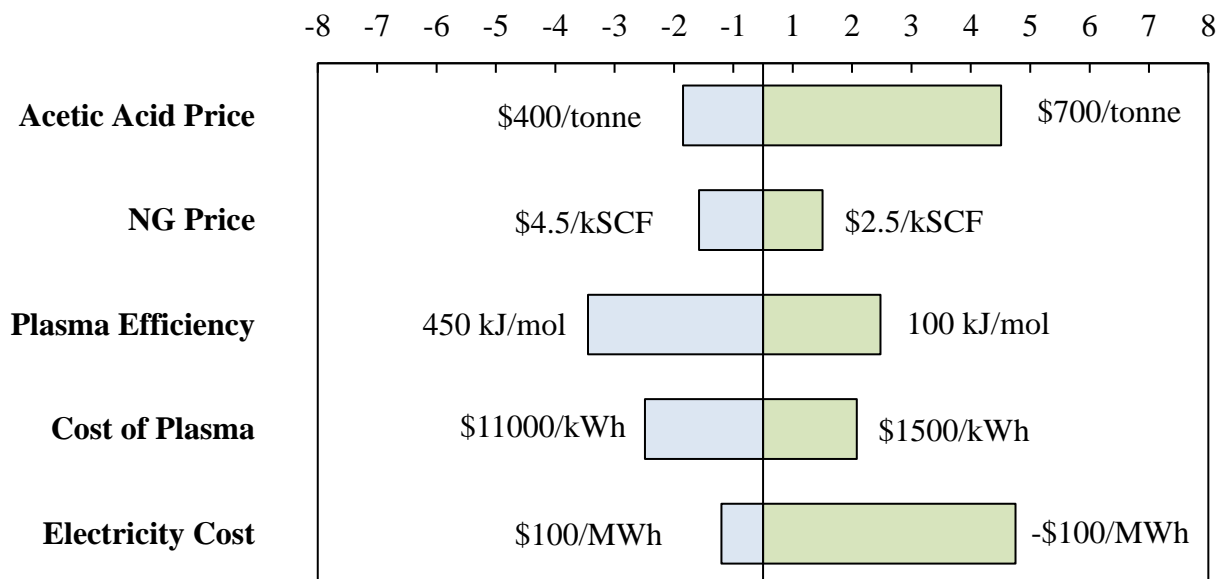


Figure 14. Tornado Plot for the Direct Pathway

To further assess the potential of the direct pathway through a sensitivity analysis model, we estimated the changes needed to move from a \$140/tonne to a \$50/tonne carbon subsidy, which is competitive with most carbon capturing technologies, and still attain the minimum 10% ROI threshold. The main operational parameters that can be improved without a significant change in the conversion and selectivity are the plasma efficiency or specific energy input (kJ/mol) and the cost per unit (\$/kWh) of a plasmatron module. Figure 15 shows that a \$50/tonne carbon subsidy or cost of capture can be obtained if these two parameters are enhanced. We assumed an increase of 33% efficiency, which is equivalent to an SEI of 100 kJ/mol, which is still within a feasible range⁸⁰. Then the plasma unit cost was assumed to be reduced by 20%, which is equivalent to \$2000/kWh. This is also within a reasonable range based on the current state of technology, according to de la Fuente et al⁷⁷.

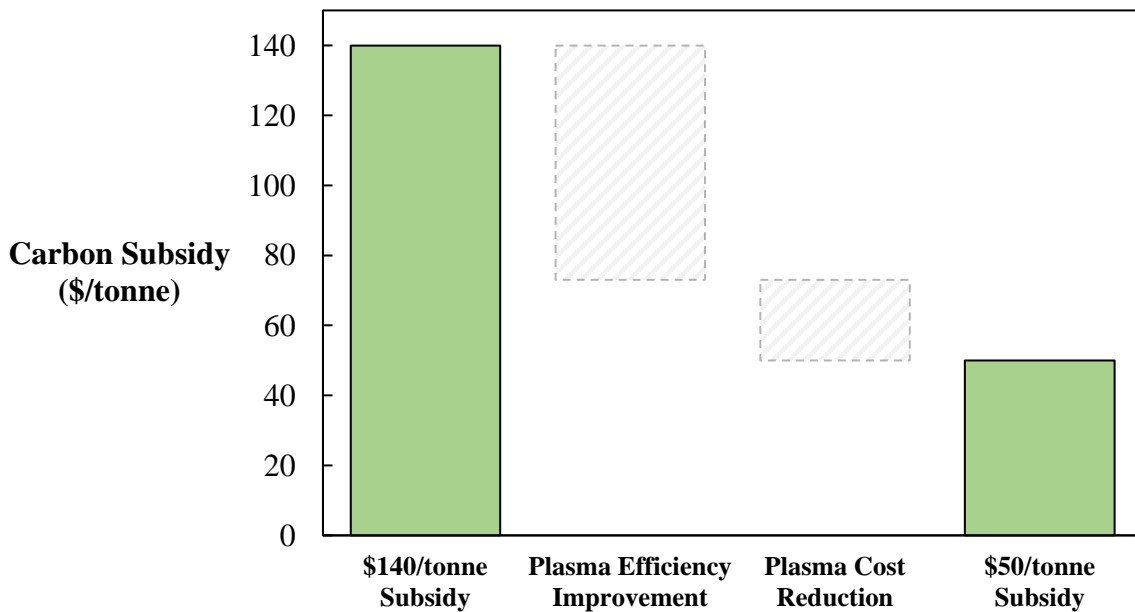


Figure 15. Achieving a \$50/tonne Carbon Subsidy through Process Improvement

As mentioned in the methodology, the entire design process was repeated for a medium and small scale plant. Figure 16 shows the results for each size and it shows first that the TCI decreases approximately linearly with respect to size (mostly due to the assumption that plasma reactor has a linear relationship with size) and second that ROI remains almost constant. It is safe to assume then that size has a very small impact in the economics of the project.

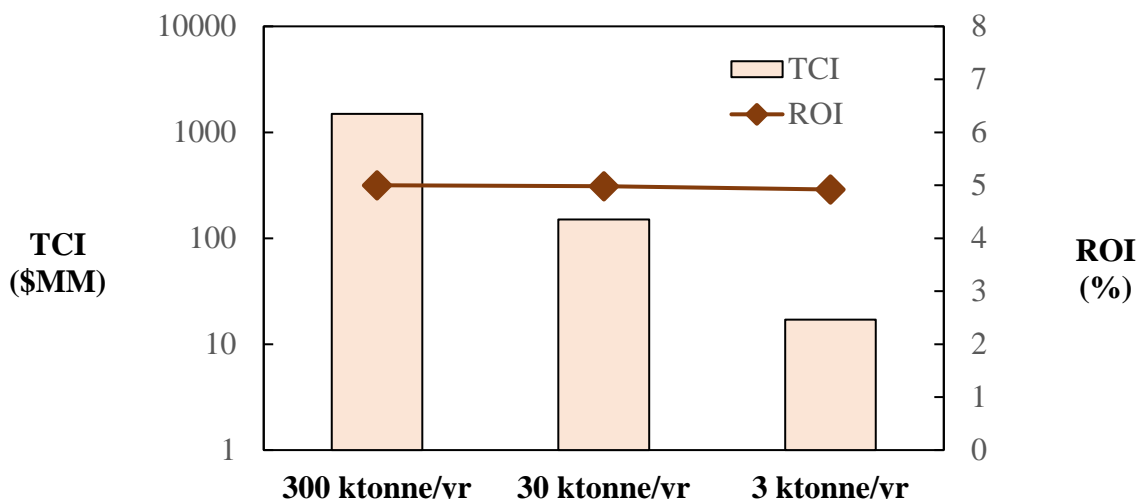


Figure 16. Effect of Plant Capacity on TCI and ROI

While the economics might not suffer from the change in plant size, which is not a common occurrence in chemical application, the sustainability would be impacted given that there would be a trade-off between a less sustainable process from lower quantities of captured carbon and a more sustainable process from a less material and energy intensive system. However, given the complexity of the process and the difficulty in obtaining the necessary equipment and investment, the medium and small scale alternatives seem to be have a more realistic implementation.

5. CONCLUSIONS

5.1. Main Conclusions

A techno-economic and sustainability analysis was assessed for the production of acetic acid from methane and carbon dioxide. Two alternative pathways were analyzed: (1) using syngas as an intermediate product and (2) through direct production using a plasma-assisted reactor. It was found that at an ROI of 19%, the commercial production of acetic acid supersedes that of indirect and direct pathways, which had calculated values of 1% and 5%, respectively. As expected, the alternative processes outperformed the commercial route in sustainability metrics, however it wasn't enough to compensate for the shortcomings on the economics side. The direct pathway was capable of attaining a SWROI of 11.7%, which makes it more attractive and made it a suitable candidate for re-design and further inspection through sensitivity analysis. Furthermore, under more efficient plasma parameters, this pathway could economically compete with the commercial route (i.e. it achieved an ROI of at least 10%) at less than \$50/tonne carbon subsidy. It was also found that the large scale plasma-assisted plant holds no advantage to small and medium processes.

5.2. Final Recommendation

Given the state of technology as well as the economic and sustainability results from this work, we recommend discarding the indirect pathway for further examination instead center the attention towards the production from methane and carbon dioxide directly. Not only did this process prove to be more successful at the combined economic and sustainability level, but it also showed little to no sensitivity to plant size. Therefore, while small and medium scale plants won't be able to capture as much CO₂ as the large scale equivalent, they will have the same return on

investment and a similar normalized environmental impact. The small and medium scale plants will also hold an advantage against the large scale in the process implementation and feasibility, as it would be easier to obtain a 10-100 \$MM investment rather than 1400 \$MM. They are also expected to have a longer life-time and such technologies would be easier to maintain and monitor at a small scale. Therefore, the final recommendation of this thesis is that large-scale industrial production of acetic acid from methane and carbon dioxide should be postponed and instead the chemicals sector should focus on implementing and carrying out these processes at a small and medium scale level.

5.3. Future Work

As mentioned previously, the indirect pathway had very little room for improvement and therefore most of the future work must be dedicated to the direct pathway or any plasma-assisted process that converts greenhouse gases into added-value chemicals. The 2020s mark the beginning of the “transition era” for plasma technology and this work is at the front end of innovation as it is one of the first techno-economic evaluations of industrial scale chemical processes⁷⁷. It is expected that by as early as 2024 there would be large-scale implementation of a plasma-assisted process if they prove to be profitable and technically feasible. As was shown in this thesis, the plasma-assisted processes have various sources and sinks of energy and heat integration and recovery can substantially reduce utility and feedstock costs. Also, superstructure and process intensification can arrange the best possible combination of units that could significantly reduce capital and operational expenses in the reactant and product recovery sections.

REFERENCES

1. EIA *Annual Energy Outlook; U.S. Energy Information Administration*; U.S. Energy Information Administration: Washington DC, 2019.
2. Kidnay, A. J.; Parrish, W. R., *Fundamentals of Natural Gas Processing*. CRC Press: 2006.
3. Elbashir, N. O., Introduction to Natural Gas Monetization. In *Natural Gas Processing from Midstream to Downstream*, 2018; pp 1-14.
4. BP *BP Energy Outlook 2019 Edition*; BP p.l.c.: London, UK, 2019.
5. Gao, J. Y.; You, F. Q., Shale Gas Supply Chain Design and Operations toward Better Economic and Life Cycle Environmental Performance: MINLP Model and Global Optimization Algorithm. *Acs Sustainable Chemistry & Engineering* **2015**, *3* (7), 1282-1291.
6. Gao, J. Y.; You, F. Q., Economic and Environmental Life Cycle Optimization of Noncooperative Supply Chains and Product Systems: Modeling Framework, Mixed-Integer Bilevel Fractional Programming Algorithm, and Shale Gas Application. *Acs Sustainable Chemistry & Engineering* **2017**, *5* (4), 3362-3381.
7. Balcombe, P.; Anderson, K.; Speirs, J.; Brandon, N.; Hawkes, A., The Natural Gas Supply Chain: The Importance of Methane and Carbon Dioxide Emissions. *Acs Sustainable Chemistry & Engineering* **2017**, *5* (1), 3-20.
8. Balcombe, P.; Brandon, N. P.; Hawkes, A. D., Characterising the distribution of methane and carbon dioxide emissions from the natural gas supply chain. *Journal of Cleaner Production* **2018**, *172*, 2019-2032.
9. EPA *United States Environmental Protection Agency*; EPA: Washington DC, 2017.
10. Al-Douri, A.; Sengupta, D.; El-Halwagi, M. M., Shale gas monetization – A review of downstream processing to chemicals and fuels. *Journal of Natural Gas Science and Engineering* **2017**, *45*, 436-455.
11. EIA *Use of Energy in the United States*; U.S. Energy Information Administration: Washington DC, 2019.
12. Al-Mohannadi, D. M.; Hassiba, R. J.; Abdulaziz, K.; Linke, P., A Natural Gas Monetization Approach with Carbon Dioxide and Excess Heat Integration in Industrial Parks. In *Computer Aided Chemical Engineering*, Espuña, A.; Graells, M.; Puigjaner, L., Eds. Elsevier: 2017; Vol. 40, pp 1963-1968.
13. Schwach, P.; Pan, X.; Bao, X., Direct Conversion of Methane to Value-Added Chemicals over Heterogeneous Catalysts: Challenges and Prospects. *Chem Rev* **2017**, *117* (13), 8497-8520.

14. Schwarz, H., Chemistry with methane: concepts rather than recipes. *Angew Chem Int Ed Engl* **2011**, *50* (43), 10096-115.
15. Horn, R.; Schlogl, R., Methane Activation by Heterogeneous Catalysis. *Catalysis Letters* **2015**, *145* (1), 23-39.
16. Karakaya, C.; Kee, R. J., Progress in the direct catalytic conversion of methane to fuels and chemicals. *Progress in Energy and Combustion Science* **2016**, *55*, 60-97.
17. Alvarez-Galvan, M. C.; Mota, N.; Ojeda, M.; Rojas, S.; Navarro, R. M.; Fierro, J. L. G., Direct methane conversion routes to chemicals and fuels. *Catalysis Today* **2011**, *171* (1), 15-23.
18. York, A. P. E.; Xiao, T. C.; Green, M. L. H.; Claridge, J. B., Methane oxyforming for synthesis gas production. *Catalysis Reviews-Science and Engineering* **2007**, *49* (4), 511-560.
19. Christian Enger, B.; Lødeng, R.; Holmen, A., A review of catalytic partial oxidation of methane to synthesis gas with emphasis on reaction mechanisms over transition metal catalysts. *Applied Catalysis A: General* **2008**, *346* (1-2), 1-27.
20. Lavoie, J. M., Review on dry reforming of methane, a potentially more environmentally-friendly approach to the increasing natural gas exploitation. *Front Chem* **2014**, *2* (81), 81.
21. Prakash, A., On the Effects of Syngas Composition and Water-Gas-Shift Reaction-Rate on Ft Synthesis over Iron-Based Catalyst in a Slurry Reactor. *Chemical Engineering Communications* **1994**, *128* (1), 143-158.
22. Wolf, A.; Jess, A.; Kern, C., Syngas Production via Reverse Water-Gas Shift Reaction over a Ni-Al₂O₃ Catalyst: Catalyst Stability, Reaction Kinetics, and Modeling. *Chemical Engineering & Technology* **2016**, *39* (6), 1040-1048.
23. Chein, R.; Yang, Z., Experimental Study on Dry Reforming of Biogas for Syngas Production over Ni-Based Catalysts. *ACS Omega* **2019**, *4* (25), 20911-20922.
24. EPA *Final ACE Rule-CO₂ Emissions Trend*; United States Environmental Protection Agency: Washington, DC, 2019.
25. C2ES *Projecting and Accelerating U.S. Greenhouse Gas Reductions*; Center for Climate and Energy Solutions: Arlington, VA, September, 2017.
26. IEA *Gloval CO₂ Emissions in 2019*; International Energy Agency: Paris, FR, 2020.
27. Nielsen, D. U.; Hu, X. M.; Daasbjerg, K.; Skrydstrup, T., Chemically and electrochemically catalysed conversion of CO₂ to CO with follow-up utilization to value-added chemicals. *Nature Catalysis* **2018**, *1* (4), 244-254.
28. Scibioh, M. A.; Viswanathan, B., Chapter 2 - Surface Chemistry of CO₂. In *Carbon Dioxide to Chemicals and Fuels*, Scibioh, M. A.; Viswanathan, B., Eds. Elsevier: 2018; pp 23-60.

29. Mane, S.; Li, Y. X.; Liu, X. Q.; Yue, M. B.; Sun, L. B., Development of Adsorbents for Selective Carbon Capture: Role of Homo- and Cross-Coupling in Conjugated Microporous Polymers and Their Carbonized Derivatives. *Acs Sustainable Chemistry & Engineering* **2018**, *6* (12), 17419-17426.
30. Yang, F. Q.; Wang, J.; Liu, L.; Zhang, P. X.; Yu, W. K.; Deng, Q.; Zeng, Z. L.; Deng, S. G., Synthesis of Porous Carbons with High N-Content from Shrimp Shells for Efficient CO₂-Capture and Gas Separation. *Acs Sustainable Chemistry & Engineering* **2018**, *6* (11), 15550-15559.
31. Ibrahim, A. F.; Nasr-El-Din, H. A., CO₂ Injection in Coal Formations for Enhanced Coalbed Methane and CO₂ Sequestration. In *Natural Gas Processing from Midstream to Downstream*, 2018; pp 89-111.
32. Hassanpouryouzband, A.; Yang, J. H.; Tohidi, B.; Chuvilin, E.; Istomin, V.; Bukhanov, B., Geological CO₂ Capture and Storage with Flue Gas Hydrate Formation in Frozen and Unfrozen Sediments: Method Development, Real Time-Scale Kinetic Characteristics, Efficiency, and Clathrate Structural Transition. *Acs Sustainable Chemistry & Engineering* **2019**, *7* (5), 5338-5345.
33. Leperi, K. T.; Chung, Y. G.; You, F. Q.; Snurr, R. Q., Development of a General Evaluation Metric for Rapid Screening of Adsorbent Materials for Postcombustion CO₂ Capture. *Acs Sustainable Chemistry & Engineering* **2019**, *7* (13), 11529-11539.
34. Scibioh, M. A.; Viswanathan, B., Chapter 10 - Perspectives—CO₂ Conversion to Fuels and Chemicals. In *Carbon Dioxide to Chemicals and Fuels*, Scibioh, M. A.; Viswanathan, B., Eds. Elsevier: 2018; pp 475-482.
35. TheRoyalSociety *The potential and limitations of using carbon dioxide. Policy Briefing*; The Royal Society: London, UK, May, 2017.
36. Drabik, N. K. Syngas-free conversion of methane to chemicals and fuels: process plant design and economical evaluation. Pd Eng Thesis, University of Twente, Enschede, ND, 2019.
37. TechNavioResearchReports *Global Acetic Acid Market 2018-2022. Abstract*; TechNavio: London, UK, 2018.
38. IHSMarkitChemicalEconomicsHandbook *Acetic Acid*; IHS Markit: London, UK, 2018.
39. Kalck, P.; Le Berre, C.; Serp, P., Recent advances in the methanol carbonylation reaction into acetic acid. *Coordination Chemistry Reviews* **2020**, *402*, 213078.
40. Afzal, S.; Sengupta, D.; Sarkar, A.; El-Halwagi, M.; Elbashir, N., Optimization Approach to the Reduction of CO₂ Emissions for Syngas Production Involving Dry Reforming. *Acs Sustainable Chemistry & Engineering* **2018**, *6* (6), 7532-7544.

41. Sellers, H.; Spiteri, R. J.; Perrone, M., CO₂ + CH₄ Chemistry over Pd: Results of Kinetic Simulations Relevant to Environmental Issues. *Journal of Physical Chemistry C* **2009**, *113* (6), 2340-2346.
42. Wang, S.; Lu, G. Q.; Millar, G. J., Carbon Dioxide Reforming of Methane To Produce Synthesis Gas over Metal-Supported Catalysts: State of the Art. *Energy & Fuels* **1996**, *10* (4), 896-904.
43. Spivey, J. J.; Wilcox, E. M.; Roberts, G. W., Direct utilization of carbon dioxide in chemical synthesis: Vinyl acetate via methane carboxylation. *Catalysis Communications* **2008**, *9* (5), 685-689.
44. Wilcox, E. M.; Roberts, G. W.; Spivey, J. J., Direct catalytic formation of acetic acid from CO₂ and methane. *Catalysis Today* **2003**, *88* (1), 83-90.
45. Huang, W.; Sun, W. Z.; Li, F., Efficient synthesis of ethanol and acetic acid from methane and carbon dioxide with a continuous, stepwise reactor. *AIChE Journal* **2010**, *56* (5), 1279-1284.
46. Zheng, X.; Tan, S.; Dong, L.; Li, S.; Chen, H., Plasma-assisted catalytic dry reforming of methane: Highly catalytic performance of nickel ferrite nanoparticles embedded in silica. *Journal of Power Sources* **2015**, *274*, 286-294.
47. Wang, L.; Yi, Y.; Wu, C.; Guo, H.; Tu, X., One-Step Reforming of CO₂ and CH₄ into High-Value Liquid Chemicals and Fuels at Room Temperature by Plasma-Driven Catalysis. *Angewandte Chemie* **2017**, *129* (44), 13867-13871.
48. Parent, K. E. *Cleaning Up with Atom Economy*; Green Chemistry Institute, ACS: United States, 2002.
49. El Ouahabi, F.; Polyakov, M.; van Klink, G. P. M.; Wohlrab, S.; Tin, S.; de Vries, J. G., Highly Efficient and Atom Economic Route for the Production of Methyl Acrylate and Acetic Acid from a Biorefinery Side Stream. *ACS Sustainable Chemistry & Engineering* **2020**, *8* (4), 1705-1708.
50. Anastasopoulou, A.; Butala, S.; Patil, B.; Suberu, J.; Fregene, M.; Lang, J.; Wang, Q.; Hessel, V., Techno-Economic Feasibility Study of Renewable Power Systems for a Small-Scale Plasma-Assisted Nitric Acid Plant in Africa. *Processes* **2016**, *4* (4), 54.
51. Anastasopoulou, A.; Wang, Q.; Hessel, V.; Lang, J., Energy Considerations for Plasma-Assisted N-Fixation Reactions. *Processes* **2014**, *2* (4), 694-710.
52. Bogaerts, A., Editorial Catalysts: Special Issue on Plasma Catalysis. *Catalysts* **2019**, *9* (2), 196.
53. Scapinello, M.; Martini, L. M.; Tosi, P., CO₂ Hydrogenation by CH₄ in a Dielectric Barrier Discharge: Catalytic Effects of Nickel and Copper. *Plasma Processes and Polymers* **2014**, *11* (7), 624-628.

54. Hu, J. Methods and Compositions for Microwave - Assisted Non - Oxidative Catalytic Direct Conversion of Natural Gas. US 2,019,284,481, September, 2019.
55. El-Halwagi, M. M., Chapter 3 - Benchmarking Process Performance Through Overall Mass Targeting. In *Sustainable Design Through Process Integration*, El-Halwagi, M. M., Ed. Butterworth-Heinemann: Oxford, 2012; pp 63-88.
56. AspenTech *Aspen Physical Property System*; Aspen Technology, Inc: Burlington, MA, November, 2013.
57. Baltrusaitis, J.; Luyben, W. L., Methane Conversion to Syngas for Gas-to-Liquids (GTL): Is Sustainable CO₂ Reuse via Dry Methane Reforming (DMR) Cost Competitive with SMR and ATR Processes? *ACS Sustainable Chemistry & Engineering* **2015**, 3 (9), 2100-2111.
58. Wang, X. Sustainable Clean Coal Technology with Power and Methanol Production. Master of Science in Chemical Engineering, University of Nebraska, Lincoln, NE, 2017.
59. Wang, X.; Demirel, Y., Feasibility of Power and Methanol Production by an Entrained-Flow Coal Gasification System. *Energy & Fuels* **2018**, 32 (7), 7595-7610.
60. Alsuhaibani, A. S. A. Optimal Selection and Design of a Methanol Process with Enhanced CO₂ Utilization. Master of Science in Chemical Engineering, Texas A&M University, College Station, TX, 2018.
61. Yoneda, N.; Hosono, Y., Acetic Acid Process Catalyzed by Ionically Immobilized Rhodium Complex to Solid Resin Support. *Journal of Chemical Engineering of Japan* **2004**, 37 (4), 536-545.
62. Albaroudi, H.; Atayi, K.; Baleca, C.; Osa, E. *Acetic acid process plant design*; University of Hull: Hull, UK, September, 2017.
63. HydrocarbonProcessing® *2014 Petrochemical Handbook*; Gulf Publishing Company: United States, 2014.
64. Roo, M. d.; Swanenburg, V.; Okkinga, O.; Smith, S. Acetic Acid Production from Steel Mill Off-gas. Bachelor Thesis Chemical Engineering, University of Groningen, Groningen, 2018.
65. Luyben, W. L., Design and Control of the Dry Methane Reforming Process. *Industrial & Engineering Chemistry Research* **2014**, 53 (37), 14423-14439.
66. Lopez, L.; Velasco, J.; Montes, V.; Marinas, A.; Cabrera, S.; Boutonnet, M.; Järås, S., Synthesis of Ethanol from Syngas over Rh/MCM-41 Catalyst: Effect of Water on Product Selectivity. *Catalysts* **2015**, 5 (4), 1737-1755.
67. Lopez Nina, L. G. Catalytic conversion of syngas to ethanol and higher alcohols over Rh and Cu based catalysts. Doctoral thesis, comprehensive summary, KTH Royal Institute of Technology, Stockholm, 2017.

68. Somiari, I.; Manousiouthakis, V., Coproduction of acetic acid and hydrogen/power from natural gas with zero carbon dioxide emissions. *AIChE Journal* **2018**, *64* (3), 860-876.
69. Young-II, L.; Jinsoon, C.; Hung-Man, M.; Gookhee, K., Techno-economic Comparison of Absorption and Adsorption Processes for Carbon Monoxide (CO) Separation from Linde-Donawitz Gas (LDG) *Korean Chem. Eng. Res* **2016**, *54* (3), 320-331.
70. Gualy, R. G.; Lamshing, W.; Gentry, J. C.; Varela, F. Method for recovering acetic acid from aqueous streams. US08/090,765, July, 1993.
71. Feyzi, V.; Beheshti, M., Exergy analysis and optimization of reactive distillation column in acetic acid production process. *Chemical Engineering and Processing - Process Intensification* **2017**, *120*, 161-172.
72. Lee, E. J.; Kim, Y. H., Energy saving in acetic acid process using an azeotropic distillation column with a side stripper. *Chemical Engineering Communications* **2018**, *205* (10), 1311-1322.
73. Haider, S.; Lindbråthen, A.; Hägg, M.-B., Techno-economical evaluation of membrane based biogas upgrading system: A comparison between polymeric membrane and carbon membrane technology. *Green Energy & Environment* **2016**, *1* (3), 222-234.
74. Tezel, F. H.; Apolonatos, G., Chromatographic study of adsorption for N₂, CO and CH₄ in molecular sieve zeolites. *Gas Separation & Purification* **1993**, *7* (1), 11-17.
75. Way, J. D. *A Mechanistic Study of Chemically Modified Inorganic Membranes for Gas and Liquid Separations*; DOE-CSM-14363 United States 10.2172/1002957 CHO English; ; Colorado School of Mines, Golden, CO (United States): 2011; p Medium: ED; Size: 45 p.
76. Dagle, R. A.; Lebarbier, V. M. C.; Lizarazo Adarme, J. A.; King, D. L.; Zhu, Y.; Gray, M. J.; Jones, S. B.; Bidy, M. J.; Hallen, R. T.; Wang, Y.; White, J. F.; Holladay, J. E.; Palo, D. R. *Single-Step Syngas-to-Distillates (S2D) Synthesis via Methanol and Dimethyl Ether Intermediates: Final Report*; United States, 2013-11-26, 2013.
77. de la Fuente, J. F.; Kiss, A. A.; Radoiu, M. T.; Stefanidis, G. D., Microwave plasma emerging technologies for chemical processes. *Journal of Chemical Technology & Biotechnology* **2017**, *92* (10), 2495-2505.
78. Puliyalil, H.; Lašič Jurković, D.; Dasireddy, V. D. B. C.; Likozar, B., A review of plasma-assisted catalytic conversion of gaseous carbon dioxide and methane into value-added platform chemicals and fuels. *RSC Advances* **2018**, *8* (48), 27481-27508.
79. Snoeckx, R.; Bogaerts, A., Plasma technology – a novel solution for CO₂ conversion? *Chemical Society Reviews* **2017**, *46* (19), 5805-5863.
80. Michielsen, I.; Uytendhouwen, Y.; Bogaerts, A.; Meynen, V., Altering Conversion and Product Selectivity of Dry Reforming of Methane in a Dielectric Barrier Discharge by Changing the Dielectric Packing Material. *Catalysts* **2019**, *9* (1), 51.

81. Sanchez, A. L. Method and apparatus for plasma gasification of carbonic material by means of microwave radiation EP 2,163,597, June, 2008.
82. EPA *Mandatory Reporting of Greenhouse Gases; Proposed Rule*; United States Environmental Protection Agency: Washington DC, 2009.
83. Alsuhaibani, A. S.; Afzal, S.; Challiwala, M.; Elbashir, N. O.; El-Halwagi, M. M., The impact of the development of catalyst and reaction system of the methanol synthesis stage on the overall profitability of the entire plant: A techno-economic study. *Catalysis Today* **2019**.

APPENDIX A

MONTE CARLO SIMULATION CODE

```
clear
clc
close all

prodrecovery=0.8;
reactrecovery=[0:.01:1];

compounds={'ch3oh'; 'co (pure)'; 'h2'; 'co (syngas)'; 'ch4'; 'co2'};

mws= [32;28;2;28;16;44];
mw_acoh=60;

molein(1:length(compounds),1)=1;

moleout=[.05;.05;.775;.775;.846;.817];
moleout_acoh=[.95;.0571;.0777875];
massout_acoh=moleout_acoh*mw_acoh;

mole_recovered=moleout*reactrecovery; %reactant
mole_feed=molein-mole_recovered;
react_feed=mole_feed.*mws; %reactant
prod_recovered=massout_acoh*prodrecovery; %product

product_low=400;
product_high=700;

r_low=[175;350;5;90;100;20];
r_high=[375;650;10;180;200;50];

c=1000;
%colorcode

for p=1:3
    for k=1:c
        r=2*p-1; %index help
        ch3cooh(k,1)=(product_low+(product_high-
product_low)*rand(1,1))*prod_recovered(p);
        reactants(k,:,p)=sum((r_low(r:r+1)+(r_high(r:r+1)-
r_low(r:r+1))*rand(1,1)).*react_feed(r:r+1,:));
        end
        misr=sort(ch3cooh./reactants,1);
        h(p)=plot(reactrecovery,misr(c*.5, :, p), 'LineWidth', 2);
        hold on
    end
end
```

APPENDIX B
ASPEN PLUS FLOWSHEETS

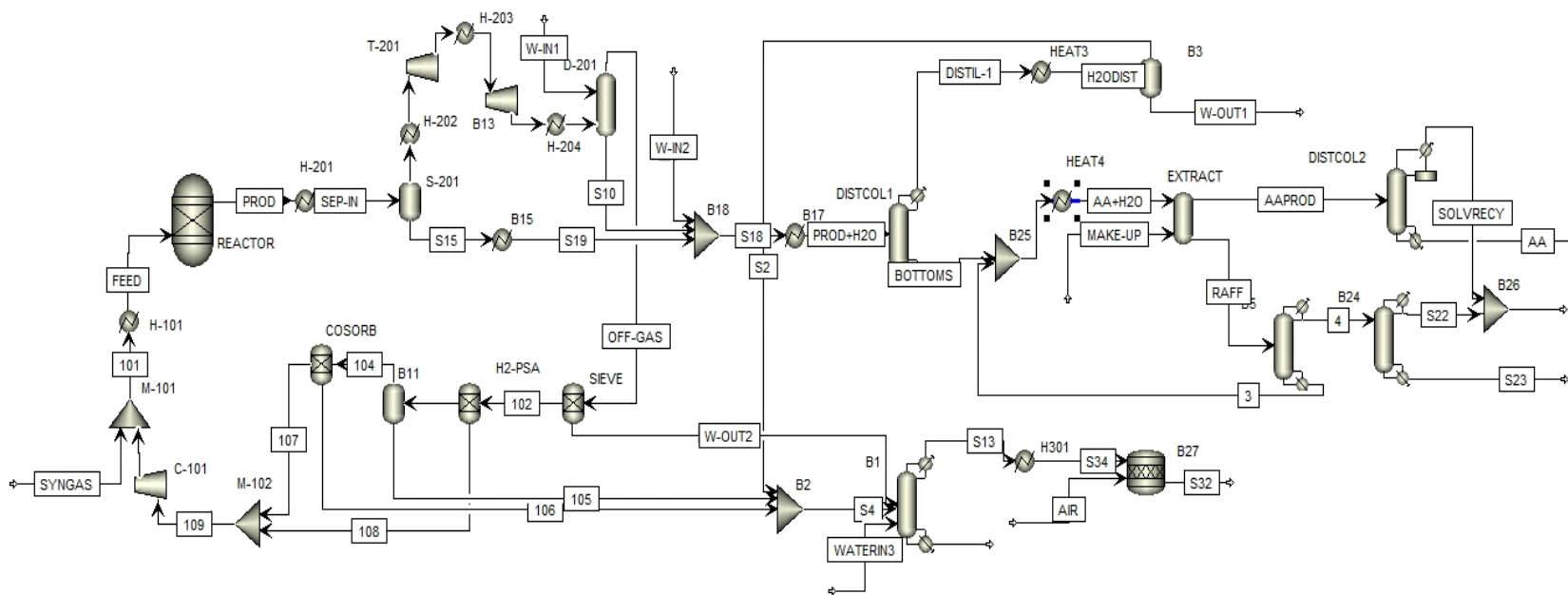


Figure 17. Indirect Pathway ASPEN Plus Flowsheet

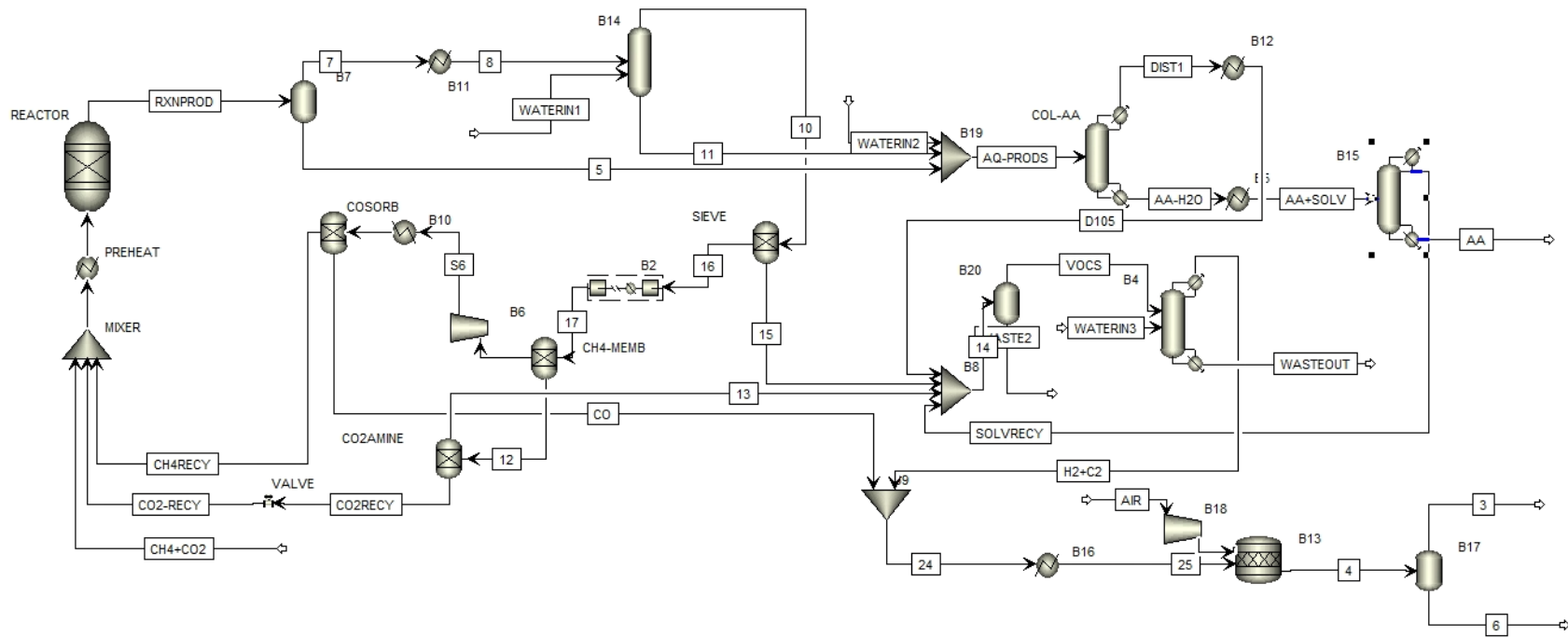


Figure 18. Direct Pathway ASPEN Plus Flowsheet

APPENDIX C

MINIMUM FRESHWATER DETERMINATION

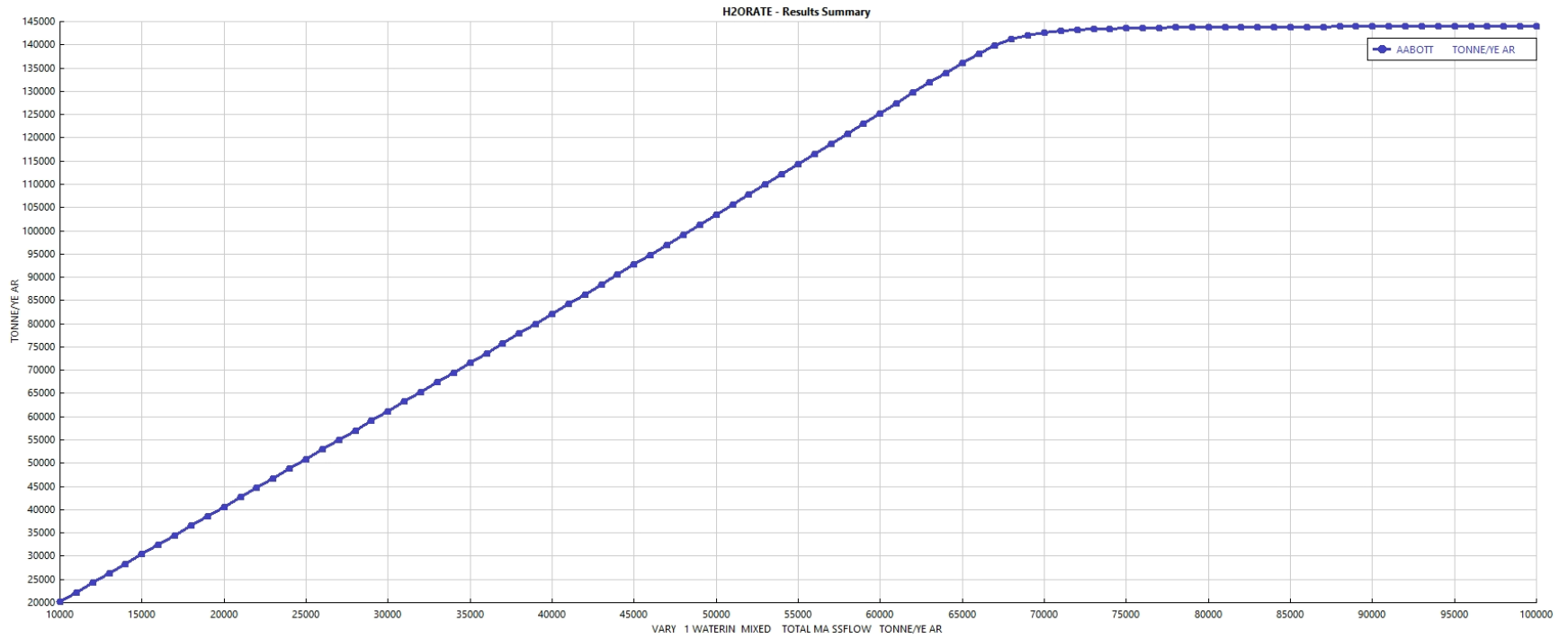


Figure 19. Minimum Freshwater Stream for Indirect Pathway Contactor

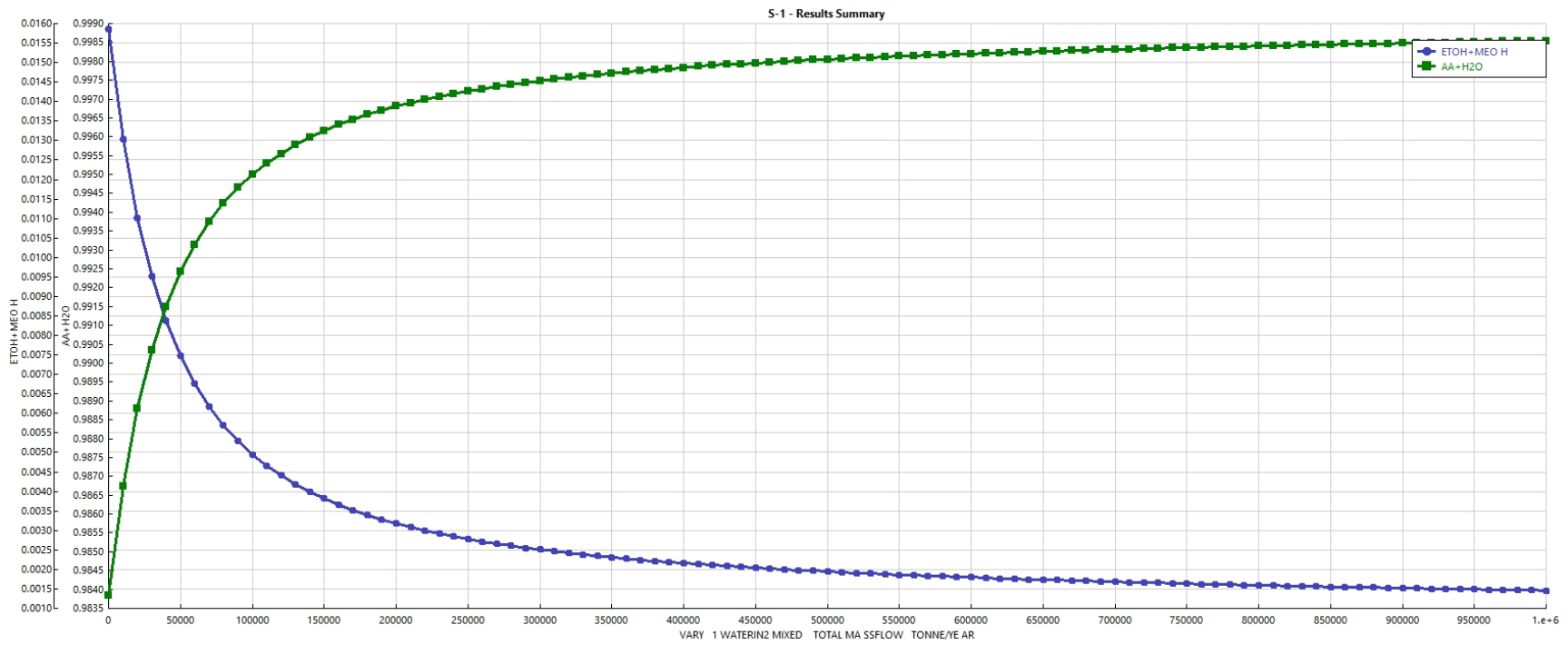


Figure 20. Minimum Freshwater Stream for Indirect Pathway Distillation Column

APPENDIX D

MODIFIED COMMERCIAL PATHWAY CALCULATIONS

Table 16. Modified Commercial Pathway Mass Balance Calculations

Color Code for all Sheets	
	Entered directly from a literature source
	Entered directly from an ASPEN Plus flowsheet simulation
	Final Value

Methanol carbonylation			
Feedstock (PetroHandbook)			
Feedstock	MT/MT	Rate (MT/yr)	Rate (kmol/hr)
Methanol	0.53	159000	567
CO	0.5	150000	612
Product (tonne/yr)			
Acetic Acid	300000		
Syngas (Material Balance) From Wang		Molecular Weight (kg/kmol)	Flow Rates (MT/yr)
H2 (MT/MT_{CH3OH})	0.14	2	22260
CO (MT/MT_{CH3OH})	0.75	28	119250
CO2 (MT/MT_{CH3OH})	0.2	44	31800

Table 17. Modified Commercial Pathway SMR/DMR Values

	SMR	DMR	
	Flow (kmol/h)	Flow (kmol/h)	
Feed			
CH4	3160	2725	
H2O	9480	0	
CO2	0	2725	
Total	12640	5450	
Product			
H2	9858	5095	
CO	2239	5261	
CH4	150	136	
H2O (waste)	5623	0	
CO2	785	53	
Total	18655	10545	
Products	Flow (kmol/h)	From SMR (kmol/h)	From DMR (kmol/h)
	Multipliers -->	0.000	0.249
H2	1271	0	1271
CO	1098	0	1312
CH4	-	0.00	34
H2O (Waste)	-	0.00	0
CO2	103	0.00	13
Total		0	2630
Feed	From SMR (kmol/h)	From DMR (kmol/h)	Total (kmol/h)
Total	0	1359	1359
CH4	0	680	680
H2O	0	0	0
CO2	0	680	680

Table 18. Equipment Cost Estimation Base Case Syngas Production and H₂ PSA Unit

Product Stream	Equipment Type	Cost (\$MM)	Cost After CEPCI (\$MM)	x exponent	Reference rate (kmol/h)	Simulation rate (kmol/h)	Delivered Cost (\$MM)
CH ₄ (SMR)	H-EXCHANGER	0.2225	0.2391	0.6	3160	0	0.0000
H ₂ O	H-EXCHANGER	0.9343	1.0039	0.6	9480	0	0.0000
CH ₄ +H ₂ O	REACTOR	10.39	11.1635	0.6	12640	0	0.0000
CH ₄ +CO ₂	REACTOR	6.79	7.2955	0.6	5450	680	1.6889
CH ₄ +CO ₂	H-EXCHANGER	2.854	3.0665	0.6	5450	680	0.7099
SMRPRODS	H-EXCHANGER	0.7387	0.7937	0.6	18655	0	0.0000
SMRPRODS	H-EXCHANGER	0.6835	0.7344	0.6	18655	0	0.0000
SMRPRODS	H-EXCHANGER	2.323	2.4959	0.6	18655	0	0.0000
SMRPRODS	DIST-COL	0.3248	0.3490	0.86	18655	0	0.0000
SMRPRODS	DIST-COL	0.4427	0.4757	0.86	18655	0	0.0000
SMRPRODS	H-EXCHANGER	0.7005	0.7526	0.6	18655	0	0.0000
SMRPRODS	DIST-COL	0.9383	1.0082	0.6	18655	0	0.0000
SMRPRODS	H-EXCHANGER	0.9554	1.0265	0.6	18655	0	0.0000
SMRPRODS	H-EXCHANGER	0.9209	0.9895	0.6	18655	0	0.0000
DMRPRODS	COMPRESSOR	10.52	11.3031	0.8	10545	2630	2.7974
DMRPRODS	H-EXCHANGER	0.6692	0.7190	0.6	10545	2630	0.2523
DMRPRODS	H-EXCHANGER	0.6501	0.6985	0.6	10545	2630	0.2451
H ₂ -PSA	COMPRESSOR	8.09847	1.7403	0.8	2894	592	0.4891
H ₂ -PSA	TURBINE	3.51499	0.7553	0.8	2894	592	0.2123
DMRPRODS-PSA	DIST-COL	99.619084	21.4070	0.86	10129	1226	3.4818
DMRPRODS PSA	H-EXCHANGER	20.7505	4.4590	0.8	10129	1226	0.8232
						Total	10.70

Table 19. Equipment Cost for Syngas to Methanol

Product Stream	Equipment Type	Cost (\$MM)	Cost After CEPCI (\$MM)	x exponent	Reference rate (kmol/h)	Simulation rate (kmol/h)	Delivered Cost (\$MM)
SYNGAS	H-EXCHANGER	0.018	0.0193	0.6	664	1839	0.0287
GAS PRODS	H-EXCHANGER	0.018	0.0193	0.6	650	5518	0.0563
GAS PRODS	H-EXCHANGER	0.027	0.0290	0.6	650	5518	0.0844
LIQ PRODS	H-EXCHANGER	0.0198	0.0213	0.6	271	567	0.0267
MEOH	H-EXCHANGER	0.0333	0.0357	0.6	271	567	0.0450
H2O	H-EXCHANGER	0.018	0.0193	0.6	50	104	0.0243
GAS PRODS	REACTOR	1.5534	1.6674	0.6	650	5518	4.8573
GAS PRODS	VESSEL	0.01324	0.0142	0.6	650	5518	0.0414
GAS PRODS	VESSEL	0.1267	0.1360	0.6	650	5518	0.3962
LIQ PRODS	DIST-COL	0.53514	0.5744	0.86	664	567	0.3692
SYNGAS	COMPRESSOR	1.673	1.7957	0.8	664	1839	3.0504
GAS PRODS	COMPRESSOR	1.705	1.8301	0.8	650	5518	7.6142
						Total	16.59

The remaining equipment cost was calculated from literature values. Utilities were calculated using the listed assumptions. The same procedure was applied for the remaining pathways.

APPENDIX E
SUSTAINABILITY CALCULATIONS

Table 20. CO₂e Emissions

CO₂e Emissions					
Direct	Emissions (tonne per yr)	CO₂e (tonnes)			
CH ₄ in	269875	80962.56			
CH ₄ out	0	0			
CO ₂ in	618464	-618464			
CO ₂ out	2500	2500			
	Total	-535001			
Off-gas Components	Mass Fraction	GHV (kJ/kg)	kg CO₂/kg comp.	GHV × mass fraction	kgCO₂/kg × mass fraction
ch ₄		45000	2.75	0	0.00
h ₂		143000	0	0	0.00
co	4.0000	11000	1.57	44000	6.29
Emission factor methane(tonne/kj)		5.90E-08			
Utilities	Duty (MW)	Yearly Usage (kJ)	Energy Factor	CO₂e (tonnes)	
Refrig	-7.15	-2.06E+11	-1	1.21E+04	
HPS	0	0.00E+00	0.85	0.00E+00	
MPS	0	0.00E+00	0.87	0.00E+00	
Natural Gas	0	0.00E+00	0.9	0.00E+00	
Power	58.2	1.68E+12	0.57	1.73E+05	
			Total	1.86E+05	