UNIVERSIDADE DE SÃO PAULO
ESCOLA POLITÉCNICA

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Technical, economic and environmental performance of formic acid production from carbon dioxide

São Paulo
2022

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Revised Version

Dissertation presented to the Graduate Program in Chemical Engineering at the Escola Politécnica da Universidade de São Paulo to obtain the degree in Master of Science.

Advisor: Prof.ª Dra. Rita Maria de Brito Alves
Co-advisor: Prof. Dr. Luiz Alexandre Kulay

São Paulo
2022

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São Paulo, 19 de outubro de 2022

Assinatura do autor: _____

Assinatura do orientador: _____

Catalogação-na-publicação

Lopes, João Vitor Monteiro
Technical, economic and environmental performance of formic acid production from carbon dioxide / J. V. M. Lopes – versão corr. -- São Paulo, 2022.
117 p.

Dissertação (Mestrado) - Escola Politécnica da Universidade de São Paulo. Departamento de Engenharia Química.

1.Captura e utilização de carbono 2. Ácido fórmico 3.Simulação 4.Hidrogênio I. Universidade de São Paulo. Escola Politécnica. Departamento de Engenharia Química II.t.

Name: LOPES, João Vitor Monteiro

Title: Technical, economic and environmental performance of formic acid production from carbon dioxide.

Dissertation presented to the Graduate Program in Chemical Engineering at the Escola Politécnica da Universidade de São Paulo to obtain the degree in Master of Science

Approved on August 19th, 2022.

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ACKNOWLEDGMENTS

I would like to thank my advisor, Prof. Rita Maria de Brito Alves for the guidance and support that helped me to get to the end. Thanks to my co-advisor Prof. Luiz Kulay for all the exciting and motivating conversations. Also, I would like to thank Dr. Antonio Esio Bresciani for the very needed technical support.

I am always grateful to my aunt Vanda and Grandma Olga for reminding me that a place to be whenever I am lost.

I also would like to thank my lab colleagues and life friends that showed me the way around in the beginning and always made the daily research journey less lonely. Special thanks to Igor Moura, Maria Clara Mendes, Kaccnny Carvalho, Kelvin Pacheco and Taofeeq Bello.

Finally, I would like to acknowledge the support of the RCGI – Research Centre for Greenhouse Gas Innovation, hosted by the University of São Paulo (USP) and sponsored by FAPESP –São Paulo Research Foundation (2014/50279-4) and Shell Brasil, and the strategic importance of the support given by ANP (Brazil's National Oil, Natural Gas and Biofuels Agency) through the R&D levy regulation.

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

RESUMO

LOPES, J. V. M. **Avaliação do desempenho técnico, econômico e ambiental da produção de ácido fórmico a partir de dióxido de carbono**. Dissertação (Mestrado em Engenharia Química) – Escola Politécnica, Universidade de São Paulo, 2022.

Implementar inovações como a captura e utilização de carbono para a produção de produtos químicos requer uma abordagem sistemática para garantir a competitividade com os processos convencionais e a capacidade de reduzir as emissões de dióxido de carbono (CO_2). A hidrogenação de CO_2 é uma rota potencial para produzir combustíveis sintéticos e produtos químicos de valor agregado, mas como é um processo de demanda energética elevada, seus custos e o impacto de mitigação precisam ser minuciosamente avaliados, considerando as fontes das matérias-primas utilizadas e seus desempenhos técnico, econômico e ambiental. Nesse contexto, o objetivo deste trabalho é avaliar a produção de ácido fórmico por hidrogenação de CO_2 como método potencial de mitigação de emissões de CO_2. A pesquisa foi desenvolvida nas seguintes etapas: (i) estudo de fontes de CO_2 e hidrogênio (H_2) para identificar combinações que resultem em processos de hidrogenação de CO_2 mais sustentáveis; (ii) modelagem e simulação das rotas selecionadas para obtenção dos balanços de massa e energia e condições operacionais do processo e; (iii) análise técnico-econômica e ambiental dos processos de produção de ácido fórmico. Resultados com base em análise de decisão multicritérios sugeriram o uso de dióxido de carbono oriundos de indústrias siderúrgicas e da produção de óxido de etileno combinados com hidrogênio provenientes do gás de coque e da produção de etileno, respectivamente, como potencialmente mais sustentáveis do que outras combinações de fontes de matérias-primas avaliadas. O processo convencional para produção de ácido fórmico e uma rota inovativa foram simulados no Aspen Plus, considerando as combinações de fontes de CO_2 e H_2 definidas. No geral, a rota inovativa custa cerca de 30% a mais que a convencional e emite 45% menos CO_2, e ambas consomem aproximadamente a mesma quantidade de energia, mas de diferentes tipos. A análise de rentabilidade mostrou que seriam necessários, no mínimo, US$ 5 em créditos de carbono por tonelada de CO_2 evitado para que o processo inovador atinja o *breakeven* ao longo da vida útil da planta e US$ 182 para torná-lo competitivo em comparação com a rota convencional.

Palavras-chave: Dióxido de Carbono; Hidrogênio; Ácido Fórmico; Simulação, Captura e Utilização de Carbono.

ABSTRACT

LOPES, J. V. M. **Technical, economic and environmental performance of formic acid production from carbon dioxide**. Dissertation (Master in Chemical Engineering) – Escola Politécnica, Universidade de São Paulo, 2022.

Implementing innovations such as carbon capture and utilization for production of chemicals requires a system-level approach to guarantee its competitiveness with the conventional process and verify its capability to reduce CO_2 emissions. Carbon dioxide hydrogenation is one of the potential routes to produce synthetic fuels and value-added chemicals from carbon dioxide (CO_2). but since it is a highly energy-demanding process, its costs and emission mitigation impact need to be thoroughly evaluated, considering raw material sources and technical, economic and environmental assessments. In this context, the objective of this work is to evaluate the production of formic acid by CO_2 hydrogenation as potential way of mitigating CO_2 emissions. The research was developed in the following stages: (i) study of CO_2 and hydrogen (H_2) sources to identify combinations that results in more sustainable hydrogenation processes; (ii) modeling and simulation of the selected routes to obtain mass and energy balances and operating conditions; (iii) technical-economic and environmental analysis of the formic acid production processes. Results from a multi-criteria decision analysis suggested that using carbon dioxide from iron and steel industries and from ethylene oxide production combined with by-product hydrogen from coke oven gas and ethylene production, respectively, are potentially more sustainable than other feedstock sources combinations evaluated. The conventional process for formic acid production and the innovative route were simulated in Aspen Plus, considering both combinations of CO_2 and H_2 sources. Overall, the innovative route costs around 30% more than the conventional and emits 45% less CO_2, and both consume approximately the same amount of energy, but of different types. The profitability analysis showed that the innovative process would need at least US$5 in carbon credit per ton of CO_2 avoided to breakeven over the plant lifetime and US$182 to make it competitive comparatively with the conventional case.

Keywords: Carbon Dioxide; Hydrogen; Formic Acid; Simulation; Carbon Capture and Utilization.

LIST OF FIGURES

Figure 1 – Scenario of carbon emission per year (a) and cumulative greenhouse gas (GHG) emissions (b) for a scenario of 1.5°C temperature increase 13
Figure 2 - Share of common CO_2 utilization applications. 15
Figure 3 – Global formic acid demand by end use. 17
Figure 4– Hydrogen sources considered in this work. 26
Figure 5 – Shares of CO_2 emissions by stationary point sources. 29
Figure 6 – General MCDA problem structure. 31
Figure 7. Selection method structure. 33
Figure 8 - Carbon footprint of the captured CO_2 to be used as feedstock. 37
Figure 9 - Overall scores of hydrogen sources. 42
Figure 10 – a) Ternary map of best hydrogen source alternative as function of the to the weight given to each criterion. b) Sensitivity analysis of the weights of the hydrogen sources. 44
Figure 11 – Overall scores of CO_2 sources calculated by TOPSIS. 45
Figure 12 – a) Ternary map of best alternative according to the weight combination. b) Monte Carlo analysis on the weights of each criterion used in TOPSIS for CO_2 alternatives, +-20% random variation. 46
Figure 13 –Top ten combined alternatives for H_2 and CO_2 sources. 48
Figure 14 –Evaluated scenarios for formic acid production. 50
Figure 15 – Formic acid process flow diagram (BASF). 51
Figure 16 – Process flow diagram of the formic acid production by CO_2 hydrogenation in ionic liquid. 56
Figure 17 – Hydrogen source integration represented in the simulation. 57
Figure 18 – Ethylene oxidation reaction. 58
Figure 19 – Conventional process flow diagram implemented on Aspen Plus. 60
Figure 20 – CO_2-based formic acid production flowsheet. 61
Figure 21 – Case 1 and 2 boundaries for analysis. 64
Figure 22 – Energy intensity (MJ/kg). 70
Figure 23 – Comparative summary of CO_2 emissions by source. 71
Figure 24 – Operational costs breakdown. 74
Figure 25 – a) total cost breakdown; b) utility cost breakdown. 75

Figure 26 – Comparative discounted cash flow of base cases. 77
Figure 27 – NPV Sensitivity Analysis. 78
Figure 28 – Carbon credits: (a) to make the CCU cases NPV breakeven – US$5 for Case 1, US$42 for Case 2. b) Carbon credit to make Case 1 NPV equal to the conventional case (US$189). 79
Figure 29 - Sketch of a formic acid process using ternary amines and a polyol solvent. 100
Figure 30 – Performance scores and sensitivity analysis for the studied conversion routes. 105
Figure 31 - Equilibrium diagrams for systems (a) Methyl formate(1)/Methanol(2) and (b) Methanol(1)/Water(2). 107
Figure 32 – Equilibrium diagrams for (a) methyl formate(1)/Formic Acid (2) and (b) Water (1)/Formic Acid (2) systems. 108

LIST OF TABLES

Table 1 – CO_2 emitting sources covered in this study. 29
Table 2 - Goal and scope definitions for life-cycle studies in the literature 36
Table 3 - Global warming potential, estimated cost and energy efficiency for hydrogen production processes.....40
Table 4 - Summary of process characteristics of top CO_2 emitting industries.....41
Table 5 - Summary of reactor configurations.....53
Table 6 – Distillation columns configuration summary.....54
Table 7 – Key input output results. 59
Table 8 – Selected indicators for performance analyses.....63
Table 9 – Summary of economic assumptions.....67
Table 10 – Operating cost input summary.....68
Table 11 – Carbon intensity of formic acid produced by different routes (kg_{CO2}/kg of product). 71
Table 12 – Total annual emissions breakdown (tons of CO_2-eq). 72
Table 13 – CCU specific indicators. 72
Table 14 – Projects economics summary.....73
Table 15 – Total annualized cost breakdown, in US$/ton of formic acid. 76
Table 16 – Project profitability indicators in the base case, considering 20 year of plant lifetime. 76
Table 17 – Coding for PC attribute. 102
Table 18 – Process characteristics for the hydrogenation routes. 104
Table 19 – Criteria values estimated for the selected routes. 104
Table 20 – Experimental datasets used for validation and regression. 106
Table 21 – Root mean square deviation NRTL e UNIQUAC 107
Table 22 - Optimal interaction parameters of UNIQUAC-HOC model. 108
Table 23 - Optimal Henry's equation parameters. 108
Table 24 – Stream conditions, mass flowrate and mass fraction for the base case. 109
Table 25 – Utilities Summary table. 110
Table 26 – Coolers and Heaters.....111
Table 27 – Separation vessels 112

Table 28 - Compressor 112
Table 29 - Pumps 113
Table 30 – Distillation Columns 114
Table 31 – Extraction Column 116
Table 32 - Reactors 116

LIST OF ABBREVIATIONS

ACCR	Annual capital charge ratio
CC	Climate Change [$CO_{2\ equivalent}$]
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CDCL	Coal direct chemical looping
CG	Coal Gasification
COM	cost of manufacturing [US$/kg]
EOR	Enhanced Oil Recovery
Ex	Reaction Exergy Approximation [kJ/mol]
EMF	Emission Factor [$kgCO_{2e}$/kJ]
FCC	Fluid Catalytic Cracking
FCI	Fixed Capital Investment [US$]
GWP	Global Warming Potential
IEA	International Energy Agency
IL	Ionic Liquids
IPCC	Intergovernmental Panel on Climate Change
LCA	Life Cycle Analysis
LPS	low pressure [steam]
MCDA	Multi Criteria Decision Analysis
MPS	Medium pressure steam
NGSR	Natural Gas Steam Reforming
NPV	Net Present value
PC	Process characteristic
PR	Production rate [kg/year]
PSA	Pressure Swing Adsorption
Q	Reaction Heat (approx. to rxn enthalpy) [kJ/mol]
R	Gas constant
r	volumetric molar reaction rate [mol/(L.min)]
ROI	Return on Investment
R_{rx}	molar reaction rate [mol/kg.min]
T	Temperature [K]

TAC	total annual cost [US$/kg]
TOPSIS	Technique of Order Preference Similarity to the Ideal Solution
DIPE	Diisopropyl ether
MA	Methanol
MF	Methyl formate
cat	Catalyst
CO	Carbon Monoxide
CO_2	Carbon Dioxide
NEt_3	triethylamine
$NHex_3$	trihexylamine
NPe_3	tripentylamine
ol	operating labor
ut	utilities
RM	raw material
∞	Environment condition
C_{XX}	liquid concentration of component XX in [mol/kg]
$\Delta G_f{}^0$	Gibbs Free energy of formation [kJ/mol]
ΔG_{rx}	Gibbs Free energy of reaction [kJ/mol]

SUMMARY

1 INTRODUCTION 13
1.1 CARBON CAPTURE AND UTILIZATION 14
1.2 FORMIC ACID 16
1.3 OBJECTIVES 17
1.4 TEXT STRUCTURE 18

2 LITERATURE REVIEW 19
2.1 HYDROGENATION OF CARBON DIOXIDE INTO FORMIC ACID 19
2.2 INTEGRATED PROCESS ASSESSMENT 21

3 FEEDSTOCK SELECTION 24
3.1 OBJECTIVE 24
3.2 BACKGROUND 24
3.3 METHODS 32
3.4 RESULTS AND DISCUSSIONS 40
3.5 CONCLUSIONS 48

4 PROCESS SIMULATION - FORMIC ACID PRODUCTION 50
4.1 CONVENTIONAL PROCESS – HYDROLYSIS OF METHYL FORMATE 51
4.2 INNOVATIVE PROCESS – CO_2 HYDROGENATION IN IONIC LIQUID MEDIA. 54
4.3 RESULTS 59
4.4 CONCLUSIONS 62

5 TECHNO-ECONOMIC AND ENVIRONMENTAL ANALYSIS 63
5.1 METHODS 65
5.2 RESULTS 69
5.3 CONCLUSIONS 80

6 CLOSING REMARKS 81
6.1 SUGGESTION FOR FUTURE STUDIES 81

REFERENCES 83
APPENDIX A - FEED SOURCES ASSUMPTIONS 96
APPENDIX B - CO_2-BASED FORMIC ACID ROUTES 98
APPENDIX C - SIMULATION INFORMATION 106
APPENDIX D - PUBLICATIONS 117

1 INTRODUCTION

In 1896, Arrhenius published one of the first papers linking the burning fossil fuels to the possible rise of earth's atmospheric temperatures (1). The debate on the consequences of increasing carbon dioxide (CO_2) emissions, however, began only after the 1950s, when alarming predictions of societal impacts mobilized the interest of the scientific community, mostly after the 1970s, leading the United Nations to create the Intergovernmental Panel on Climate Change (IPCC), in 1988, to synthesize and publish reports on climate change and its global effects (2). The latest predictions indicate that worldwide carbon emissions must decrease at least 49% of its 2017 levels by 2030 and achieve carbon neutrality by 2050 to limit the temperature increase to 2°C, even that 1.5° C is as a more desirable goal (3–5). These scenarios are illustrated in Figure 1.

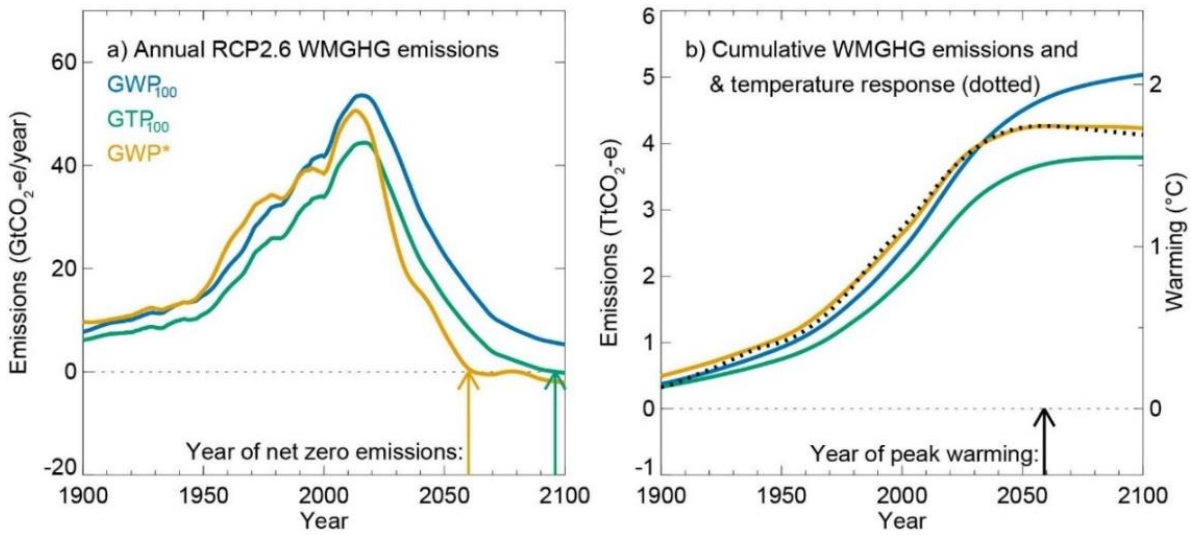

Figure 1 – Scenario of carbon emission per year (a) and cumulative greenhouse gas (GHG) emissions (b) for a scenario of 1.5°C temperature increase
Source: IPCC (4).

Despite the historical concerns and looming deadline, anthropogenic carbon dioxide emissions increased at an average rate of 2.6% per year from 2000 to 2014, reaching 35.5 Gt_{CO_2} per year (6). In this scenario of pressing change, several options are considered to help towards the mitigation target, including Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU)(7,8). This work will consider CCU only.

1.1 CARBON CAPTURE AND UTILIZATION

Carbon capture and utilization (CCU) is an attractive technological alternative to the greenhouse-gas emission issues and the ever-growing energy demand. CCU aims to transform the waste CO_2 into economically viable input to a given process. First, CO_2 is captured from different sources, including power plants and industries, or directly from air, via several existing carbon capture and separation technologies. Then, it is used in process systems or for generation of value-added chemicals, generating value to support the transition into a low carbon economy (9). CCU technologies are divided into wide-ranging categories: CO_2 conversion to chemicals and fuels, mineral carbonation, enhanced oil recovery, biological conversion and direct CO_2 utilization.

The use of carbon dioxide as a feedstock for chemicals and fuels has attracted substantial scientific and technological interest, since the CO_2 conversion technologies are promising to the reduction of its emissions and the captured CO_2 is considered a renewable source to complement or alternate the conventional fossil sources (10). By selling some CO_2 derived products, for example, may be possible to further finance larger CCU and CCS projects (11).

According to IPCC (12), CCU has been envisioned as part of the “circular economy” but expectations on CCU sometimes leads to different and contested interpretations. While the environmental assessment of CCS projects is relatively simple, this is not the case for CCU technologies. The GHG mitigation impact of CCU depends on several factors such as capture rate, energy requirements, lifetime of products utilization, production route that is substituted and associated room for improvement of the conventional route. For example, gases containing carbon monoxide (CO) and carbon dioxide and even hydrogen (H_2) from steel mills can be used as feedstock to produce chemicals. In this way, the carbon originally contained in the coke used in the blast furnace is reused, and the emissions is reduced, but not zeroed.

Nowadays, around 230 million tons of CO_2 per year have been used, mainly in the urea industry to produce fertilizers, with consumption around 130 Mt_{CO_2} per year, followed by the oil sector, for enhanced oil recovery (EOR), using 70 - 80 Mt_{CO_2}. There are also smaller consumers in the food and beverage industry, metal production,

cooling, fire suppression and in greenhouses to stimulate plant growth (13). Figure 2 shows these main CO_2 uses.

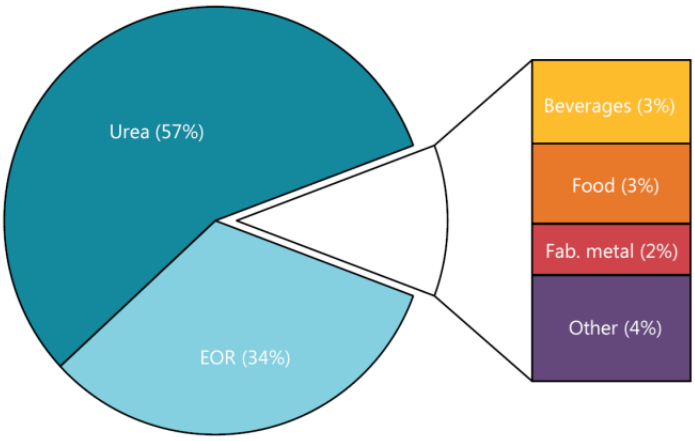

Figure 2 - Share of common CO_2 utilization applications.
Source: IEA (13).

Additionally, carbon captured from point sources (bioenergy, chemical recycling, or from industrial processes emitting fossil CO_2) can be combined with hydrogen to form synthesis gas (syngas) or other chemicals for its valorization (14).

A rich literature reports the potential products to be manufactured using carbon dioxide as feedstock. Otto et al. (15) investigated a total of 122 chemicals derived from carbon dioxide. From bulk chemicals, for example, formic acid, oxalic acid, formaldehyde, methanol, urea and dimethyl ether were appointed as promising candidates to be produced from CO_2.

IEA (13) pointed out different carbon capture processes together with electrolytic hydrogen production as being of high importance to reach net zero emissions, including methane pyrolysis, electrified steam cracking and biomass-based routes for ethanol-to-ethylene and lignin-to-BTX. Moreover, macro-level analyses show that large-scale utilization of carbon circulation through CCU is possible in the chemical industry as primary strategy, and it would be very energy intensive and the climate impacts depend significantly on the CO_2 source and processes for its capture (12). Synergies could be found when combining circular CCU approaches with virgin carbon feedstocks from biomass (16).

Since CO_2 is a highly stable molecule, its conversion into fuels and chemicals requires high energy reactants, such as hydrogen. From the possible conversion

pathways, carbon dioxide hydrogenation is considered to be the most important reaction as it may produce valuable chemicals and fuels, and, at the same time, offer a good opportunity for sustainable development in the energy and environmental sectors, since the hydrogen may be generated from renewable resources (17).

Given the potential contribution to CO_2 emission reduction, replacing fossil-based products by CO_2-based alternatives must be evaluated holistically, accounting for the CO_2 and hydrogen sources, the conversion processes and the comparison against the conventional fossil product/service. In this context, this work evaluates the production of formic acid (FA) by carbon dioxide hydrogenation, including a previous selection of feed sources, and assesses the potential of the proposed innovative route compared to the conventional process.

1.2 FORMIC ACID

Formic acid (FA) is an environmentally acceptable and highly efficient organic acid. It is an important basic chemical, has been currently considered as a promising candidate for hydrogen storage and can potentially be upgraded to higher added value CO_2 synthetic products.

Nowadays, applications of formic acid include silage and animal feed preservation, leather and tanning, textiles, pharmaceuticals/food chemicals, rubber chemicals (antiozonants and coagulants), catalysts, and plasticizers as seen in Figure 3 (18). In many instances, it is used to regulate the pH of chemical processes. Recently, it has attracted attention as a H_2 carrier (19). The global production was estimated to be around 760 kt in 2019 (20) and the market has been expected to grow about 4% – 5% from 2020 to 2024 (21). The Asia-Pacific region leads the global market, with China being the largest producer, consumer and exporter (22). Accounting for nearly 2.5% of the global demand and without domestic production, Brazil imported approximately 19 kt of FA for internal consumption in 2019 (23).

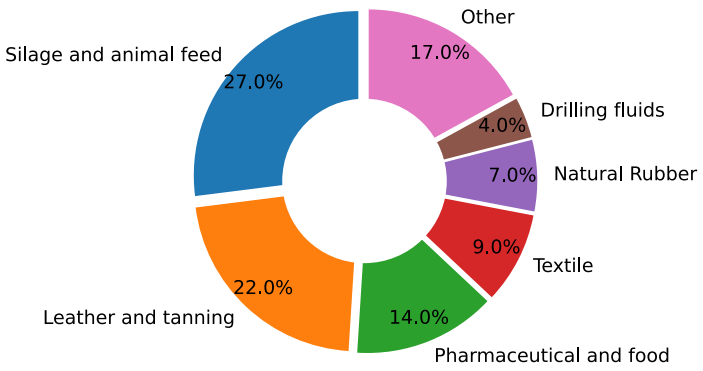

Figure 3 – Global formic acid demand by end use.
Source: Hietala et al. (18)

FA is available in grades of 85%, 95%, 98% or 99% in mass, and its price was estimated at 0.83 US$/kg (85 wt%) in 2021. the FA global market is historically dominated by a handful of companies, with BASF leading with 32% of market share in 2013 (24) followed Perstorp, Eastman Chemical Company, Luxi Chemical, among others (18).

FA is typically obtained by hydrolysis of methyl formate, and a new technology for FA synthesis from CO_2 and H_2 was introduced by British Petroleum (BP) in the 1980s and further developed by BASF. The first concept suggested that the hydrogenation of carbon dioxide in alcohol produces formic acid in an almost water-free environment. Soluble Ru complexes are the preferred catalysts (18). After the first patent, several developments on CO_2 hydrogenation to formic acid have been published, however the technology is still in the early development stage, with most studies focusing on catalysts and reaction systems at laboratory scale.

1.3 OBJECTIVES

The objective of this work is to evaluate technical, economic and environmental aspects of formic acid production by CO_2 hydrogenation as a potential route for reducing CO_2 emissions.

The specific objectives include:

- Assessment and selection of synergetic sources of hydrogen and CO_2 considering the potential impacts on the process sustainability.

- Comparison of a new proposed route for CO2-based FA production with an established FA production technology based on their technical, economic and environmental performances.

1.4 TEXT STRUCTURE

This work is organized in 6 chapters as follows. Chapter 1 lays out the context and objective of the work. Chapter 2 provides a literature review on formic acid production from carbon dioxide hydrogenation in homogeneous media in a process engineering perspective. Chapter 3 discusses and evaluates the methodology proposed to select CO_2 and H_2 sources to be used in the CO_2-based FA production. A multi-criteria decision Analysis (MCDA) is used to rank technical, economic and environmental aspects. Chapter 4 describes the development and implementation of a base case process simulation of the conventional route for FA production, as well as the new CO_2 hydrogenation route. Chapter 5 details the technical, -economic and environmental analysis of the simulated processes, quantifying and comparing key indicators of the CCU route. Finally, Chapter 6 summarizes the study and suggests future developments.

2 LITERATURE REVIEW

As an early development technology, most research published about CO_2 hydrogenation to FA discuss reaction mechanisms, catalysis and, just recently, few studies have evaluated the reaction in a process engineering perspective, tackling economic and environmental aspects. This chapter reviews the recent advances in formic acid production by carbon dioxide hydrogenation and the process engineering publications and findings.

2.1 HYDROGENATION OF CARBON DIOXIDE INTO FORMIC ACID

The hydrogenation of carbon dioxide to formic acid has been studied exhaustively since the 1970s. This conversion is an endergonic reaction, with standard Gibbs energy of formation, ΔG_f^0, equal to 32.5 kJ/mol. However, in the presence of an additive, such as Na_2CO_3, triethylamine (NEt_3), or ammonia, the reaction becomes exergonic (for example, $\Delta G^0 = -9.5$ kJ/mol) and takes place spontaneously, as shown in the Equations 1 – 3 (25,26).

	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)	
$CO_2 + H_2 \rightleftharpoons HCOOH$	32.8	-31.5	-216	(1)
$CO_2 + H_2 + NH_3 \rightleftharpoons HCOO^- + NH_4^+$	-9.5	-84.3	-250	(2)
$CO_2 + H_2 + NHMe_2 \rightleftharpoons HCONMe_2 + H_2O$	n.a.	-131	n.a.	(3)

Most recent studies focus on the development of new catalyst systems, and many are directed to the mechanism of the homogeneously catalyzed conversion, although few heterogeneous-catalyzed mechanisms are also being studied (26). However, since the use of a catalyst can only make the reaction to reach the equilibrium more rapidly, other studies have emphasized the importance of the reaction media to influence the unfavorable equilibrium (27).

Yoshio et al. (28) reported one of the first investigations indicating the promoting effect of water for the homogeneously catalyzed hydrogenation of carbon dioxide. Small amounts of water can shift the thermodynamic equilibrium. Besides water, organic solvents, such as mostly amines, ionic liquids, and even supercritical carbon dioxide can be used as solvents for the conversion.

Ehnes et al. (27) studied the effect of various alkylamines on the reaction and the particular activity of the combination of ethanol with triethylamine. Results showed that the activity increases with increasing solvent permittivity. Protic solvents such as alcohols stabilize the FA-amine intermediate, inhibiting the reverse reaction. The positive influence on the reaction only occurs with NEt_3 in comparison with other amines.

Shaub and Paciello (29) introduced a process for CO_2 hydrogenation to formic acid using homogeneous ruthenium catalysts and amines such as trihexylamine ($NHex_3$) instead of the commonly used NEt_3 to shift the unfavorable equilibrium. The authors affirm that intermediate adducts, such as $NHex_3 \cdot FA$, are advantageous as they can be thermally cleaved under relatively mild conditions, allowing isolation of the formic acid formed. A patent for preparing formic acid based on this study was issued in 2014 (30). This patent describes a process using a tertiary amine with at least 12 carbon atoms per molecule and a polar solvent (monoalcohols and water), forming FA in a three-phase reaction.

Apart from amine-solvents, ionic liquids (IL) are also the focus of substantial researches. Yasaka et al. (31) described the use of ionic liquids based on imidazole for the hydrogenation of carbon dioxide to formic acid and compared it with the equilibrium in water promoted reaction. The comparison showed that the pressures required to transform hydrogen and carbon dioxide into formic acid can be reduced by a factor of ~100 when the IL medium is used instead of water. The authors claim that FA formation can be achieved most efficiently in ILs due to the use of mild operating temperatures and pressures, making the FA synthesis substantially advantageous for industrial applications.

Weilhard et al. (32) reported the selective and efficient catalytic hydrogenation of CO_2 to formic acid using a combination of an ionic liquid (IL) with basic anions and catalysts derived from the precursor $[Ru_3(CO)_{12}]$. The authors argue that the tunable nature of ILs and its interaction with the reactants enable the transformation at low pressure with a broad range of solvents. Additionally, it facilitates the separation at the end of the synthesis. The authors also reported that IL may prevent catalyst deactivation via protonation due to a shift in acid equilibrium.

In contrast with homogeneous catalyzed hydrogenation, studies in heterogeneous catalysis have shown low catalytic activity, low product selectivity, and reported harsh reaction conditions (33). Reymond et al. (34) showed that the

conversion using $Cu/ZnO/Al_2O_3$ and Ag/Al_2O_3 catalysts resulted in low selectivity and led to the production of DME and methyl formate as byproducts.

2.2 INTEGRATED PROCESS ASSESSMENT

From a process engineering perspective, many publications have evaluated technical, economic and environmental aspects of CO_2 hydrogenation. Most of them investigated the methanol production (35–37). Just recently, some concept-level process design of FA production by hydrogenation have been published.

Pérez-Fortes et al. (20) used process flow modeling, with simulations developed in CHEMCAD, to obtain the mass and energy balances. The purchase equipment costs of the formic acid plant were also provided. The reaction model is based on the previously cited patent by Schaub et al. (30), using a tertiary amine and Ruthenium catalyst complex. The authors performed a technical-economic analysis using the net present value as a financial indicator. The estimated cost of FA produced this way was 1.53 €/kg, against 0.47 €/kg for the conventional process, thus they argued that FA CCU plant is technically viable, but economically infeasible and more R&D is necessary.

Regarding emissions, Pérez-Fortes et al. (19) claim that the CCU plant avoids up to 92% of the CO_2 when compared to the conventional process. However, when estimating the emissions, the authors neglected the carbon footprint of the hydrogen, which was assumed to be carbon-free. Moreover, the CO_2 utilized in the plant did not account for its purification, only its compression (the plant receives pure CO_2 at atmospheric conditions).

Surywanshi et al. (38) presented a case study of of formic acid synthesis using captured CO_2 and co-generated H_2 from a coal direct chemical looping (CDCL) power plant. A steady-state simulation was developed in Aspen Plus to represent the power and H_2 co-generation CDCL plant integrated with formic acid synthesis. The study focus was on the effect of integrating a CCU process to a CDCL power plant, and the authors used the same process flowsheet developed by Pérez-Fortes et al. (20). However, the CO_2, hydrogen and power integrated to FA plant were generated by the CDCL plant. The integration resulted in a 5.8% penalty on the electric energy and overall efficiency of the power plant.

Barbera et al. (39) studied technological parameters of the CO_2 conversion to different C1 chemicals by catalytic hydrogenation using process simulation. Formic acid production was built starting from the same aforementioned BASF patent (30). A kinetic model based on the catalyst turnover frequency was implemented and tripentylamine (NPe_3) was chosen as tertiary amine instead of NEt_3. The results revealed that the FA production, despite requiring high thermal and power energy inputs, can still be promising under the assumption that H_2 is available from renewable sources. If non-renewable energy is used to produce H_2, the actual environmental benefits, in terms of net CO_2 emissions, strongly depend on the country-specific carbon intensity for electricity generation.

Kim and Han (40) present two commercial-scale processes for the catalytic production of formic acid from CO_2 and their economic, energy and environmental performances. The first process is the previously discussed hydrogenation in triamine media proposed by Schaub et al. (30), and the second process is similar, but it uses NEt_3 and Au/TiO_2 catalyst instead of the Ruthenium based catalyst. Both processes use about 0.83 ton_{CO_2}/ton of FA. Economic analysis showed a similar cost of FA for both processes, 1,029 and 1,037 US$/$ton_{FA}$, respectively, with differences mainly on capital costs. The environmental analysis showed that the second process presents lower net CO_2 emissions (0.07 ton_{CO_2}/ton_{FA}) compared with the first route (0.36 ton_{CO_2}/ton_{FA}). However, in the environmental analysis, the study did not consider environmental impacts such as production and transportation of H_2 and CO_2 as raw materials.

Lastly, Kang *et al.* (41) evaluated the environmental feasibility of different FA production strategies using an Life Cycle Analysis (LCA). Two major environmental impact factors, Climate Change (CC) and Fossil Depletion (FD) were quantified. The analysis considered conversion and separation steps, and data was acquired from the literature and from a simulation study. The study considered a conventional route, a catalytic CO_2 hydrogenation route and an electro-catalytic conversion route. In all strategies, the utilities significantly affected both the CC (29–126% of total CC) and FD (21–96% of total FD) impacts. The authors showed that the use of environmentally friendly utility sources, such as wood chips (heat) and hydropower (electricity), made the electro-catalytic route stand out as the most environmentally feasible option. The study provided quantitative information on environmentally feasible strategies for FA

production, which can be used as a reference for improving CO_2-based FA production. However, it did not consider economic factors.

As seen from the implementations of FA CCU processes, the most used technology is the implementation by Schaub et al. (30) process with tertiary amine. Furthermore, the environmental and economic impacts of feedstock hydrogen and CO_2 used are generally neglected, which may be significantly relevant in this context. Therefore, is necessary to conduct a study considering both the environmental and economic aspects of the entire process, from the production of raw materials to the conversion to the target products in order to identify bottlenecks and synergies.

3 FEEDSTOCK SELECTION

The first step to a realistic implementation of CO_2 hydrogenation processes would be the comprehensive evaluation of hydrogen and CO_2 sources, as they play a strategic role in the system sustainability. Here, CO_2 is a raw material, hence, parameters such as quality and price must be considered. Moreover, H_2 can be expensive and its production greatly impacts the costs and environmental loads of the final product.

Although hydrogen and carbon dioxide sources have been thoroughly reviewed in the literature, little attention has been given to the combined sustainability evaluation of these sources in the context of carbon dioxide utilization, considering possible synergetic scenarios and unconventional sources (by-product hydrogen is rarely considered, except in the iron and steel industry).

3.1 OBJECTIVE

The objective of this section to propose a systematic framework to evaluate and select potential sources of CO_2 and H_2 to be used in CO_2 conversion processes by hydrogenation. Different sources of CO_2 (from power plants to ethanol fermentation) and H_2 (from dedicated production to by-product hydrogen) were evaluated, considering environmental and economic aspects associated with the usage of each source. Most content in this chapter was published in scientific journal with selective editorial policy (42) as seen in Appendix D.

3.2 BACKGROUND

The main sources of CO_2 and hydrogen and a description of the multicriteria decision analysis are presented in this section.

3.2.1 Hydrogen Sources

Hydrogen can be generated from fossil sources (i.e. natural gas and coal), and renewable sources, such as water electrolysis using solar and wind energy and biomass (43). The current global hydrogen industry is based mostly on fossil fuels, accounting for 96% of global production, while water electrolysis is responsible for the

remaining 4.0%. Natural gas steam reforming (NGSR) holds the highest proportion of hydrocarbon-based production, the second largest part is oil-based, followed by coal gasification (CG).

Hydrogen production alternatives was reviewed and evaluated by Dincer and Acar (44)using six different criteria (objective and subjective values) and computing the overall performance of energy sources. Later, Acar and Dincer (45)evaluated the sustainability of hydrogen produced from renewable sources, classifying them according to scores of sustainability performance (social, environmental, technical, reliability and economics). These processes focused on dedicated hydrogen production in a general scenario.

CO_2 conversion into chemicals is often energy-intensive. Consequently, a broad scope analysis of such processes, based on the life-cycle approach, should reveals that CCU may emit more CO_2 than which is consumed if customary routes for hydrogen and power production are used (20). Hence, a comprehensive search for hydrogen sources and production technologies is necessary to select a favorable alternative so that CO_2 hydrogenation routes can become economically and environmentally attractive. In the long term, large-scale hydrogen production by electrolysis of water with electricity from renewable sources would be ideal from an environmental standpoint. However, with an increasing, but yet insufficient, supply of renewable energy, other options must be evaluated. In this context, the sources of hydrogen considered in this work, as shown in Figure 4, were classified according to their origins into fossil fuel derived, including Carbon Capture – CC, renewable energy and by-product hydrogen, not commonly mentioned. A brief description of each group is also presented.

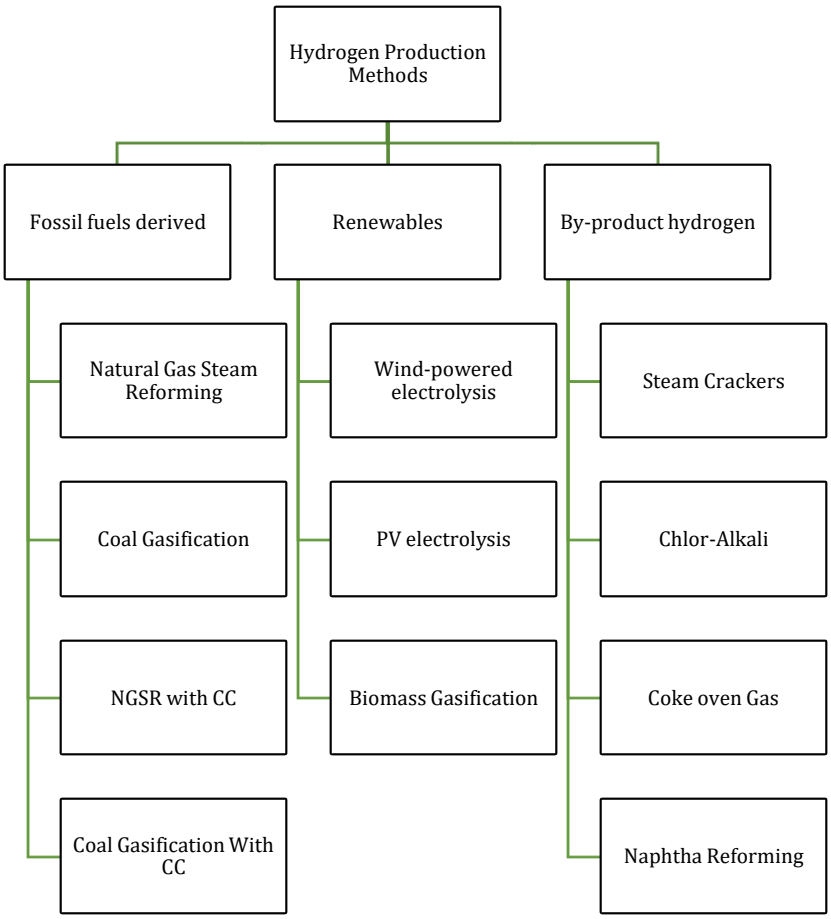

Figure 4– Hydrogen sources considered in this work.

3.2.1.1 Hydrogen from fossil fuels

The demand for pure hydrogen is around 94 million tons per year in 2021. This hydrogen is almost entirely supplied from fossil sources (46) and, therefore, produce large amounts of CO_2, obviously undesired for the application at hand. Current industrial production from conventional fossil sources such as natural gas steam reforming (NGSR) or coal gasification (CG) has a lower cost if compared to the rising alternatives (47).

According to Muradov et al. (48), the overall energy efficiency of a modern NGSR without CO_2 capture is estimated at 76%. However, if a CO_2 capture unit (e.g. the combination of an amine scrubber with PSA) is added to the NGSR plant with the same capacity, the efficiency would drop to 73%, with CO_2 removal rate reduced to 8.0 kg of CO_2 per kg of H_2 (-72%).

3.2.1.2 Renewable hydrogen production

The hydrogen produced from renewable energy sources is a prospect for sustainable energy carrier, but it requires technological advances in its production and storing processes (49). Water electrolysis powered by renewable energy is expected to enable the scale-up of hydrogen production (50). The costs of hydrogen produced by electrolysis are higher than those produced by fossil sources due to the electricity costs. In this case, photovoltaic power plants may supply the electricity necessary for water splitting, closing the cycle for water electrolysis with no direct carbon emissions (47).

Biomass can be an alternative source for renewable hydrogen. In biomass gasification, a thermal transformation that can convert low-value organics or biomass carbonaceous materials into electricity and transportation components such as H_2, CO, CO_2, CH_4, light hydrocarbons, tar, char, ash, and minor contaminants (51). Synthesis gas (syngas) is the main product of biomass gasification and consists of a mixture of mainly hydrogen and carbon monoxide. In order to increase the hydrogen fraction in the syngas, the reactor, feedstock and reaction conditions have to be improved (52). Biomass conversion is roughly twice as expensive as NGSR or CG and has high acidification potential due to the co-emission of SO_2 and potential amounts of inorganics and/or ashes. Biomass conversion routes have in common high SO_2 emissions of over 10 g/kg of H_2, comparable to NGSR (47).

3.2.1.3 By-product hydrogen

Several industrial processes produce hydrogen as by-product: the chlor-alkali industry (53), iron and steel industries (coke production) (54), ethylene/olefins production (steam cracker units) (55) and some units in the petroleum refinery (fluid catalytic cracker units, catalytic reforming units etc.) (56). The destination of the by-product hydrogen depends on the specific plant and could even be a waste.

In the US chlor-alkali industry, it is estimated that between 10-30% of the hydrogen produced in the brine electrolysis is flared or vented, the remaining may be used on site for hydrochloric acid production or heat generation or sold to other industries (57). In the iron and steel industry, only around 20 – 40% of the coke oven gas, a stream containing hydrogen, is used to generate heat or in other on site

operations, and the remaining is burned in chimney or torches (58) – this value varies due to the dynamic nature of the steel-making process (59). In the case of petrochemical plants, by-product hydrogen produced in steam crackers is usually mixed with natural gas and/or surplus methane and burned to generate heat required for the cracking operations (55). Since these processes may provide the necessary amount of hydrogen to CCU, which otherwise would be wasted, it is advantageous to include them among the alternatives to be explored.

3.2.2 Carbon dioxide sources

The feasibility of a carbon dioxide source for carbon capture and utilization (CCU) is directly related to its composition, flowrate and pressure in the emitting stream. Higher concentrations allow for rather inexpensive separations and, therefore, lower cost per ton of CO_2 (60).

A detailed report elaborated by the Intergovernmental Panel on Climate Change (IPCC) (61) presents the most significant stationary carbon dioxide sources as well as other key information about average emission per plant and process conditions. Bains et al. (62) reviewed CO_2 from the industry sector and presented an estimation of the capture cost of each industry. Lastly, Assen et al. (63) classified CO_2 sources from industrial processes using environmental merit order curves, preferring the most environmentally friendly, from a European perspective.

The emissions from boilers, furnaces and process streams are potential opportunities for carbon capture and utilization due to its high flow rate and continuity. Most of these sources emits CO_2 at concentrations under 15% $_{v/v}$. However, a small fraction of these sources emits CO_2 at concentrations above 95%$_{v/v}$, making them highly attractive to CCU (61). This is mainly related to the difference between "combustion" and "process" CO_2. Combustion emissions are those resulting from the burning of fossil/carbonaceous fuels, usually for power generation, while process emissions refer to CO_2 released from other process units, typically as a by-product of chemical reactions. Combustion CO_2 and process CO_2 are typically on quite different scale and concentration. Most emissions from point sources comes from combustion; however, process CO_2 has higher CO_2 concentration. Figure 5 shows the estimated shares of CO_2 emissions per source (62).

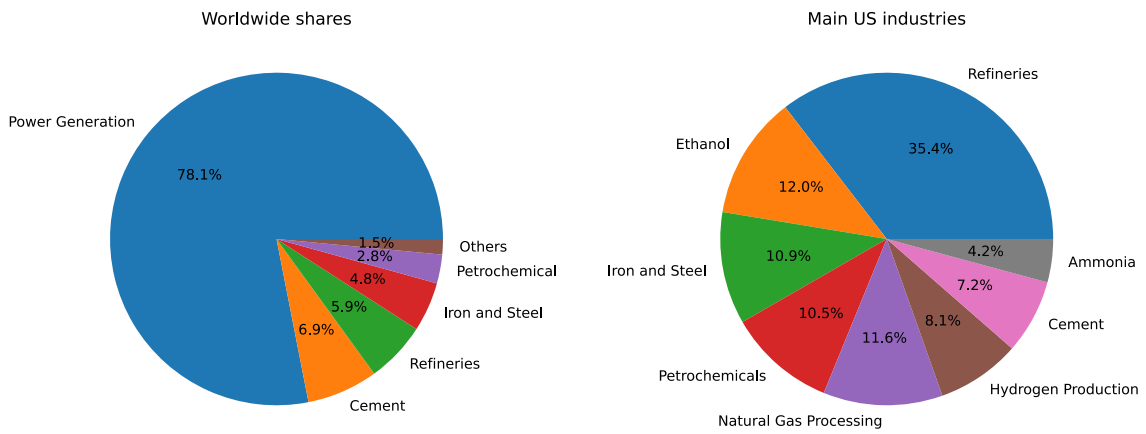

Figure 5 – Shares of CO_2 emissions by stationary point sources.

IPCC global estimates (61) show that the majority of the emissions are attributed to the energy sector. Bains et al. (62) reported emission of the US industrial sector.

Table 1 presents the list of CO_2 sources covered in this analysis The list is based on the most relevant global sources presented by IPCC (61) and US industrial sources by Bains et al. (62).

Table 1 – CO_2 emitting sources covered in this study.

CO_2 Sources	Power Plants	Natural gas
		Coal
	Industrial	Iron and Steel
		Cement
		Oil Refineries
		Ethylene oxyde
		Natural Gas Processing
		Ethanol Production
		Steam Crackers
		Ammonia Production
		NGSR

3.2.2.1 Carbon dioxide from power plants

Power plants are the largest stationary sources of CO_2, accounting for almost 80% of global stationary emissions. Generally, when using coal, natural gas or petroleum as fuel, the exhausting carbon dioxide content in the flue gas varies between 3.0% - 15%. Therefore, capture and separation are necessary (64).

Capture of CO_2 from flue gas streams at atmospheric pressure can be achieved by various physical and chemical separation methods, such as absorption, membranes, adsorption and cryogenic processes. The most applied technology for this purpose is absorption with amine solvents, which have been verified at full commercial scale (65). Typically, 85 to 90% of the CO_2 is captured with these technologies at costs highly defined by the energy required to regenerate the amine solution (66).

3.2.2.2 Carbon dioxide from industrial processes

When compared to the total amount of carbon dioxide emitted in combustion processes, the CO_2 released from industrial processes is substantially lower. On the other hand, high CO_2-concentration streams emitted by some industries (>95%) may contribute to an easier separation and, consequently, a lower cost per ton of CO_2, turning these sources promising targets for capture. In general, when the CO_2 concentration in a gas stream is high, CO_2 recovery costs will be lower. In addition, the advantage of scale suggests that recovery will be cheaper if there are large sources of CO_2 (67). Some highlights of high CO_2 concentration produced from process streams include iron and steel production (20 – 42%)(68), natural gas processing (96 – 92%) (69), ethylene oxide production (98-99%) (69), ethanol production (98-99%) (70) and others.

3.2.3 Multi-criteria decision analysis

Traditionally, the Decision Making (DM) process is carried out in a single criteria approach, normally focused on identifying the most efficient options at low cost. However, the increasing environmental awareness in the 1980s modified the single criteria decision framework to a broader method. The decision-making in the field of sustainability must encompass the multiple factors considered in the triple bottom line,

i.e., economic, environmental and social aspects. A Multi-Criteria Decision Analysis (MCDA) can be a method to facilitate decision making in complex systems, evaluating multiple criteria, not always directly comparable. MCDA is an integrated evaluation and several methods have been widely applied to social, economic, agricultural, industrial, ecological, biological and energy systems (71). The problem structure is presented in Figure 6. Several attributes (A_n) are evaluated according to certain Criteria (C_n) to be later aggregated to reach a final score (goal).

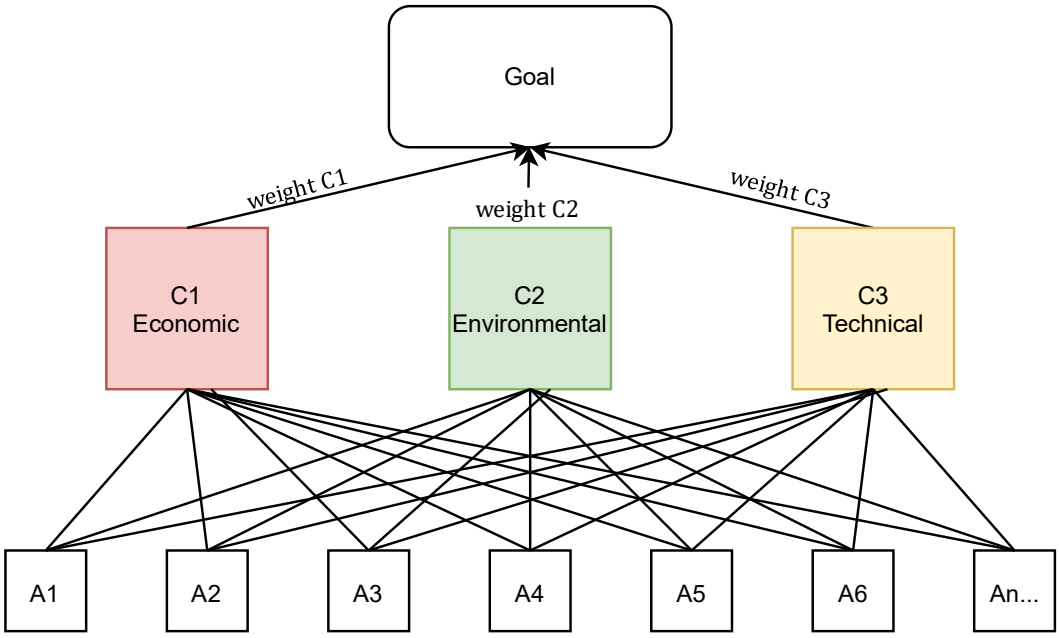

Figure 6 – General MCDA problem structure.
Notes: Cn – criteria; An - attributes

There are numerous methods and variations in MCDA. Wang et al. (72) and Kumar et al. (73) reviewed the usage of MDCA on sustainable energy systems. An MCDA problem involves m alternatives to be evaluated with respect to n criteria. The decision matrix can be expressed by Equation 4 (72):

$$\begin{array}{ll} & \text{criteria} \quad C_1 \quad C_2 \cdots \quad C_n \\ & (\text{weights} \quad w_1 \quad w_2 \cdots w_n) \\ X = \begin{array}{c} A_1 \\ A_2 \\ \vdots \\ A_m \end{array} & \begin{pmatrix} x_{11} & x_{12} & \cdots & x_{1n} \\ x_{21} & x_{22} & \cdots & x_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ x_{m1} & x_{m2} & \cdots & x_{mn} \end{pmatrix}_{m \times n} \end{array} \tag{4}$$

Where x_{mn} is the performance of m_{th} alternative (*A*) in the n_{th} criterion (*C*), and w_n is the weight of criterion n. Each alternative with n criteria must be summarized in a unique score per an MCDA method.

The MDCA methods can be divided into three main categories: elementary methods, unique synthesizing criteria methods and outranking methods (72). Elementary methods include the Weighted Sum Method (WSM) (74), where the score of an alternative is calculated as the sum of the criteria multiplied by its respective weight, and it is, then, used to rank the options. The Weighted Product method (WPM)(75) is similar to WSM, but with the score calculated by the product of the criteria elevated to the weightth power. The Analytical Hierarchy Process (AHP) (76), Technique for Order Preference by Similarity to Ideal Solutions (TOPSIS) (77), Multi-Attribute Utility Theory (MAUT) (78) are examples of unique synthesizing criteria. Outranking methods include the ELimination Et Choice Translating Reality (ELECTRE), the Preference Ranking Organization Method for Enrichment Evaluation (PROMETHEE) and their variations (79).

In this work, the chosen MCDA method is the Technique of Order Preference Similarity to the Ideal Solution (TOPSIS).

3.3 METHODS

The approach for the overall system evaluation consists of four major steps as shown in Figure 7.

3.3.1 Criteria definition

Assessing the overall sustainability of a chemical technology is a complex problem. However, authors seem to agree that sustainable processes must satisfy the three global requirements: environment, economy and society. A review of indicators for process sustainability is presented by Ruiz-Mercado et al. (80).

Although hydrogen production methods have been extensively reviewed regarding its fundamental principles (24, 54), sustainability (13, 20) and classification criteria (82,83), few or no objective data is available regarding the social aspect of sustainability from hydrogen production processes.

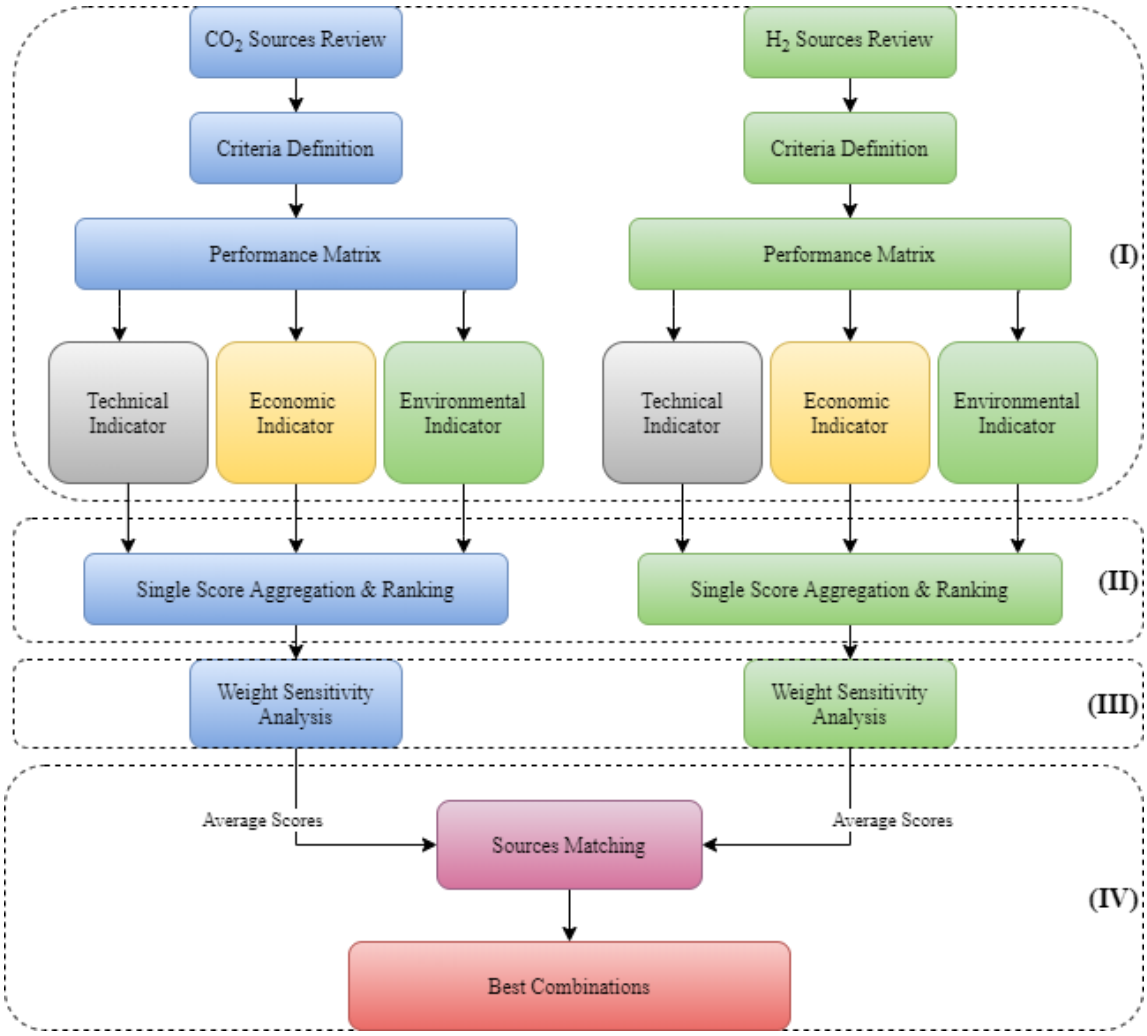

Figure 7. Selection method structure.

Characteristics of carbon dioxide sources were thoroughly presented in the IPCC report (61). Commonly, carbon capture studies focus on technologies to recover CO_2 from power plants (84,85), and a few studies review the capture from other point source (62). These studies disclose information regarding the technical, economic and environmental aspects of the CO_2 to be used as feedstock.

Recent data from hydrogen production systems and CO_2 emitting sources were collected from literature to build a simplified selection framework based on economic, environmental, and technical performance aspects. Details for each indicator used herein are given in the following sections.

3.3.1.1 Economic indicators

There are several uncertainties associated with the cost estimation of hydrogen production, due to various technologies are still in development and the overall cost is

strongly affected by the advancement level, existing infrastructure availability and prices of feedstock (86).

Indicators that describe process costs and profitability, such as the Net Present Value, discounted, payback period and rate of return on investment are commonly used to assess the economic sustainability of a process. These indicators require a thorough evaluation of cash flows and are highly dependent on the project size (80). To simplify the analysis of multiple sources, the economic indicator used in this work is the average cost for producing 1.0 kg of hydrogen and the estimated cost for 1.0 ton of captured CO_2.

The literature data provide average values for hydrogen production cost for a given technology, such as wind-powered electrolysis (87), biomass and coal gasification (81). The costs of the CO_2 capture were retrieved from an assessment presented by Bains et al. (62), which employed an analysis based on the minimal work necessary to separate CO_2 from a given gas stream. Capture efficiency of 90% with a $95\%_{mol/mol}$ purity was assumed to estimate the cost of 1.0 ton of CO_2 for each type of source. These values were adjusted for inflation from the year of study (between 2005 and 2016) to 2019 using U.S. Official Inflation data (88). It is important to notice that the correction does not consider technological advancement for these processes.

Regarding hydrogen production from natural gas steam reforming with and without carbon capture, as well as PV electrolysis, and detailed data is reported by the International Energy Agency (89) and will be used for comparison.

For by-product hydrogen, the cost is associated with the cost of separation, if necessary, and the cost of heat substitution. Hydrogen from steam cracker, catalytic naphtha reforming, coke oven gas may be partially used to produce heat, therefore if they are removed from the process this heat must be replaced by other sources. The price of substitution is calculated by the sum of the cost of heat substitution and separation.

3.3.1.2 Environmental indicators

Concerning the environmental performance of a chemical process, the main goal is to optimize the process design to minimize and/or eliminate the production of waste and pollutants that would need to be treated by end of the line remediation processes. It is important to realize that the life-cycle of products and materials are not

usually considered, as the process designer focuses mostly on gate-to-gate aspects. In a review of sustainability indicators, Ruiz-Mercado et al. (80) imply that although cradle-to-grave is important, the level of complexity required to make such analysis is not considered practical to employ it in processes evaluation.

Despite the idea presented by Ruiz-Mercado et al. [53], to truly evaluate the environmental performance of a process, outer contributions/environment alterations caused, for example, by raw material extraction, energy source, plant building and decommissioning should not be neglected. As the main purpose associated with research on CO_2 utilization processes is to reduce impacts caused by fossil fuel usage, it is vital to assess production processes in terms of detailed environmental indicators.

In this context, the Global Warming Potential (GWP) per kg of H_2 for each technology is used in this work to evaluate the impact of selected hydrogen production methods, except for by-product-hydrogen estimates.

In this study, values for GWP were extracted from results and evaluations published in the literature as shown in Table 2. In these studies, the LCA methodology was implemented to evaluate GWP. Most authors reported follow the international standard ISO 14044 and 14040 guidelines to evaluate environmental impacts. The ISO guidelines comprise four main phases: goal and scope definition, inventory analysis, impact assessment, and interpretation. Since each study has slightly different objectives, the goal and scope definition for each reference used in this study is summarized in Table 2.

It is important to notice that the GWP (expressed in $kg_{CO_2\text{-}eq}/kg_{H_2}$) is dependent on the technology employed, energy sources, transportation, raw material extraction and other aspects of the product life cycle. The cases and GWP values presented herein represent a base model for each technology.

The environmental criterion for CO_2 emitting sources is the carbon footprint associated with capturing CO_2 from a given source. A merit order curve and the carbon footprint of CO_2 sources calculated for a European scenario are presented by Muller et al. (90). The authors employ strict LCA guidelines and standards to estimate the carbon footprint of CO_2 sources in Europe, reporting cradle-to-gate footprint of captured CO_2 varying from -0.95 to -0.59 kg of CO_2-equivalent per kg of feedstock CO_2 as seen Figure 8. Here, the average value of the carbon footprint of each source is used as the environmental indicator.

Table 2 - Goal and scope definitions for life-cycle studies in the literature

	Study Goal	Scope	Ref.
NGSR and NGSR-CCS	A LCA assessment of chemical looping combustion thermally coupled natural gas steam reforming for H_2 production. Compare with traditional NGSR	Includes the process to be studied, the functional unit and the system boundary	(91)
Coal Gasification, PV electrolysis, and Wind-powered electrolysis	A comprehensive LCA for commercial hydrogen production methods by including all major steps for every method. Comparison of energy consumption, and carbon dioxide equivalent emissions to examine their environmental impact.	The system boundaries cover the following major processes: Infrastructure for fuel production; Feedstock production and transport, fuel production and distribution; Vehicle body and fuel cell production; Vehicle use; Vehicle disposal and recycling.	(92)
Coal Gasification CCS	Analyze the Carbon Footprint of the hydrogen production process from sub-bituminous coal and lignite using gasification technologies.	The scope includes: mining, mechanical processing, and transport of coal to the gasification plant, as well as gasification and capture of CO_2 and its sequestration.	(93)
Biomass Gasification	Evaluate the life-cycle environmental and energy performance of a hydrogen-production system based on indirect poplar gasification.	Five subsystems were considered: poplar production and transport, pre-treatment, gasification and tar reforming, syngas cleaning, water gas shift and hydrogen purification, cooling water supply, and power generation.	(94)
By-product Hydrogen	Evaluate the emissions associated with the recovery of H_2 from a by-product stream.	If the H_2 stream is vented or flared, there is only the environmental emissions for separating it or purifying it. If H_2 is burned for heat, it is necessary to account for the substitution of the energy previously provided by the recovered hydrogen, and energy for purification and compression.	(55,95,96)

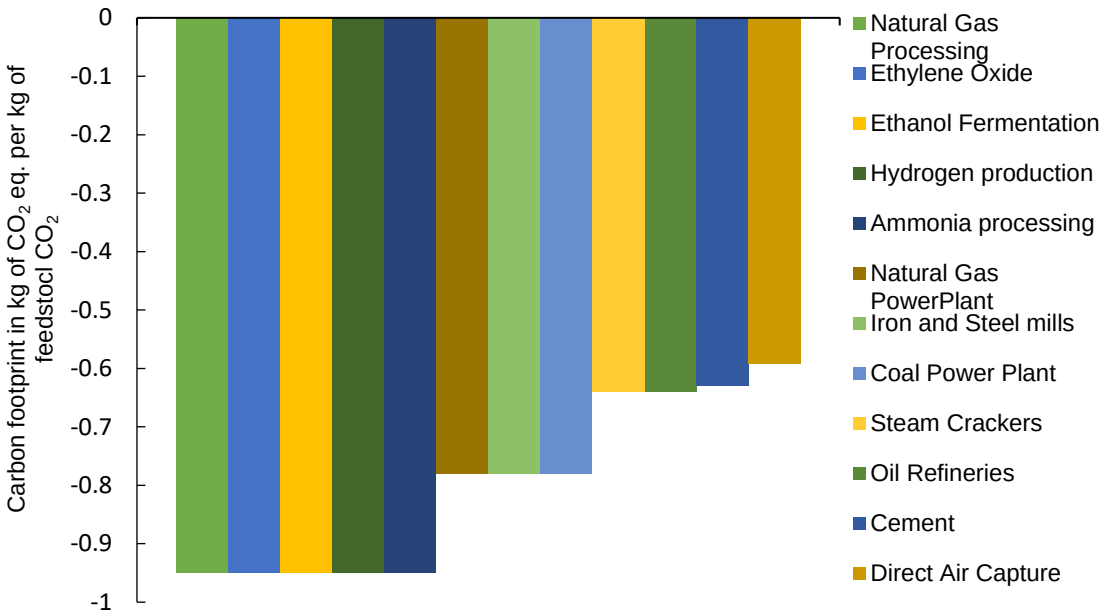

Figure 8 - Carbon footprint of the captured CO_2 to be used as feedstock.
Source: Müller et al. (90).

In this context, the calculated lower carbon footprint of capturing CO_2 from hydrogen production, ammonia and ethanol fermentation plants are around -0.95kg of CO_2-eq. per kg of captured CO_2. Direct air capture is approximately -0.59kg of CO_2-eq per kg of CO_2.

3.3.1.3 Technical indicators

According to Ruiz-Mercado et al. (80), some common technical performance indicators are the total energy consumption, waste treatment energy, resource energy efficiency, energy and exergy efficiency. Additionally, based on the consensus among international experts in hydrogen production, technical performance is the key aspect to sustainable hydrogen production, especially energy and exergy efficiencies. An energetic efficient hydrogen production implies that the process uses its resources less wastefully, which consequently lowers its costs and environmental impacts (82). Therefore, the technical performance indicator for the hydrogen sources (tec_{H_2}) is computed as shown in Equation 5.

$$tec_{H_2} = Energy\ efficiency \times f_{tech\ factor} \quad (5)$$

The overall energy efficiency of the hydrogen production processes given as the product hydrogen energy content per input process energy is multiplied by a technology reliability factor ($f_{tech\ factor}$). The $f_{tech\ factor}$ multiplier is 1.0 for a fully developed continuous process (NGSR, coal gasification) and 0.5 for non-commercial/development processes (by-product recovery) or process based on intermittent energy sources (solar, wind, biomass).

The technical performance for carbon dioxide sources (tec_{CO_2}) is calculated according to Equation 6.

$$tec_{CO_2} = Average\ CO_2\ flow \times f_{continuity} \quad (6)$$

Where the *Average CO_2 flow* is multiplied by a continuity factor ($f_{continuity}$) of 1.0 for continuous processes (refineries, NGSR, iron and steel plants) and 0.5 for non-continuous processes (ethanol fermentation) and the ammonia process (since the CO_2 in ammonia plants are generally used for urea production).

3.3.2 Aggregation and ranking

The Technique of Order Preference Similarity to the Ideal Solution (TOPSIS) is applied as the MCDA method to carry out this study. Furthermore, three criteria were adopted to represent the system sustainability: economic, environmental and technical. This method was chosen due to the application convenience, simplicity and computational efficiency. According to Kiliç et al. (97), TOPSIS has similar performance to the methods that use additive weights and outperforms other methods in some cases when assessing the sustainability of manufacturing companies. Additionally, the result index calculated by the method known as “similarity to positive-ideal solution” is defined by combining the closeness to positive-ideal solution and remoteness to negative-ideal solution. This index is used to rank the competing alternatives and interpret the ranking (98).

In brief, TOPSIS is based on the idea that the best strategy should have the shortest distance from an ideal solution. It assumes that if each attribute takes a monotonically increasing or decreasing change, it is easy to define an ideal solution (99). The TOPSIS method can be summarized in 6 steps:

1. Normalization of the decision matrix (making them dimensionless);

2. Calculation of the weighted normalized decision matrix - the weights are the only subjective parameter in the method. The second step multiplies the normalized decision matrix by the weight attributed to each criterion;
3. Determination of ideal solutions – it calculates the best performance for each criterion;
4. Calculation of the separation measures – it calculates the geometric distance of each alternative to the ideal solution;
5. Calculation of the relative closeness to the positive and negative ideal solutions – a score between 0 and 1, where 1 is the ideal solution;
6. Ranking of the preference order –ranking the alternatives according to their proximity to the positive ideal solution.

Detailed mathematical description of each step and its variations is given elsewhere (71). In this work, a code was implemented in Python, using the Scikit-Criteria library, (100) to analyze the problem and using vector normalization as the normalization step.

The scores for the alternatives of CO_2 and hydrogen sources were ranked individually and the results were used to perform the third assessment in order to evaluate the pair-wise combination of the best performing sources.

3.3.3 Weighting and sensitivity analysis

In most multi-criteria decision analysis, a numerical value is assigned to each criterion, conveying its relative significance. In renewable energy planning, a decision maker may feel unsure to provide explicit values for the criteria since there is usually not sufficient time to be devoted to this procedure. Similarly, it is extremely expensive and time consuming for weights to be confirmed by consistency checks or by applying different elicitation procedures(101).

In this work, the weights are attributed according to the importance of each criterion to the final score. Herein, a weight of 0.4 is assumed for the economic and environmental criteria since these values are obtained through various methodological frameworks in the given literature. As the technical performance indicator is composed of an objective value and a subjective correction factor, as described in Section 3.1.3, a weight of 0.2 is attributed to this criterion to reduce the impact of a subjective factor in the analysis.

Finally, to assess how these weights affect the MCDA outcome, a sensitivity analysis is performed using the Monte Carlo method varying the weights 20% around its base value, as applied by Pacheco et al. (102). This procedure is implemented sampling 1000 random weight values for each criterion, evaluating the resulting scores and sumarizing the results into box plots. Also, a ternary colour coded plot, showing which alternative would have the higher score in the given weight combination is shown. The individual scores of the base cases were used to perform a combined assessment of the best scoring alternatives.

3.4 RESULTS AND DISCUSSIONS

This section presents a summary of the data obtained on each source, the results of the TOPSIS ranking and sensitivity analysis. Table 3 summarizes the hydrogen source options considered in this work and the average value for each criterion.

Table 3 - Global warming potential, estimated cost and energy efficiency for hydrogen production processes[a].

	GWP [kgCO_2-eq/kg]	Hydrogen cost [US$/kg]	Energy Efficiency [%]
Natural Gas Steam Reforming	11.893 (87,92)	1.31 (89)	76 (91)
NGSR– with CCS	3.009 (91)	1.86 (89)	73 (91)
Coal Gasification	11.299 (92)	1.04 (87)	75 (103)
Coal Gasification - with CCS	5.497 (87)	1.8 (104)	64 (103)
Wind-Powered Electrolysis	0.970 (105)	2.12[a]	69[b] (89)
PV Electrolysis	2.412 (92)	2.6 (89)	69 [b] (89)
Steam Cracking	1.8 (55)	1.1 (55)	92[d] (95)
Biomass Gasification	0.405 (81)	5.01 (81)	46 (51,106)
Chlor-Alkali Processes	5.4[e]	2.4(57)	55
Coke Oven Gas	8.4(54)	1.1(54)	92(95)
Naphtha Catalytic Reforming	6.8[e]	0.8(56)	92(95)

[a] Average price of US wind electricity (0.053 kWh) (107) and hydrogen electrolytic production, accounting for losses, of 40 kWh/kg of H_2(108).
[b] Values found in the corresponding references. If there are multiple values, these are averaged.
[c] Average energy efficiency of alkaline water electrolysis (89).
[d] Energy efficiency of PSA units (used to separate hydrogen from the crackers stream) (55).
[e] Estimated by energy consumption and substitution fuel substitution, only accounting for CO_2

Table 4 presents information on the main stationary sources of CO_2. Here, large stationary sources are considered the ones that emit more than 0.1 Mt_{CO_2}/year.

Table 4 - Summary of process characteristics of top CO_2 emitting industries.

CO_2 Source	CO_2 Content (mol %)	Average emissions/source (Mton CO_2/day)[a]	Emitting Unit	Estimated Cost ($/ton CO2 Captured)[b]
Coal Power Plant	10 - 15	10.79	Furnace	41 - 51
Natural gas power plant	3 - 5	2.77	Furnace	75 -100
Iron and Steel	20 -27; 16 -42	10.05	Blast Furnace and Basic oxygen furnace	31 – 35; 23 – 39
Cement production	14 - 33	2.16	Precalciner and calcination	26 – 42
Petroleum Refineries	3 - 20	3.42	Process heaters, furnaces, FCC	35 – 100
Steam Crackers	7 - 12	2.96	Steam cracking	46 - 62
Ethylene oxide production	30; 98 - 100	0.41	Absorption unit to purify EO (air oxidation and oxygen oxidation)	14 – 28
Ammonia Process	98 – 100	1.59	H_2 purification	14
Natural Gas processing	96 - 99	0.32	Acid gas removal/ CO_2 absorption	14
Hydrogen production	30 - 45; 98 - 100	1.00	H_2 purification (PSA and or CO_2 specific separation)	14 – 28
Ethanol production	98 - 99	0.55	Fermentation	14

[a] Based on average yearly emissions per source, reported by IPCC (61).
[b] Estimated by using Sherwood analysis and minimal work of separation method, values reported by Bains et al (62).

3.4.1 Hydrogen Performance

In this general overview of feedstock sources, potential sources of CO_2 and hydrogen were ranked according to specific criteria. Figure 9 shows the ranking of hydrogen alternatives. The scores are the TOPSIS *proximity to the ideal solution* calculated for each source. The results indicate the chosen process in a general scenario, using average literature values.

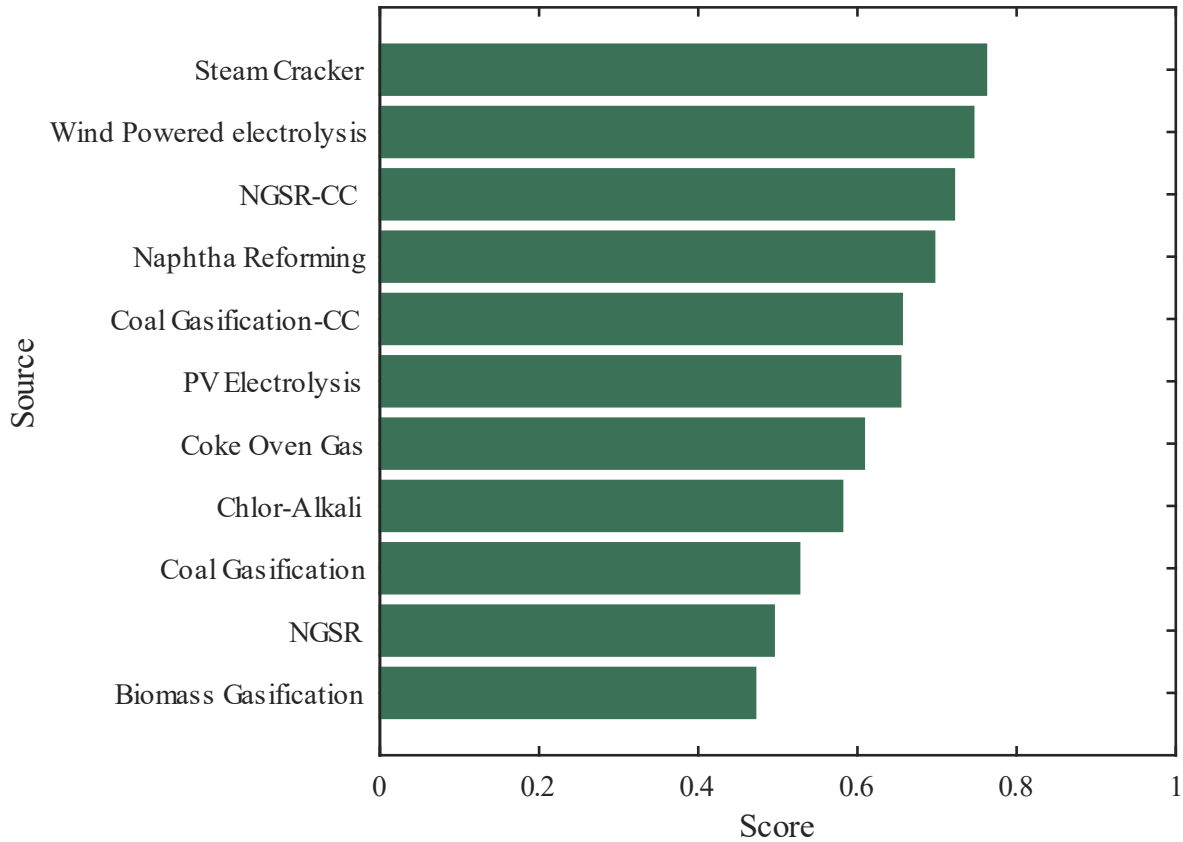

Figure 9 - Overall scores of hydrogen sources.

The process closer to the ideal solution is the recovery of hydrogen from steam crackers in petrochemical plants, with an overall score of 0.76. This can be attributed to its low costs, low associated emission, and high estimated energy efficiency. Wind-powered electrolysis follows directly with a 0.70 proximity to the ideal solution. Following is the hydrogen production from natural gas reforming with carbon capture, coke oven gas and coal gasification with carbon capture.

The sustainability performance of fossil-based H_2 alternatives with carbon capture is higher than some renewable sources, for example, PV-electrolysis and

biomass gasification. This might be explained by the overall low cost and efficiency of the fossil-based production when compared to the economic and technical performance of PV-electrolysis, for instance. These results represent a generic scenario, a prospect in which the electrolytic cell energy efficiency is higher (future technological development), the electricity is produced by a cleaner grid, and fluctuation in oil and gas prices could shift the score of the renewable alternatives to a higher place.

The weights subjectivity was tested on a sensitivity analysis. The score distributions are showed in Figure 10a. The ternary diagram shows that, regardless of the weight combination, only four H_2 sources achieve the higher score: by-product hydrogen from steam crackers and naphtha reforming if the economic and technical aspects are prioritized and wind powered electrolysis or biomass gasification when to the environmental aspect is given more importance.

The Monte Carlo variation on weights, as seen in Figure 10b, shows the possible rank that the alternative could assume if the weights varied by $\pm$20% from the base. This variation did not impact the final ranking significatively, as the ideal solution still is the recovery of hydrogen from steam crackers with a median score of 0.76, the same as the base case, now followed by naphtha reforming, with a score of 0.70 (Figure 10b).

It is important to observe that the viability of the top-scoring alternatives is also constrained by their specific availability. Peramanu et al. (56), for instance, reported that all hydrogen-containing off-gases in the naphtha reforming unit are burned to produce heat, and, if this hydrogen is recovered, there is already an internal demand for hydrogen in hydrotreating units, therefore it may not be available for a CCU demand. In US chlor-alkali industries 40-50% of the hydrogen is burned for steam generation, 30-40% is sold and 10-30% is vented/flared (57), so the only “free” hydrogen, in this case, is the remainder 10-30%. The H_2 combusted for steam generation might be redirected to CCU. In this case, its heating value must be substituted by a fuel source.

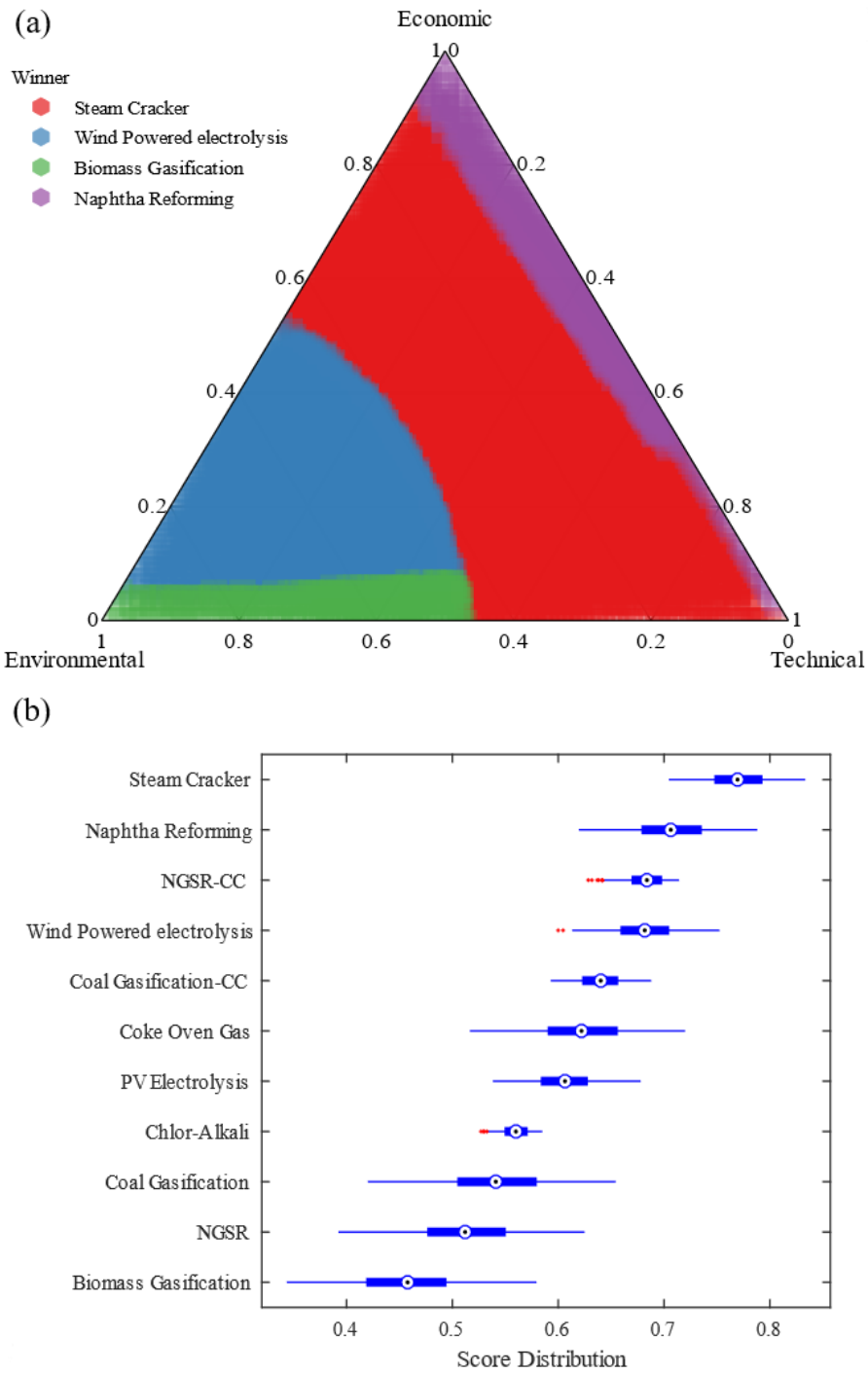

Figure 10 – a) Ternary map of best hydrogen source alternative as function of the to the weight given to each criterion. b) Sensitivity analysis of the weights of the hydrogen sources. Note: The black dots in the box plot represent the median score of the sensitivity results for each alternative.

3.4.2 Carbon dioxide ranking

Figure 11 shows the distribution of the overall scores for CO_2 sources. In general, the higher-scoring technologies are those that produce high concentration

CO_2 streams at a constant rate (i.e., not seasonal): production of hydrogen by natural gas reforming, ethylene oxide production (with direct oxygen oxidation), natural gas processing, iron and steel mills (blast oxygen furnace).

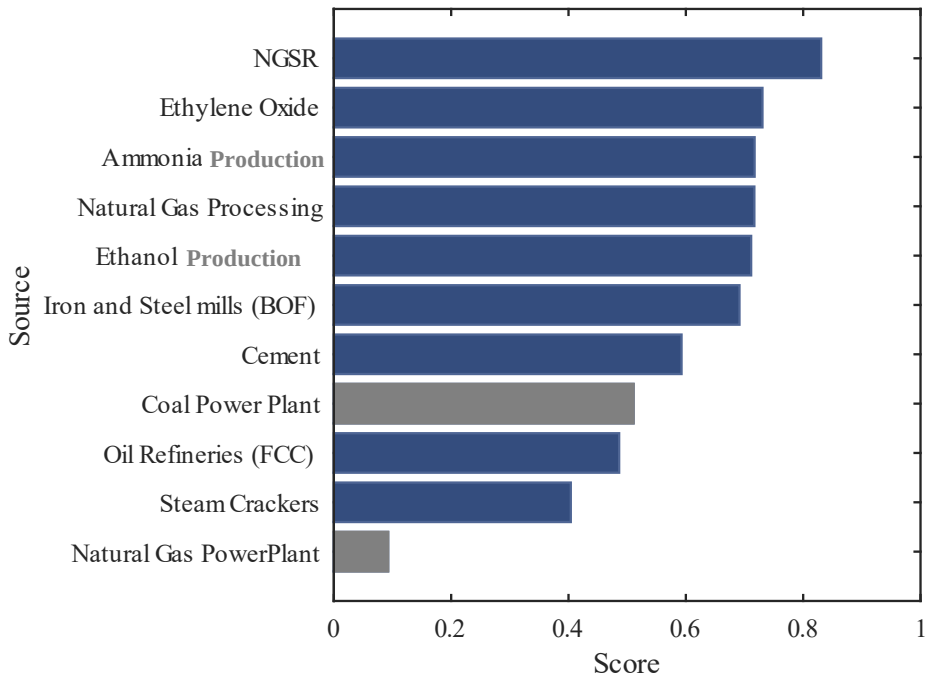

Figure 11 – Overall scores of CO_2 sources calculated by TOPSIS.
Note: Process CO_2 in blue and combustion CO_2 in grey.

As expected, CO_2 emitted at high concentrations is more advantageous for utilization due mainly to its low cost of separation and, therefore, lower energy consumption, which consequently reduces its environmental impact. The technical criteria were decisive in classifying high concentration sources. Although CO_2 from the fermentation step in the ethanol production from sugarcane is almost pure, the smaller availability and intermittent nature of biomass lowered the overall score of this alternative. The same is considered for the ammonia industry, as the CO_2 generated has a captive use in the urea production.

Score distributions are showed in Figure 12a. The ternary diagram shows that four CO_2 sources achieve higher scores: CO_2 captured from NGSR, iron and steel industries, ethanol production and ethylene oxide production. Overall, results point predominantly to iron and steel, if the technical aspect is prioritized, and to NGSR, if more importance is given to economics. Ethanol and ethylene oxide production appear in an unrepresentative part of the results, mostly when the technical aspect is disregarded.

The Monte Carlo analysis on the weights shows the scores of the alternatives with higher availability increased, changing the base rank as seen in Figure 12b. Highlights are for the iron and steel industry, with large production and moderate concentration of CO_2 and coal power plant, with high CO_2 production.

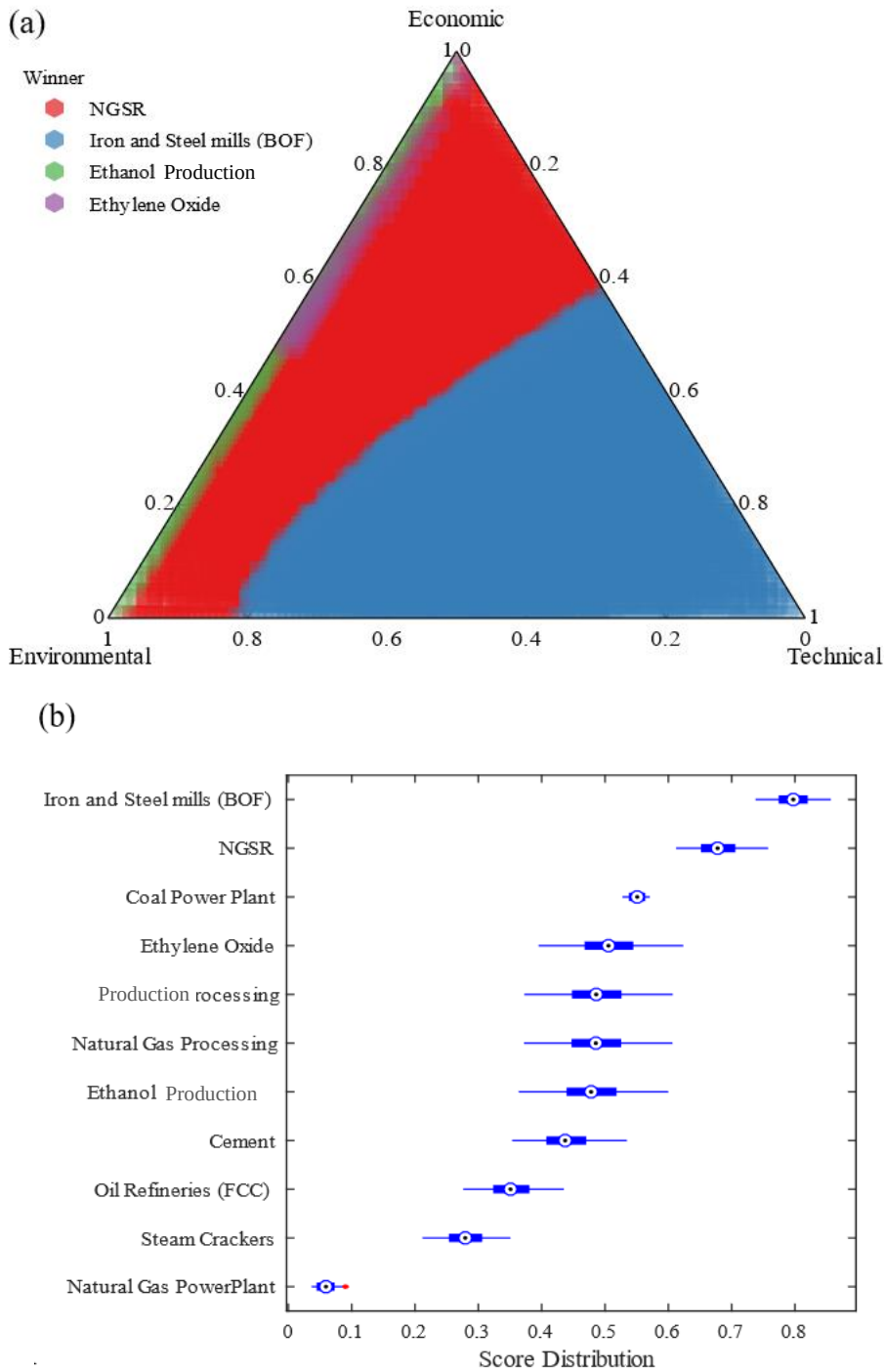

Figure 12 – a) Ternary map of best alternative according to the weight combination. b) Monte Carlo analysis on the weights of each criterion used in TOPSIS for CO_2 alternatives, +-20% random variation.

3.4.3 Combined assessment

In the context of CCU, the scores can infer possible connections between higher-ranking sources. Some high scoring CO_2 emitter processes, such as H_2 production in petrochemicals and ethylene oxide production may be linked to potential hydrogen sources such as NGSR-CC and by-product hydrogen from steam crackers. These interactions may represent the best scenario for CCU, for example, when hydrogen and CO_2 sources are in the same or nearby facility, the environmental and economic impact of the final product of CO_2 conversion may be reduced. The following assessment combines CO_2 and hydrogen scores into one indicator for a pair-wise comparison. The 11 carbon dioxide sources and 11 hydrogen alternatives were combined, totaling 121 pairs.

The indicators used were the proximity to the ideal solution for CO_2 and H_2 from the previous analysis and a Boolean criterion to indicate if the combination is produced in the same or nearby plant. For the weights in this combined assessment, the scores of the CO_2 sources are assumed to have a higher impact in the decision making, considering that a CCU project intends to mitigate the emissions of a CO_2 source itself. Moreover, since the Boolean criterion might impact disproportionately the other criteria, the weight of the Boolean criteria will be set to 10%. Therefore, the weights of the source combinations are: 0.5 for the CO_2 score, 0.4 for the H_2 score and 0.1 for the proximity Boolean. The decision matrix is presented in Appendix A. Figure 13 shows the top ten alternatives.

The solution indicate that use hydrogen produced from natural gas reforming together with CO_2 capture would be the best alternative to use in CO_2 conversion processes. This result was expected considering that this process has the lowest cost, is technologically mature and emits a high concentrated CO_2 stream. However, it cannot be assumed as a viable combination since the hydrogen production process is itself responsible for the CO_2 generation.

Therefore, disregarding fossil-based hydrogen sources, the by-product hydrogen, from coke oven gas and steam crackers, and wind-powered electrolysis combined with high concentrated CO_2 are expected to be suitable to integrate into a CCU process.

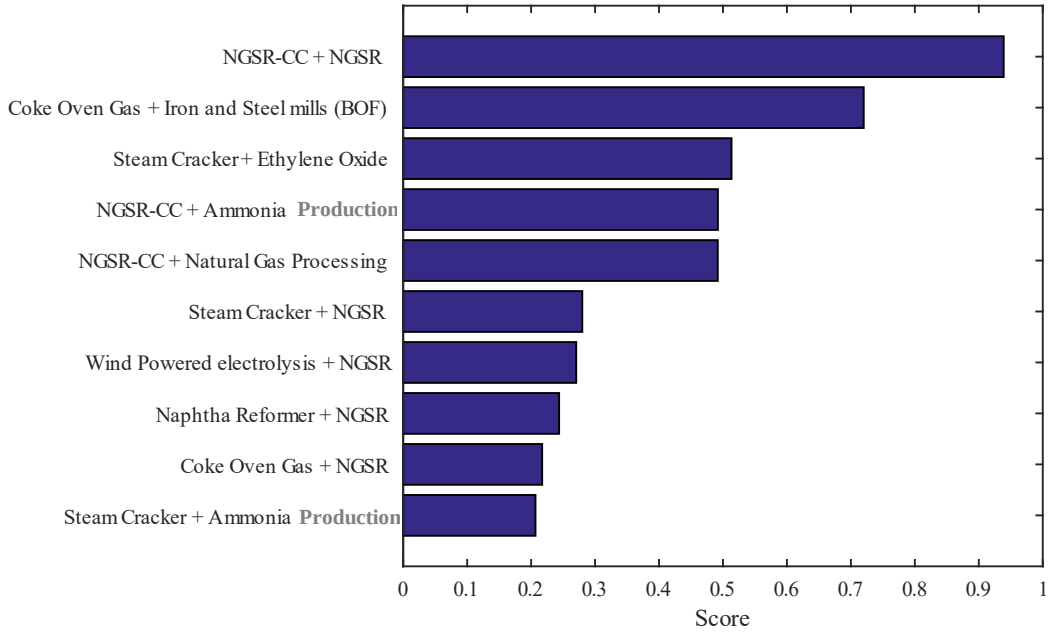

Figure 13 –Top ten combined alternatives for H_2 and CO_2 sources.

This procedure may be used to provide insight into which sources of CO_2 and H_2 should be chosen for a CCU project given a limited set of available information. The impact of this choice in the project will be evaluated in a model-based assessment in Chapter 5.

3.5 CONCLUSIONS

This section focused on evaluating and ranking potential sources of hydrogen and carbon dioxide to be used in CCU. Individually, the analysis showed that capturing CO_2 from refineries (hydrogen production unit), ethylene oxide production (oxygen oxidation process), natural gas processing and steel mills (blast-oxygen furnace) may be considered as potential sources, as they emit high concentration of CO_2 continuously. By-product hydrogen produced in steam crackers (petrochemicals), wind-powered electrolysis and natural gas steam reforming with carbon capture was the highest-scoring processes given the scenario.

A combined assessment suggested that a dedicated production of hydrogen by NGSR with carbon capture should be the chosen combination. A contra-intuitive result linked to the criteria used to perform the assessment. Disregarding the first alternative,

the combinations of coke oven gas + iron/steel industry (BOF) and the steam crackers + ethylene oxide plant were presented as plausible choices.

The performance of the by-product hydrogen sources was significantly better than the other alternatives, therefore is important to further investigate such sources, mainly if facilities are near high concentration CO_2 sources, such as by-product hydrogen from coke oven gas in steel mills.

Finally, the combinations indicated are further explored in the following sections to measure how the different sources of CO_2 and H_2 impact the performance of formic acid production by carbon dioxide hydrogenation.

4 PROCESS SIMULATION - FORMIC ACID PRODUCTION

Formic Acid is conventionally obtained from the combination of methanol and carbon monoxide, and its production through carbon dioxide utilization routes have gained significant attention in recent years (18,109,110). This section presents the modeling and simulation methods used to evaluate both the conventional and CO_2-based formic acid production, considering the hydrogen and CO_2 sources discussed in the previous chapter. The cases studied are summarized in Figure 14.

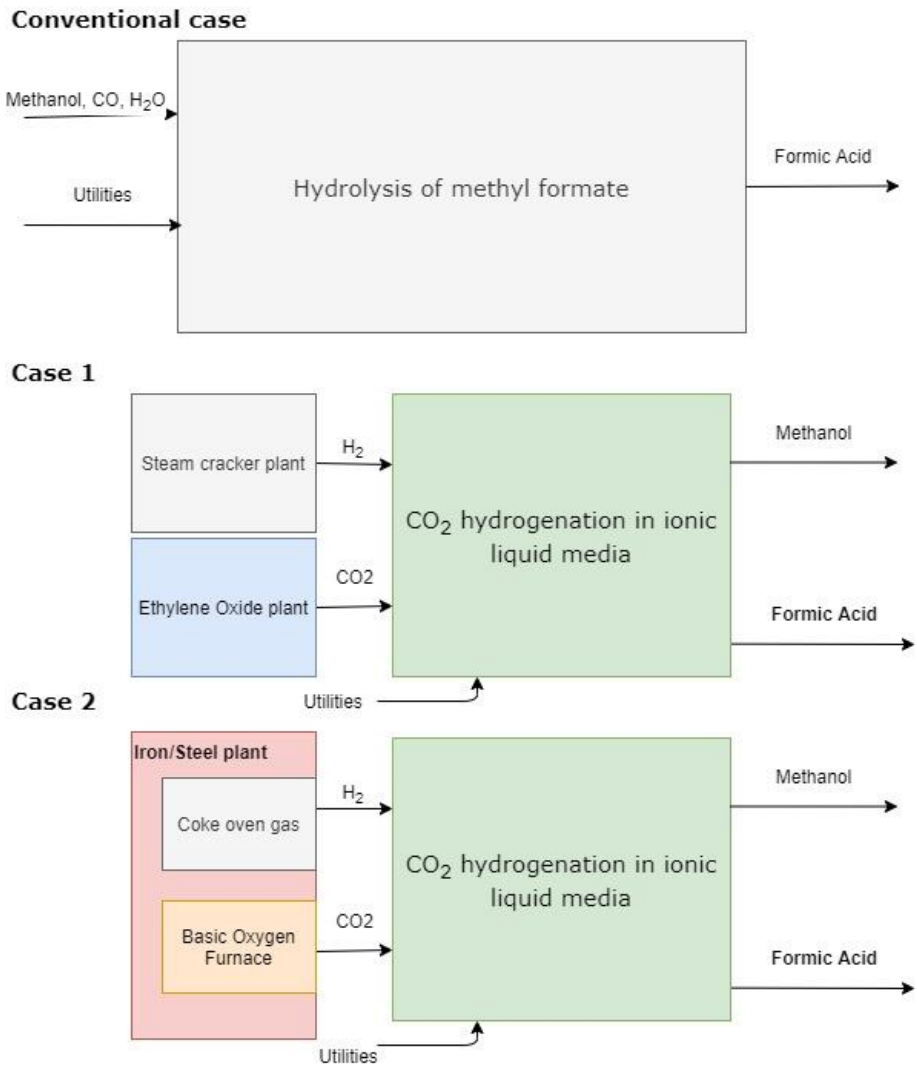

Figure 14 –Evaluated scenarios for formic acid production.

Thus, this section describes the procedures and assumptions used in the modeling and simulation of FA production case studies, which are further the base cases for the techno-economic and environmental analysis.

4.1 CONVENTIONAL PROCESS – HYDROLYSIS OF METHYL FORMATE

Given its importance and market participation, the conventional process chosen for comparison with the CCU case is the used at BASF, based on the carbonylation of methanol followed by hydrolysis of methyl formate with a liquid-liquid separation step to obtain almost anhydrous formic acid (111). Figure 15 shows the key steps involved in this method.

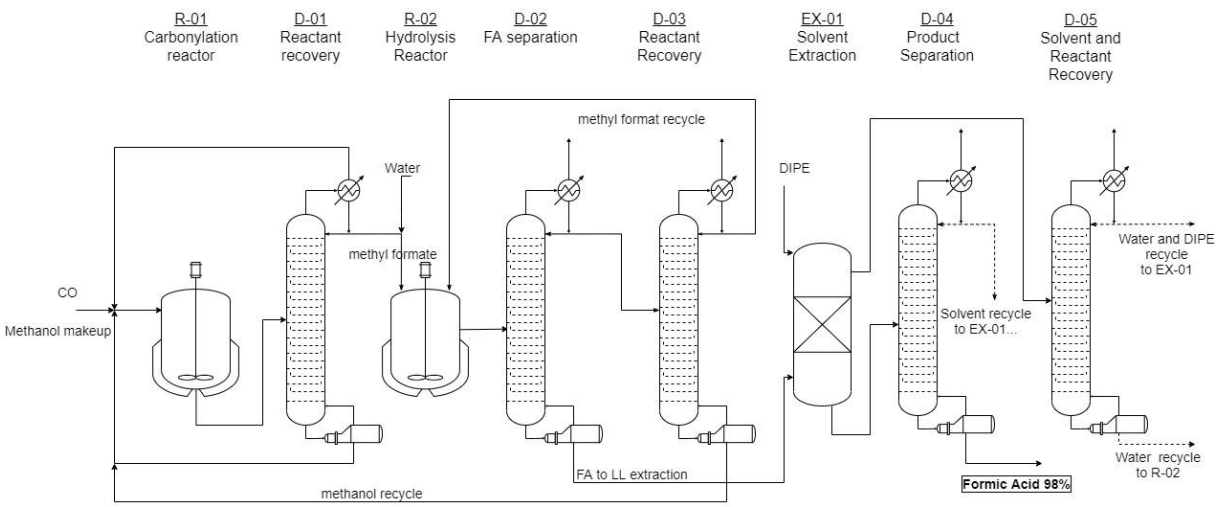

Figure 15 – Formic acid process flow diagram (BASF).
Source: Adapted from da Cunha et al. (24)

First, the carbonylation reaction (Eq. 7) is carried out in a CSTR (R- 01).

$$\mathrm{CO} + \mathrm{C}H_3\mathrm{OH} \rightarrow H\mathrm{COOC}H_3 \tag{7}$$

The outlet stream of the reactor (R-01) is sent to a distillation column (D-01) to separate unreacted methanol and methyl formate, the intermediate product. Methanol is recycled back to R-01, while the distillate is sent to the hydrolysis stage (R-02).

$$\mathrm{HCOOC}H_3 + H_2\mathrm{O} \rightarrow H\mathrm{COOH} + \mathrm{C}H_3\mathrm{OH} \tag{8}$$

The outlet stream of the reactor goes to a second distillation column (D-02), in which methyl formate and methanol are separated at the top, and the aqueous FA leaves in the bottom stream. Methanol and methyl formate are separated in the distillation column D-03 and recycled to R-01 and R-02, respectively. The aqueous FA is sent to an extraction column (EX-01), where a solvent is used to separate formic acid from the aqueous mixture. The extraction raffinate is mostly formic acid and

solvent, which are finally separated in a distillation step (D-04), the remaining liquid phase is sent to the last distillation column (D-05) to recover solvent and water.

Industrial data on plant operating conditions are restricted, so operating conditions used in the simulation are based on works published in the literature (18,111,112).

4.1.1 Process modeling

The simulation study was performed using Aspen Plus V10, following the process description in a BASF patent (111) and other simulation available in the literature (24,113,114). The next sections show brief descriptions of general considerations used in the modeling process, such as reaction, equilibrium thermodynamics and operating conditions.

4.1.1.1 Reaction and Kinetics

In the first reaction stage, methanol carbonylation occurs in the presence of sodium methoxide in the reactor R-01 and the reaction kinetics is described by Equation 9.

$$\begin{aligned} \mathrm{r} = 1.419 \times 10^{9} \exp\left(-\frac{70748}{RT}\right)[cat][MA][CO] \\ - 2.507 \times 10^{12} \exp\left(-\frac{92059}{RT}\right)[\mathrm{cat}][MF] \end{aligned} \tag{9}$$

Where r is given in mol/(L.min); cat is the catalyst; MA, CO, MF correspond to methanol, carbon monoxide and methyl formate, respectively; and the square brackets indicate liquid concentration in mol/L. The catalyst concentration is assumed to be 0.408 mol/L, corresponding to 3 wt % in the reactor for the final simulation. The catalyst was not considered in the simulation. In the second reaction stage, the methyl formate hydrolysis kinetics is given by Equation 10.

$$R = 0.39(K_d C_{FA})^{0.5} \exp\left[-\frac{67{,}800\left(\frac{1}{T} - \frac{1}{368.15}\right)}{R}\right]\left(C_{water}C_{MF} - \frac{C_{FA}C_{MA}}{0.18}\right) \tag{10}$$

Where R is the reaction rate in mol/(kg.min); K_d is the FA dissociation constant (1.8×10^{-4}), and C refers to liquid concentration in mol/kg. Since the kinetics are given per kg of mixture and such a choice of kinetic basis is not a built-in option in Aspen Plus, an average density value of 0.92 kg/L was used to characterize the mixture. Table 5 summarizes the rector conditions, which were optimized by da Cunha (24).

Table 5 - Summary of reactor configurations.

	R-01	R-02
Model type	CSTR	CSTR
Temperature (°C)	102	100
Pressure (bar)	24	20
Residence time (h)	0.717	0.202

4.1.1.2 Thermodynamics

According to da Cunha et al. (24), the UNIQUAC-HOC model shows a good representation of the system phase equilibrium at simulation conditions, therefore it was the chosen property method in this simulation. Using Hayden-O'Connell equation is recommended to handle the solvation of polar compounds and dimerization of the vapor phase in the mixtures containing carboxylic acids (115).

To validate the model performance, experimental phase equilibrium data for the binary systems (component-component combination) were used to optimize the model parameters. Experimental data were selected, preferably, when taken close to the estimated operating conditions. Most of the data studied were available in the simulator database, specifically the NIST ThermoData Engine, except for CO solubility data.

This model describes the binary systems with satisfactory accuracy at the given conditions. Phase equilibrium is predicted with notable accuracy for the MF-FA system but there is a positive deviation in predicting the saturation pressures of the pure components for the system Water-FA even after parameter optimization. Phase equilibrium plots and analysis are shown in Appendix C

4.1.1.3 Equipment

Besides thermodynamics and kinetics assumptions, some operating conditions are given by the original BASF patent and some optimized conditions can be found in the literature (24,114). Table 6 shows the distillation configuration optimized by Cunha et al. (24), which was the reference for the base case.

Table 6 – Distillation columns configuration summary

	D-01	D-02	D-03	D-04	D-05
N° of stages	16	34	38	22	8
Feed stage	7	25	32	11	5
Pressure	4.05	3.78	1.01	1.01	1.01
Condenser	Partial	Partial	Partial	Partial	Total

4.2 INNOVATIVE PROCESS – CO_2 HYDROGENATION IN IONIC LIQUID MEDIA

The conversion of carbon dioxide and hydrogen into formic acid commonly involves a phase change from gaseous reagents into a liquid product, yielding an entropically disfavored reaction when gas phase reactants are considered (Equation 11)

$$H_{2(g)} + CO_{2(g)} \Leftrightarrow HCOOH_{(l)} \qquad \Delta G°=32.8 \text{ kJ mol} \qquad (11)$$

On the other hand, the presence of solvents alters the thermodynamics of the reaction and the reaction becomes slightly exergonic, when operated in the aqueous phase (Equation 12).

$$H_{2(aq)} + CO_{2(aq)} \Leftrightarrow HCOOH_{(aq)} \qquad \Delta G°=-4 \text{ kJ mol} \qquad (12)$$

Besides water, other substances, such as ammonia and amines can be used to improve the equilibrium of the CO_2 hydrogenation into formic acid. A multi-criteria decision analysis was performed to select a suitable reaction path based of process

characteristics, and the CO_2 hydrogenation in Ionic Liquid media was chosen to be further evaluated. This is discussed in Appendix B.

Ionic liquids (ILs) can be viewed as a new and outstanding class of solvents as they are liquids comprised of cations and anions (organic and inorganic) with unique properties, such as better solvating properties and low vapor pressure (116).

According to Bello et al (117), a significant benefit of using ILs as solvent in CO_2 hydrogenation reactions is the ability to adjust its properties, selecting different cations and anions, to lead to a reduction in the Gibbs energy of formation, and improve the reaction yield, acting as solvent and catalyst.

In this study, the reaction of CO_2 hydrogenation into formic acid implemented by Bello et al. (117) was used as base case to build the CO_2-based formic acid production. The work consisted in a thermodynamic analysis for hydrogenation of CO_2 to formic acid and methanol in a single-step reaction promoted by the IL- 1-ethyl-2,3-dimethylimidazolium nitrite ([Edmim][NO2]). Details of simulation and assumptions are given next.

4.2.1 Base case modeling

Bello et al. (118) carried out a thermodynamic analysis of CO_2 hydrogenation into methanol and formic acid promoted by the IL 1-ethyl-2,3-dimethylimidazolium nitrite ([Edmim][NO2]). The study investigated the effect of variables such as temperature, pressure, IL flow and H_2 and CO_2 concentrations over the formic acid production. Methanol was considered as a by-product.

The simplified process flowsheet is presented in Figure 16. CO_2 and H_2 feeds originate from different sources depending on the studied case The reaction part of the process (F-01, R-01, F-02, and F-03) was implemented by a PhD candidate (Bello et al. (117)) in the research group where this work was developed and handed for further modifications, scaling-up and addition of separation processes to be compatible with the conventional process also evaluated in this study. In summary, first, in the reaction step, the absorption of CO_2 in the ionic liquid (F-01) takes place, forming an adduct and releasing off-gas, the CO_2-IL mixture is then sent to the reactor (R-01) where the reaction takes place with excess H_2 to form FA, methanol and water. For this process, the mass ratio IL/CO_2 is approximately 2.5/1, while de ratio H_2/CO_2 is about 35/1.

After the reaction stage, the mixture of IL-Adduct, H_2, CO_2, formic acid and methanol is separated - the IL and H_2 not reacted are recycled and the product mixture containing FA, methanol and water is directed to the separation step.

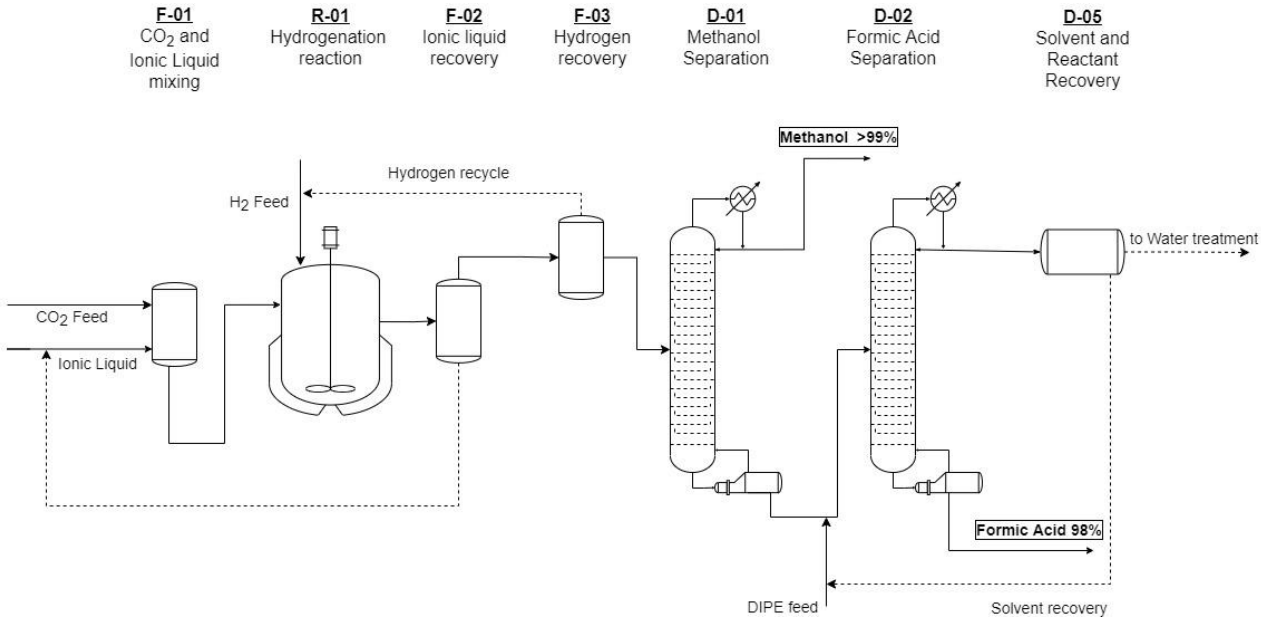

Figure 16 – Process flow diagram of the formic acid production by CO_2 hydrogenation in ionic liquid.

First, the methanol is separated from FA and water mixture in a distillation column (D-01). At this point, methanol is already at commercial grade. Then the FA-water mixture enters an extractive distillation column for separation, using the same solvent used in the conventional case (Diisopropyl ether). Formic acid is purified to the commercial grade of 98%. The extractive distillation configuration step was based on the conventional process (24).

4.2.1.1 Thermodynamics properties of the IL

The thermodynamics assessment of the reaction was carried out by Bello et al. (117) in Aspen Plus, using the thermodynamic package COSMO-ESR, which was used whenever dealing with the ionic liquid (reaction stage). Then in the separation stage, the UNIQUAC-HOC model was used, as in the conventional case, to deal with the dimerization of formic acid in the vapor phase.

Additionally, since IL is not present in the simulator database, it was considered as a hypothetical component, and its properties needed to be estimated. The normal

boiling point of [Edmim][NO_2] was estimated by the extended group contribution method, the density was estimated by conductor-like screening method for real solvents (COSMO-RS), while the molecular weight was known. Properties such as standard enthalpy and Gibbs energy of formation and vapor pressure were estimated by Joback group contribution method in Aspen Plus.

4.2.2 Hydrogen recovery

Aside from the CO_2 conversion process itself, the sources of hydrogen and CO_2 are also considered in the model as black boxes. In the case of H_2 sources, two scenarios are considered as previously described steam cracking and coke oven gas. The representation in the simulation is given in Figure 17.

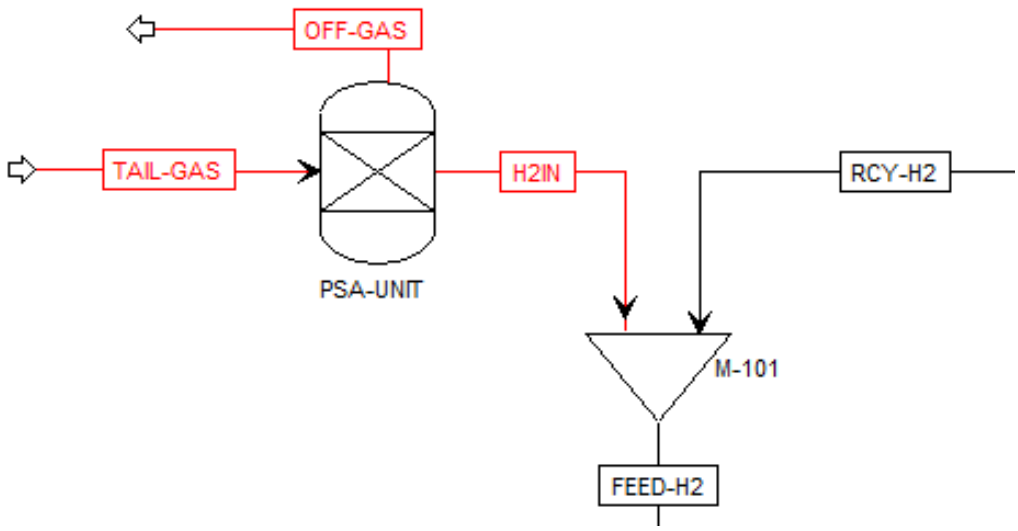

Figure 17 – Hydrogen source integration represented in the simulation.

The *tail-gas* refers to the gas containing hydrogen coming from the steam cracking or coke oven gas process. This gas passes through a separation process, in this case, a pressure swing adsorption system (PSA) to purify the hydrogen into the desired quality to be sent to the conversion stage (H2IN). The purge gas from the PSA unit, containing hydrocarbons and hydrogen not separated, is then sent back to the source, where it is usually burned for heat or flared.

The PSA parameters are incorporated into the model to account for energy use and capital costs. Despite being similar, off-gas composition from those sources are quite distinct.

The output composition of the steam cracker depends mainly on the raw material used in the reaction. In 2017, in the United States industry, 67% of steam crackers operated using ethane as raw material (RM). The composition varies but the final mixture exiting the ethylene fractionation column consists basically of 1/1 of hydrogen and methane in mass (55).

Hydrogen from a coke oven gas may carry considerably more impurities and needs to be pre-treated before being sent to the PSA unit, but it also consists mostly of hydrogen and hydrocarbons (58,119).

A major issue in separating the hydrogen from the respective off-gases is that it is generally used as fuel in the originating process, therefore the energy content of the hydrogen removed must be compensated with other fuel. Herein, it is assumed its substitution by natural gas. So proper costs and emissions are considered.

4.2.3 Carbon dioxide feed

Similarly, carbon dioxide comes from two distinct sources, ethylene oxide industry and steel and iron industry. Herein, the differences are not as subtle, since the ethylene oxide CO_2 is assumed to be almost pure, while the CO_2 steelmaking has a much lower concentration (36% m/m), making necessary to implement a carbon separation unit before directing the stream to the reaction step.

According to Bains et al (62), an ethylene oxide plant operating with direct air oxidation generates about 10 ton of CO_2 per hour at 99% m/m. The CO_2 from the process comes from the complete oxidation of the raw material in a parallel reaction to the production of ethylene oxide, as in the reaction scheme showed in Figure 18. When the reaction occurs with pure O_2, the only products are carbon dioxide and EO. After the purification step, a virtually pure CO_2 stream is generated.

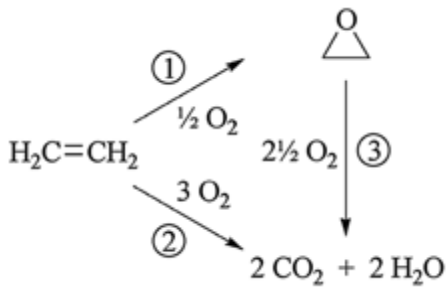

Figure 18 – Ethylene oxidation reaction.
Source: Ullman's Encyclopedia of Industrial Chemistry (120).

An integrated iron and steel mill (ISM) consists of several complex series of interconnected plants, where emissions come out from many sources (10 or more). Large quantities of CO_2 are produced in the blast furnace by the reduction reaction ($Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$) and by the combustion reaction of carbonaceous materials (coke breeze, etc.) and carbon-containing gases such as blast furnace gas, sintering machine and others (62). The largest CO_2 flow comes from the blast furnace, which accounts for 69 % of the total steel mill emissions. CO_2 capture is modeled as a black box unit, based on carbon capture using amine absorption technology as given by Sundqvist et al. (121). Capital costs and energy consumption are considered according to Minh et al. (122).

4.3 RESULTS

The stream data calculated for the base case process is presented in Appendix C. The conventional process flow diagram as implemented in Aspen Plus process simulator is shown in Figure 19.

Regarding the CO_2-based process, the process was simulated without major issues and show reasonable comparability with the conventional process. Figure 20 shows the current process flowsheet. Note that the sources of H_2 and CO_2 are not explicit. Process flow details are presented in Appendix C. Table 7 shows key input/output values for each simulation.

Table 7 – Key input output results.

Variable	Unit	**Conventional**	**Case 1[a]**	**Case 2[b]**
FA production	ton/year	26,016	21,424	21,424
Methanol production	ton/year	-	3,654	3,654
CO_2 usage	ton/year	-	25,095	25,095
H_2 usage	ton/year	-	1,942	1,942
Electricity usage	kW	77	7,862	7,884
Heating duty	MJ/h	75,179	29,269	30,524
Colling duty	MJ/h	77,477	65,700	67,600

[a] CCU formic acid production using hydrogen from Steam Crackers and CO_2 from ethylene Oxide production.
[b] CCU formic acid production using hydrogen from Coke oven gas and CO_2 from basic oxygen furnace, both from iron and steel production.

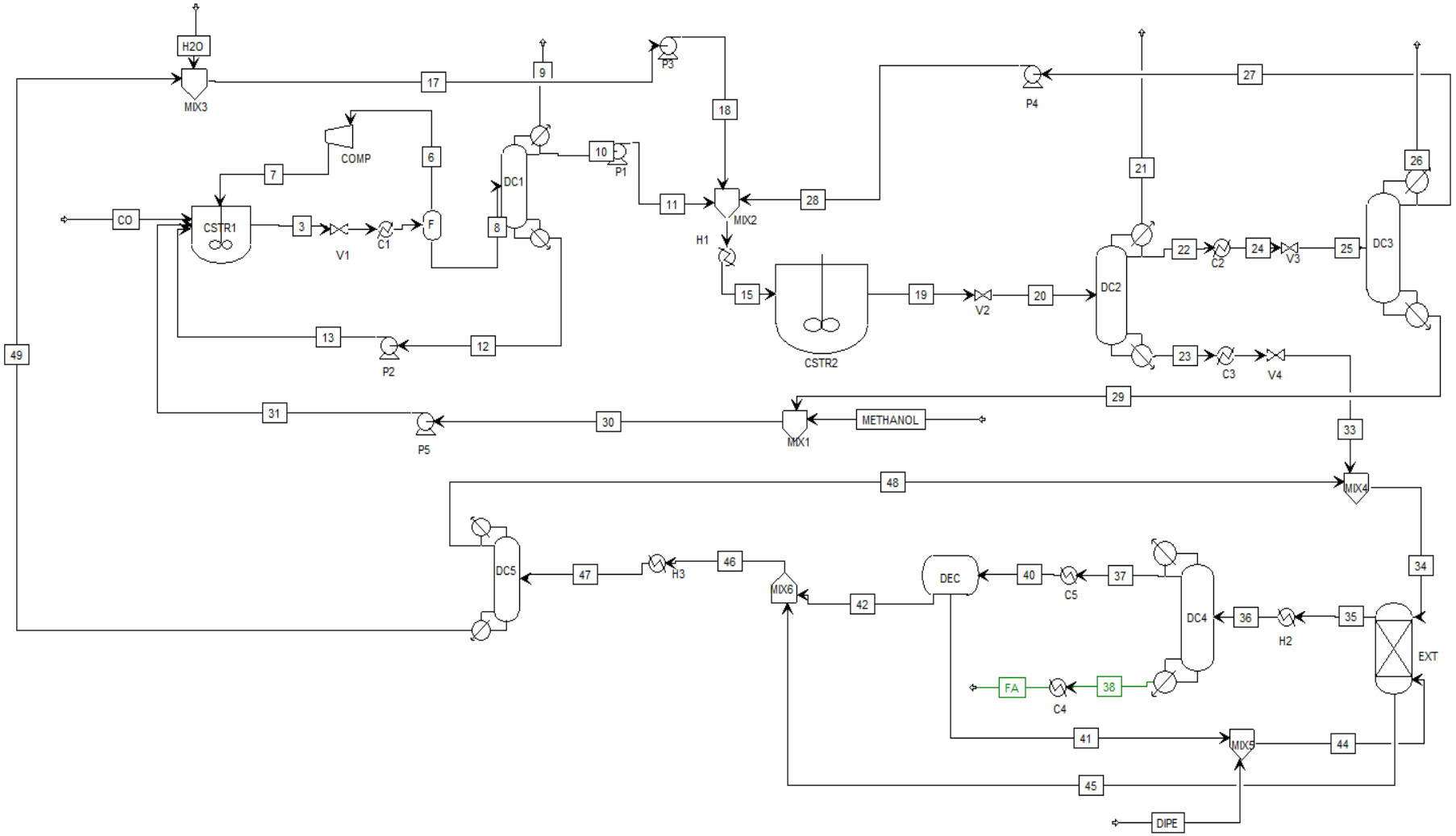

Figure 19 – Conventional process flow diagram implemented on Aspen Plus.

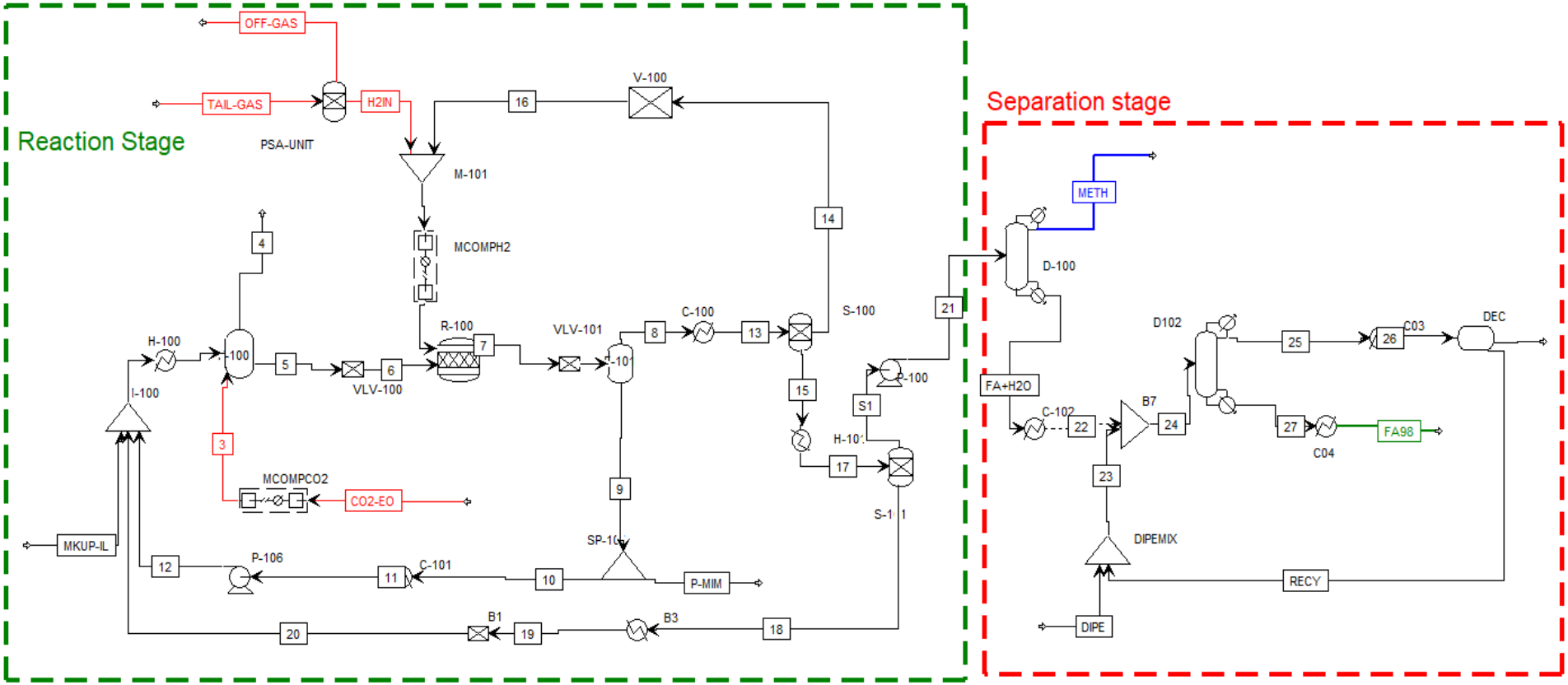

Figure 20 – CO_2-based formic acid production flowsheet.

4.4 CONCLUSIONS

Complete processes for FA production via hydrolysis of methyl formate and by CO_2 hydrogenation were simulated based on data available in the literature. The objective of implementing rigorous flowsheets as base for future comparison was achieved. However, since the ionic liquid process is still at theoretical development stage, for its comparison with the conventional case, it is important to consider that the conventional case is a mature technology and has been optimized over the decades, therefore it is expected to be more efficient.

In the next section, the simulation results are used to draw detailed technical-economic analysis of the CCU processes and its comparison with the conventional case.

5 TECHNO-ECONOMIC AND ENVIRONMENTAL ANALYSIS

As previously discussed, evaluating a CCU process can easily become a highly complex task. The process being coupled to CCS or a hub, multiple products, employed technology are some examples of which can be considered. In this work the evaluation of the process is based on the data obtained from the simulation and aims to compare the performance of CCU processes with the performance of the conventional process. For this, the indicators presented in Table 8 are computed and compared. In addition, the performance difference between Cases 1 and 2 are also quantified with the appropriate indicators.

Table 8 – Selected indicators for performance analyses

	Indicator	Description	
Technical	Total energy consumption (123)	$E_{total} = Total\ energy\ consumed\ by\ the\ process$	(13)
	Energy intensity(80)	$EI = \frac{Net\ energy\ used}{Mass\ of\ product}$	(14)
	Mass intensity (80)	$MI = \frac{Total\ mass\ of\ input}{Total\ mass\ of\ of\ product}$	(15)
Environmental	**Carbon intensity**	$CI = \frac{Net\ CO_2\ emissions}{Mass\ of\ product}$	(16)
	Emissions (CO_2) avoided (124)	$C_{avoid} = CI_{conventional} - CI_{CCU}$	(17)
	Cost of avoidance(125)	$C_{avoid_{cost}} = \frac{CI_{conv} - CI_{CCU}}{Cost_{CCU} - Cost_{conv}}$	(18)
Economic	**Capital Cost**(123)	$CAPEX = Equipment\&land\ cost + indirect\ costs + working\ capital$	(19)
	Manufacturing Cost	$COM = Direct\ Manufac.cost + fixed\ manufac.\ costs + plant\ overhead\ costs$	(20)
	Total Annualized Cost (24)	$\mathrm{TAC} = COM + \mathrm{ACCR} \times \frac{\mathrm{FCI}}{PR}$	(21)
	Net Present Value	NPV = Total of the present value of all cash flow, minus the present value of the capital investments.	
	Internal Rate of Return	IRR = discount rate that makes the NPV equals to zero (break even)	

Additionally, a hypothetical scenario considers carbon credit to assess the condition in which the CO_2-based process might be competitive when compared to the conventional one. A sensitivity analysis is performed for the key indicators.

The conventional process assessment considers the equipment and utilities shown in Figure 19. For Cases 1 and 2, it is necessary to expand the CCU process to account for separation units and fuel substitute as shown in Figure 21. Since these are multi-product plants, producing FA and methanol, the indicators values were allocated by mass.

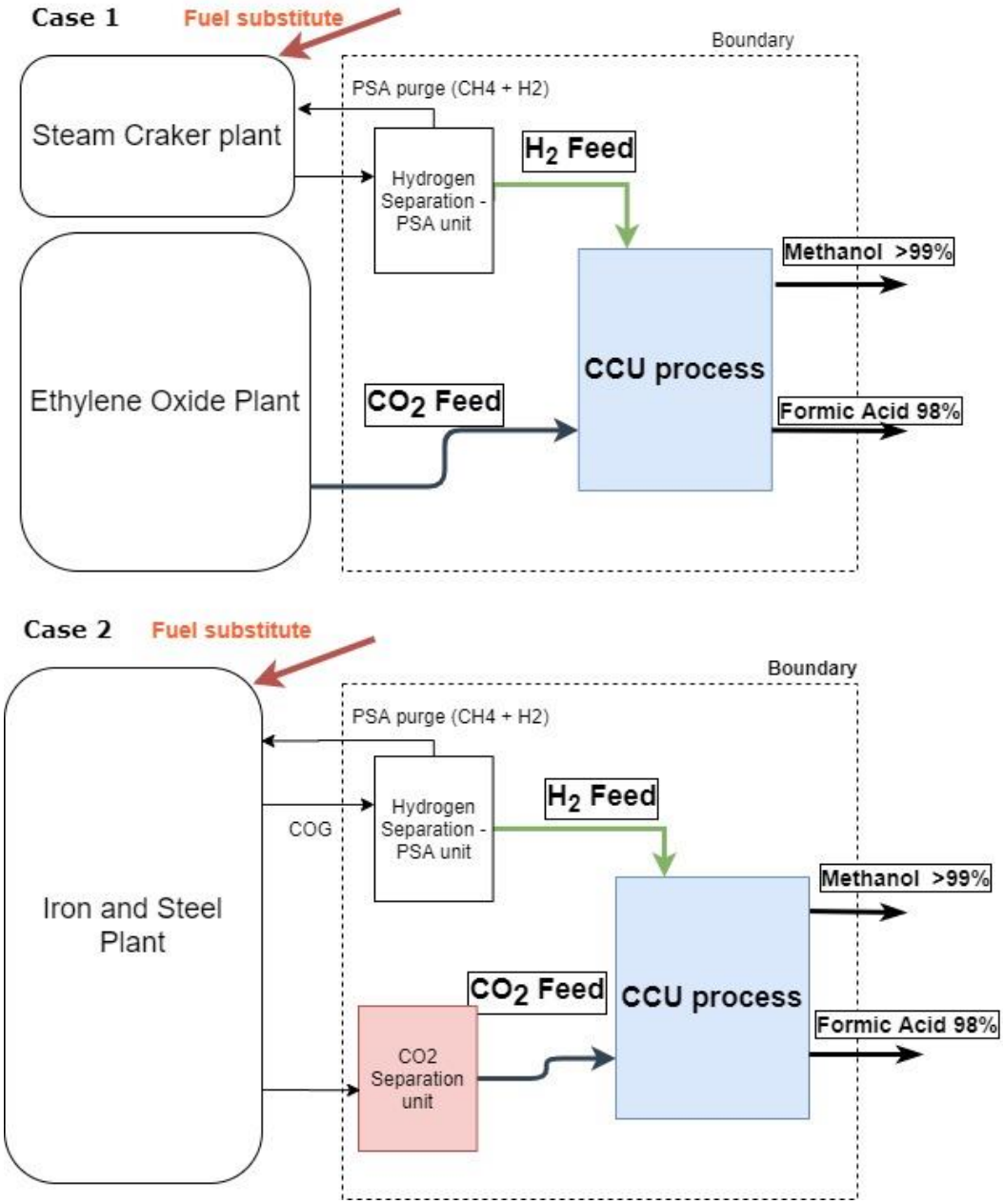

Figure 21 – Case 1 and 2 boundaries for analysis.

5.1 METHODS

This section describes the major assumptions used when computing the mentioned indicators.

5.1.1 Technical indicators

The technical maturity of a project is also an indicative of the risk that the project holds. A mature process, besides being tested at commercial scale before, was likely optimized over the time, to reduce waste material and improve energy efficiency. Therefore, technical indicators should reflect how efficient the technology is in terms of the amount of material and services required to generate the desired product or complete a specific process task (e.g., separation). These indicators can also be useful in detecting opportunities in process design at the conceptual stages (80).

Herein, three technical indicators are calculated: total energy demand, and energy intensity.

5.1.2 Emissions assessment

In this analysis, only direct and indirect emissions of CO_2 are considered inside the boundaries previously discussed. The CO_2 emitted by each plant is assumed to be the sum of direct CO_2 emissions, from process streams and combustion fuel substitute, and indirect emission estimates from electricity usage, steam generation and cooling. Process energy consumption is calculated by simulation.

For computing emissions, natural gas was assumed to be the ultimate fuel source to generate heat. For each utility employed, the emissions are calculated based on the amount of energy used. The emission factor is given by the US Environmental Protection Agency Rule of 2009 (126), in the case of natural gas 50.23 gCO_2/MJ. It assumes the ultimate fuel source is burned, providing the net heating value of the components, and all carbon atoms are converted to the emitted CO_2. The electricity emission factor used is based on its global average carbon intensity of 340gCO_{2e}/kWh (127).

The analysis is limited to evaluating CO_2 emissions. Other environmental indicators that consider toxicity of liquid/solid/gas waste have been left out of the scope

of this work. It is possible to estimate these indicators with data provided by the simulation, but these can be calculated more accurately in a life cycle analysis.

5.1.2.1 Carbon pricing

There are several ways to price carbon. According to the World Bank (128), a carbon tax consists of a fixed amount of tax that a given entity must pay to the government according to the amount of carbon emitted.

Carbon credits, on the other hand, are baseline-and-credit market systems, where baseline emissions levels are defined for individual regulated entities and credits are issued to entities that have reduced their emissions below this level. These credits can be sold to other entities exceeding their baseline emission levels. In this sense, carbon credits values are not fixed, but fluctuate with the market. Well known examples of credit systems are the European Emission Trading System (ETS) (129) and California's Low Carbon Fuel Standard program (LCFS) (130).

Brazil recently implemented a prototype decarbonization credit system similar to the LCFS, inside the national biofuel program (RenovaBio), and also finalizing legislation to implement a carbon market to expand the coverage for other industries.

Here, in a simplified scenario analysis, the carbon credit is used to estimate the amount of financing needed to make the CCU process viable or competitive compared to the conventional case. In this case, the number of credits that a CCU process generates is given by Equation 22.

$$C_{credit} = C_{avoided} \left(\frac{ton_{CO_2}}{year}\right) \tag{22}$$

Where the number of carbon credits generated is equal to the tons of CO_2 avoided each year. The values of these credits are set to zero in the base case analysis, then its influence is investigated in a sensitivity analysis.

5.1.3 Economic Assessment

A positive economic outcome is the main objective of a business. Therefore, it needs to be evidenced at the time that a new process or modification is proposed to be implemented at commercial scale.

To establish a fair economic evaluation, the framework conditions for the study have to be defined as similar as possible. Base case variables used in the calculation of economic indicators are given in Table 9 and Table 10.

Table 9 – Summary of economic assumptions

	Conventional	**Cases 1 e 2**
Tax Rate	30%	30%
Discount rate	10%	10%
Economic Life of Project (years)	20	20
Salvage Value (% of Initial Capital Cost)	15%	15%
Hours per year	8,000	8,000
Formic Acid Production (ton/year)	26,016	21,424
Methanol production (ton/year)	-	3,654
Hypothetical site location	United States	
Reference Capital Cost year	2021	
Depreciation Method	Straight Line, for 10 years	

Information about mass and energy balances and equipment sizing were obtained from Aspen Plus simulations. The equipment sizing and costing were carried out using Aspen Process Economic Analyzer (APEA) v10, which employs a 2016 pricing basis and it is integrated to Aspen Plus v10, which then was adjusted to their respective valuea in 2021 according to the increase in the Chemical Engineering Plant Cost Index (CEPCI).

Aspen Process Economic Analyzer was used to estimate the Fixed Capital Costs (FCI) and Cost of Operating Labor (C_{ol}). Costs of raw material (C_{RM}) and utilities (C_{ut}) were based on their consumption estimated by the process simulation, and the prices are given in Table 10. The cost of water treatment (C_{wt}) was neglected for this assessment.

Table 10 – Operating cost input summary.

	Material Cost (US$/ton)
Water	1[a]
Diisopropyl Ether	2125[b]
CO	70[a]
Methanol	430[c]
Formic Acid	830[d]
Natural Gas[e] (US$/1000 m^3)	5.50
Ionic Liquid[f]	50,000
	Utilities cost (US$/GJ)[d]
Cooling Water	0.244
Chilled Water	4.43
LP Steam	13.28
MP Steam	14.19
Electricity	16.8

[a]Turton et al.(131); [b] Average vendor price at Alibaba.com (132); [c] Sharma et al.(114); [d](24).
[e] Average 2021 natural gas price for industrial users in the United States (133);
[f] Ionic liquid is charged once, and 10% of its volume is replaced yearly.

Economic performance was assessed by calculating the indicators shown in Table 8. NPV, IRR and cash flow analysis of plant profitability were calculated following the procedure described in Turton et al. (131).

The cost per kg of product described by the total annualized cost (TAC) is defined by Equation 23 (134).

$$\mathrm{TAC} = COM + \mathrm{ACCR} \times \frac{\mathrm{FCI}}{PR} \tag{23}$$

Where FCI is the Fixed Capital Investment, PR is the production rate, ACCR is the annual capital charge ration (a time correction of capital). The cost of manufacturing without depreciation (COM), describes the operating costs, as shown in Equation 24 (131).

$$COM = 0.18 \times \frac{\mathrm{FCI}}{\mathrm{PR}} + 2.73 \times \mathrm{C_{ol}} + 1.23 \times (\mathrm{C_{ut}} + \mathrm{C_{rm}} + \mathrm{C_{wt}}) \tag{24}$$

5.1.3.1 Ionic liquid cost

As a novel material, the cost of ionic liquids can vary widely. Since no reference cost is available for ([Edmim][NO2]), an estimate price of 50 US$/kg is estimated, based on literature reference prices for other ionic liquids (116).

Since the IL is not expected to evaporate and is considered stable at the operating conditions, it is assumed to be almost fully recovered in the recycles streams, with only 10% of the total volume of IL circulating lost yearly. Therefore, despite being the most expensive component in the material list, the IL cost is considered an initial investment. The 10% of the IL lost is replaced annually and computed as an operating cost.

5.2 RESULTS

The analyses showed that the indicators energy intensity, CO_2 emissions and economic indicators vary widely from project to project. The conventional process is by far the most economically attractive but emits almost the double of the amount of CO_2. Case 1 performs slightly better than the Case 2, since no carbon capture unit is needed. Detailed assessment is given next.

5.2.1 Technical performance

Since the studied processes are at different levels of technological development, it was expected that the conventional process would show technical performance clearly superior to CCU processes, but this was not the case.

The total energy demand of the processes, disregarding mild cooling, was 75.4, 84.0 and 85.2 GJ/h for the conventional, Case 1 and Case 2, respectively. Considering energy as function of the product mass, the difference is clearer, and CCU processes are at least 15% more energy intensive than the conventional case, as seen in Figure 22. Note that cooling duty does not translate directly to energy consumption, it refers to “Ex. Cooling” line to the direct energy use. Since fluids are cooled to ambient temperatures by cooling towers and similar equipment, the actual energy consumed to cool a fluid is given by the electricity used to pump the fluid through the cooling equipment, for example.

It is important to highlight that, although the absolute energy intensity is similar, the nature of these energies is notably different – the elevated contribution of electricity in the total energy consumed by CCU processes is caused mainly by the work required to compress CO_2 and H_2. In fact, more than 95% of the electricity consumed at the CCU plants goes to the hydrogen compression.

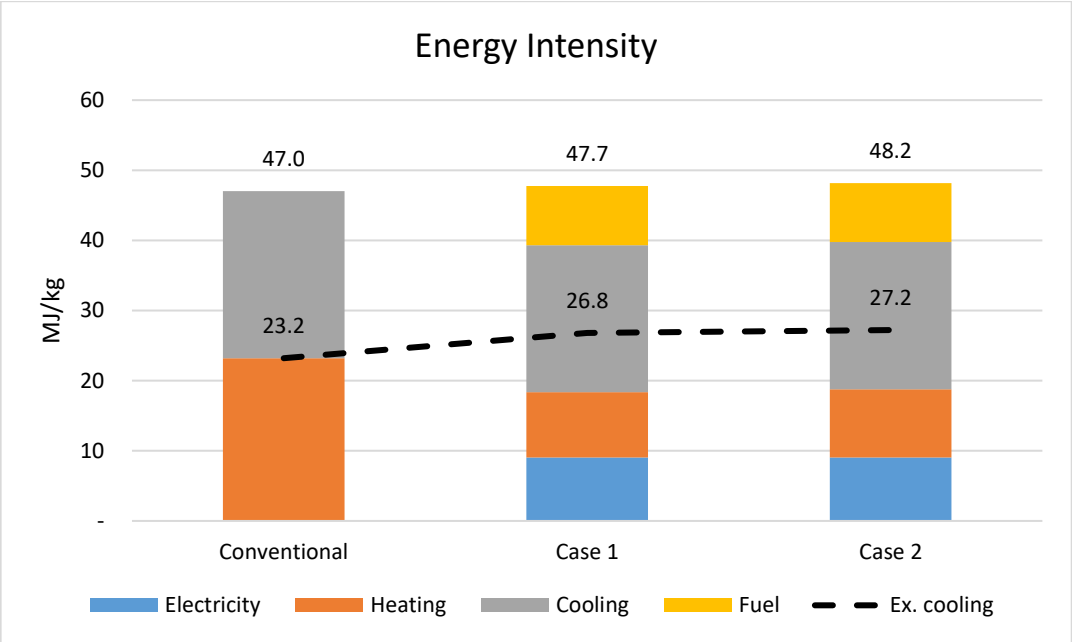

Figure 22 – Energy intensity (MJ/kg).

In addition, in both CCU cases, about 8.4 MJ of energy from substitute fuel is required for each kilogram of product. Both compressor work and substitute fuel energy are aspects that can be improved to make the CCU process more competitive.

5.2.2 Environmental performance

The simulated FA production routes emit about the same amount of carbon dioxide in total, if only energy consumption and fuel switching is considered. However, the value drops almost by half when the CO_2 converted is subtracted from the absolute emission value, giving the net emissions shown in Figure 23.

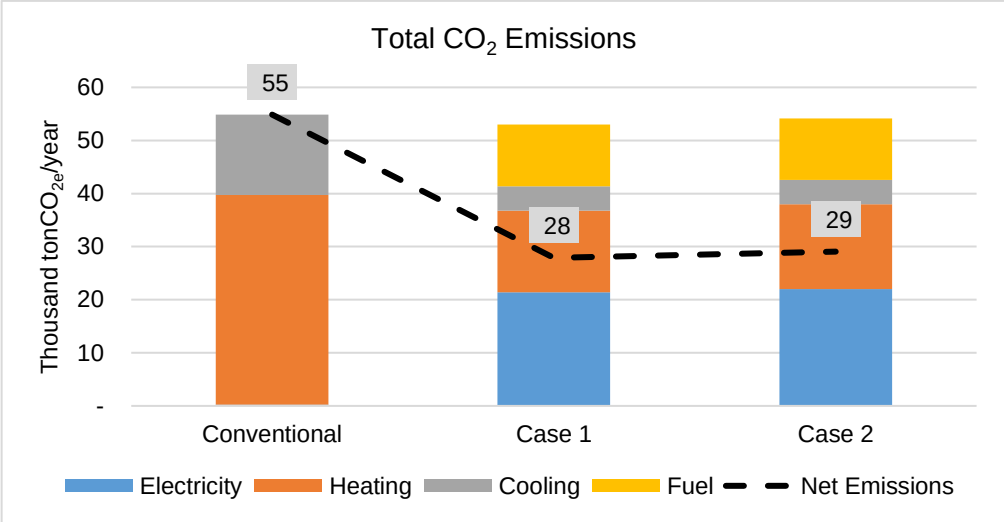

Figure 23 – Comparative summary of CO_2 emissions by source.
Notes: Net emissions discount the CO_2 converted in the CCU reaction. Fuel emissions refer to the emission from burning natural gas to substitute hydrogen.

According to Perez-Fortes et al.(20), a conventional FA plant emits about 2.18 kg_{CO_2}/kg_{FA}, while the value estimated by this work is 2.11 kg_{CO_2}/kg_{FA} for the conventional process and 1.11 kg_{CO_2}/kg_{FA} and 1.16 kg_{CO_2}/kg_{FA} for cases 1 and 2 as seen in Table 11.

Table 11 – Carbon intensity of formic acid produced by different routes (kg_{CO_2}/kg of product).

	Conventional	Case 1	Case 2
Carbon intensity	2.11	1.11	1.16
Utilities emissions	2.11	1.65	1.70
Electricity	0.01	0.85	0.88
Heating	1.52	0.61	0.64
Cooling	0.58	0.18	0.18
Direct emissions	-	-0.54	-0.54
Process CO_2	-	-1.00	-1.00
Combustion CO_2	-	0.46	0.46

In absolute terms, 72% of the CO_2 emitted by the conventional process is allocated to the steam production, mainly in the distillation units, 28% for cooling and less than 1% in emissions are associated to the electricity consumption.

For CCU processes, emissions are more spread between utilities and the burning of substitute fuel. In cases 1 and 2, about 29% of the CO_2 emitted is related to steam generation, 9% for cooling, 22% directly in the burning of H_2 substitute fuel, and finally 40% is attributed to indirect emission from the electricity use. Absolute annual emissions are shown in Table 12.

Table 12 – Total annual emissions breakdown (tons of CO_2-eq).

	Conventional	Case 1	Case 2
Total Emissions	**54,868**	**27,889**	**29,071**
Utilities emissions	**54,868**	**41,392**	**42,574**
Electricity	209	21,377	21,998
Heating	39,546	15,396	15,957
Cooling	15,113	4,619	4,619
Direct emissions		**-13,503**	**-13,503**
Process CO_2		-25,095	-25,095
Combustion CO_2		11,593	11,593

As previously mentioned, most of this electricity consumption from cases 1 and 2 and, and consequently, occur at the H_2 compression stage, which operates compressing 5 ton/h of H_2 in a ΔP of 15 bar.

Other important indicator is the amount of CO_2 not emitted when the CCU process is used to produce formic acid. This is merely the difference between the carbon intensity of the conventional process minus the carbon intensity of FA in the other cases. In this study, 1 ton of formic acid produced through CCU emits 1 ton less CO_2 in case 1, and 0.95 ton less in case 2, as seen in Table 13.

Table 13 – CCU specific indicators.

	Case 1	Case 2
CO_2 Avoided (ton_{CO_2}/ton)	1.0	0.95
Avoidance cost (US$/$ton_{CO_2}$)	223	275

Rubin et al. (134) estimated the avoidance costs for various CCS alternatives and showed that the cost of avoidance of implementing CCS in a Natural Gas Power Plant can vary from to US$67 to US$140 per ton of CO_2 avoided (adjusted for inflation). Making the current CCU processes less competitive with $C_{avoided}$ at U$233 to 275 per ton. At the same time, it is lower than the €400/ton estimated by Hank et al. (135). Cost breakdown is detailed in the next section.

Another notable outcome is the cost to avoid this emission. The cost of avoidance (Eq. 18) compares emissions and costs of the conventional process with the CCU process, i.e., how much would cost to mitigate each ton of CO_2 in through this route. Avoidance costs are displayed in Table 13. The avoidance cost is useful in comparisons with other mitigation alternatives such as CCS. The avoidance cost difference between Cases 1 and 2 shows that the difference in capital cost and energy consumption due to the difference in hydrogen and CO_2 sources add up to more than US$50/ton of CO_2 avoided.

5.2.3 Economic performance

Table 14 summarizes the key indicators of the economic performance calculated for the FA processes. It is clear that the conventional process has both lower capital and operating costs. On the other hand, regarding CCU processes, the most evident difference is the comparison between the plants CAPEXs. The CAPEX of Case 1 is 44% higher than in the conventional process and Case 2 is about 8% higher than in Case 1.

Table 14 – Projects economics summary

	Conventional	**Case 1**	**Case 2**
Total Project Capital Cost (Million US$)	26.84	36.85	39.23
Total Operating Costs (Million US$/year)	12.04	14.25	14.58
Total Raw Materials Cost (Million US$/year)	2.26	1.08	1.08
Total Utilities Cost (Million US$/year)	5.23	7.61	7.75
Total Products Sales (Million US$/year)	21.59	19.94	19.94

The CAPEX difference between the conventional and CCU cases is attributed mostly to the high cost of investment in CO_2 and, mainly, to H_2 compression. Between the CCU cases, the requirement of a capture unit to separate the CO_2 from the iron and steel industry increases both the capital and operational costs, when compared to Case 1.

At the same time, the investment and operation costs are higher. The CCU processes also earn slightly less annually from the sale of products, since the conventional process has moderately higher total capacity (+3.5%) and that part of the production of the CCU process (14.6%) is methanol, a product of lower added value.

On the OPEX, 43% of the cost is associated with the utility needs in the conventional process and 53% in CCU processes. On the other hand, 19% of the operating costs of the conventional process are of raw material cost against 8% in CCU processes, as illustrated in Figure 24.

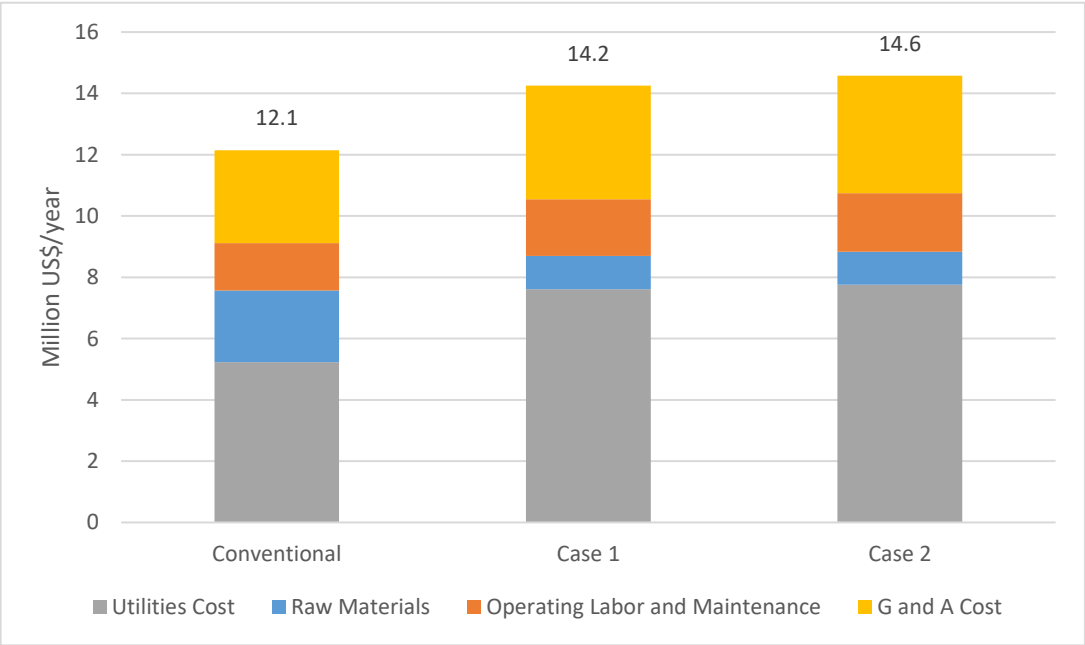

Figure 24 – Operational costs breakdown.

As seen in the technical and environmental performance analysis, most of the utility duties in the CCU processes are from the use of electricity in CO_2 and, particularly, to H_2 compression.

The total annualized cost (TAC) shows how much the CAPEX and OPEX values are reflected in the product cost. Figure 25 shows how much of the total cost of FA

refers to operating and capital expenses. At the same time, how much of the utility expenses are associated to each type of energy used.

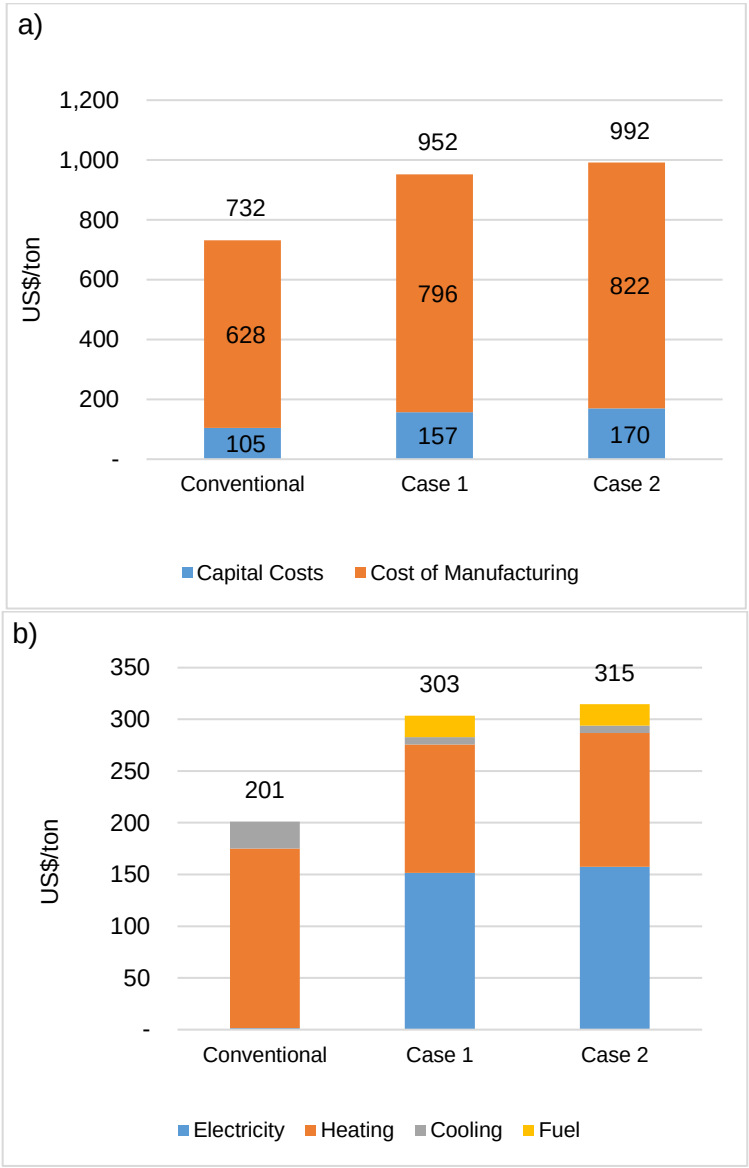

Figure 25 – a) total cost breakdown; b) utility cost breakdown.

The TAC is about 732 US$/ton of FA in the conventional case, comparable to the US$741/ton reported by da Cunha et al. (24). The CCU based FA costs were estimated at US$952 and US$992 per ton for Case 1 and Case 2, respectively, with slightly over US$300/ton in utility costs. Table 15 details the costs per ton of formic acid produced in each case and compares with the values reported by da Cunha et al. (24).

Table 15 – Total annualized cost breakdown, in US$/ton of formic acid.

	da Cunha et. al (24)[a]	**Conventional**	**Case 1**	**Case 2**
Capital Costs	110	105	157	170
Cost of Manufacturing	622	628	796	822
Utility Costs	234	201	303	309
Raw Materia Costs	95	87	43	43
Operating Labor Costs	39	42	47	47
Total Annualized Cost	**741**	**732**	**952**	**992**

[a] conventional process (adjusted for inflation).

Finally, profitability analysis shows that the conventional process can be profitable in the plant lifetime, with NPV above US$300 M and IRR of 26%. The CCU processes do not reach the break-even point during the operating life if 10% discount is considered, with IRR 9.7% and 7.9% for cases 1 and 2, respectively. Table 16 compares the NPV and IRR values of the projects and Figure 26 shows the evolution of cash flows.

Table 16 – Project profitability indicators in the base case, considering 20 year of plant lifetime.

	Conventional	**Case 1**	**Case 2**
NPV (Million US$)	309	- 9.6	- 72
IRR (%)	26	9.7	7.9

Again, the difference in the CAPEX is the key reason for the sizable difference in NPVs, added to improved revenue of the conventional case, which produces more formic acid than the other cases.

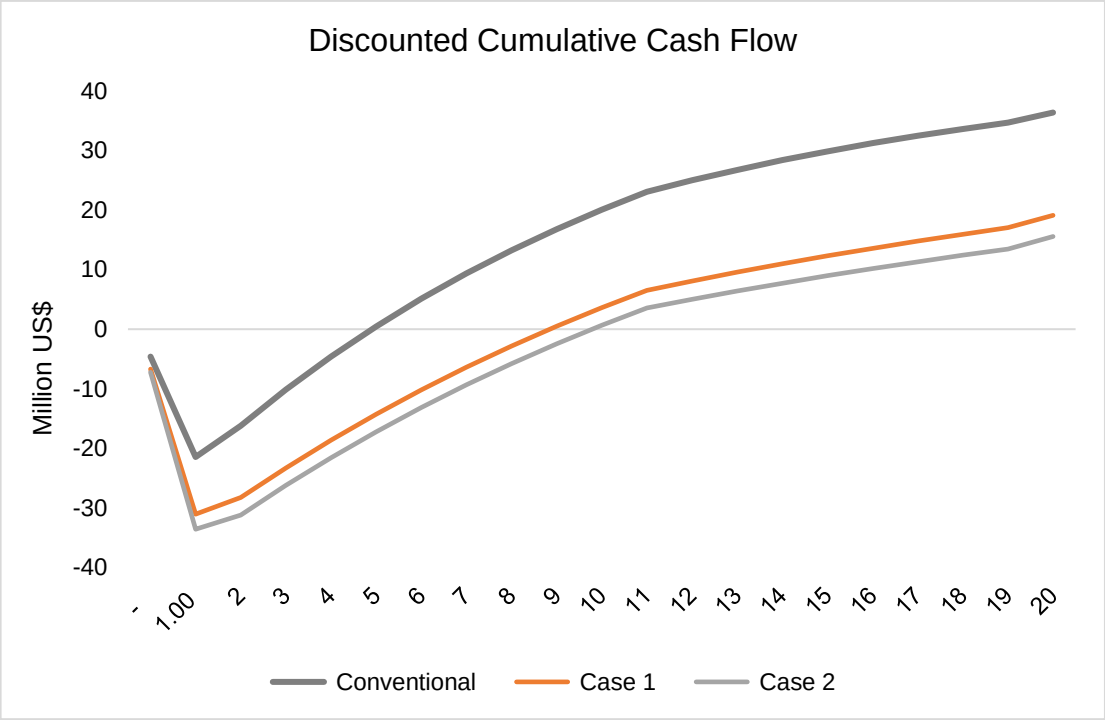

Figure 26 – Comparative discounted cash flow of base cases.

5.2.4 Sensitivity analysis

The economic feasibility of CCU is influenced by several parameters, and it is essential to know which have higher impacts on the process economy. Therefore, a sensitivity study was performed to investigate which variables affected most the NPV.

The variables evaluated in this work were the heating and electricity costs, tax rate and the addition of a carbon credit per ton of CO_2 avoided (see Carbon pricing section). Only one parameter was varied at a time. Besides the capital costs, the most important factors were the cost of electricity and the addition of a carbon credit. Since the electricity impacts the utility usage the most, decreasing it also reduces the NPV and the carbon intensity of the product. Adding a carbon credit also has an immediate impact on the economics. With only U$10 of credit per ton of CO_2 avoided already turns the Case 1 NPV positive. Figure 27 shows the results of this analysis, the yellow line outlining NPV in different carbon credit values (10 – 50).

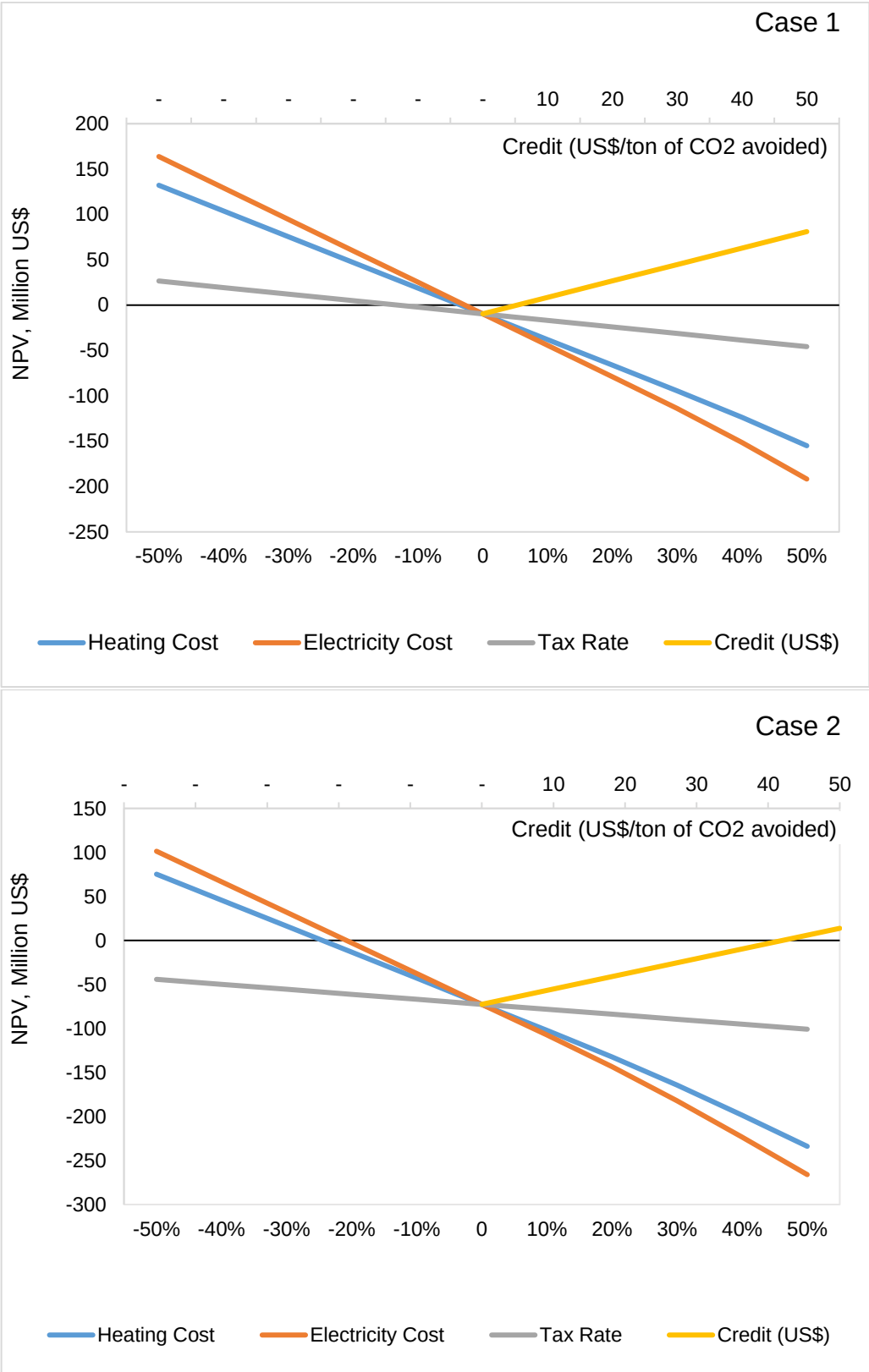

Figure 27 – NPV Sensitivity Analysis. Bottom x *axis as* % change from the base value (except carbon credit). Top axis: added carbon credit (yellow line)

Seeing that a carbon credit impacts positively in the plant profitability, 2 scenarios in which a carbon credit is given to the FA producer are explored:

- What should be the credit price to make the cases breakeven? (NPV=0)
- At which credit value the Case 1 would be competitive compared to the conventional case?

Figure 28 shows the cash flow analysis of these cases. In summary, case 1 would need only U$5/ton of CO_2 avoided to reach the NPV=0, while Case 2 would need U$42.

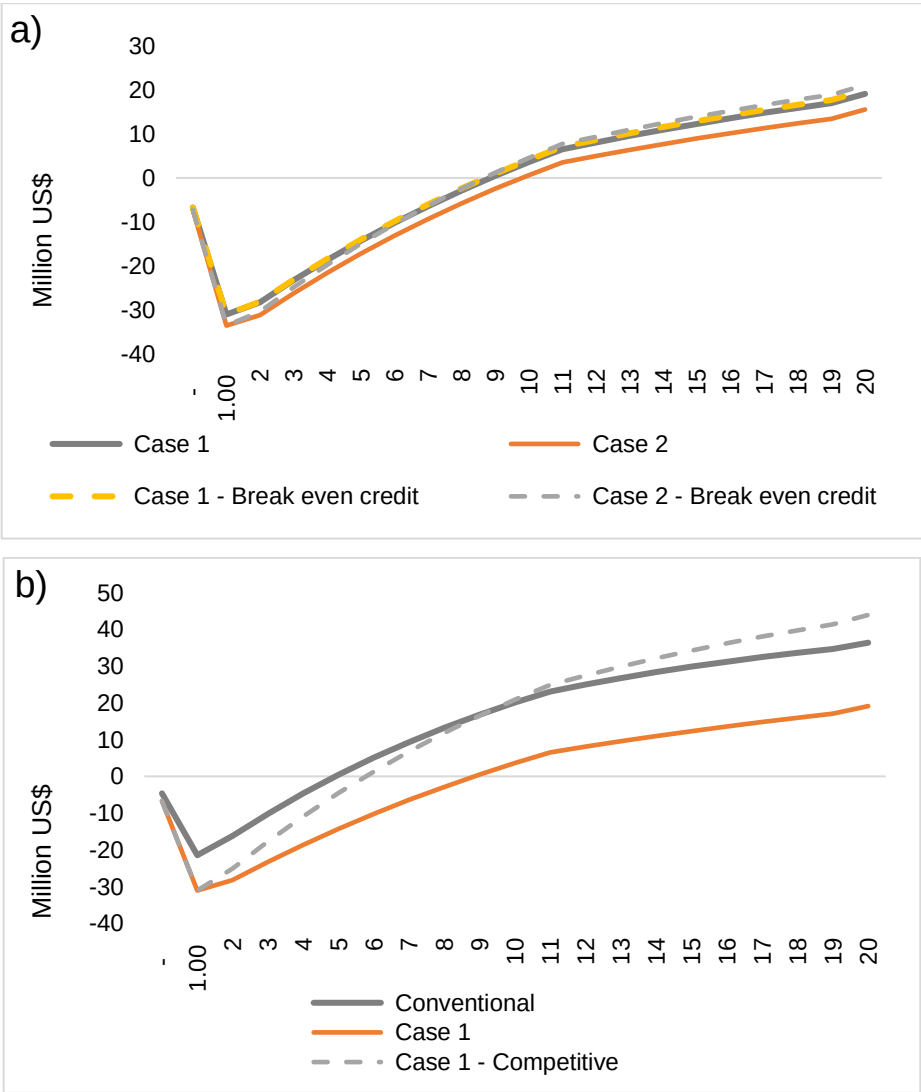

Figure 28 – Carbon credits: (a) to make the CCU cases NPV breakeven – US$5 for Case 1, US$42 for Case 2. b) to make Case 1 NPV equal to the conventional case (US$189).

In the case of competitiveness with the conventional process, Case 1 would need at least US$189 credit per ton of CO_2 avoided to reach the same NPV of the

conventional case, considering that the conventional process would operate as usual, with no added taxes or carbon emissions expenses.

As seen from the analysis, several improvements can be made to enhance the CCU process competitiveness, but the additional value of a carbon credit showed to be essential to make it competitive with the conventional case. Additionally, the addition of carbon taxes, levied at the conventional case, would turn it less profitable and attractive, making more reasonable for investors to consider improving the process or invest in less carbon intensive technologies.

5.3 CONCLUSIONS

In this chapter, comparative evaluations were carried out between the conventional process and the CO_2-based processes for FA production, studying technical, economic and environmental indicators.

In the technical aspect, the three cases evaluated presented similar total energy consumption, and the CCU cases consume much more electrical energy than the conventional due to the work of recompression of H_2 and compression of CO_2.

In the environmental aspect, since this analysis considers mainly the energy expenditure to account for emissions, all cases present similar results concerning utility emissions. However, when the CO_2 consumed by the reaction is taken into account, the net emissions are reduced almost by half. Case 1 always performs slightly better than Case 2.

In the economic aspect, the conventional process still has competitive advantage given its relatively lower production costs compared to the innovative cases, which would need financial incentives such as carbon credits to become more competitive.

6 CLOSING REMARKS

In this work, a thorough assessment of CO_2 and H_2 sources was performed to select a synergetic combination to be used in the CO_2 based formic acid production. A method was developed to evaluate technical, economic and environmental aspects and rank sources according to a sustainability criterion. Results suggested that using CO_2 from iron and steel industries and hydrogen from a coke oven gas may be advantageous, as well as CO_2 from ethylene oxide and hydrogen from steam crackers.

Under the assessment conditions in this study, the CCU route costs around 30% more than the conventional route and emits 45% less CO_2 – both routes consume approximately the same amount of energy, the difference being that the conventional process uses mostly heat, while the CCU cases consume a sizable share of electricity. The profitability analysis showed that the innovative process would need at least US$5 in carbon credit per ton of CO_2 avoided to breakeven over the plant lifetime and US$182 to make it competitive with the conventional case.

The CCU production of FA is currently not economically competitive with fossil-based production with significantly lower cost. However, process improvements and taxation/credit systems for CO_2 emissions could create appropriate market conditions for an industrial business case for CO_2-based formic acid. The work allowed a clearer view of the challenges and opportunities in the implementation of innovative processes in relation to conventional route.

6.1 SUGGESTION FOR FUTURE STUDIES

A CCU process, even simple it may be, can have several developments that make the analysis extremely complex. Each case can be divided into several others, i.e., changes in energy cost, location, utility emission factors and even comparing with another conventional process. Some suggestions for future studies are:

- Within the scope of H_2 sources, it would be valuable to compare the current process with and electrolysis-based H_2. Is it more advantageous to produce H_2 by electrolysis or separate H_2 from a by-product and use this electricity in another process? Where is the renewable eletricity better applied?
- To deepen in the taxing and carbon credits scenarios to identify alternatives where carbon mitigation projects can become economically viable.

- To expand the system boundaries, so that it is not only limited to the formic acid but also to the industries from which H_2 and CO_2 are sourced. Is it possible to integrate energy with these industries? Iron and steel industries are known to have sizable amount of excess heat. How much would it reduce environmental impact and cost?

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APPENDIX A

FEED SOURCES ASSUMPTIONS

By-product hydrogen emissions

Life-cycle CO_2 emissions in a *well-to-use* scope was employed by (55) to estimate hydrogen recovery from steam crackers. The equation used was:

$$EM_{LC} = EM_{WTU,feed} + EM_{WTU,FG} + EM_{Furnace} + EM_{CH_4,comp} + EM_{H_2,PSA} \qquad (25)$$

Where EM_{LC} is the life-cycle air emissions for by product hydrogen (g/kg of H_2); $EM_{WTU,feed}$ is the emissions associated with steam cracker feedstock production (well to use); $EM_{WTU,FG}$ is the emission associated with the fuel production and delivery to the Fuel Gas; $EM_{Furnace}$ emissions of Fuel Gas combustion; $EM_{CH_4,comp}$ is the emission of compressing the surplus CH_4 used to substitute H_2 in the FG; $EM_{H_2,PSA}$ is the emission associated with PSA operation. Since this study is focused on gate-to-gate analysis, the well-to-gate emissions will not be considered yielding the following equation:

$$EM_{LC} = EM_{Furnace} + EM_{H_2,PSA} \qquad (26)$$

$$EM_{Furnace} = E_{FG(1kgH_2)} \times EMF_{Substitution\ fuel} \qquad (27)$$

Where $E_{FG(1kgH_2)}$ is the energy of 1 kg of H_2 (LHV = 120MJ) and the EMF is the emission factor of the fuel substituting hydrogen (here, natural gas = 0.055kg/MJ).

$$EM_{H_2,PSA} = E_{H_2,PSA} \times EMF_{PSA} \qquad (28)$$

The energy for hydrogen purification is estimated at 0.5kWh/kgH_2, the Emission factor for PSA is the average electricity matrix emission factor of 0.34kgCO_2/kWh. Therefore the Emissions associated with recovering hydrogen from steam cracker, is:

$$EM_{LC} = 120MJ \times 0.0556\frac{kg_{CO_2}}{MJ} + 0.5kWh \times 0.34\frac{kg_{CO_2}}{kWh}$$
$$EM_{LC} = 6.84\frac{kgCO_2}{kgH_2} \qquad (29)$$

Combined CO_2 and H_2 sources decision table:

CO_2 Score[w=0.5]		*Hydrogen Score[w=0.4]*		*Synergy [w=0.1]*	*Result*
NGSR	0.8306	Steam Cracker	0.7614	0	0.2800
NGSR	0.8306	Wind Powered electrolysis	0.7454	0	0.2705
NGSR	0.8306	NGSR-CC	0.7211	1	0.9389
NGSR	0.8306	Naphtha Reformer	0.6963	0.5	0.2437
NGSR	0.8306	Coke Oven Gas	0.6079	0	0.2173
Ethylene Oxide	0.7306	Steam Cracker	0.7614	0.5	0.5133
Ethylene Oxide	0.7306	Wind Powered electrolysis	0.7454	0	0.1957
Ethylene Oxide	0.7306	NGSR-CC	0.7211	0	0.1701
Ethylene Oxide	0.7306	Naphtha Reformer	0.6963	0	0.1430
Ethylene Oxide	0.7306	Coke Oven Gas	0.6079	0	0.0712
Ammonia processing	0.7172	Steam Cracker	0.7614	0	0.2068
Ammonia processing	0.7172	Wind Powered electrolysis	0.7454	0	0.1900
Ammonia processing	0.7172	NGSR-CC	0.7211	0.5	0.4920
Ammonia processing	0.7172	Naphtha Reformer	0.6963	0	0.1343
Ammonia processing	0.7172	Coke Oven Gas	0.6079	0	0.0478
Natural Gas Processing	0.7168	Steam Cracker	0.7614	0	0.2067
Natural Gas Processing	0.7168	Wind Powered electrolysis	0.7454	0	0.1899
Natural Gas Processing	0.7168	NGSR-CC	0.7211	0.5	0.4918
Natural Gas Processing	0.7168	Naphtha Reformer	0.6963	0	0.1340
Natural Gas Processing	0.7168	Coke Oven Gas	0.6079	0	0.0471
Ethanol Fermentation	0.7113	Steam Cracker	0.7614	0	0.2050
Ethanol Fermentation	0.7113	Wind Powered electrolysis	0.7454	0	0.1881
Ethanol Fermentation	0.7113	NGSR-CC	0.7211	0	0.1608
Ethanol Fermentation	0.7113	Naphtha Reformer	0.6963	0	0.1313
Ethanol Fermentation	0.7113	Coke Oven Gas	0.6079	0	0.0372
Iron and Steel mills (BOF)	0.6914	Steam Cracker	0.7614	0	0.2014
Iron and Steel mills (BOF)	0.6914	Wind Powered electrolysis	0.7454	0	0.1842
Iron and Steel mills (BOF)	0.6914	NGSR-CC	0.7211	0	0.1565
Iron and Steel mills (BOF)	0.6914	Naphtha Reformer	0.6963	0	0.1262
Iron and Steel mills (BOF)	0.6914	Coke Oven Gas	0.6079	1	0.7200
…..	…..	…..	…..	…..	…..
…..	…..	…..	…..	…..	…..

APPENDIX B

CO_2-BASED FORMIC ACID ROUTES

The conversion of carbon dioxide and hydrogen into formic acid commonly involves a phase change from gaseous reagents into a liquid product. Yielding an entropically disfavored reaction when the gas phase reactants are considered

$$H_{2(g)} + CO_{2(g)} \Leftrightarrow HCOOH_{(l)} \qquad \Delta°G=32.8 \text{ kJ mol} \qquad (30)$$

On the other hand, the presence of solvent alters the thermodynamics of the reaction and the reaction becomes slightly exergonic when operated in the aqueous phase.

$$H_{2(aq)} + CO_{2(aq)} \Leftrightarrow HCOOH_{(aq)} \qquad \Delta°G=-4 \text{ kJ mol} \qquad (31)$$

Additionally, to the water phase reaction, several other routes are being developed, varying catalyst, solvent, operation conditions and feed proportions, all in the early development stage, thus with limited information available in the public literature (47). As novel chemical conversions are developed, it is important to analyze these processes within a broader economic, environmental to help identify promising alternatives and direct investments accordingly (135).

There is a vast amount of CO2 hydrogenation into FA routes, some cited in Chapter 2, comprehending a realm of possibilities. However, as time and resources are limited, the selection of a promising alternative to carry out a detailed study is essential to achieve meaningful results. Thus, only 3 alternatives are being studied by the present research group and, for this work, one of these alternatives must be chosen to be further investigated.

To assess the potential sustainability of a route, generalist methods incorporate features such as techno-economic analysis, environmental and social life cycle assessment. Unfortunately, most of these methods are either qualitative and overly broad or extremely information-intensive, demanding significant investment of time and resources.

Hence, the use of early development sustainability indicators will be employed to assess the potential of the studied CO_2 conversion routes. These shortcut methods

use qualitative and quantitative information as is available at an early stage in process development. The method used here is based on a mix of indicators by (135–138).

Objectives

The objective of this section is to point a promising sustainable conversion alternative for formic acid production through CO_2 hydrogenation. The information on each route is accessed and a MCDA method is used to rank the alternatives.

CO_2 hydrogenation routes

The routes evaluated are among the four main reactions studied by the research group, however, only three routes have sufficient information to be considered. The data acquired for the analysis of the respective routes were obtained in the literature or by the responsible for studying it in the research group.

CO_2 hydrogenation into formic acid in tertiary amine media

This route is the same as the one mentioned before Ref. (30), where FA is produced in a combination of a tertiary amine, polyalcohol, catalyst and water (or no water). The process takes place in a 3-reaction system at temperatures around 50°C and pressures over 100 bar. The free energy of reaction, enthalpy and other operational parameters are being studied by advanced group contribution methods and thermodynamic analysis. A general scheme for the reactor media is presented in Figure 29. Additionally, various examples are presented in the BASF patent application.

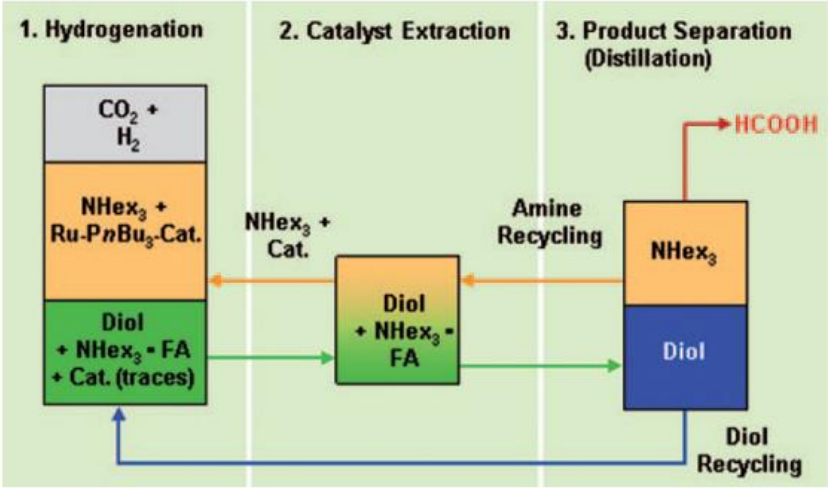

Figure 29 - Sketch of a formic acid process using ternary amines and a polyol solvent. (Adapted from the literature (29))

CO_2 hydrogenation into formic acid in ammonia media

This route studies the manufacture of formic acid (salt - ammonium formate CO_2 hydrogenation considered here to be described by the following overall reaction

$$\mathrm{CO_2 + H_2 \rightarrow HCOOHCO_{2_g} + H_{2_g} + NH_{3_g} \leftrightarrow NH_{4_{aq}}^{+} + HCOO_{aq}^{-} \Delta G = -9{,}5\,\frac{kJ}{mol}\,CO_{2_g} + H_{2_g} + NH_{3_g} \leftrightarrow NH_{4_{aq}}^{+} + HCOO_{aq}^{-} \Delta G = -9{,}5\,\frac{kJ}{mol}\,CO_2 + H_2 \rightarrow HCOOH}$$

The reaction is conducted at 10-100 °C and 1-50. Aside from the formic acid precursor, the reaction of CO_2 and ammonia is already well documented due to its importance in the urea synthesis, where the carbon dioxide reacts with ammonia to form the ammonium carbamate:

$$CO_2 + 2NH_3 \leftrightarrow NH_2CO_2NH_4$$

Thus, the reaction was studied to find the most suitable conditions that favored the formation of the FA salt. The thermodynamic analysis was carried out in Aspen Plus using the ELECNRTL model in an RGibbs reactor. The thermodynamic analysis showed that promising yield of FA at a temperature close to 10°C and pressure of 50 bar. The water content was also studied, showing that the equilibrium conversion increases with the increase in water concentration.

CO_2 hydrogenation into formic acid in ionic liquid media

As mentioned before, IL may be a potential candidate for CO_2 hydrogenation, due to its selectivity, the capability of being tuned and for promoting reactions at mild operation conditions. Here, Ref. (118) performed a thermodynamic analysis of CO_2 hydrogenation to systems of methanol and formic acid promoted by the IL (1-ethyl-2,3-dimethylimidazolium nitrite, ([Edmim][NO2]). The analysis was conducted in the Aspen Plus process simulator, using the Gibbs free energy minimization approach using the vapor-liquid equilibrium to account the CO_2 solvation in the IL.

The results showed promising outcomes in the CO_2 conversion into FA and methanol. The thermodynamic analysis indicated that the best operating condition among the studied was at 24-25°C and 17 bars, right in the shift of selectivity for each product. Lowering the temperature could increase the selectivity of FA.

Method

This section describes the methodology used to assess the prospect hydrogenation route to be further studied. Since the available information is rather limited, a simplified evaluation was performed using shortcut sustainability measures. The sustainability indicators for each alternative were then used as input to an MCDA method, like the previous chapter.

Multi-Criteria Decision Analysis

The TOPSIS method and a sensitivity analysis on weights were done to compare the CO_2 hydrogenation routes, refer to Section 3.2.3 for information on the method.

Given the early development of these FA production routes, a shortcut method based on Multi-Criteria Decision Analysis was performed to assess the performance of each reaction route. These are evaluation criteria for an early-stage assessment of chemical processes, mentioned by (135,137,139,140) and will be discussed briefly in the following sections.

Criteria

Process Characteristics

Given the nature of initial technology development, it is difficult to obtain quantitative information regarding the costs and environmental impacts involved in the conversion of raw materials to products and subsequent downstream processing. Thus, this parameter serves as a substitute to indicate impacts based on quantitative/qualitative data inherent to the reaction and products. The index used here is a combination of indexes proposed by Audus and Oonk, Sugiyama et. al. and Patel et. al. (135,137,138) and serves as a preliminary indication on how the process would operate. It is mostly concerned about system complexity and energy usage.

$$PCHs = \sum_{i=0}^{8} PC \tag{32}$$

This indicator must be minimized, the coding for each character is given in Table 17. The lower the PCH indicator, the better the route suitability.

Table 17 – Coding for PC attribute.

Process Characteristic (PC)	*PC value*[a]		
	0	*0.5*	*1*
Product Concentration in the reactor outlet	>25%	5%	<1%
Minimal Boiling Point Difference for products and co-products	>20 K	Up to 10 K	< 5K
Reaction Enthalpy	< 100kJ/mol	200kJ/mol	>300kJ/mol
Number of sub-products	0	Up to 3	7
Value-added co-products?	Yes	No co-product	No
Reaction-phase characteristics	1 phases	2 phases	>2 phases

Separation Steps	Up to 2	3	>3
Presence of Water	0 – 5%	Up to 50%	>50%
Mild process conditions (relative to ambient)	Ambient T and P	$P > 10\ bar$ or Vacuum > 50°C or < 10°	$P > 30\ bar$ $T > 100$°C

[a] Here, if a route has a product concentration in the reactor outlet higher than 25%, a value o *0* is attributed to the PC.

Thermodynamics of reaction ($\Delta G°_{rx}$)

The Gibbs free energy of reaction was used to indicate the reaction feasibility. Thermodynamic data for evaluation were acquired from the respective thermodynamic studies mentioned in Section 0.

Process Energy Demand

Associated with the process overall energy consumption, the estimate on exergy demand proposed by Muller et. al.(136) is given by the following relation:

$$Ex = Q\left(1 - \frac{T^{\infty}}{\mathrm{T}}\right) \tag{33}$$

This approach assumes Q to be approximately equal to the reaction enthalpy. T is the reaction temperature and T^{∞} is the reference ambient temperature (298 K).

Results

The shortcut evaluation was employed in this work. Table 18 presents the results for the process characteristics for the studied FA production routes.

The IL route performed significantly better in this criterion. As previously stated, the nature of IL allows for mild operation conditions, moreover, this study found promising results regarding conversion to FA in a simpler system than the others.

Table 18 – Process characteristics for the hydrogenation routes.

	Ionic Liquid	**Ammonia**	**Amine**
Product Concentration	>25%	<5%	5%-9%
Minimal BP difference	<10K	<10K	<10K
Number of Co-products	1	1	None (expected)
Value-added co-products	Methanol	Undesirable	No co-product
Reaction phases	Gas/liquid	Gas/liquid	Gas/Liquid/Liquid
Separation steps	~2	~3	~3
Presence of Water	< 50%	>50%	<50% (product phase)
Operational conditions	Mild	Medium/Mild	Harsh

Table 19 shows the decision matrix used as input to the MCDA method, as well as the weight of importance given to each aspect.

Table 19 – Criteria values estimated for the selected routes.

	Gibbs Free Energy (kJ/mol)	Exergy Estimate (kJ/mol)	Process Characteristics
Ionic Liquid	-15.806	0.013	2
Ammonia	-9.5	2.970	5.5
Amine	-4.34	2.385	5
Weights	*0.4 (minimize)*	*0.3 (minimize)*	*0.3 (minimize)*

The assessment scores for the evaluated routes and a sensitivity analysis on the weights are presented in Figure 30. A sensitivity analysis was performed to deal with the uncertainty of the scoring method, but even with +-20% variation on each weight, the ranking still favors the choice of the Ionic-liquid conversion route.

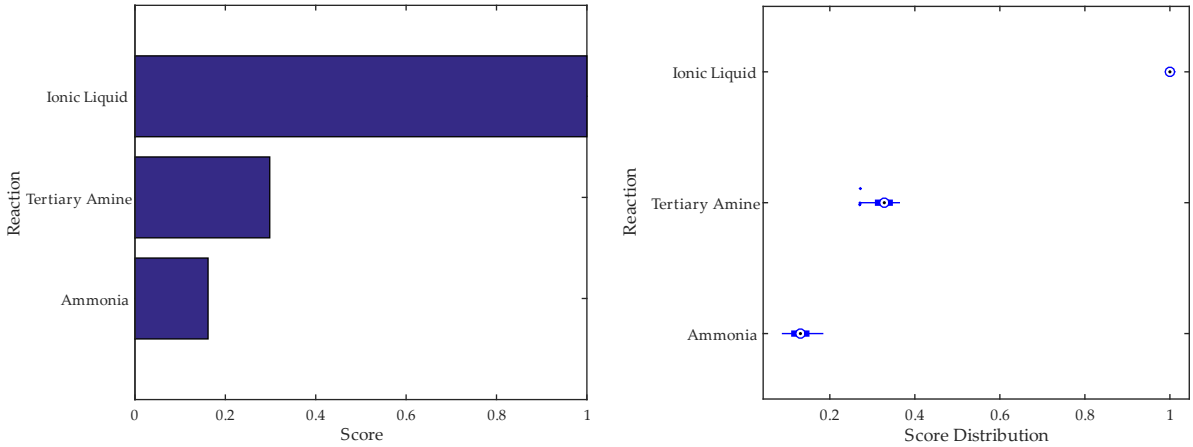

Figure 30 – Performance scores and sensitivity analysis for the studied conversion routes.

TOPISIS results in a score indicating the overall proximity of an alternative to the ideal solution, the IL route score here is 1 because it represents the ideal solution among the routes investigated (performed better in all criteria). The performance of the Ionic-liquid route may be attributed mainly to its process characteristics (low water concentration, less reaction, its value-added co-product).

Conclusion

The three CO_2 hydrogenation routes were compared, and the ionic liquid route was selected for detailed analysis through multi-criteria decision analysis. The MCDA with shortcut criteria framework was used here to assist in integrating data from a variety of sources to enable a comparative assessment of process routes. Nevertheless, when using these results, it is important to consider that the analysis is based on several specific data inputs and assumptions. It is important to examine the validity of these inputs. Additionally, with this methodology, a lower score does not mean that the alternative is not worth pursuing, it was used here to prioritize the most suitable route for further investigation in this context.

APPENDIX C

SIMULATION INFORMATION

Thermodynamic Model Validation

To validate the model performance, experimental data of phase equilibrium of the binary systems (component/component combination) was used to optimize the model parameters. Experimental data was chosen, preferably, when taken close to the estimated operating conditions. Most of the data studied were available in the simulator database (NIST ThermoData Engine), except for the CO solubility data. Table 20 shows the dataset used and their references.

Table 20 – Experimental datasets used for validation and regression.

System	Temperature (°C)	Pressure (bar)	Source
Water +Methanol	107 – 146	4.27	(141)
Water + Formic Acid	134 - 141	3.13	(142)
Methanol + Methyl Formate	51 - 80	2.06	(143)
Water + Methyl Formate	31 - 100	1.01	(144)
Methyl Formate + Formic Acid	31 -100	1.01	(142)
CO + Methanol	20 - 50	1.01	(145)
CO + Water	5 - 50	1.01	(146)

The Relative Root Mean Square Error (RRMSE) evaluated the performance of the UNIQUAC-HOC model. This indicator is available in the results of the calculations performed by the simulator itself. To ensure we use the best model, regressions were compared with the NRTL-HOC model (Table 21).

Using RRMSE as an indicator, both models can describe systems with similar accuracy, but the UNIQUAC-HOC model performs with slightly lower error and, therefore, was chosen to model the system. Figure 31 presents the equilibrium diagrams of the methyl formate/methanol and methanol/water systems.

Table 21 – Root mean square deviation NRTL e UNIQUAC

System	UNIQUAC-HOC	NRTL-HOC
Water + Methanol	12.33	4.3616
Water + Formic Acid	20.90	20.635
Methanol+Methyl Formate	5.647	24.771
Water + Methyl Formate	20.23	23.804
Methyl format + Formic Acid	32.87	33.39
CO + Methanol	62.56	67.57
CO + Water	145.60	269.76
Average	43.6	67.3

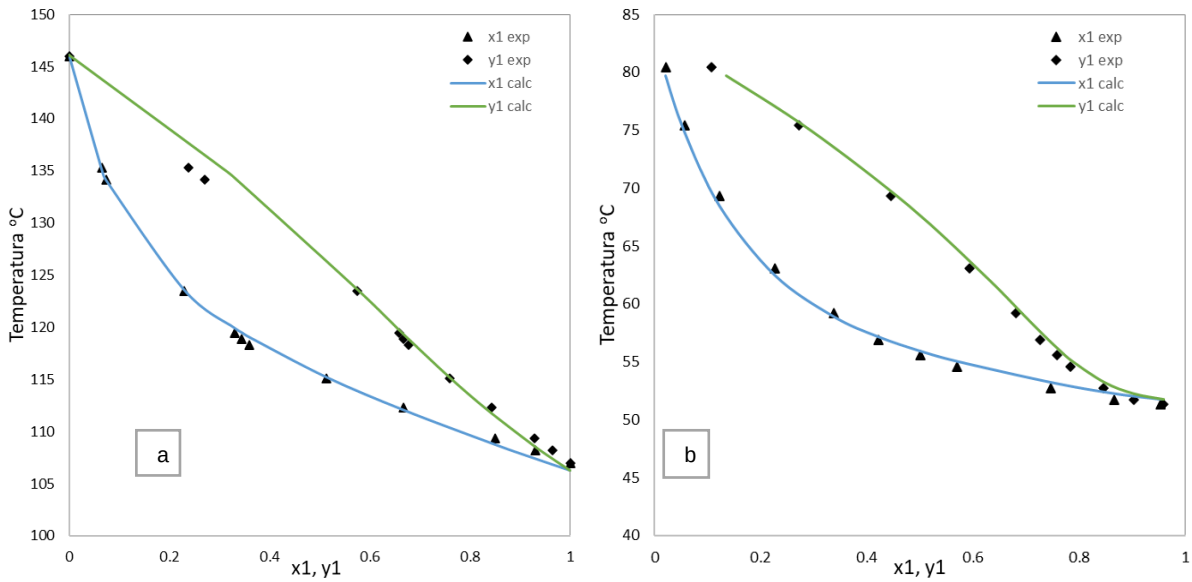

Figure 31 - Equilibrium diagrams for systems (a) Methyl formate(1)/Methanol(2) and (b) Methanol(1)/Water(2).

The model could describe the above systems with satisfactory accuracy in the given conditions. The methyl formate/formic acid and the water/formic acid system are presented in Figure 32. Equilibrium is predicted with notable accuracy for the MF/FA system (Figure 32a) but there is a positive deviation in predicting the saturation pressures of the pure components for the system Water/FA (Figure 32b) even after parameter optimization.

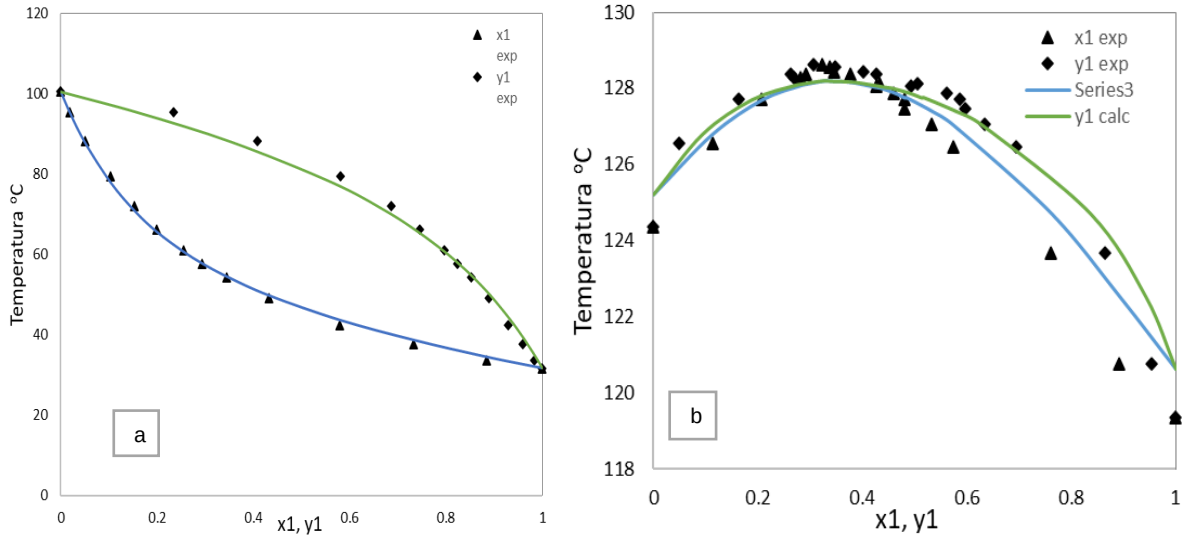

Figure 32 – Equilibrium diagrams for (a) methyl formate(1)/Formic Acid (2) and (b) Water (1)/Formic Acid (2) systems.

The data from Table 20 was used to optimize the parameters A, B and C of the UNIQUAC-HOC and Henry models (for binaries with CO).

Table 22 and Table 23 presents the optimal parameters calculated from these regressions.

Table 22 - Optimal interaction parameters of UNIQUAC-HOC model.

Comp. i	Comp. j	Aij	Aji	Bij	Bji	Cij
Water	Methanol	2.7322	-0.693	-617.26	172.98	0.3
Water	Formic acid	-2.5864	4.5156	962.29	-1756.1	0.2103
Methanol	Methyl Formate	-3.6412	0	1340.38	217.046	-0.2980
Water	Methyl Formate	1.7473	0	672.78	0	0.2943
Methyl Formate	Formic acid	1.862	1.4652	132.65	-471.54	-0.32

The parameters of the Henry equation optimized for the UNIQUAC-HOC model are in Table 18.

Table 23 - Optimal Henry's equation parameters.

System	Aij	Bij	Cij
CO + Methanol	161.46	-5204.66	-23.9091
CO + Water	393.823	-18209.1	-56.5108
CO + Methyl Formate[a]	2.92	1721	-

[a] Parameters retrieved from da Cunha et al. (2018).

Stream Results

Table 24 – Stream conditions, mass flowrate and mass fraction for the base case. (Figure 19)

Stream Name	Temp. (°C)	Pressure (bar)	Mass Flows (kg/h)	Mass Fractions (Water, CO, Methyl Formate, Methanol, Formic Acid, Diisopropyl ether)					
3	101.7	23.61	18683.9	0.0003	0.0107	0.2323	0.7567	0.0000	0.0000
4	86.7	4.05	18683.9	0.0003	0.0107	0.2323	0.7567	0.0000	0.0000
5	50.0	4.05	18683.9	0.0003	0.0107	0.2323	0.7567	0.0000	0.0000
6	50.0	4.05	301.59	0.0000	0.5950	0.2839	0.1211	0.0000	0.0000
7	242.7	23.61	301.518	0.0000	0.5950	0.2839	0.1211	0.0000	0.0000
8	50.0	4.05	18382.3	0.0003	0.0011	0.2315	0.7671	0.0000	0.0000
9	15.9	4.05	24	0.0000	0.7676	0.2173	0.0151	0.0000	0.0000
10	15.9	4.05	4998.52	0.0000	0.0004	0.8396	0.1600	0.0000	0.0000
11	17.9	20	4998.52	0.0000	0.0004	0.8396	0.1600	0.0000	0.0000
12	104.3	4.05	13359.8	0.0004	0.0000	0.0040	0.9956	0.0000	0.0000
13	105.6	23.61	13359.8	0.0004	0.0000	0.0040	0.9956	0.0000	0.0000
14	59.5	20	19130.1	0.4384	0.0001	0.5149	0.0466	0.0000	0.0000
15	78.0	20	19130.1	0.4384	0.0001	0.5149	0.0466	0.0000	0.0000
17	89.8	1.01	8386.69	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
18	90.6	20	8386.69	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
19	100.0	20	19130.1	0.3731	0.0001	0.2973	0.1627	0.1668	0.0000
20	92.5	3.78	19130.1	0.3731	0.0001	0.2973	0.1627	0.1668	0.0000
21	72.2	3.78	9.06602	0.0000	0.0742	0.7694	0.1565	0.0000	0.0000
22	72.2	3.78	8792.89	0.0000	0.0002	0.6461	0.3538	0.0000	0.0000
23	147.9	3.78	10328.2	0.6911	0.0000	0.0000	0.0000	0.3089	0.0000
24	40.0	3.78	8792.89	0.0000	0.0002	0.6461	0.3538	0.0000	0.0000
25	35.5	1.01	8792.89	0.0000	0.0002	0.6461	0.3538	0.0000	0.0000
26	16.3	1.01	4.59954	0.0000	0.2822	0.7086	0.0092	0.0000	0.0000
27	16.3	1.01	5744.9	0.0000	0.0000	0.9841	0.0159	0.0000	0.0000
28	18.8	20	5744.9	0.0000	0.0000	0.9841	0.0159	0.0000	0.0000
29	63.6	1.01	3043.47	0.0000	0.0000	0.0079	0.9921	0.0000	0.0000
30	63.5	1.01	3053.35	0.0000	0.0000	0.0079	0.9921	0.0000	0.0000
31	66.4	23.61	3053.35	0.0000	0.0000	0.0079	0.9921	0.0000	0.0000
32	40.0	3.78	10328.2	0.6911	0.0000	0.0000	0.0000	0.3089	0.0000
33	40.1	1.01	10328.2	0.6911	0.0000	0.0000	0.0000	0.3089	0.0000
34	40.1	1.01	10588.6	0.6835	0.0000	0.0000	0.0000	0.3013	0.0152
35	45.3	1.01	39869.7	0.0113	0.0000	0.0000	0.0000	0.0800	0.9087
36	66.5	1.01	39869.7	0.0113	0.0000	0.0000	0.0000	0.0800	0.9087
37	60.5	1.01	36614.5	0.0123	0.0000	0.0000	0.0000	0.0000	0.9877
38	98.8	1.01	3255.27	0.0000	0.0000	0.0000	0.0000	0.9800	0.0200
40	40.0	1.01	36614.5	0.0123	0.0000	0.0000	0.0000	0.0000	0.9877
41	40.0	1.01	36377.9	0.0060	0.0000	0.0000	0.0000	0.0000	0.9940
42	40.0	1.01	237.387	0.9783	0.0000	0.0000	0.0000	0.0000	0.0217
44	40.0	1.01	36442.2	0.0060	0.0000	0.0000	0.0000	0.0000	0.9940
45	40.0	1.01	7161.01	0.9782	0.0000	0.0000	0.0000	0.0000	0.0217
46	40.0	1.01	7398.4	0.9783	0.0000	0.0000	0.0000	0.0000	0.0217
47	63.9	1.01	7398.4	0.9783	0.0000	0.0000	0.0000	0.0000	0.0217
48	46.2	1.01	260.411	0.3830	0.0000	0.0000	0.0000	0.0000	0.6170
49	99.9	1.01	7138.24	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO	30.0	23.61	1969.1	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
DIPE	30.0	1.01	64.2265	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000
FA	40.0	1.01	3255.27	0.0000	0.0000	0.0000	0.0000	0.9800	0.0200
H2O	30.0	1.01	1248.45	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL	30.0	1.01	9.87864	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000

Utilities Summary Table

Table 25 shows the utilities specification (blue) and results (black).

Table 25 – Utilities Summary table.

Name	CHILLWAT	COOLWAT	ELEC	LPSTEAM	MPSTEAM
Utility type	**WATER**	**WATER**	**ELECTRICITY**	**STEAM**	**STEAM**
Specified electricity price [$/kWhr]			**0.06048**		
Specified energy price [$/GJ]	**4.43**	**0.244**		**13.28**	**2.2**
Specified inlet pressure [bar]	**1.01325**	**1.01325**			
Specified outlet pressure [bar]	**1.01325**	**1.01325**			
Specified inlet temperature [C]	**5**	**20**		**125**	**175**
Specified outlet temperature [C]	**10**	**25**		**124**	**174**
Specified CO2 emission factor [kg/GJ]	56.1	56.1	**94.4**	55.89	55.89
Specified CO2 energy source efficiency factor	**1**	**1**	**1**	**0.85**	**0.85**
Calculated heating/cooling value [kJ/kg]	-20.96	-20.88		2191.88	2034.75
Calculated inlet enthalpy [kJ/kg]	-15949.45	-15886.67		-13258.70	-13200.13
Calculated outlet enthalpy [kJ/kg]	-15928.48	-15865.80		-15450.57	-15234.88
Calculated inlet pressure [bar]	1.01	1.01		2.32	8.93
Calculated outlet pressure [bar]	1.01	1.01		2.25	8.72
Calculated inlet temperature [C]	5	20		125	175
Calculated outlet temperature [C]	10	25		124	174
Calculated purchase price [$/GJ]	4.43	0.244	0.06048	13.28	2.2
Calculated total cost [$/hr]	69.1	15.1	4.6	479.0	86.0
Calculated total usage rate [kg/hr]	744085.2	2964139.5	76.9	16457.2	19219.6
Calculated CO2 emission factor [kg/cal]	0.0	0.0	0.0	0.0	0.0
Calculated CO2 emission rate [kg/hr]	875.1	3471.4	26.1	2371.9	2571.4

Equipment Summary Tables

The following tables presents the equipment model summary and results. Values in Blue are the simulation specification, and in black are calculated by AspenPlus.

Table 26 – Coolers and Heaters

Name	C1	C2	C3	C4	C5	H3
Property method	**UNIQ-HOC**	**UNIQ-HOC**	**UNIQ-HOC**	**UNIQ-HOC**	**UNIQ-HOC**	**UNIQ-HOC**
Specified temperature [C]	**50**	**40**	**40**	**40**	**40**	**63.9**
Calculated pressure [bar]	4.05	3.78	3.78	1.01	1.01	1.01
Calculated temperature [C]	50	40	40	40	40	63.9
Calculated vapor fraction	0.0172	0	0	0	0	0
Calculated heat duty [MJ/hr]	-3017.6	-412.6	-1427.8	-248.5	-1623.9	715.1
Net duty [MJ/hr]	-3017.6	-412.6	-1427.8	-248.5	-1623.9	715.1
Utility CO2e production [kg/hr]	169.3	23.1	80.1	13.9	91.1	47.0
Utility usage [kg/hr]	144551.5	19763.4	68394.8	11902.8	77788.7	326.3
Utility cost [$/hr]	0.736	0.101	0.348	0.061	0.396	9.497
Utility ID	**COOLWAT**	**COOLWAT**	**COOLWAT**	**COOLWAT**	**COOLWAT**	**LPSTEAM**
Equipment Cost [US$]	$ 13,100.00	$ 11,000.00	$ 11,000.00	$ 8,700.00	$ 14,200.00	$ 8,700.00
Installed Cost [US$]	$ 72,200.00	$ 59,000.00	$ 60,900.00	$ 58,900.00	$ 70,600.00	$ 59,900.00

Table 27 – Separation vessels

Name	F	DEC
Property method	**UNIQ-HOC**	
Henry's component list ID	**CO-HRY**	
Temperature [C]	**50**	**40**
Pressure [bar]	**4.05**	**1.01**
Outlet temperature [C]	50	40
Outlet pressure [bar]	4.05	1.01
Vapor fraction	0.0172	0
Equipment Cost [US$]	$ 23,100.00	$ 26,100.00
Installed Cost [US$]	$ 113,500.00	$ 162,500.00

Table 28 - Compressor

Name	COMP
Property method	**UNIQ-HOC**
Henry's component list ID	**CO-HRY**
Model Type	**ISENTROPIC**
Specified discharge pressure [bar]	**23.61**
Indicated horsepower [kW]	19.6
Calculated brake horsepower [kW]	19.6
Net work required [kW]	19.6
Efficiency (polytropic / isentropic) used	0.72
Calculated discharge pressure [bar]	23.61
Calculated pressure change [bar]	19.56
Calculated pressure ratio	5.8
Outlet temperature [C]	242.7
Isentropic outlet temperature [C]	193.8
Head developed [m-kgf/kg]	17188.8
Isentropic power requirement [kW]	14.13
Inlet heat capacity ratio	1.30
Inlet volumetric flow rate [cum/hr]	58.73
Outlet volumetric flow rate [cum/hr]	16.22
Inlet compressibility factor	0.99
Outlet compressibility factor	0.99
Utility CO2e production [kg/hr]	6.67
Total CO2e production [kg/hr]	6.67
Utility usage [kW]	19.62
Utility cost [$/hr]	1.19
Utility ID	**ELEC**
Equipment Cost [US$]	$ 807,000
Installed Cost [US$]	$ 921,800

Table 29 - Pumps

Name	P1	P2	P3	P4	P5
Property method	**UNIQ-HOC**	**UNIQ-HOC**	**UNIQ-HOC**	**UNIQ-HOC**	**UNIQ-HOC**
Specified discharge pressure [bar]	**20**	**23.61**	**20**	**20**	**23.61**
Fluid power [kW]	2.3	10.5	4.8	3.1	2.6
Calculated brake power [kW]	7.3	20.4	11.7	9.1	8.7
Electricity [kW]	7.3	20.4	11.7	9.1	8.7
Volumetric flow rate [cum/hr]	5.2	19.3	9.0	5.9	4.1
Calculated discharge pressure [bar]	20	23.61	20	20	23.61
Calculated pressure change [bar]	15.95	19.56	18.99	18.99	22.6
Head developed [m-kgf/kg]	170.0	288.8	208.4	197.4	308.7
Pump efficiency used	0.32	0.51	0.41	0.34	0.30
Net work required [kW]	7.26	20.44	11.74	9.15	8.68
Utility CO2e production [kg/hr]	2.47	6.94	3.99	3.11	2.95
Utility usage [kW]	7.26	20.44	11.74	9.15	8.68
Utility cost [$/hr]	0.44	1.24	0.71	0.55	0.52
Utility ID	**ELEC**	**ELEC**	**ELEC**	**ELEC**	**ELEC**
Equipment Cost [US$]	$ 17,100.00	$ 49,900.00	$ 17,300.00	$ 16,900.00	$ 47,200.00
Installed Cost [US$]	$ 44,100.00	$ 87,700.00	$ 49,000.00	$ 45,200.00	$ 78,400.00

Table 30 – Distillation Columns

Name	DC1	DC2	DC3	DC4	DC5
Property method	**UNIQ-HOC**	**UNIQ-HOC**	**UNIQ-HOC**	**UNIQ-HOC**	**UNIQ-HOC**
Henry's component list ID	**CO-HRY**	**CO-HRY**	**CO-HRY**	**CO-HRY**	**CO-HRY**
Number of stages	**16**	**34**	**38**	**22**	**8**
Condenser	**PARTIAL-V-L**	**PARTIAL-V-L**	**PARTIAL-V-L**	**TOTAL**	**TOTAL**
Reboiler	**KETTLE**	**KETTLE**	**KETTLE**	**KETTLE**	**KETTLE**
Top stage pressure [bar]	**4.05**	**3.78**	**1.01**	**1.01**	**1.01**
Specified reflux ratio	**1.2**	**3.5**	**1.7**	**1.4**	**1.4**
Specified bottoms rate [kg/hr]	**13359.8**	**10328.4**	**3041.30**	**3255.39**	
Calculated molar reflux ratio	1.2	3.5	1.7	1.4	1.4
Calculated bottoms rate [kmol/hr]	416.3	465.5	94.6	69.9	396.3
Calculated boilup rate [kmol/hr]	270.9	740.7	212.8	1238.2	44.0
Calculated distillate rate [kmol/hr]	95.6	191.8	97.0	379.0	7.1
Condenser / top stage temperature [C]	15.9	72.2	16.3	60.5	46.3
Condenser / top stage pressure [bar]	4.05	3.78	1.01	1.01	1.01
Condenser / top stage heat duty [MJ/hr]	-7035.1	-25265.2	-7833.7	-28494.5	-729.4
Condenser / top stage reflux rate [kmol/hr]	114.3	671.5	164.9	530.6	10.0
Reboiler pressure [bar]	4.05	3.78	1.01	1.01	1.01
Reboiler temperature [C]	104.3	147.9	63.6	98.8	99.9
Reboiler heat duty [MJ/hr]	8744.3	27606.7	7522.2	27834.9	1789.8
Utility CO2e production [kg/hr]	969.6	3232.6	934.1	3428.8	158.6
Condenser utility usage [kg/hr]	335599.0	1210265.3	373692.2	1364955.5	34794.1
Condenser utility cost [$/hr]	31.2	6.2	34.7	7.0	3.2
Condenser utility ID	**CHILLWAT**	**COOLWAT**	**CHILLWAT**	**COOLWAT**	**CHILLWAT**
Reboiler utility usage [kg/hr]	4297.5	13567.6	3431.8	12699.1	879.6
Reboiler utility cost [$/hr]	19.2	60.7	99.9	369.6	3.9
Reboiler utility ID	**MPSTEAM**	**MPSTEAM**	**LPSTEAM**	**LPSTEAM**	**MPSTEAM**

Calculated molar boilup ratio	0.65	1.59	2.25	17.71	0.11
Calculated mass boilup ratio	0.65	1.35	2.31	18.33	0.11
Equipment Cost [US$]	$ 159,500.00	$ 379,400.00	$ 340,400.00	$ 489,800.00	$ 67,400.00
Installed Cost [US$]	$ 577,200.00	$ 933,200.00	$ 820,500.00	$ 1,210,100.00	$ 417,700.00

Table 31 – Extraction Column

Name	EXT
Property method	**UNIQ-HOC**
Henry's component list ID	**CO-HRY**
Number of stages	**16**
Top stage temperature [C]	45.3
Top stage first liquid flow [kmol/hr]	453.2
Top stage second liquid flow [kmol/hr]	448.9
Bottom stage temperature [C]	40
Bottom stage first liquid flow [kmol/hr]	390.4
Bottom stage second liquid flow [kmol/hr]	366.8
Equipment Cost [US$]	$ 381,000.00
Installed Cost [US$]	$ 1,680,000.00

Table 32 - Reactors

Name	CSTR1	CSTR2
Property method	**UNIQ-HOC**	**UNIQ-HOC**
Henry's component list ID	**CO-HRY**	**CO-HRY**
Specified pressure [bar]	**23.61**	**20**
Specified temperature [C]	**101.7**	**100**
Reactor residence time [hr]	**0.717**	**0.202**
Outlet temperature [C]	101.7	100
Calculated heat duty [MJ/hr]	-1388.60	966.33
Net heat duty [MJ/hr]	-1388.60	966.33
Reactor volume [cum]	18.62	4.56
Liquid phase volume [cum]	18.62	4.56
Condensed phase volume [cum]	18.62	4.56
Reactor residence time [hr]	0.72	0.20
Utility CO2e production [kg/hr]	77.90	63.54
Utility usage [kg/hr]	66517.32	474.91
Utility cost [$/hr]	0.34	2.13
Utility ID	**COOLWAT**	**MPSTEAM**
Equipment Cost [US$]	$ 265,400.00	$ 134,000.00
Installed Cost [US$]	$ 456,900.00	$ 283,700.00

APPENDIX D

PUBLICATIONS

6.1.1.1 Full paper in conference proceeding:

Lopes, J. V. M.; Carvalho, K. M.; Reis, A. C.; Kulay, L. A.; Alves, R. M. B. *Systematic Selection of Potential CO_2 and Hydrogen Sources for Carbon Dioxide Utilization***.** 2nd Latin American Conference on Sustainable Development of Energy, Water and Environment Systems. Feb, 2020. Buenos Aires, Argentina.

6.1.1.2 Full paper in indexed journal:

Lopes JVM, Bresciani AE, Carvalho KM, Kulay LA, Alves RMB. *Multi-criteria decision approach to select carbon dioxide and hydrogen sources as potential raw materials for the production of chemicals*. **Renew Sustain Energy Rev** 2021;151:111542. https://doi.org/10.1016/J.RSER.2021.111542.