Front-End Techno-Economic and Environmental Analysis on CCU Technologies

Identifying the most business critical pathways for valorization and utilization of carbon dioxide

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by

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to obtain the degree of Master of Science
at the Delft University of Technology,
to be defended publicly on Monday August 29, 2022 at 04:00 PM

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Preface

The climate is changing and the transition towards a more sustainable society might be one of the biggest challenges we have to face this day and age. Temperatures are rising, we are experiencing an unprecedented drought, and the concentration of carbon dioxide in the atmosphere has never been as high. Fortunately, many positive developments are happening, ambitious technologies are being developed and encouraging research initiatives are being set up. A promising contribution to this whole is carbon capture and utilization. Which might be the key in eliminating the rise of CO_2 concentrations and closing the carbon loop by converting CO_2 to valuable products.

The study I have performed for the past months includes all aspects of the challenges of engineering I get enthusiastic about. I got to explore novel state-of-the-art technologies, how they are applied in real life situations, and what is required for the process to be commercial feasible. I got the opportunity to evaluate the environmental impact and how this novel technology can contribute to one of the biggest challenges of modern time. The subject of CCU appealed to me because of the possibility to utilize a harmful product towards something valuable. During this study, I learned a tremendous amount about how to conduct a research, the technologies used for CCU, and challenges the future might bring. I got the opportunity to work in a pioneering environment surrounded with very ambitious and skilled people. I am grateful for the opportunity to be a part of this research.

I would like to start by thanking my daily supervisor Carlos. Thank you for your commitment and great guidance. I could always consult you with questions and you have always helped me in the right direction when I got stuck. You taught me how to approach problems at a systematic level and to remain realistic when it comes to promising system performance. I am sure this has contributed to taking my results to a higher level. Next, I would like to thank my supervisor Earl Goetheer for the overall support and the enthusiastic discussions. Through our meetings, I have often come to new valuable insights. You helped me keep the focus on my results and schedule, but also remembered me to take a break from time to time. Furthermore, I would like to thank everyone at TNO who helped me gain a better understanding and for the valuable feedback on my intermediary presentations. Everyone has always been open to a discussion and showed interest in my results.

I am very grateful to my parents, their partners, and my sister for always supporting me and showing interest in my work. Also, I would like to thank them for giving me the opportunity to pursue mu study. Finally, I would like to thank my friends for encouraging me to keep pushing and for providing the necessary occasional distraction.

Jelmer Dielwart
Delft, August 2022

Abstract

Carbon capture and utilization (CCU) is an emerging technology for reducing the CO_2 concentration in the atmosphere and to limit the negative effects on the global warming. Different from carbon capture and storage (CCS), in CCU the carbon captured from point sources or direct from air is processed to valuable carbon containing products. Several studies have been conducted on the technological and economic viability of CCU. However, no detailed process analyses with a system-level approach have been reported. Performance and challenges on pre-treatment and downstream processing of product streams have been ignored or generalized. This work aims to perform a detailed front-end techno-economic and environmental analysis on CCU pathways, focused on thermocatalysis (TC) and low- and high temperature electrolysis (LTE and HTE) of CO_2. Identifying the most business critical pathways for valorization and utilization of CO_2.

The scope of this study focuses on the identified single-step chemicals, that can directly be produced from CO_2 without intermediates. KPI's selected for both conversion technologies are used to determine performance. A parametric analysis is carried out to evaluate the marginal costs of production per unit of weight for the selected chemicals. Based on costs, TRL and phase of product stream a selection of chemicals is made. Products identified as potential viable for industrial scale production and selected for further study are carbon monoxide (LTE, HTE and TC), formic acid (LTE and TC) and oxalic acid (LTE).

Conceptual process designs are made using reported system performance with all required units identified. A model is developed to simulate input- and product streams, scale size of units, calculate required utilities and costs of investment and operation. All processes are modulated according to generic battery limits, use cases and analysis methodology to provide an equal comparative study. It is found that state-of-the-art electrochemical processes are dominated by capital investment costs and are too immature for commercial application. For TC processes, production costs are primarily driven by H_2 and CO_2 costs. CO shows the most potential in this respect and is competitive with the market price. A sensitivity analysis is performed to gain understanding of the sensitivity of the parameters. Conversion pathways that could gain significant technical improvements are most sensitive to CAPEX varying and are less affected by variance in operating expenses. Main focus for investments on EC technologies should be current density. More mature technologies are most sensitive to varying the costs of feedstock and market parameters.

Opportunities for process improvements are evaluated by a performance analysis for current base-case versus the expected near-term and optimistic future scenarios. The parameters used for modulation vary according to the expected improvements in technical performance, economic performance and electricity price. Opportunities for EC processes lie within extensive R&D on conversion technology. For TC process, and on the long term for EC, opportunities lie within further development of green H_2 production and CO_2 capture. EC CCU pathways demonstrate great potential for future performance with potential reduction up to 71% for near-term future. To quantify the environmental impact of the pathways and their improvements compared to conventional processes, a gate-to-gate life cycle assessment is performed. Switching to a more renewable energy mix offers serious improvements to minimize global warming impact. The most emission reducing pathways are CO TC and OA LTE which utilize more CO_2 than is emitted during the process, -0.16 and -0.26 $\frac{kgCO_2-eq}{kg}$.

Contents

Nomenclature

Abbreviations

Abbreviation	Definition
CAPEX	Capital expenditures
CEM	Cation exchange membrane
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CD	Current density
CO_2R	Carbon dioxide reduction
CRF	Capital recovery factor
CV	Cell voltage
DSP	Downstream process
EC	Electrochemical conversion
FA	Formic acid
FE	Faradaic efficiency
FLL	Full load hours
GAP	Gas antisolvent precipitation
GDE	Gas diffusive electrode
GWI	Global warming impact
HTE	High temperature electrolysis
ISBL	Inside boundary limits
KPI	Key performance indicator
LCA	Life cycle assessment
LTE	Low temperature electrolysis
MeOH	Methanol
MSP	Minimal selling price
NPV	Net present value
OA	Oxalic acid
OPEX	Operational expenditures
OSBL	Outside boundary limits
OSM	Oxygen storage material
PEM	Polymer electrolyte membrane
PC	Propylene carbonate
PSA	Pressure swing adsorption
RWGS	Reverse water gas shift
RWGS-CL	Reverse water gas shift chemical looping
SEC	Specific energy consumption
SHE	Standard hydrogen electrode
SME	Subject matter experts
SOEC	Solid oxide electrolyzer cell
SOT	State of technology
SOTA	State of the arte
TC	Thermocatalytic conversion
TEA	Techno-economic assessment
TEACL	Tetraethylammoniumchloride
TIC	Total investment costs
TRL	Technology readiness level

Symbols

Symbol	Definition	Unit
E^0_{cell}	Standard electrode potential	V
F	Faraday's constant	[-]
FE	Faradaic efficiency	[%]
ΔG	Gibbs free energy	[J]
ΔH	Change in enthalpy	[J/mol]
i	Current density	[mA/cm^2]
M	Molar mass	[g/mol]
n	Number of electrons	[-]
$\dot{n}$	Molar flow rate	[mol/s]
Q	Applied current	[A]
R	Gas constant	[-]
ΔS	Change in entropy	[J/K]
SEC	Specific energy consumption	[kWh/kg]
T	Temperature	[K]
w_{max}	Maximum work performed in chemical cell	[J]
x_i	Molar fraction of product i	[%]
α	Charge transfer coefficient	[-]
η	Activation potential	V

Subscripts

Symbol	Definition
red	reduction
ox	oxidation
cathode	at cathode side of reaction
an	at anode side of reaction
at	anodic transfer
ct	cathodic transfer

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1
Introduction

1.1. Background

For the past decades, the concentration of carbon dioxide (CO_2) in the atmosphere of the earth has been rising exponentially since the start of the industrial revolution. Since this era, the concentration of CO_2 has been rising for over 50%, to a total of 418 parts per million (ppm) in 2021 [1]. This rise is mainly caused by human activity and their use of fossil fuels. The rapidly increasing concentration of CO_2 in the earth's atmosphere is considered to be a serious contributor to the global warming [2]. Due to the serious effects of global warming and the greenhouse gas effects, largely caused by the rising CO_2 concentration in the atmosphere, the emissions of this greenhouse gas should be seriously reduced. According to the latest EU Green Deal goals, the European Union sets the target of the reduction of global greenhouse gas emission to 55% by 2030. The long term strategy and objective is total carbon neutrality by 2050 [3]. The reduction of CO_2 and conversion to valuable chemicals is a promising route to contribute to the road to a carbon neutral economy.

Promising technologies of reducing the CO_2 concentration are Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU). CCS and CCU involve the capture of CO_2 from large point sources or directly from ambient air. Point source capture is the capture of carbon directly from industrial facilities to lower their emissions [4]. CCS is the process of capturing, transporting and storing carbon dioxide in log term storage sites. CCU so-called closes the carbon cycle by processing the captured CO_2 to valuable products. Using renewable energy as a source, CO_2 is reduced (CO_2R) and recycled to valuable chemicals and fuels for further usage. Such a process can offer a sustainable way to reduce the carbon concentration in the atmosphere.

Conversion of CO_2 in CCU can be done via two different pathways, direct- and indirect conversion. Direct conversion directly utilizes the electricity to drive the CO_2R reaction such as electrolysis and microbial electrosynthesis, while indirect conversion utilizes the electricity via energy carriers such as hydrogen via thermocatalytical and biological conversion [5]. Combined with renewable electricity, these reduction pathways can offer a sustainable solution for the decarbonization of the global atmosphere. CO_2 could be converted to a broad range of valuable carbon products starting at C_1 molecules, such as formic acid [6][7], to C+ products containing more than 2 carbon atoms, such as n-propanol. However CCU and the electrochemical or thermocatalytical conversion of CO_2 can be a serious contributors, these technologies are not yet available on industrial scale. Technologies of the mentioned pathways are often novel and emerging and therefore their economical viability is uncertain. For evaluation of the different pathways, their technological maturity and economic viability, a consistent comparison of all pathway combinations is required.

Research done on CCU focuses on the conversion technology and the financial viability of those pathways [5][8][9]. However, comparing front-end techno-economical and environmental analyses (TEA) including pre- and post-treatment of the process are missing. A total evaluation of technical and economical aspects is necessary for identifying the potential and possibilities for CCU. To explore the potential of CCU, a group of conversion technologies has to be analyzed. Considering the direct- and indirect conversion technologies, the focus will be on the low-temperature electrolysis (LTE), high temperature electrolysis (HTE) and thermocatalytical conversion (TC). Using these conversion routes and their respective operational conditions, a broad range of valuable carbon products can be achieved. An analysis on all possible products is carefully made and by use of techno-economical criteria a selection of most promising CO_2R products is made in this research. These products will further be analyzed on system-level approach on their commercial and environmental potential.

1.2. Scope

In this study, a techno-economic and environmental analysis is performed on the a selection of the possible process pathways-product combinations and the most relevant pathways for valorization and utilization of Co_2 is determined. The term relevant here refers to the potential of the molecule itself, its current conversion performance, and its expected future performance. A selection of possible and promising production routes is established by means of an marginal costs analysis and a parametric analysis. Based on the selected products and technologies, conceptual process designs are developed used for the techno-economical analysis at system level. By means of a mathematical model and several analyses, the techno-economic performances are determined and limitations and opportunities are identified. The analysis at system level will include the pre-treatment, carbon dioxide conversion and downstream processing. The capture and purification of CO_2, heat generation, and H_2 production will be considered out of scope for this research and will be considered as available as feedstock in a pure stream.

1.3. Research Questions

The research and its goals will be conducted by answering the main research question and its sub-questions. Based on the answers to the formulated sub-questions, the main question of the study can be answered.

Main Research Question:

- *What are the most relevant pathways for the valorization and utilization of carbon dioxide based on their techno-economical and environmental performance?*

Sub-questions:

- *What products can be produced via CO_2R and what are the routes towards these products?*
- *What products and routes are economically and technically viable for large scale production?*
- *How are the conversion routes structured at system level and what technologies are used?*
- *How do the system designs perform technically and economically?*
- *What is the environmental impact of the process design and how does it perform compared to conventional process designs?*

1.4. Methodology

The study on the most relevant pathways for CCU is divided into five consecutive phases. A flow diagram of the five phases in which the study is conducted is visualized in figure 1.1. The five phases can be divided into two overarching phases: the literature phase and the design phase. The first two phases, feasibility- and selection of CCU products, will be carried out during the literature study. The literature phase will result in a selection of products to be passed on to the design phase. During the first two phases, an extensive literature study was carried out on previous TEA's on CCU and state-of-the-art scientific reports on CO_2 conversion towards valuable carbon containing products. Data and information was gathered on technology, performance, economics and future prospects for CCU. With the comprehensive collection of quality references, several analysis were performed using an Excel model. At first, the key performance indicators were identified for both processes, electrochemical and thermocatalytical. Next, previous TEA's were analyzed and earlier findings on CCU product feasibility were gathered to identify similarities and contradictions between the reports to identify opportunities and crucial issues for this study. A broad framework of possible CCU pathways towards valuable chemicals was constructed based on the most recent developments on conversion technologies and visualized using a mind map. On selected conversion routes, a parametric analysis was carried out determining the marginal costs of production. With the results of the parametric analysis, a selection of products is made by means of a criteria assessment. Taking into account the technology KPI's, financial performance, technology readiness level and phase of product, a selection of products is made promising for CCU.

The results of the literature study are taken into the design phase. This phase involves an extensive techno-economic and environmental analysis of the selected products. First, for the selected process pathways, conceptual process designs are constructed at system level. Involving pre-treatment of input streams, conversion towards the desired product and downstream processing of product streams. The process designs are based on state-of-the-art reports on recent studies on electrochemical or thermocatalytical conversion of CO_2. Using the conceptual designs, techno-economic analyses have been performed on production costs, parameter sensitivity and future performance. Using the results of the techno-economic analysis, limitations and opportunities are identified for improvements and performances. Finally, an environmental analysis is performed on the global warming impact of each conventional and CCU production route by means of a life-cycle assessment. An schematic overview of the research methodology is visualized in figure 1.1.

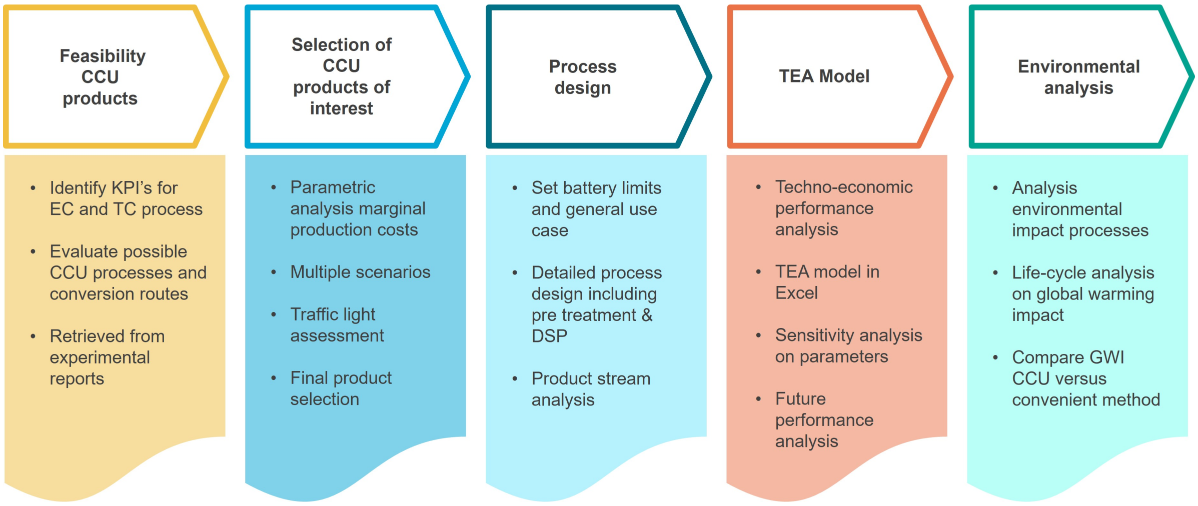


Figure 1.1: Flow diagram of the five consecutive phases in which the study is conducted. First two phases correspond to the literature phase, the following three phases correspond to the design phase in which the TEA and LCA are performed.

2

Literature Review

2.1. Conversion Technologies

The conversion technologies assessed in this research are covered in this section. A distinction is made between direct- versus indirect carbon dioxide conversion. For the process of CCU to be meaningful, the electricity must be renewable and no carbon emissions can be involved during the complete process. Therefore, both conversion technologies are driven by renewable generated electricity or heat from sources such as solar radiance or wind. Direct conversion of CO_2 directly utilizes the electricity via an electrochemical cell for the conversion toward valuable products. This process is referred to as electrochemical CO_2R. Indirect conversion of CO_2 involves in the process renewable generated heat and energy carriers, like hydrogen. In the coming subsections, both technologies will be discussed in more detail.

2.2. Electrochemical Conversion

Direct conversion of CO_2 is the utilization of renewable electricity directly for the process. In this process, electrons are directly used by the system to convert the inlet stream to reduced carbon products. Direct conversion can be done in an electrochemical cell, via so called CO_2 electrolysis. An electrochemical cell is a device which can create an electrical current by spontaneous chemical reactions that occur when different compartments are connected, or could stimulate chemical reactions when an electrical current is applied. A cell in which spontaneous reactions occur and a current is generated is called a galvanic cell. Electrochemical cells were a potential is applied to start a chemical reaction is called an electrolytic cell. Such a cell can be used to convert electrical energy to chemical energy and use it as storage.

The basic principle of an electrochemical cell is driven by the reduction and oxidation reactions at the electrodes, so called redox-reactions. The reduction reaction is when an atom, molecule or ion reduces its oxidation state by receiving one or more electron(s). Oxidation is when an atom, molecule or ion increases its oxidation state by the loss of one or more electron(s). Inside an electrochemical cell both phenomena occur, forming each a half-reaction and combined a redox reaction. The compartments, or cells, in which those reactions occur consist both of an electrode and electrolyte through which ions can be transported. The compartments and its electrodes are in general kept apart by a separator to prevent electrical short circuits, depending on the setup.

The half-reactions occur at each electrode at different potentials, these are called the oxidation- and reduction potential. The potential of a reaction that takes place under standard conditions (1M concentration, T = 298 K, p = 1 atm), the cell potential is called the 'standard electrode potential', E^0, and is measured in volts (V). Each species has its on standard electrode potential and the more positive the potential, the greater the attraction of electrons and therefore the chance of reduction is. In general, the standard reduction potential is referred to by means of the standard hydrogen electrode (SHE) reference electrode, which is set to be at 0.00 V. The standard electrode potential of a electrochemical cell can be expressed in the reduction potential at the cathode and anode, shown in equation 2.1. The standard cell potential states the potential, voltage, at which initially the reaction would take place. However, the potential of a reaction is influenced by its activation barrier, concentration-, and resistance potential, which are all related to the cell design, reaction type and operation conditions. The difference between the standard electrode potential and actual required potential is called overpotential. The overpotential compared to the standard electrode potential of the reaction, requires additional energy to initiate the reaction [10].

$$E^0_{cell} = E^0_{red,cath} - E^0_{red,an} \tag{2.1}$$

$$E^0_{red} = -E^0_{ox} \tag{2.2}$$

The performance of the electrochemical cell and its products depends on electrical energy, in terms of the Gibbs free energy. The change in Gibbs free energy is a measure of work that can be performed by a chemical cell, w_{max}. The Gibbs free energy can be expressed by means of the cell potential, E_{cell}, and the electrical current, nF, as shown in equation 2.3 [11]. A spontaneous reaction is initiated by a negative ΔG. And subsequently, an non-spontaneous reaction is initiated by a positive ΔG and therefore would need a form of an applied energy to run the reaction. Gibbs free energy of a chemical reaction is also related to the entropy term and enthalpy term of the redox process, equation 2.4. The enthalpy and entropy, ΔH and ΔS respectively, both strongly influence the activity of the redox reaction, together with the temperature of reaction [12]. The enthalpy can be seen as an indication for the bond strength and the total heat content of the reaction. Redox reactions have their own standard entropy change at certain temperatures. A negative entropy change, ΔS, will cause an increased cell potential at lower reaction temperatures. Reactions with a large positive entropy change will allow a lower cell potential at lower reaction temperatures. Temperature dependence of redox-reactions and their cell potentials can make the distinction between HTE and LTE. Where HTE is performed at elevated temperatures and part of the energy is supplied as heat from renewable heat sources [11] [13].

$$\Delta G_f = -nFE_{cell} \tag{2.3}$$

$$\Delta G = \Delta H - T\Delta S \tag{2.4}$$

2.2.1. Electrochemical CO_2 Reduction

The most well-known electrochemical cell is a water electrolyzer, where H_2O is reduced into H_2 and O_2. However, an electrochemical cell can also be used to reduce CO_2 into valuable C production and O_2 as a byproduct, equation 2.5. Electrochemical reduction of CO_2 can be performed in gaseous and liquid phase and carried out using several types of catalyst, electrode types and electrolytes, resulting in a wide range of reaction products. Depending on the operation conditions, several product pathways can be obtained. Low temperature electrolysis (LTE) is typically performed at moderate temperatures (70-90°C) in aqueous and non-aqueous electrolytes using metal electrodes. Examples of LTE are alkaline or polymer electrolyte membrane (PEM) electrolysis. High temperature electrolysis (HTE) is performed at elevated temperatures (800-1000 °C) utilizing electricity and also steam to reach the required temperatures. HTE is carried out using solid oxide electrochemical cells (SOEC)[13]. A SOEC is characterized by its solid oxide electrolyte that transferring oxygen ions formed at the cathode to the anode. Where the atoms form oxygen molecules and are released from the system [14]. The range of products that can be produced using LTE is broader than HTE. However, energy consumption and selectivity of HTE often exceed those of alkaline and PEM devices [15] [16].

$$CO_2 + H_2O \rightarrow C_xH_yO_z + O_2 \tag{2.5}$$

As in a normal electrochemical cell, the process is driven by an external applied voltage and the electrons that are fed to the system will be capable of reducing the CO_2 molecules towards many possible carbon products. Varying on the applied voltage and operation conditions, different reduction products are obtained. Utilizing CO_2R technology renewable produced electricity can be stored as chemical energy in useful products [17].

Electrolysis of CO_2 is influenced by the thermodynamics the reaction. The thermodynamics of the conversion determine the minimum amount of energy required for the reaction to occur and sustain. Depending on the operation conditions, the amount of electrons transferred and catalyst used, different products are produced at the cathode side. The conversion towards other carbon products are expressed as half-reactions and are balanced with the water oxidation reaction at the anode. As example, below the two half-reactions and overall-reaction for the electrochemical reaction towards methanol (CH_3OH) is shown.

$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH\ (l) + H_2O\ (l)$	E_0 = - 0.02 vs. SHE
$3\ H_2O\ (l) \rightarrow 6H^+ + 6e^- + 1.5\ O_2$	E_0 = 1.23 vs. SHE
$CO_2 + 2H_2O \rightarrow CH_3OH + 1.5\ O_2$	E_0 = 1.21 vs. SHE

Table 2.1: Overall reaction methanol formation [18]

Later in this chapter, all possible CO_2R redox-reactions are reviewed in more detail. In a detailed review, a more in-depth analysis on reaction characteristics, current state of technology, and future possibilities will be performed.

2.3. Thermocatalytic Conversion

Thermocatalytic reduction of CO_2 refers to the catalytical reaction under influence of added energy in the form of heat. In general, this reaction is carried out in the presence of a metal (heterogeneous) catalyst and an added reactant. The conversion of a molecule like CO_2 towards other products under influence of applied heat and a catalyst is called thermocatalysis. CO_2 is a very thermodynamically stable molecule with a high oxidation rate and a double carbon bond. Which makes it a thermodynamically very unfavorable molecule to react and which requires a serious input of heat to initiate the reduction. In figure 2.1 an overview is given of the Gibbs free energy of formation (equation 2.4) for a selection of carbon molecules and for the molecules H_2, N_2 and H_2O [19]. The oxidation state of CO_2 is substantial compared to other carbon products ($\Delta G_0 = -394.0\, kJmol^{-1}$), indicating the high stability of the molecule.

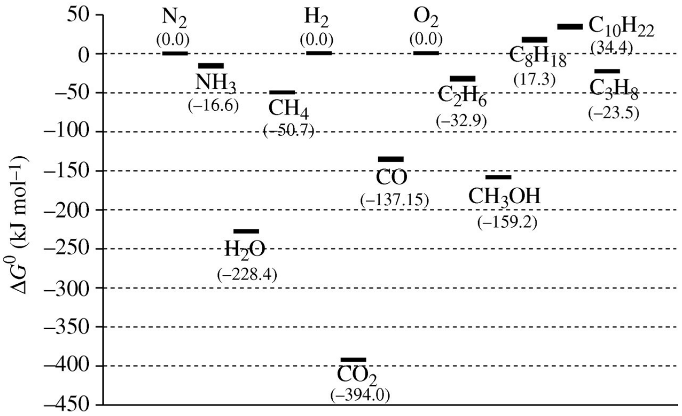


Figure 2.1: Gibbs free energy of formation of several molecules adapted from Jiang et al. [19]

2.3.1. CO_2 Hydrogenation

The thermodynamic favorability of CO_2 conversion towards reduced carbon products can be enhanced by the presence of a reactant with an higher Gibbs free energy of formation. As stated by De et al. the Gibbs free energy required for the production of CO from CO_2 is subsequently higher than formation when H_2 is added to the process (equation 2.6 and 2.7) [20]. The addition of the energy carrier H_2 to the chemical reaction to favor the thermodynamics is called hydrogenation. Which offers a promising solution for energy storage and emission reduction. Hydrogenation offers a potential pathway for sustainable production of hydrocarbons like methanol and formic acid [21] overcoming the thermodynamic barrier of CO_2.

The first hydrogenation process, related to CO_2 reduction, deployed on industrial scale was the Sabatier process [22]. In this process CO_2 is reacted with H_2 in the presence of a nickel catalyst for the production of methane (CH_4). Later, the Fischer-Tropsch process dominated the industry of hydrocarbon production. The Fischer-Tropsch process operates at elevated temperatures (150 - 300 °C) and produces a range of hydrocarbons from syngas (gaseous mixture of CO, H_2 and diluted CO_2) on metal catalyst surface. The main advantage of hydrogenation reactions is that no intermediate reduction of CO_2 is required. Products of CO_2 hydrogenation are primarily formic acid, formaldehyde, methanol and methane. However, by selection of multi functional catalytic sites, high selectivity towards desired products can be achieved and tuned, resulting in a wide range of possible products [23].

$$CO_2 \rightarrow CO + 0.5\,O_2 \qquad \Delta H_0 = 293.0\,kJmol^{-1} \quad \Delta G_0 = 257.2\,kJmol^{-1} \tag{2.6}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H_0 = 41.2\,kJmol^{-1} \quad \Delta G_0 = 28.6\,kJmol^{-1} \tag{2.7}$$

$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H_0 = -49.5\,kJmol^{-1} \quad \Delta G_0 = 3.5\,kJmol^{-1} \tag{2.8}$$

Because of the thermal stability of CO_2, it is challenging to decompose the molecule. Resulting in relative low conversion rates of CO_2, significant role of catalyst type, and limited operation conditions. Electrochemical reduction can be achieved at high temperatures (HTE) but also, and most commonly, at room temperature (LTE). Which is not possible for thermocatalytical processes, those processes are mostly operated at elevated temperatures around 200-300 °C due to the thermal stability of CO_2[24]. Thermocatalytic reactions can be endo- or exothermic, depending on the product of the reaction. For endothermic reactions, such as RWGS (equation 2.7), increasing the temperature of reaction can lead to a more efficient conversion. An example of an exothermic reaction is the reaction towards methanol, equation 2.8. Exothermic reactions could perform better at lower temperatures. However, for both endo- and exothermic reactions, altering the temperature of reaction could affect the catalytic performance.

Selection of the catalyst used in the reaction is a crucial part of the process. Efficiency and performance of the reaction are dependent of the intermediates towards the final product and therefore of the identifying of the catalyst. The metal used as catalyst and the surface geometry must be selected and designed carefully for optimal efficiency and selectivity to overcome the thermodynamic and kinetic barrier [20]. Several parameters are of importance while designing the thermocatalytic reaction process towards the reduced products, including CO_2 conversion (%), yield towards C-product, and CO_2:H_2 ratio. depending on whether the reaction is endo- or exothermic, the supply of heat also plays a role in the performance and especially the efficiency of the process. For optimal system performance and efficient thermocatalytical conversion, the catalyst design and catalytic performance, conditions of operation and selection of added reactant are of importance [25].

Later in this chapter, all possible thermocatalytical CO_2R pathways are reviewed in more detail. In a detailed review, a more in-depth analysis on reaction characteristics, current state of technology, and future possibilities will be performed.

2.4. State of the Art Technology

In this section, state of the art technology and developments on CCU are assessed. First the technology's key performance indicators are determined for both conversion technologies, electrochemical and thermocatalytical. Next the results of previous TEA's on CCU are discussed and with the findings of reports on recent CCU technologies the possible pathways towards valuable products are determined.

2.4.1. Technology Performance Indicators

Identifying business critical CCU pathways requires measurements of performance for the production technologies and products. By conducting a marginal costs analysis on the possible products, a selection of business relevant molecules is made. In order to perform this analysis the key performance indicators (KPI's) are identified. These KPI's will also be of interest for the techno-economic analysis performed later in this study. For both conversion technologies, the performance of the system are dependent on key performance indicators. The majority of the possible products and their technologies are premature and their performance is rapidly improving according to recent reports. For the performance indicators of both conversion technologies, three different scenarios are introduced to be able to estimate future performance of the technology and make equivalent comparisons between the products: (1) a current state with performance based on recent reports, (2) a near-term future scenario with performance that can be realised on short-term, and (3) an optimistic scenario with optimal performance.

2.4.2. Electrochemical KPI's

Electrochemical conversion and its performance strongly depends on the electrons transferred during the process. Performance indicators determined for electrochemical conversion are therefore, as expected, related to the electrical performance of the cell. The performance indicators, used for the marginal cost- and the techno-economic analysis, of an electrochemical cell are *faradaic efficiency* [%] (FE), *current density* [mA/cm^2] (CD), and *cell voltage* [V] (CV).

Faradaic efficiency refers to the efficiency with which electrons are transferred in an electrochemical cell towards the desired product. FE is relevant for systems where simultaneously more reactions can occur at an electrode. The fraction of the total electrons (current) that ends up in the desired product is called '*faradaic efficiency*' (equation 2.9). A FE of 100 % indicates that only one reaction is occurring at the electrode and all electrons are used for one product. Reduction of FE can be caused by e.g. reducing or oxidizing solvent, electrolyte type, electrode material, etc. [26]. Equation 2.9 gives the FE of an EC where n represents the numbers of electrons required for the half reaction, F Faraday's constant which is 96,485.33 $\left[\frac{s\,A}{mol}\right]$, x_i the molar fraction of product i in the final stream $\left[\frac{mol\ product\ i}{total\ moles}\right]$, $\dot{n}$ the molar flow rate in $\left[\frac{moles}{s}\right]$, and Q_{total} the total applied current in Ampere.

$$FE = \frac{Q_{product}}{Q_{total}} = \frac{n * F * x_i * \dot{n}}{Q_{total}} \tag{2.9}$$

Current density is the rate at which current is passed per surface area during a electrochemical reaction. In other words, CD is the rate of charge proportional to the amount of material at the interface of the reaction. The current at the electrodes interfaces can directly be related to the overpotential and expressed by the Buttler-Volmer equation, 2.10. Where i_0 the exchange current density, α the charge transfer coefficient, n the number of electrons involved at the charge-transfer reaction and η the activation overpotential is. The higher the CD, the better the EC performance and the more efficient the EC operates.

$$i = i_0 \left[exp\left(\frac{\alpha n F}{RT}\eta_{ct}\right) - exp\left(-\frac{(1-\alpha)nF}{RT}\eta_{ct}\right)\right] \tag{2.10}$$

Cell voltage refers to the total cell potential of the redox-reaction, as discussed in section 2.2. The total cell voltage is determined by the standard electrode potential of the redox-reactions and the overpotential. The overpotential is the difference between the thermodynamically determined cell potential and the actual observed applied potential. Overpotential represents the energy losses due to heat during the reaction activities in the EC. The higher the cell voltage, and therefore the overpotential, the larger the losses due to heat and the less efficient the cell operates [27]. Overpotential is typically divided into three different categories; *activation-*, *concentration-*, and *resistance* overpotential [28].

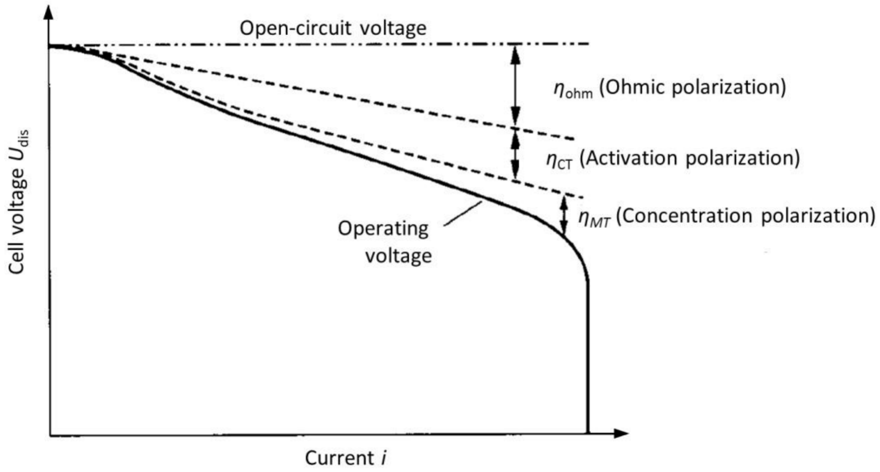


Figure 2.2: Cell voltage and overpotentials as function of current applied. Adapted from Buchberger et al. [28]

Activation overpotential is caused by the the kinetics of the reaction current at the interface between the electrolyte and the anode and cathode. The current at the electrode/electrolyte interface, i, is determined by the Buttler-Volmer equation, equation 2.10, and is directly related to the activation overpotential (η_{ct}). Reactions with larger i_0 have lower overpotentials and therefore more desired for electrochemical cells. Concentration overpotential is related to the mass-transport at the anode and cathode surface and the diffusion of active species. When diffusion of active species within the electrolyte at electrode surface is hindered, the cell works less efficient and overpotential increases. To increase cell performance, available surface area of the electrode can be increased to maximize diffusion and efficiency of the cell. Resistance overpotential, or ohmic overpotential, is caused by the ionic resistance within the electrolyte and resistance in conducting electrons. The resistance overpotential is related to the current within the system and the total resistance [28].

2.4.3. Thermocatalytical KPI's

Thermocatalytical conversion and its performance strongly depend on the amount of feedstock used and the efficiency of conversion towards the desired product. The thermocatalytic processes analyzed in this research are hydrogenation reactions with CO_2. Therefore, the performance indicators used for thermocatalytical processes are all related to the amount and efficiency of H_2 and CO_2 used. The performance indicators, used for the marginal costs- and techno-economic analysis in this study, for thermocatalytical processes are *single-pass CO_2 conversion* [%], *product selectivity* [%], and *yield* [%].

Single-pass CO_2 Conversion refers to the percentage of CO_2 fed to the system that is converted the first time it enters the reactor. The amount of CO_2 that is converted is an important factor for the performance of the system. DSP costs are strongly influenced by the composition of the final product stream. The more unreacted CO_2 is present in the final product stream, the less of the desired product is present. Consequently, the production capacity of the reactor must be increased to produce the desired amount of product. Resulting in increased production- and separation costs per kilogram of desired product. The maximum amount of CO_2 that can be converted in the process is limited by operation parameters such as feeding rate, purity, temperature, etc. The amount of feed conversion is often neglected in literature, however looking at system level it is a highly important figure of merit. Single-pass CO_2 conversion will not have an effect on the marginal costs, since unreacted CO_2 is recycled back to the reactor unit. However, it will affect the economics of the process design and scale of DSP.

Product selectivity refers to the percentage of desired product present in the final product stream of the process. Similar to the single-pass CO_2 conversion, product selectivity has a substantial influence on the DSP costs. Insufficient product selectivity could kill the feasibility of a process. For optimization of product selectivity, an understanding of the reaction mechanism of CO_2 towards the product on catalytic surface is essential. Product selectivity is dependent on catalyst selection and the structure of catalyst surface, together with the operation conditions [29].

Yield or reaction yield, is the measure of amount of moles of reactant transformed to the desired product during a chemical reaction. Yield differs from selectivity in that yield refers to the percentage of mole reactant that actually ends up as the desired product, where selectivity refers to the percentage of desired product present in the final stream. Similar to product selectivity, yield is dependent on catalyst selection and morphology of the catalyst surface [29]. Yield is determined for both, CO_2 and H_2, as an influence on the conversion performance.

2.5. Previous Work

In this section research and analysis of previous reports on CCU are discussed. An overview is given on previous conducted TEA's and their results. In the reports, feasible products and technologies for CCU are analyzed and their potential for commercial/industrial scale are examined. Each report has its own approach on determining the feasibility of the reduced product. In this section the reports are discussed and their outcomes and approaches are compared. Based on the analysis of previous results, opportunities on CCU will be explored and essential missing areas for system-level analysis completed.

2.5.1. CO_2R Products

Theoretically, a very wide range of different products can be produced via EC or TC. Each product differs in the amount of electrons or moles of H_2 required for the reaction. Each reaction has its own characteristics and optimal operation conditions. Those aspects make some carbon reduced products more attractive to produce than others. Several TEA's have been performed on the feasibility, opportunities and challenges of a selection of products.

The broad selection of carbon dioxide reduced products that can be made, depends on conversion technology, materials used and conditions of operating. An extensive literature research has been conducted on previous performed techno-economic analyses on electrochemical and thermocatalytical CO_2R products. Followed by a literature research towards additional and novel conversion technologies reported in recent state-of-the-art studies. An overview of all reported products, together with the technology of conversion, is given in table 2.2.

Product	**Technology**	**Reference**
Carbon Monoxide	LTE, HTE, TC	[5] [9] [17] [30] [31] [32] [33]
Formic Acid	LTE	[5] [9] [17] [30] [31] [32] [33]
Oxalic Acid	LTE	[5] [9]
Methane	LTE, HTE, TC	[5] [9] [17] [8]
Methanol	LTE, TC	[5] [9] [17] [8] [30]
Ethylene	LTE	[5] [9] [17] [30] [31] [33]
Ethanol	LTE	[5] [9] [17] [30] [31] [32] [33]
Dimethyl Ether	TC	[5] [8]
Oxalic Acid	LTE	[9] [17]
1-Propanol	LTE	[9] [30]
Acetic Acid	LTE	[9]
Allyl alcohol	LTE	[9]
Glycoaldehyde	LTE	[9]
Acetaldehyde	LTE	[9]
Propionaldehyde	LTE	[9]
Ethylene glycol	LTE	[9]
Acetone	LTE	[9]
Hydroxyacetone	LTE	[9]
Glyoxal	LTE	[9]
Formaldehyde	LTE	[17]

Table 2.2: Possible CO_2R products mentioned in previous TEA studies

As shown in the table, several molecules are named in multiple reports. However, not all molecules tend to have the potential for a positive net present value (NPV) in a hypothetical up-scaled industrial production process. NPV is the difference between present value of cash inflows and outflows over a period of time. A positive NPV is necessary for a profitable investment or project. Carbon monoxide and formic acid are the most mentioned products, as shown in table 2.2, and also identified as most economical feasible by all of the reports. Other often mentioned products, such as methane, methanol, ethylene and ethanol are not immediately feasibly due to their current state of technology. Current cell performance are not sufficient and the costs of production are substantially higher than competing market prices. However estimation of future performances and simulations of several scenarios show promising results for further research[31][32]. The improvements and barriers to overcome discussed in previous reports, are discussed in this section and the findings will be taken into consideration throughout this thesis.

For both technologies, TC and EC, high-value and high-margin or products that could act as intermediates for further processes are likely to dominate the near-term future market of sustainable produced carbon products. Grim et al. [9] suggests that, based on an TEA performed on multiple C_1-C_3 products, C_1 molecules used as intermediates paired with thermochemical formation of C_+ products offer the most promising sustainable driven CO_2 reduction on short notice. However, on the long term, direct reduction towards longer carbon molecules will be possible and overcome limitations indirect routes. Huang et al. [5] performed an extensive TEA on a selected number of promising products and technologies and the effect of the expected future developments. The effect on the minimum selling price (MSP) is analyzed. The MSP is the minimum price at which a product must be sold to generate a positive NPV taken a set internal rate of return in account. For the future performance of electrochemical and thermocatalytical reduced products, improving current density must be prioritized. Cell stacks that can obtain already sufficient current densities will likely have the focus for near-term future process designs [17] [5].

Jouny et al. [30] finds that under state-of-the-art conditions of technology and the chemical markets, carbon monoxide (CO) and formic acid (FA) are the only economically viable products. Insights gathered in this report are on large-scale production of common CO_2R products. Similar to previous mentioned reports [5][17], current densities tend to have a important influence on the economical viability of EC produced products. Remarkable, when the current density reaches a certain range (400 mA/cm^2), the influence on the process becomes minimal [30][5].This is visualized in figure 2.3 by Huang et al. that shows the impact of current density on the MSP. Beyond this point, the role of the selectivity and overpotential during the process become more important parameters. The more electrons transferred during the reaction, the more critical these parameters of performance become. The economical viability of TC processes is mostly dependent on hydrogen yield towards the desired product and catalyst activity. Green hydrogen and catalyst materials are major costs contributors and therefore have a big influence on the financial feasibility of the process.

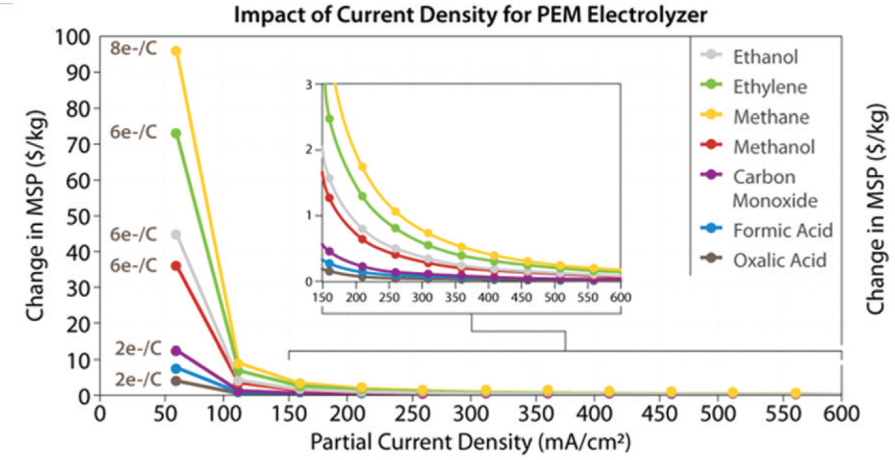


Figure 2.3: Impact of current density of a PEM CO_2 electrolyzer on the minimum selling price. Increasing current density reduces minimum selling price. Beyond 400 mA/cm^2 influence becomes minimal. Adapted from Huang et al. [5]

To obtain improvements on electrochemical conversion on short notice, and to obtain the ability to produce a variety of products with high purity and selectivity, care must been taken in research on the cell design. R&D on CO_2 electrolysis can take advantage on developments taking place on PEM and SOEC water electrolysis. Developments on these fields of technology are rising and similarities between those techniques should be used. A solution given by Chen et al. [17] for increasing purity and selectivity, and overcoming barriers regarding current densities and activity are gas diffusion electrodes (GDE). Enabling increased activity and selectivity towards desired products.

The majority of the comparative TEA's performed on CO_2R are focused on electrochemical conversion. Limited researches are reported on the techno-economic viability of TC products. While this conversion technology, similar to EC, has potential and could play a significant role in future developments regarding CO_2R. Especially since the electrochemical production of H_2 is developing at a rapid pace and therefore the use of green H_2 in TC processes is becoming more and more attractive. For now, in order to rapidly scale up potential reduction processes, the primary focus should be on technologies that are sustainable, reliable, and capable of achieving high production rates on short notice.

2.5.2. Product Feasibility

The TEA's performed in the reports mentioned above, all have their outcomes on product feasibility, MSP and future performance. This section outlines these results and includes the conclusions and opportunities for further research. The different reports are similar in many aspects, this will provide a good lead for the comprehensive research. However, also certain aspects of research are missing, those will bee taken as opportunities to gain new and more complete insights.

According to Grim et al., the technical feasibility of reduced carbon products has all to do with ease of formation. In the report, four factors are identified for the qualitative determination of ease of formation: (1) rate of formation, (2) faradaic efficiency/selectivity, (3) energy/catalyst efficiency, and

(4) TRL of the process [9]. A selection of products produced via EC CO_2R and their feasibility are assessed according to those aspects. As expected, carbon monoxide is mentioned as top performer, together with methanol and methane. Other products that stand out are formate, ethylene and acetate. However, due to their low TRL and insufficient efficiency, production of those products will not be feasible on short notice. Taking the market forces and global production rates into account, methane is identified with the highest potential for CO_2 utilization according to Grim et al. [9].

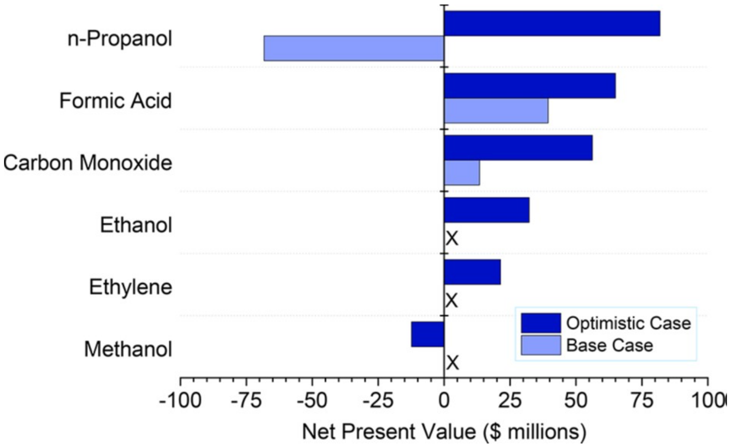


Figure 2.4: End-of-life NPV for EC production of C-molecules under base and optimistic conditions [30]

Jouny et al. performed an extensive analysis on the current state-of-the-art figures of merit and performed calculations on the end-of-life NPV of numerous EC processes. Two types of scenario's were written in the report: a base-case scenario and an optimistic. Where the optimistic scenario represents the near-term future performances. In figure 2.4 the results of the NPV analysis are shown. Their analysis on NPV for methane and syngas resulted in excessively high production costs compared to their current market value, therefore they are not included in the bar chart. At base case conditions, only the relative simple products, CO and FA, are economic feasible. It should be mentioned that the market for FA is relatively small and this will have a negative influence on the business case. According to Jouny et al., focus should be on liquid products due to the transportation difficulties of gaseous products. Liquid products such as ethanol and n-propanol could be more profitable in future scenarios because of their technological and market potential [30]. The selection of these two molecules can be seen as debatable since the production technologies of multi-carbon molecules cannot yet be seen as mature in the near-term future.

Huang et al. took the analysis on the NPV further and used the expected future performance to determine the percentage reduction in minimum selling price for a selection of carbon molecules. When conversion performance increase and feedstock or utility prices decrease, it will have a positive effect reducing the MSP, resulting in a more optimistic scenario for a positive NPV. Within this analysis, a distinction is made between performances of high temperature-, low temperature electrolysis and thermocatalytical processes. A visualization of the percentage change in MSP is given in figure 2.5. Relevant in this figure are the two left columns (LTE and HTE) and the most right column (TC). The middle two columns represent reduction for microbial electrosynthesis (MES) and biological conversion (BC). These two technologies will not be considered in this study. Significantly reduction in costs are shown due to the improvements of future scenarios. Product MSP's are reduced from 54% to 87% depending on the conversion route. The greatest improvements can be obtained for the EC pathways. This is due to the current low TRL of EC compared to TC technologies. TC production of chemicals is a more established industry and therefore performs better at current state-of-the-art processes. MSP improvement for TC is therefore mainly driven by developments of market parameters, such as green hydrogen and renewable electricity prices. Improvements of the MSP for EC pathways are mainly driven by technical parameters. To realize these future scenarios, further R&D is needed towards efficient EC processes and reduced hydrogen and green electricity production costs.

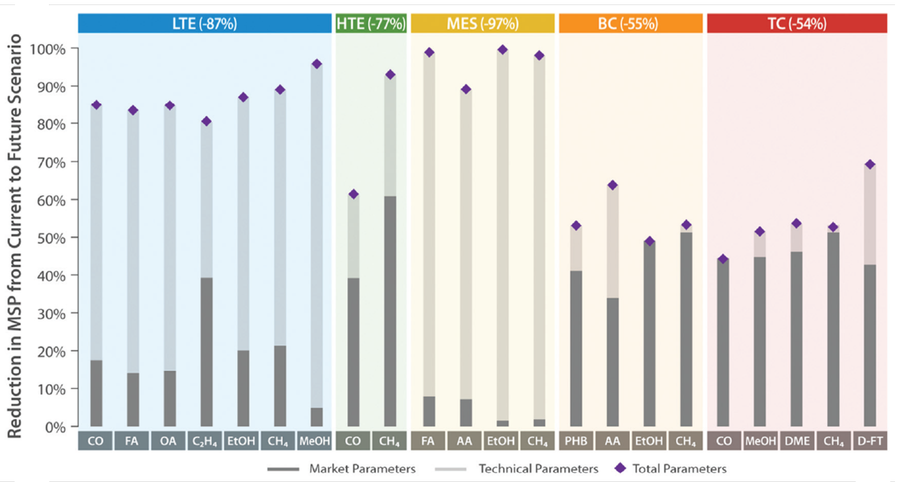


Figure 2.5: Percentage reduction in MSP moving from current to near-term future scenario for different conversion technologies by Huang et al. [5]. Total percentage reduction in MSP is distinguished in improvement of market- (dark shaded) and technical parameters (light shaded).

Similar analysis to the ones mentioned above are performed in TEA's on the products mentioned in table 2.2. In all reports CO and FA are identified most feasible at current state of technology (SOT). Even though the high TRL of the two pathways, separation costs need to be improved to be ready for large-scale production since those are a large contributor of production costs. [31]. Spurgeon et al. identifies formic acid as the most readily product to be commercialised for production on industrial scale [32]. However, formic acid is not always seen as favorite due to the relative small market for the molecule as product. The market size parameter is not considered in each result, which could cause to misleading comparisons. Other molecules stated as promising are ethylene, ethanol, and methanol. At current SOT, TEA shows the technology and economics for these products are insufficient but opportunities for feasible pathways are present [31][9][8]. An opportunity for improving near-term feasibility of low TRL pathways is considering the economics of produced byproducts, such as hydrogen. Selling byproducts has a positive influence on the NPV but increases the downstream processing (DSP) costs.

After reviewing a variety of TEA reports on CCU, it can be concluded that formic acid and carbon monoxide have the most potential for the current state of technology and economics. For the near-term future, ethanol, ethylene, methanol and methane are mentioned multiple times. However, there is no unanimity between the different analysis on those products depending on the approach and parameters taken. Study on the literature shows that there are also conflicting results between the different analyses. Chen et al., for example, states that for short term feasibility high-volume fuel market are ultimately desired [17]. While Spurgeon et al. states that combustion products, which are used as fuels, will not be desirable since the thermodynamics suggest that reducing CO_2 requires more energy input than combustion releases. Other conflicts between different analyses are on economic feasibility, market size, application of the final product et cetera. Contradictions like these require a careful approach as not to make misguided selections. In the reviewed literature assumptions were made and general approaches applied for different products. This could have the consequence that production pathways and processes are sometimes simplified and the performance and costs analysis are not specific. The complexity of DSP is in most cases reduced to general cost factors. To deliver a more specific analysis on product feasibility, the complete production pathway is analysed in detail in this research. Distinction is made between product stream phases and modes of separation. Costs on CAPEX and OPEX will be addressed as detailed as possible to identify the most business critical pathway on legitimate calculations and comparisons. More attention will go out in this research to thermocatalytical pathways. Even though the technology for TC pathways is more mature, most of the TEA's are focused on electrochemical pathways. This study will focus on legitimate comparisons between product and conversion technology and will examine all pathways using a similar approach.

2.5.3. Possible CO2R Pathways

The characteristics and molecular properties of the different CO_2 derived products are all different. Each molecule has its own thermodynamics and kinetics influencing the conversion process and its economical feasibility. Depending on technology, operation conditions and materials used a substantial amount of pathways is possible. Extensive research is conducted on those pathways ranging from low TRL laboratory scale to conversion routes that are almost applicable on industrial scale. Based on published reports on the technologies discussed in previous sections, a overview of possible products for CO_2R and their pathways are visualized in a mind map (figure 2.6). A visualization is given for all C_1, C_2 and C_+ products able to be reduced via single- or multi-step conversion. A broad selection of carbon products is included that theoretically can be produced, supported by literature on state-of-the-art technology. This includes well known products that are mostly discussed in the previous section (CO, FA, MeOH, CH_4, etc.) and more complex C_2 and C_+ products. In table A.1 in appendix A, all products from the mind map are listed.

The mind map in figure 2.6 includes all pathways towards the desired product. Pathways are denoted by blue arrows between the molecules. The method of conversion is mentioned by abbreviations for the conversion technologies. Electrochemical conversion is denoted by *EC* and thermocatalytical conversion is denoted by *TC*. Pathways can be directly towards the final molecule, single-step, or via intermediate products towards the desired molecule, multi-step. Some molecules may act as intermediates for a large amount of different products, these can be seen as '*spiders in the web*'. These spiders in the web can be especially of interest due to the diversity of potential applications beyond the traditional market. Products that act as intermediate for several products can be visualized in the mind map multiple times at different locations. Molecules are categorized in the mind map in the categories C_1 (left), C_2 (right) and C_+ (bottom). This is done deliberately to limit complexity and to improve the readability and understanding of the mind map.

Based on the molecules and pathways shown in the mind map, values for the key performance indicators are obtained. This is done via extensive a literature study on state-of-the-art research reports on CCU. The key performance indicators for EC conversion were faradaic efficiency, current density and cell voltage. Those for TC conversion were single-pass CO_2 conversion, product selectivity and yield. To limit the scope of the project, a first selection will be made based on the performance of conversion via single-step pathways. Later in this study, use of intermediate products and multi-step conversion will be considered.

The first feasibility analysis is performed on single-step conversion molecules to reduce complexity of analysis and to avoid jumping into conclusions. Single-step products tend to have lower CAPEX and OPEX since less conversion steps and downstream processing is involved. Single step conversion is less complex so near-term feasibility is more likely to happen than for multi-step. Additionally, the conversion and purification process for single-step products must be economical viable for the multi-steps to be considered for technical and economical analysis. If the intermediate product already is not feasible to be produced via CO_2R, then the follow-up product most likely will be neither. In some cases, multi-step products can be produced directly by letting the initial products react within the cell or reactor. However, these reactions are very difficult to control and many unwanted side reactions would occur. Therefore, these type of reactions are left out of scope.

As in earlier sections, the feasibility is determined by means of the KPI's. Using those indicators, a selection is made by means of a costs analysis. In order to collect all KPI's per product, an extensive literature research is performed on all single-step products, including the C_2 products. As many different reports and researches are analyzed, different values of performance are mentioned. The researches studied for the first analysis all differ in process design, production scale, process performance, operating times and level of maturity. The most relevant and legit reports are selected and used for further analysis. An overview of the selected reports of study and their parameters of performance are listed in table 2.3.The numbers mentioned in the table are current state performance as obtained from the different reports. Based on this selection, the most commercial representative parameters will be used for further research. Hereby the scale of the system, terms of stability and production rates will determine the

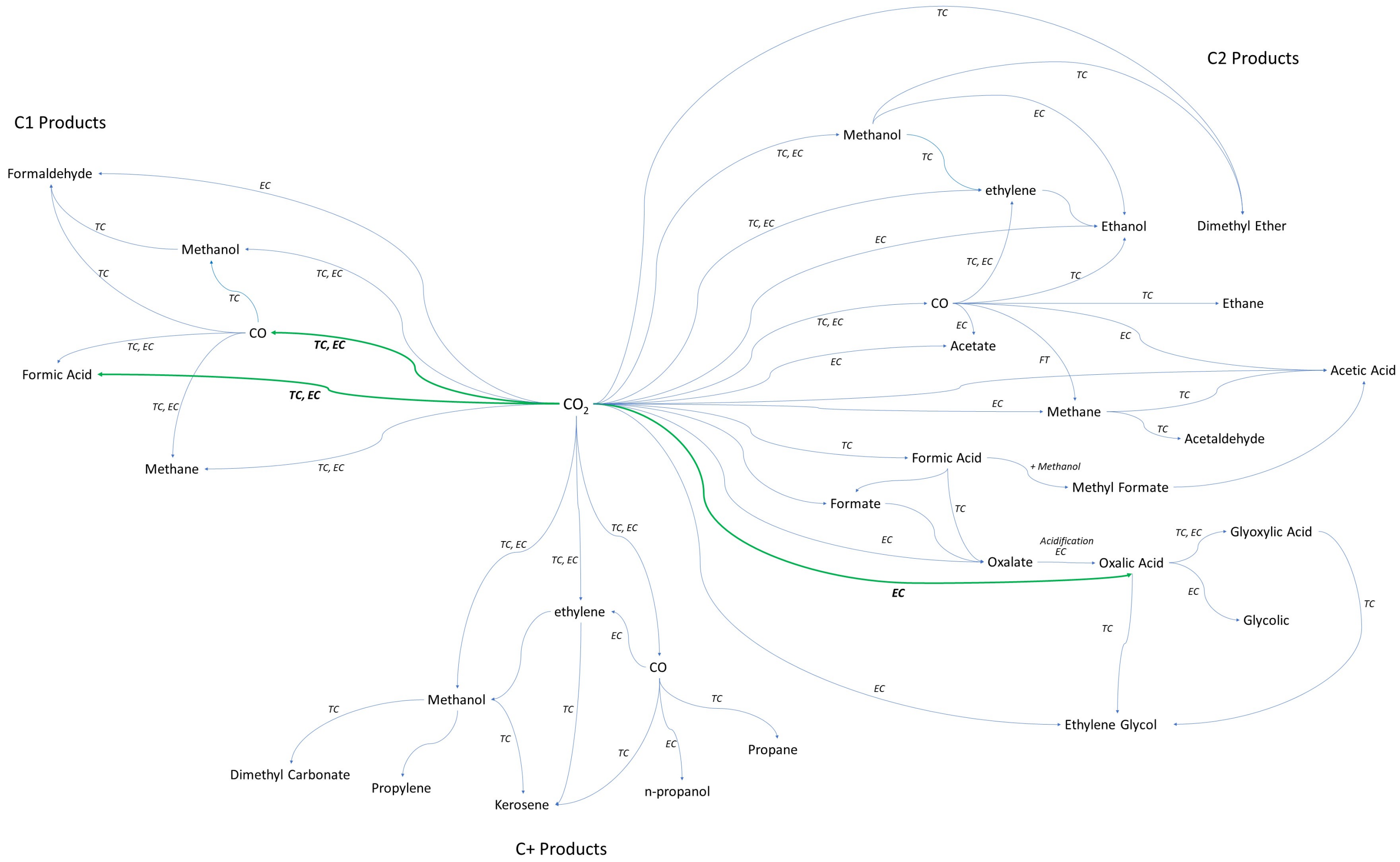


Figure 2.6: Mind map visualizing possible pathways for CO$_2$ reduction. EC representing electrochemical conversion and TC representing thermocatalytic conversion. Finally selected pathways for this study highlighted in green. Selected conversion technologies highlighted in bold.

prioritized results. Metrics of performance and commercialization potential of reported technologies are based on the different KPI's defined in section 2.4.1. Based on the marginal costs analysis on the first selection of products, using the KPI's mentioned in table 2.2, a selection of products is established for further analysis. As the marginal costs analysis is performed, it is expected that the majority of the products will turn out to be not economical viable and only a small selection will be feasible for further research.

Pathway	**product**		**Performance**		**Reference**
LTE		**CD [mA/cm^2]**	**FE [%]**	**CV [V]**	
	Carbon Monoxide	200	98	3	[5]
	Carbon Monoxide	200	95	3	[13]
	Carbon Monoxide	350	100	3	[34]
	Methanol	41.5	77.6	2.67	[35]
	Methanol	31.8	80		[36]
	Methane	225	48	2.94	[37]
	Methane	100	42		[38] [39]
	Methane	225	48		[40] [39]
	Formic Acid	140	95	3.5	[35]
	Formic Acid	50	95	2.8	[7]
	Formic Acid	133	86	4.1	[34]
	Formaldehyde	0.1	74	2.5	[41]
	Ethylene	1550	60	3.23	[5]
	Ethylene	1340	70		[42]
	Ethylene	100	70		[43]
	Ethylene	100	70	2.4	[34]
	Ethanol	300	52		[37]
	Ethanol	300	51	2.21	[34]
	Oxalic Acid	19.22	51	3	[44]
	Oxalic Acid	19.6	62.4	-3.5 vs. Ag/Ag+$^{(1)}$	[45]
	Oxalic Acid		50	6.5	[5]
	Ethylene Glycol	0.4	80	3	[46]
HTE		**CD [mA/cm2]**	**FE [%]**	**CV [V]**	
	Carbon Monoxide		99.5	1.3	[13]
	Carbon Monoxide	200	99.5	1.41	[5]
	Carbon Monoxide	750	99	1.47	[47]
	Methane	1800	12	1.45	[5]
	Methane	1385	20	1.45	[48]
TC		**Selectivity [%]**	**Yield [%]**	**CO$_2$ Conv [%]**	
	Carbon Monoxide	100	68	68	[49]
	Carbon Monoxide	100	40	40	[50]
	Methanol	68	18	27	[51]
	Methanol	80			[52]
	Methane	99	84	85	[53]
	Methane	99	79	80	[54]
	Formic Acid	81	79	98	[49]
	Formic Acid	81	81	100	[55]
	Ethylene	90	35	20	[56]
	Dimethyl Ether	73	23	31	[57]
	Dimethyl Ether	85	73		[58]
	Dimethyl Ether		70		[59]
	Ethanol	98	55	57	[60]

Table 2.3: Selection of technology performance single-step CO2R Products. (1) Is the applied cathode potential versus a Ag/Ag+ reference electrode.

2.6. Marginal Costs Analysis

In this section, a comparative analysis is performed on the marginal production costs of the selected products identified in section 2.5 on the previous conducted TEA's on CCU. The marginal costs analysis will determine the costs per kilogram of product for several different scenarios. Depending on the feedstock prices and system performance. The results of this analysis are used, along with other fields of criteria, for a selection of products. This selection of products will be used in this research and the whole process will be modelled in detail at system level.

The marginal costs is defined as the change in total production costs by the production of one additional unit of product [61]. This analysis thus only includes the additional costs in terms of feedstock usage (e.g. electricity use) and feedstock costs (e.g. electricity price). This excludes any costs of capital expenditures or maintenance costs et cetera. The purpose of a marginal costs analysis is to determine at what scenario a production plant could gain profit from CCU. In other words, if the production price per additional unit of product is below the conventional market price, then the opportunity to develop a profitable process design exists. Assuming that the technologies covered in this study are very rapidly developing and not all parameters are fully representative, multiple scenarios will be included in the analysis. This does not only apply to the technical parameters but also to the parameters on renewable feedstock costs. Due to the speed of current developments, a lot is happening in the field renewables and their economic parameters as well.

2.6.1. Analysis Parameters

The marginal costs analysis is performed based on several metrics of performance that differ per conversion technology. The production costs of EC converted products will be dependent on different aspects than TC converted products. For all reactions, the first metric of costs is based on the stoichiometry of the reaction. And for both process technologies the costs of the captured CO_2 and other used feedstock are an influence on the eventual feasibility of the product. For TC processes, especially the H_2 costs will be of influence, since the reactions demand the usage of it. For EC processes the specific energy consumption (SEC) and electricity costs will have a large influence. This is due to the fact that EC reactions are driven by electricity. In this section all costs drivers used for the marginal costs analysis will be addressed and their influence on the production costs per product will be discussed.

Economic Scenarios

For the analysis of the marginal costs, three different economical scenarios are considered. Throughout the study the following scenario's are considered: a current scenario based on reported state-of-the-art technologies and their performance indicators, a near-term future scenario using more progressive values for the performance indicators that could be achieved in the next few years, and as third the theoretical scenario based on optimal operation conditions and optimal case feedstock price assumptions. The three different scenarios for feedstock costs will be discussed later in this section.

Reaction Stoichiometry

The stoichiometry is the balance of a chemical reaction. It states the reactants, the products and the numerical relationships between those. The stoichiometry of a reaction is used in this analysis to determine the balance of reactant and product and determine how much CO_2 and other feedstocks are consumed and products produced in the chemical reaction. Reaction 2.11 shows how the relation between reaction and product is visualized by means of the stoichiometry. The numbers represent the amount om moles of a specific molecule is required. E.g. the stoichiometry of reaction 2.11 states that for the production of one mole methanol (CH_3OH) one mole of CO_2 and three moles of H_2 are required. Based on this relationship an assumption of feedstock costs and product revenue is made in the costs analysis.

$$1\,CO_2 + 3\,H_2 \rightarrow 1\,CH_3OH + 1\,H_2O \qquad (2.11)$$

Feedstock Costs

For both conversion technologies, the feedstock costs are of importance for the production costs. The feedstocks used for the single-step products are CO_2, H_2, H_2O and electricity. It is of importance that those feedstocks, especially CO_2, H_2 and the electricity, are produced or captured via a sustainable route where no polluting emissions are released. To limit the complexity of the processes designs made later in this research it is assumed that from the atmosphere captured carbon dioxide and green hydrogen are available as pure streams directly for the process. The feedstock prices used for the marginal costs analysis and analyses later in this research are based on state-of-the-art capture and production technologies. A price range is applied based on three scenarios: a worst case-, a base case- and an optimal case scenario. Where the feedstock prices vary between the lowest and highest costs reported in literature. The hydrogen price is obtained from the analysis by Huang et al. [5], corrected for inflation and exchange rates. Where based on the U.S. Department of Energy's H_2A Hydrogen Production Cash Flow Analysis Tool an estimation on the H_2 price for all three scenario's is made [62]. Assuming H_2 is obtained via green PEM electrolysis. The other feedstock prices are adopted from an earlier model in consultation with experts from TNO. In table 2.4 all feedstock prices used for the marginal costs analysis are listed per scenario.

Feedstock		**Worst**	**Base**	**Optimal**	**Ref**
Carbon Dioxide	$\frac{€}{kg}$	0.15	0.05	0.02	[5]
Hydrogen	$\frac{€}{kg}$	3.71	2.37	1.71	[5]
Water	$\frac{€}{kg}$	0.002	0.001	0.0005	[5]
Electricity	$\frac{€}{kWh}$	0.05	0.03	0.02	[5]

Table 2.4: Feedstock prices per economic scenario

Specific Energy Consumption

The marginal production costs of products obtained via EC pathways is mostly affected by the electricity use and costs. To determine the electricity use and thereby the costs per produced unit of product, the specific energy consumption is calculated. SEC is defined as the ratio between the consumption of energy in kWh and the unit weight of produced product in kg. The unit of SEC is represented by kWh per kilogram of product $[\frac{kWh}{kg_{product}}]$ [63]. The SEC of a process can be a good performance indicator and can be used to evaluate or measure the performance of energy efficiency [64].The SEC of a given product is calculated using equation 2.12. Where ne^- represents the number of electrons required for the reaction to take place, F Faraday's constant ($F = 96.485\,C/mol$), ΔV the applied cell voltage [V], FE the faradaic efficiency of the cell stack in percentage [%], and $M_{product}$ the molar mass of the final product in grams per mole of product $\left[\frac{gram}{Mol_{product}}\right]$.

$$SEC = \frac{Energy\,Used}{Product's\ Amount} = \frac{ne^- \times F \times \Delta V}{FE \times M_{product}} \tag{2.12}$$

Product Prices and Annual Production

The calculated marginal costs are compared to the actual current market prices of the to be produced products. Market prices used for the analysis are gathered from various research papers. As market prices depend on location of production, sales location, purity of product, year of production et cetera, it is hard to determine a fixed price per kilogram of sold product. Therefore, prices that have been used in earlier performed TEA's have been adapted and a general price per kg of product is established based on the reported values [30][9][34][58][65][66][67]. Taking into account that the market prices can vary greatly by report and can fluctuate, makes it an uncertain variable in the analysis. Given the current situation in Ukraine and uncertainty in gas and oil prices, the market prices prior to this crisis are used. Another factor that contributes to the interest of a product is the market size and thereby the annual production of the product. The correlation between annual production and market price is not significant. However, products with a large market size, tend to have lower production costs. This is not unusual, given that with large-scale production, the production costs per kilogram of product goes down. The market prices and global annual production per product are listed in table A.2 in Appendix A. A visualization of the annual production of each single-step product in tonnes against the production price per kilogram in euro's is shown in figure 2.7. This visualization shows the variation in annual production across the different products. A difference in consumption of almost a fourth-order magnitude is observed between the most produced product, methane, and the least produced product, formic acid. The insights in variance in annual production and market prices will be of use in a later stadium of the analysis of molecules to produce and their process design.

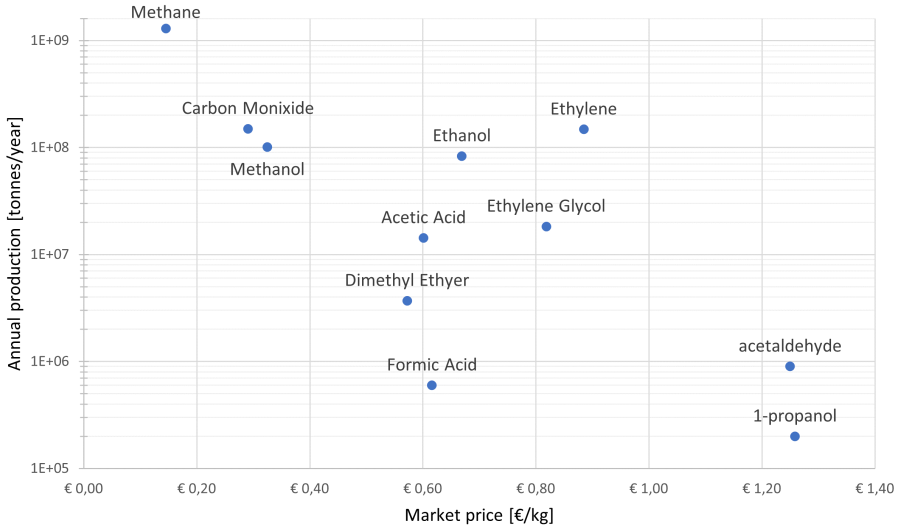


Figure 2.7: Annual production of each single-step product in tonnes against market price per kilogram. Reference values used are listed in Appendix A in table A.2.

2.6.2. Marginal Costs Calculation

The marginal costs $[\frac{€}{kg_{product}}]$ are determined using the costs for feedstock utilized in the reaction, and costs of utilities used. Between the two conversion technologies, a distinction is made on what parameters are affecting the production costs. The costs calculations for both conversion technologies are given by equations 2.13 and 2.14. For both equations, *Required CO*$_2$ represents the amount of CO$_2$ required for the reaction in $\frac{kg_{CO2}}{kg_{product}}$. The required amount of CO$_2$ is determined based on the reaction stoichiometry. In electrochemical reactions the reaction is driven by electrons applied to the electrolyzer system. The costs of electricity are calculated using the *SEC* in kWh per kg of product together with the electricity price for the corresponding economic scenario. In thermocatalytical reactions, hydrogen is used as feedstock in the reaction. The *Required H*$_2$ represents the amount of hydrogen required for the thermocatalytic reaction in $\frac{kg_{H2}}{kg_{product}}$. The costs of captured CO$_2$, electricity and hydrogen are based upon the price per kg or kWh for the corresponding economic scenario.

$$Marginal\ cost\ EC = \left(SEC * \frac{€}{kWh}\right) + \left(Required\ CO_2 * \frac{€}{kg_{CO2}}\right) \tag{2.13}$$

$$Marginal\ cost\ TC = \left(Required\ H_2 * \frac{€}{kg_{H2}}\right) + \left(Required\ CO_2 * \frac{€}{kg_{CO2}}\right) \tag{2.14}$$

2.6.3. Results Marginal Costs Analysis

After the extensive literature on possible products and parameters for the performance of single-step conversion products, the marginal costs analysis is performed using the parameters mentioned above.

First the ratio between feedstock and product are determined using stoichiometry for the chemical reactions. Based on those ratios the initial required feedstock consumption and obtained product is determined. For the EC processes, the cell voltage and faradaic efficiencies obtained from literature are used to determine the SEC. For the TC processes the technology performance indicators mentioned in section 2.4, yield and product selectivity, are used for determining the feedstock consumption, especially the H_2 consumption. The marginal production costs per kilogram of product are determined for three different economical scenario's using three different price scenario's.

Figure 2.8 gives deviation in percentage of the marginal costs for the three different economic scenarios from the average market price in Euro's per kilogram listed in table A.2, represented by the red line. The marginal costs are determined for all technical and economic scenarios (table 2.4). The dots represent the marginal production costs for the corresponding products mentioned on the horizontal axis. Each color represents a technical scenario and each shape of marker represents an economic scenario. The distinction is indicated in the legend. The spread between the dots indicates the difference in performance over the scenarios. A positive deviation from the middle line indicates a costs of production greater than the reported market price. A negative deviation indicates a marginal production price below the reported market value. Evidently, a negative deviation implies more potential and opportunities for a economic feasible conversion process. Keeping in mind that the market prices can fluctuate significantly and depend on various aspects, for the market prices where it applies a range of price deviation is indicated by means of the green shaded bars around the mid line. The outlined text boxes on top of the graph indicate the conversion method for the corresponding products listed on the horizontal axis.

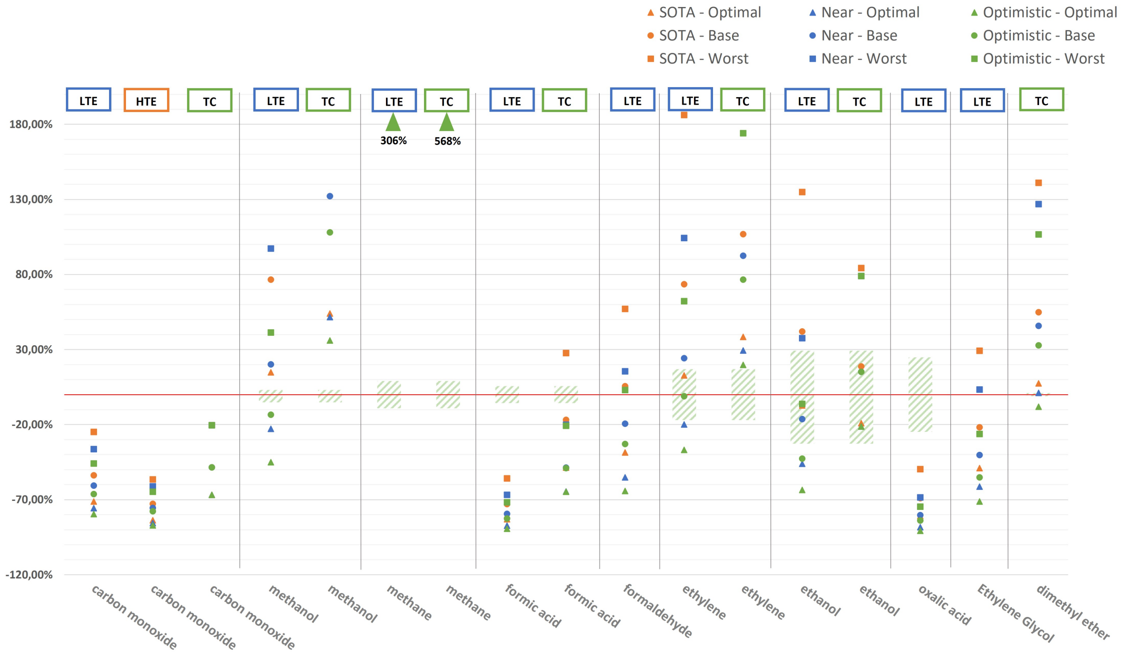


Figure 2.8: Deviation marginal production costs from reported market prices [%]. Market price indicated by horizontal red line, deviation in reported values indicated by green shaded bars. SOTA, Near & Optimistic refer to the scenario's for the performance of KPI's. Numbers used are listed in Appendix A in table A.3. Optimal, Base & Worst refer to the economic scenario's listed in table2.4.

From the graph can be observed that at under current SOTA conditions, indicated by the orange markers, only the marginal costs of CO, FA and oxalic acid (OA) are below the average market prices. Implying potential economical viable conversion at current technologies. When the more progressive values for system performances are observed, indicated by the blue dots, marginal costs for all products decrease. For some products the improvements on performance have an bigger influence than others.

Formaldehyde almost hits the mid line, however still has a positive deviation. Products that cross the mid line or reach the area of market price deviation are now ethylene glycol and dimethyl ether. Looking at the performance at the theoretical scenario, more products get to compete with the average market price. However, methanol, methane and ethylene are still above the competitiveness level of the market prices. Methane is the outlier in this regard. Even under the optimal conditions, the deviation is well off the chart with more than 300% and 500% for EC and TC respectively. This is mainly due to the competing low price of natural gas from which methane is obtained, prior to the situation Ukraine and increase of gas prices. Given the uncertainty in today's production costs and the lack of current prices, this analysis is performed using market prices prior the war in Ukraine. These results show that near-term feasibility for methanol, methane and ethylene can be excluded. Ethylene does not perform well in this analysis due to the current system performance for EC or TC conversion and due to competitiveness of the conventional production methods, which is steam cracking of naphtha or natural gas [68]. Methanol is a somewhat notable one in this list given the current focus around CO_2 reduction towards this product. The disappointing performance of conversion towards methanol is mainly caused by the challenge of reaching high faradaic efficiencies at high current densities [35]. Another contributing cause is the market size and thus the competitive price of methanol. Under these conditions, renewable produced methanol is not yet ready to win over conventional production methods.

Products that reach the mid line or shaded area within the deviating price range have potential of competing in the near-term future with the current production methods. Molecules that are of interest and should be considered in further analyses are CO, FA, formaldehyde, ethanol and oxalic acid. However, not every molecule performs equally well in the analysis. A distinction must also be made between these products as to which are potentially economic viable in the near-term future and which are not. The analysis shows that a major factor that influences the economic viability of a product is the yield to mass. The more atoms of feedstock end up in the desired product, the less mass is lost into the process of conversion. CCU is based on converting carbon atoms towards useful valuable products. However, the more oxygen atoms of the CO_2 end up in final product in addition to the carbon atoms, the more mass of feedstock end up in the final product per mol. In general, products are marketed in weight and sold for a price per unit of mass. Thus, products that have a higher mass per produced mole, tend to be more valuable per mol. This trend is reflected in the analysis, where the three most well performing products (CO, FA and OA) are the most oxygenated products. More than 55% of their molar weights exists of oxygen atoms, which have a very high molar mass compared to hydrogen atoms (15.999 grams per mole vs. 1.008 grams per mole). Compared to the other molecules, these products consume less feedstock and have a higher mass output resulting in a better system performance.

2.7. Product selection

With these findings based on analysis of the literature and reports on previous conducted research, a selection of potential CCU products interesting for further research can be made. The selection is based on the performance on the marginal costs analysis, the state of the current technology and the phase in which the final product stream is obtained. These criteria are selected based on their influence on economical-, system- and downstream processing performance. Since the process of CO_2R towards these products will be analyzed at system level, including pre- and post-treatment, economics and conditions for DSP cannot be ignored.

Selecting the molecules of interest is done according to a so-called 'traffic light assessment'. A traffic light assessment is a rating system where the performance of each process is rated according to specified criteria. In this research, a hard line between *pass* and *not pass* is drawn, resulting in two colours/scenarios. A green light is assigned when criteria have been met meaning the conversion of the product can potentially be achieved at viable performance. A red light is assigned when a product cannot pass the criteria and therefore will not be considered for further research.

Besides the performance on the marginal costs analysis, other parameters must be considered as criteria for the selecting procedure. An important factor on the economics of the system, especially on the costs of DSP, is the phase in which the product stream leaves the cell stack or reactor. Separation of liquid mixture (via e.g. distillation) is energy intensive and could possibly be crucial for the economic viability of the complete system and is often an overlooked challenge in designing a process [69]. Thus, in the assessment on system performance a distinction must be made between product streams in liquid phase and product streams in non-liquid phase.

Another important parameter for the traffic light system is the technology readiness level (TRL). TRL is a method to classify the maturity of a technology, in this case the maturity of the conversion technology per product. A methodology introduced by the NASA in 1974 and later accepted by the European Union (EU) as a general innovation policy tool. Over the past decades, the TRL has formed and adjusted to the present day. The current definition of TRL and includes nine following levels of different stages of technology readiness. The current nine levels of TRL stated in the EU Horizon 2020 Program are [70]:

1. TRL 1: Basic principles observed
2. TRL 2: Technology concept formulated
3. TRL 3: Experimental proof of concept
4. TRL 4: Technology validated in lab
5. TRL 5: Technology validated in relevant environment
6. TRL 6: Technology demonstrated in relevant environment
7. TRL 7: System prototype demonstrated in operational environment
8. TRL 8: System complete and qualified
9. TRL 9: Actual system proven in operational environment

To pass the criteria of the assessment, an minimal amount of points must be achieved based on properties and performance of the process. Points are are assigned when the performance meet certain requirements. Under some conditions, also points can be deducted. This is the case when the conversion process has complexities or drawbacks that negatively influences the economics of the process and the system performance. All points assigned or deducted based on criteria on the marginal costs analysis, TRL and phase of product stream are listed in table 2.5. The minimal threshold of points to be achieved by a pathway is set at value of five points. A pathway with a score of five points or more is seen as interesting for research at system level. Anything below the threshold is categorized as red-light and thus a no-pass. The point distribution per criteria is based on the impact and influence on the technical and economic performance of the process [70][69].

Criteria	**points assigned**
Marker below average market price	1
Marker above average market price inside deviating price range	0,5
Marker above average market price outside deviating price rang	0
Technology readiness level <3	-2
Technology readiness level 3-5	-1
Technology readiness level >5	0
Product stream in liquid phase	-2

Table 2.5: Criteria and points assigned for traffic light assessment based on marginal costs analysis, current TRL and phase of product stream.

The point distribution is based on reference literature, interviews with subject matter experts (SME's), and assumptions on the effect on the overall system performance. The system performance was measured in total for three different economic scenario's at three different price scenarios. Resulting in nine values of marginal production costs per product. The threshold was set to be 5 points. This criteria was selected such that at least half of the marginal costs scenario's was performs feasible on the costs analysis. In the event of a low TRL, the opportunities for a technology may be overestimated from their actual performance. To prevent situation of overestimating performance, points of deduction are assigned. The quantity at which points are deducted are based on amount of development required to reach higher levels and the economic impacts of that based on Héder [70]. The penalty for liquid product streams is based on the economical impact on DSP by liquid-liquid separation [69]. The penalty is set to be equal to the deduction for TRL below 3. While a TRL is evolving, the product flow remains in the same phase and therefore the separation method as complex. Thus, the effect of the phase in which a product is obtained can be crucial for the economics of a conversion process.

An overview of the parameters and results of the traffic light assessment per pathway is listed in table 2.6. The system performance and phase of the product streams are obtained from reports on novel state of the art conversion systems along with the criteria stated by Héder [70]. In the tables, the points assigned using the results of the marginal costs analysis (MCA) are reported before any penalties are assigned. In the column next to it, the final points are listed. Based on those results, the traffic light assessment will be performed. Using the criteria and point assignment according to table 2.5, only five pathways pass the threshold of the traffic light assessment. The pathways selected for research into their process design and technical economic performance are carbon monoxide (LTE, HTE and TC), formic acid (LTE and TC), and oxalic acid (LTE). In line with the expectations, these products are consistent with the outcome of the marginal costs analysis. The selected pathways are selected according to the data reported in literature and results obtained from several analysis on that data.

Product	**Technique**	**TRL**	**Phase**	**Points MCA**	**Final Points**	**Pass [y/n]**	**Ref to TRL**
Carbon Monoxide	**LTE**	**4**	**Gaseous**	**9**	**8**	**Y**	**[13]**
Carbon Monoxide	**HTE**	**8**	**Gaseous**	**9**	**9**	**Y**	**[13]**
Carbon Monoxide	**TC**	**8**	**Gaseous**	**9**	**9**	**Y**	**[50]**
Methanol	LTE	3-5	Gaseous	3	2	N	[71]
Methanol	TC	6-7	Gaseous	0	0	N	[71]
Methane	LTE	5	Gaseous	0	0	N	[71] [37]
Methane	HTE	6	Gaseous	0	0	N	[48]
Methane	TC	6	Gaseous	0	0	N	[53]
Formic Acid	**LTE**	**5**	**Liquid**	**9**	**7**	**Y**	**[71]**
Formic Acid	**TC**	**4**	**Liquid**	**8**	**6**	**Y**	**[71]**
Formaldehyde	LTE	2	Gaseous	5	3	N	[71] [41]
Ethylene	LTE	5	Gaseous	3.5	2.5	N	[71] [43]
Ethylene	TC	3	Gaseous	0	0	N	[56]
Ethanol	LTE	3	Liquid	6	3	N	[71] [37]
Ethanol	TC	5	Gaseous	4.5	3.5	N	[60] [72]
Oxalic Acid	**LTE**	**3**	**Liquid**	**9**	**8**	**Y**	**[44] [71]**
Ethylene Glycol	LTE	3-5	Liquid	7	4	N	[71]
Dimethyl Ether	TC	5	Gaseous	2	2	N	[58]

Table 2.6: Numbers and results traffic light assessment per product and conversion technique. Values for TRL and phase of product stream are obtained from the references. Initial points per production route assigned after the results of the MCA visualized in figure 2.8 are listed before any point reduction. Final points includes assigned penalties according to TRL and product stream phase.

2.8. Objectives

The objective of this study will be an front-end analysis on the possible products of CCU and the most feasible production routes using electrochemical and thermocatalytical conversion. The goal of the study is to determine the most economical and environmental relevant pathway for valorization and utilization of carbon dioxide. For that, research will be done on the production of different molecules, different conversion pathways and technologies and the downstream processing. To do so, all possible routes will be defined and their feasibility for large scale production is determined. For a selection of products, conceptual process designs are made at system level evaluating state of the art technologies. Taking into account, the operational conditions and downstream processing. Technical and economical performances are analyzed in detail and their environmental impact is determined. Comparing their performance with conventional production methods.

3

Process Design and Analysis

In this chapter, the process designs for the selected products and the techno-economic analyses for each design are made. In the previous chapter, potential CCU products have been evaluated. Based on marginal costs, TRL and product properties a selection for further analysis is made. Thereby completing the literature phase and taking the selection of promising products into the design phase. To perform a complete front-end techno-economic analysis, first the battery limits of the process and a generic use case must be defined. The battery limits will determine what process units and which details will be included in the process designs. A generic use case is necessary to perform a comparative analysis on the different systems. With the battery limits set and use case defined, the process designs are made. Next the analysis methodology is set and a techno-economic analysis is performed for each product and conversion pathway. The designs will give a good insight in all processes involved, including pre- and post-treatment, compositions and conditions of product streams and utilities required for the process. The process designs for each pathway are made according to state of the art technologies based on recent reports and findings. The techno-economic assessment is performed by developing a mathematical model using Excel. The model simulates all input- and output flows, utilities required and calculates the OPEX and CAPEX of the process. The techno-economical analysis is performed based on the reported system performance, composition of input and output streams and costs of materials and utilities. In the techno-economic analysis, the levelized production costs are calculated, sensitivity analyses on costs parameters are performed and eventually the expected future performance are determined.

3.1. Battery Limits

The battery limits refer to the area around a process unit, encompassing all parts parts and processes included in the unit or plant. Before a detailed process design is made for each pathway, the battery limits for the electrochemical and thermocatalytic routes are required. All processes, regardless of the conversion technology, are assessed at front-end system level. All pathways will include pre- and post treatment, conversion towards the desired product and downstream processing. Excluded will be the generation or production of inlet streams. Those will be seen as available in pure stream for a given price per unit. Below is listed what processes or units are considered as inside battery limits (ISBL) and outside battery limits (OSBL).

Inside battery limits:

- *Pre- and post-treatment of in- and outlet streams*
- *Electrolyzer cell stack or thermocatalytic reactor*
- *Down stream processing*

Outside battery limits:

- *CO_2 capture and purification*

- *Electricity generation*
- *Heat generation*
- *Hydrogen production*

Pre- and post-treatment of the in- and outlet streams includes the heating/cooling and compressing of the material streams of interest. Electricity is assumed to be produced by renewable sources and heat is generated using e-boilers. Heat required during the process is expressed in terms of kWh. During the process of generating heat by means of e-boilers, energy is lost. This loss is accounted for by applying an e-boiler efficiency. Similar to the pre-treatment, electricity or heat input required for the EC and TC conversion of CO_2 is delivered via renewable produced electricity. The last process considered to be ISBL is the downstream processing (DSP) of the product streams. DSP includes the separation of product- and recycle-streams and purification of the final product. Recycle streams may include streams of unconverted CO_2, H_2, catalyst or electrolyte recycled back into the conversion process. Processes considered to be OSBL are generation and production of the utilities and raw materials used during the process. The CO_2, H_2, electricity and heat consumed during the ISBL processes are considered to be available in pure streams into the system. The inlet streams are assumed to be available for a given price per unit sold. For raw materials the units will be Euro per kilogram and for utilities Euro per kWh. The design and modelling is carried out for a complete process at system level. The process will be designed as an autonomous conversion plant in order to provide an equivalent comparison between the different production pathways. The economics of by-products or integration possibilities to existing systems will not be considered. This is done to prevent routes from being wrongfully identified to be more favourable due to an advantage in, for example, downstream processing. If a part of a process design could be combined with an existing industrial process, it could affect the system boundaries and economics, causing a misleading comparison.

3.2. Use Case

For the design and modelling of the complete system, a generic use case must be defined that can be applied to all CO_2 conversion pathways. The use case must be applicable and reasonable for both electrochemical and thermocatalytical pathways. The purpose of the use case is to define the scale of operations, in terms of production capacity, assumed range of feedstock prices, and site of production. Scale of operations is of importance to be able to draw a comparison between the different pathways. To make a comparable analysis for the technical performances of the pathways, the same volume at the same rates must be produced. For the inlet streams of raw materials and electricity, a range of prices per unit is set. Similar as the scale of operations, the feedstock and utility prices are equal for all production pathways. A range is used to perform the analysis for several economic scenario's. The prices selected for the use case are based on the numbers used for the marginal costs analysis listed in table 2.4. Below an overview is given for the selected parameters for the generic use case.

Parameter	**Value**	**Motivation/Ref.**
Geographical location	Netherlands	Determined
Production rate [kg prod /hr]	1000	Determined
Full load hours [hrs/year]	8000	Determined
CO2 price [€/kg]	0.02 - 0.15	[5]
Electricity price [€/kWh]	0.02 - 0.05	[5]
Hydrogen price [€/kg]	1.71 - 3.71	[5]

Table 3.1: Overview of parameters selected for a generic use case applied to all process designs

3.3. Process Designs per Pathway

In this section, the process design of each CO_2R pathway is made and discussed in detail. Depending on the type of system, the cell stack or reactor are selected. The base case performance and operation conditions will be analyzed and the composition of products streams are determined. Based on the product streams and their composition, a design for the downstream processing is made. Scaling of the units is done base done molar streams and desired output. In the following sections, an extensive techno-economic assessment will be performed on the process designs discussed in this section. Figure 3.1 visualizes a schematic overview of how the process designs are structured. Included in the process designs are the pre-treatment units, CO_2 conversion units and DSP units. Feedstock materials and electricity are fed to the system, recycle streams are purified and recycled back to the relevant unit and by-products streams leave the system separated from the desired product and unconverted CO_2. All units are powered by renewable generated electricity. First the conceptual process designs are discussed. After that, analyses on the process performance are performed.

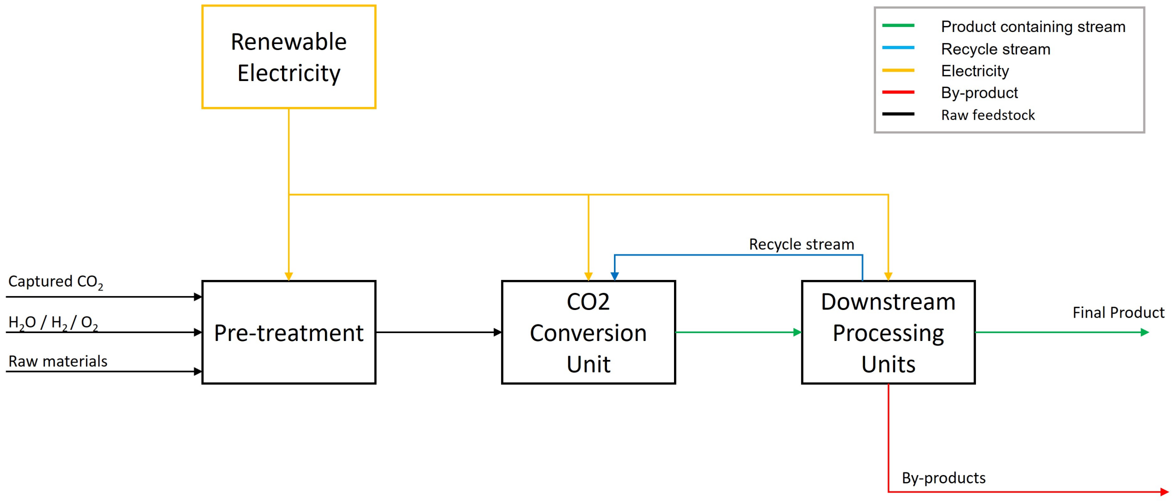


Figure 3.1: Schematic overview what is included in conceptual process design. Color-coded streams indicating type of stream. Corresponding stream types to colors indicated in legend.

3.3.1. Low Temperature Electrolysis Carbon Monoxide

The first process to be designed and analyzed is carbon monoxide produced via low temperature electrolysis. Carbon monoxide is a molecule that is used in a very broad range of applications for industrial operations and can be produced via various production pathways. Carbon monoxide is used for numerous applications and can be used for the fabrication of various chemicals. Another application for CO is as component in fuel gas mixtures and other gases for industrial heating. In this section the process design will be discussed along with the metrics of system performance.

In the process design, an electrolyzer stack and several DSP units are used. Figure 3.2 shows the schematic drawing of the process design with the corresponding composition of the product streams. The molar flow rates are calculated using the system's state-of-the-art performance mentioned in recent scientific reports and given in table 3.2. The composition of the product stream leaving the cathode is calculated using results reported by Jeng et al. [73]. The composition the stream leaving the anode compartment is calculated using the CO_2 utilization degree, faradaic efficiency and reaction stoichiometry.

Carbon monoxide can be produced via low temperature electrolysis in a 2-compartment cell stack, existing of an anodic and cathodic compartment separated by an ion exchange membrane [31][74]. For the LTE cell stack design, a membrane-electrode assembly was selected, utilizing Sustanion imidazolium-functionalized membranes. Base case conditions for the cell stack are adapted from Küngas et al. and Liu et al. [13][75]. A fixed current of 200 mA/cm^2 and a voltage of 3 V is applied, reaching high selectivity. The system operates with an Ag cathode and IrO_2 anode with both catalyst layers facing the membrane [75]. A schematic drawing of the cell with its electrochemical reactions and transport of ions through the membrane is pictured in figure 3.3.

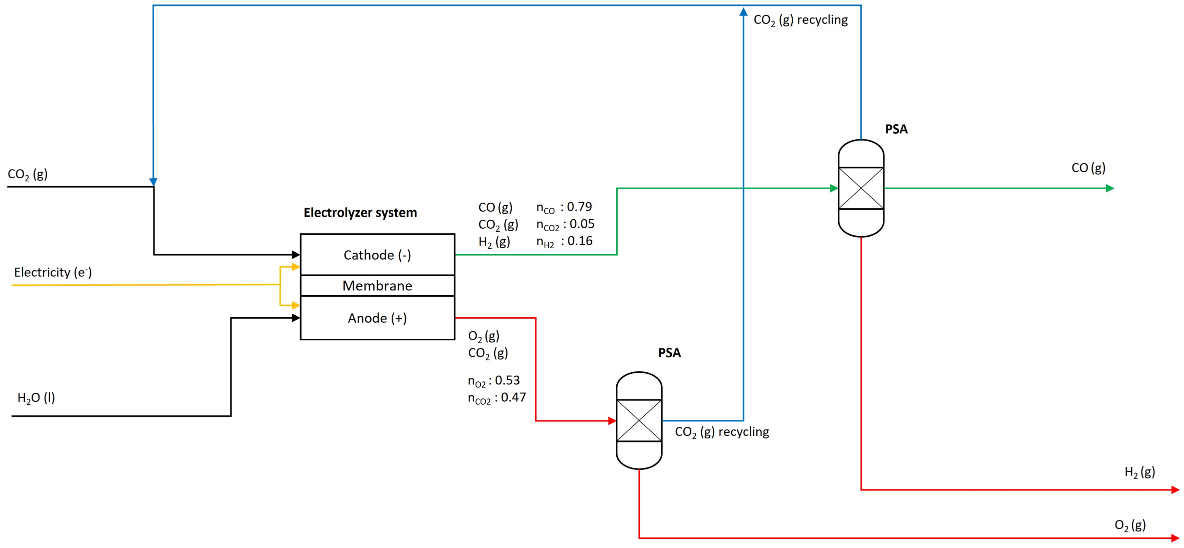


Figure 3.2: Process design low temperature electrolysis carbon monoxide production

Humidified CO_2 enters the system at the cathode and a 10 mM $KHCO_3$ solution at the anode. In an alkaline environment under influence of applied current, the CO_2 is reduced at the cathode to CO. As side reaction, water is reduced to H_2. During these reactions, OH^- anions are produced and transferred via the membrane to the anode, where O_2 is produced. The overall reactions occurring in the cell stack are given by equations 3.1 and 3.2. Due to unwanted side-reactions, carbonates and bicarbonates are generated and crossed over to the anode compartment via the membrane, as shown in figure 3.3. By-products from the reacted CO_2 are HCO_3^- and CO_3^- [73]. As the time of operational hours progresses, the reactivity and selectivity towards CO decrease and more by-products will leak to the anode compartment [76][77]. At the anode, the by-products react with O_2 to unwanted CO_2. Thus, the DSP design must take into account the presence of CO_2 in the product stream leaving the anode. The base case performance and operation conditions are listed in table 3.2.

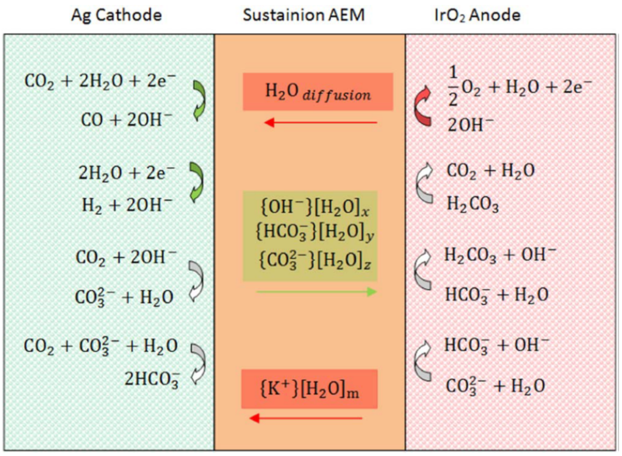


Figure 3.3: Proposed cell stack design for LTE CO production including reactions at anode and cathode and transport through membrane [75]

$$2CO_2 \rightarrow 2CO + O_2 \qquad E^0 = 1.33\,V \tag{3.1}$$

$$2H_2O \rightarrow 2H_2 + O_2 \qquad E^0 = 1.23\,V \tag{3.2}$$

Mixed gaseous streams leave the system at both compartments, the anode and the cathode. The process design consist of two pressure swing adsorption (PSA) units for the separation of the gaseous products. The stream leaving the anode compartment consists of O_2 and CO_2. Inside the first PSA unit, adsorbents are used to separate the CO_2 from the entering gas stream by attracting it to its surface. According to to Perez-Carbajo et al. PSA can be used for separating CO_2 from a mixture with O_2. Zeolites observed to be ideal for CO_2 separation are faujasite (FAU) zeolites[78]. Using zeolites as adsorbents, recovery rates over 90% are achieved [79]. Inside this PSA unit, the O_2 is separated and can be used as valuable product in other processes. To optimize the CO_2 utilization rate of the system, the unreacted and generated CO_2 is recycled back into the electrolyzer stack, closing the carbon loop.

The product stream leaving the cathode compartment consists of CO, CO_2 and H_2 in gaseous phase. The desired CO is obtained via adsorption in the PSA unit. The PSA process is developed to adsorb CO with high selectivity [80]. Since CO_2 binds more strongly to adsorbents, such as zeolites. An adsorbent is selected which has high selectivity towards CO. Using an activated alumina carrier with an impregnated carbon and copper compound as the active chemisorption species, CO can be recovered at high purity in a single stage, according to Kasyya et al. [80]. The purified H_2 stream leaves the system as by-product and can be used as valuable feedstock in other processes or sold as product. The unreacted CO_2 recovered from the product stream is recycled back into the system towards the electrolysis stack.

		Base	**Reference**
Cell voltage	V	3.00	[13][75]
Current density	A/m2	2000	[13][75]
CO faradaic efficiency	%	97%	[13][75]
CO_2 utilization degree	%	49%	[13][75]
Specific Energy Consumption	kWh/kg	5.92	Eq. 2.12
Installed capacity	MW	6.21	Calculated
Required electrode area	m2	1036	Eq. 3.14
Purity CO after PSA	%	99	[80]
Yield of CO	%	90	[80]

Table 3.2: Base case operation conditions and performances LTE CO production for a production capacity of 1000 kg CO per hour

3.3.2. High Temperature Electrolysis Carbon Monoxide

The second production pathway for carbon monoxide analyzed in this study is high temperature electrolysis of CO_2. Similar to LTE, the process design consist of an electrolyzer system and downstream processing units. The reaction is carried out under elevated temperatures and therefore a different type of cell stack is required and the product streams leaving the electrolyzer are different. In this section the process design of HTE CO production will be discussed along with the metrics of performance.

Figure 3.4 shows the schematic drawing of the HTE process design, including the cell, pre- and post-treatment units and DSP unit. Since no by-products are observed at the anode compartment and no CO_2 cross over occurs through the solid electrolyte [13][81][82], only a single DSP unit is required to process the stream leaving the cathode. The system operates at elevated temperatures, thus heating and cooling units are required. The composition of the flow leaving the cathode compartment is determined using the reported cell performance. The FE is 100% and the CO_2 utilization degree is 50% according to table 3.3. Due to the difference in molecular weight, the CO/CO2 ratio is 0.65/0.35. At the anode, only O_2 is produced so no molar ratio has to be determined.

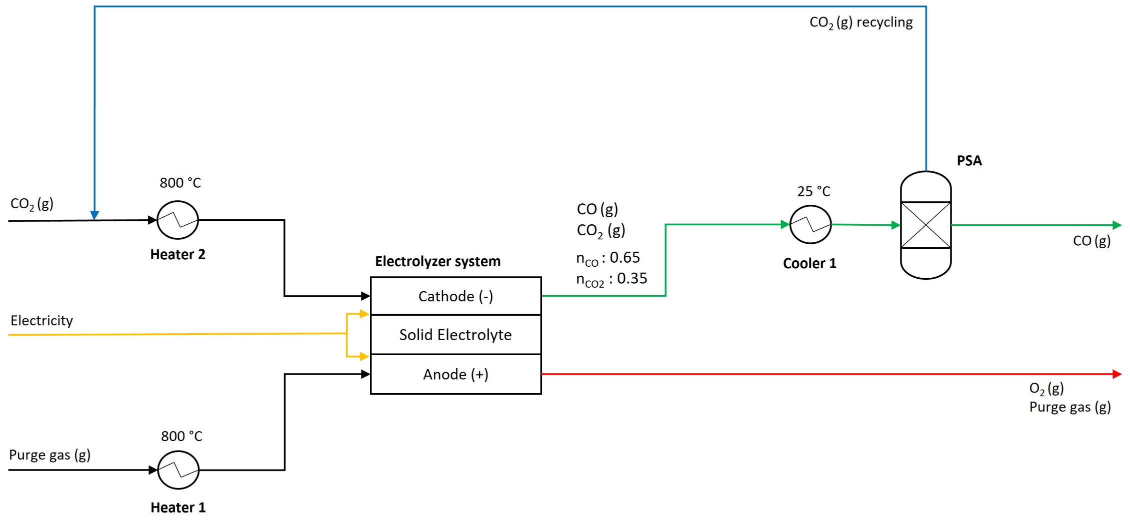


Figure 3.4: Process design high temperature electrolysis carbon monoxide production

For HTE cell stack design, a solid oxide electrochemical cell is used and set up as currently produced by Haldor Tospøe [83]. The base conditions for operations of the SOEC are adapted from Foit et al. and Küngas et al. [47][83]. A high current density of 750 mA/cm^2 was maintained at steady state at an applied voltage of 1.47 V. This results in high conversion rates. A schematic drawing of the SOEC with occurring electrochemical reactions is pictured in figure 3.5

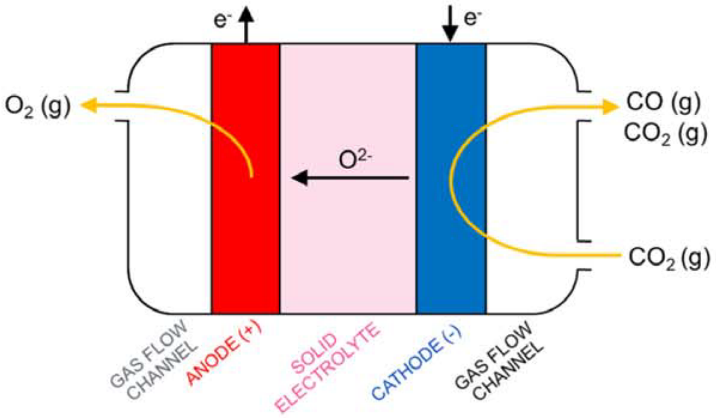


Figure 3.5: Proposed cell stack design for HTE CO production including reactions at anode and cathode and transport of anions through membrane [13]

The SOEC setup makes use of an solid ceramic electrolyte through which the oxide anion (O^{-2}) transfers towards the anodic compartment. The CO_2 enters the porous cathode in gaseous form and is reduced to CO and oxide anions. The O^{-2} anions are transferred through the electrolyte to the anode, where it reacts to O_2. The oxygen is then released from the anodic compartment via an purge stream of heated air [84]. Since there is no unwanted carbon cross-over, no separation unit is required for the oxygen stream. The desired CO leaves the cathode in a gaseous mixture of product and unreacted CO_2. In this process no H_2O is involved, therefore no unwanted side reactions occur. The overall chemical cell reaction is given by equation 3.3. The base case performance and operation conditions are listed in table 3.3.

$$CO_2 \rightarrow CO + \frac{1}{2}O_2 \qquad E^0 = 1.33\,V \tag{3.3}$$

One DSP unit is necessary for purification of the product stream leaving the SOEC system. Similar to

LTE production of CO, a stream of gaseous product is purified and CO_2 must be recovered. Again, a PSA unit is used in the process design. A similar unit is used, where the PSA is designed to adsorb CO with very high selectivity using an activated alumina carrier as stated by Kasuya et al. [80]. Unlike the product stream in the LTE CO process, there is no H_2 or other compound present. The purification process can be performed in a single stage PSA unit. Reducing the complexity, capital investment and operational costs of the unit. The unreacted CO_2 is recovered and recycled back to the SOEC. The desired CO is purified and leaves the system as product.

		Base	**Reference**
Cell voltage	V	1.47	[47]
Current density	A/m2	7500	[47]
CO faradaic efficiency	%	100%	[47] [83]
CO_2 utilization degree	%	50%	[47] [83]
Specific Energy Consumption	kWh/kg	2.84	Eq. 2.12
Installed capacity	MW	2.98	Calculated
Required electrode area	m2	271	Eq. 3.14
Purity CO after PSA	%	99	[80]
Yield of CO	%	90	[80]

Table 3.3: Base case operation conditions and performances HTE CO production for a production capacity of 1000 kg CO per hour

3.3.3. Thermocatalytical Carbon Monoxide

The final pathway for the production of CO analyzed in this study is thermocatalytical conversion. The conversion towards CO is achieved via hydrogenation of CO_2 under influence of heat in the presence of a catalyst. No current is applied to to run the reaction, however the heat required for running the reaction and pre-heating the streams will be generated using e-boilers powered by renewable electricity. Hydrogenation of CO_2 towards CO takes place via the catalytic reverse water gas shift reaction (RWGS). The product of the RWGS reaction is CO that can be applied industrially or a mixture of CO and H_2 (syngas). Whether the product is syngas or pure CO depends on the reactor design and H_2/CO ratio of the feed into the reactor [50]. Besides the reactor, heating-, cooling- and DSP units are included in the process design.

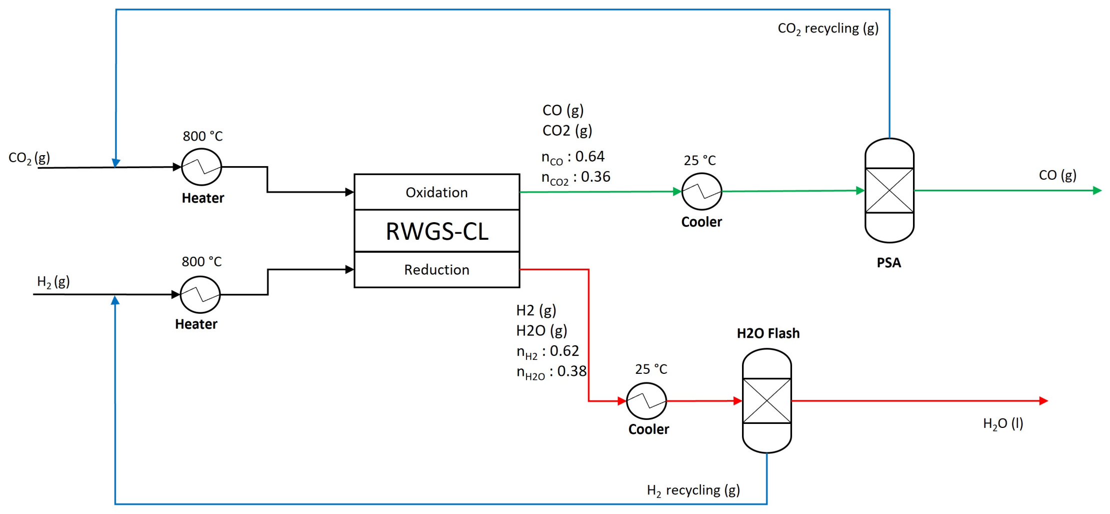


Figure 3.6: Process design thermocatalytical carbon monoxide production

Figure 3.6 shows the schematic process design of TC CO production including additional processing units. Inside the RWGS reactor the CO_2 is converted to CO by reacting with the H_2. The design of the reactor is based on a cyclic two-step process using a metal oxide as an oxygen storage material (OSM) [85]. This process is known as reverse water-gas shift chemical looping (RWGS-CL). The design splits the reactor into an oxidation and reduction compartment, similar to a electrolysis cell. Chemical looping improves the process efficiency since the reaction is split and yields in two different process streams [85][86][87]. Unwanted side-reactions are eliminated because the separated reactants and favorable thermodynamics. Hydrogenation via RWGS takes place at temperatures around 400°C, creating a thermodynamic unfavorable scenario at which the equilibrium is shifted towards the feed. RWGS-CL operates at temperatures around 800 °C, creating favorable thermodynamics resulting in less required excess of H_2 [86]. For the process design we adapted the cell design and OSM selection from Wenzel et al. [85]. Figure 3.7 illustrates the principles of process inside the RWGS-CL reactor. Two separate gas streams enter the reactor, in reaction with the Fe OSM the streams are reduced and oxidized. After some time the OSM is exhausted and the gas inlet compositions are switched, repeating the same process from opposite direction. The process is repeated creating a quasi-continuous yield of CO and H_2O over separate streams. The oxidation and reduction reactions occurring inside the reactor are expressed as equation 3.4 and 3.5 respectively. Reactor performance and conditions are adapted from Wenzel et al. [85] and Daza et al. [86] using mentioned reference values for RWGS stated by Pastor-Pérez [88] and listed in table 3.4.

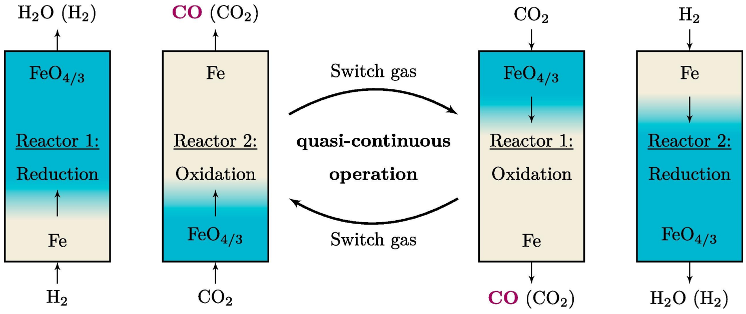


Figure 3.7: Schematic overview of RWGS-CL concept using two fixed bed reactors [85]

$$\frac{3}{4}Fe + CO_2 \rightarrow \frac{3}{4}FeO_{4/3} + CO \qquad \Delta H_R(1073K) = 8.98\,kJ/mol \tag{3.4}$$

$$\frac{3}{4}FeO_{4/3} + H_2 \rightarrow \frac{3}{4}Fe + H_2O \qquad \Delta H_R(1073K) = 27.86\,kJ/mol \tag{3.5}$$

Selecting the RWGS-CL reactor instead of RWGS reactor or other unit is because of the yield into split product streams. Increasing the selectivity and simplifying the DSP process. A gaseous mixture of CO and unreacted CO_2 leaves the system at at an elevated temperature. Before it enters the PSA unit for separation, the stream is cooled down to a temperature of 25 °C. Separation of CO and CO_2 is done similarly as previous processes, by using a PSA unit equipped with adsorbent material as described by Kasuya et al. [80]. Resulting in a pure stream CO and a recycle stream of CO_2 that is fed back to the reactor. The outlet of the reduction part of the reactor contains a mixture of H_2O and H_2. The stream is separated by a H_2O flash and the H_2 stream is recycled back to the reactor. Inside the flash unit, water is separated from the hydrogen via condensation [89]. The flash unit operates at a temperature of 35 °C. However, the reactor operates at an elevated temperature of approximately 800 °C. Thus, the stream is cooled down before it enters the separation unit. The separated H_2 is recycled back to the inlet stream, where it is heated again, and the H_2O leaves the system as by-product.

		Base	Reference
CO_2 selectivity towards CO	%	100	[88]
CO_2 utilization degree	%	64	[88]
H_2 selectivity towards CO	%	100%	[88]
H_2 utilization rate	%	38%	[88]
Reactor required flow capacity	m^3/hr	2162	Calculated
Purity CO after PSA	%	99	[80]
Yield of CO	%	90	[80]

Table 3.4: Base case operation conditions and performances TC CO production for a production capacity of 1000 kg CO per hour

3.3.4. Low Temperature Electrolysis Formic Acid

Formic acid is a carbolyxic acid and has several applications. Formic acid (FA) is mainly used as preservative and as antibacterial agent in livestock feed. Further, it can be used as an element of several chemical processes in various industries [90]. FA can be used as source for carbon monoxide and also act as intermediate in other production processes. FA can be produced via multiple CO_2R conversion routes. The first pathway analyzed in this study is LTE of CO_2 towards Formic acid. The selection of cell stack design, pre- and post-treatment and DSP is discussed in this section. A schematic drawing of the process design for the LTE FA production is shown in figure 3.8.

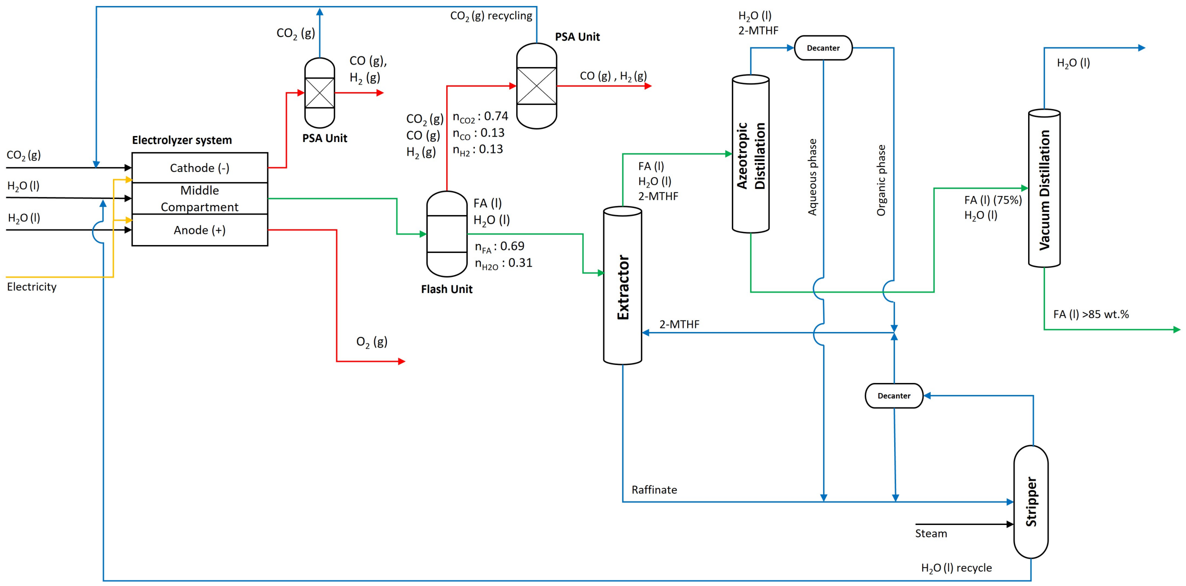


Figure 3.8: Process design low temperature electrolysis formic acid production

Low temperature electrolysis of CO_2 towards FA can be performed in various types of electrolyzer stacks. Both a 2- and 3-compartment cell can be utilized and a broad range of electrode materials and catalyst may be used. Proietto et al. performed an extensive comparative analysis on the different types of cell design and catalyst type [91]. The cell design considered to be most competitive with conventional production technologies was the 3-compartment cell design. For the process design, a 3-compartment cell was selected, using Sn-based gas diffusive electrodes (GDE's). Several studies have been performed on this cell setup showing high performances and steady long-term operation hours [92][93]. This design divides the cell into three compartments, separated from each other by Sustanion membranes. Reduction of CO_2 takes place in the cathode compartment by the electrochemical reaction with H_2O and electrons in the presence of the catalyst. Formate ($HCOO^-$) is formed together with hydroxide (OH^-) anions. In the anode compartment, H_2O is oxidized towards H^+ protons and O_2. The formate, OH^- and H^+ ions migrate through the membranes towards the center compartment where they react towards liquid H_2O and formic acid. The product is obtained from the center compartment via a stream of deionized water. Figure 3.9 illustrates the design of the cell stack including input and product streams. The desired chemical reaction inside different compartments are given by equation 3.6, 3.7, 3.8 and 3.9. According to Yang et al. [93] the only liquid products formed inside the cell were water and formic acid, and the only gaseous products that were showed by a GC analysis were H_2 and CO. According to Yang et al. H_2 and CO are formed due to decomposition of formed FA inside the middle compartment. Potential FA losses due to decomposition may be about 10% or less observed from GC. The H_2 and CO formed in the middle compartment were observed in equimolar amounts. Meaning undesired by-product is generated inside the cell and an additional DSP unit is required. Reported cell performance and and operation conditions are adapted from Yangt et al. [93] and Kaczur et al. [92] and listed in table 3.5.

$$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^- \tag{3.6}$$

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2 \tag{3.7}$$

$$H^+ + OH^- \rightarrow H_2O \tag{3.8}$$

$$H^+ + HCOO^- \rightarrow HCOOH \tag{3.9}$$

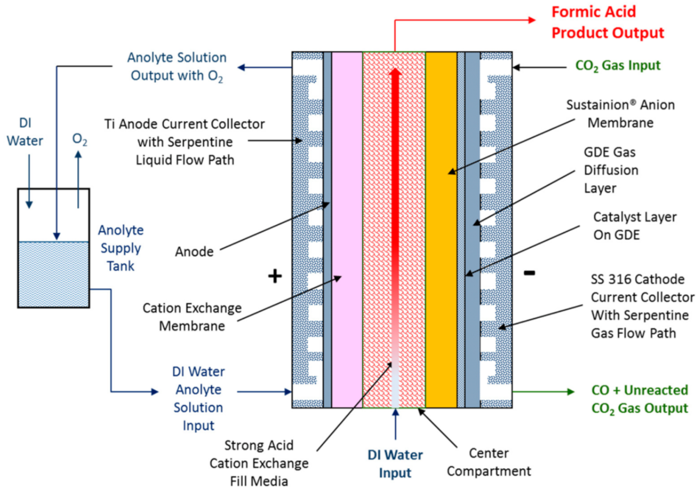


Figure 3.9: Proposed three compartment cell stack design for LTE FA production including input and product streams [92]

In the middle compartment, a mixture of gaseous and liquid products is formed. The mixture leaves the middle compartments due to deionized water put into the system. First, the different phases leaving the electrolyzer system are separated by flashing the gaseous products. The product stream, containing liquid FA and H_2O is now free from gaseous by-products. The further processing of the aqueous FA consist of several following distillation stages for the separation of FA and water. The process is designed based on recent reports on FA purification. This method consists of four distillation columns and is patented by BASF [94]. This process design is used in recent reports for the downstream separation of water and formic acid using the low boiling solvent 2-MTHF forming an azeotrope with H_2O [95][96][97]. The stream of dilute FA and water is fed into an extraction column which extracts the FA from the water using the solvent. The extract, containing the FA, is then sent to an azeotropic distillation column where the 2-MTHF-water azeotrope leaves via the top of the column and the FA via the bottom. The product stream is then fed into a vacuum distillation column to purify the FA. The concentrated FA leaves the column as distillate from the top with purity $\geq 85\%$. Separated H_2O leaves the distillation column at the top and can be recycled back to the electrolyzer system (the stream is not recycled in figure 3.8 to enhance readability). The heterogeneous 2-MTHF-water azeotrope is further processed using a stripper, condenser and decanter to separate the water and recover the solvent.

The gaseous products formed inside the middle compartment leave the flash unit as a mixture of H_2, CO and CO_2. A similar composed stream is encountered in the design of the LTE CO production. However, since were not interested in CO as product, a less complex separation unit is required. The separation unit is designed to separate the CO_2 from the gaseous stream and recycle it back to the cell stack. The CO and H_2 leave the system as syngas and can be used for other processes. The recovery of the CO_2 is done by a PSA unit using zeolites as adsorbent. A similar unit as in previous process designs is used as described by Wiheeb et al. [79] and Wilson et al. [98]. Using pressure swing on zeolite adsorbent, the CO_2 can be recycled back to the process. From the cathodic compartment, a gaseous mixture of CO, H_2 and unreacted CO_2 leave the system. Again, a similar PSA unit is used and the separated CO_2 is recycled. Inside the anodic compartment only O_2 is formed, no further DSP is necessary. The economics of the process design will be analyzed in the TEA section. The costs for the PSA units will be determined using the equations described in the methodology. However, the purification of FA from the product stream is not as generic as PSA and therefore requires a specific approach. Luckily, the separation of FA from H_2O is known and industrially applied process. Costs calculation for the extractor and distillation columns were adapted from Laitinen et al. [97]. Resulting in a total uninstalled investment costs for the distillation purification process of 6.7 M€. Further DSP costs, for the PSA and flash columns will be determined using the costs calculations discussed in the coming methodology section.

		Base	**Reference**
Cell voltage	V	3.75	[93]
Current density	A/m2	2000	[47]
FA faradaic efficiency	%	82%	[47] [83]
CO_2 utilization degree	%	41%	[47] [83]
Specific gy Consumption	kWh/kg	4.53	Eq. 2.12
Installed capacity	MW	4.75	Calculated
Required electrode area	m2	633.74	Eq. 3.14

Table 3.5: Base case operation conditions and performances LTE FA production for a production capacity of 1000 kg 85%wt. FA per hour

3.3.5. Thermocatalytical Formic Acid

The second pathway towards the production of formic acid is thermocatalytical reduction of CO_2. In the TC process design, formic acid is synthesised by the hydrogenation of captured CO_2 using H_2 produced via electrolysis. The synthesis of FA is performed via homogeneous thermocatalysis based on the process designed and patented by Schaub et al. [99]. The design by Schaub et al. is modelled and analyzed on its performance and economics by Pérez-Fortes et al. [49]. The process design based on the patent is visualized in figure 3.11.

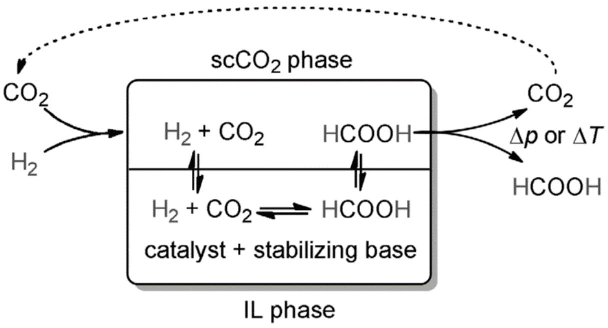
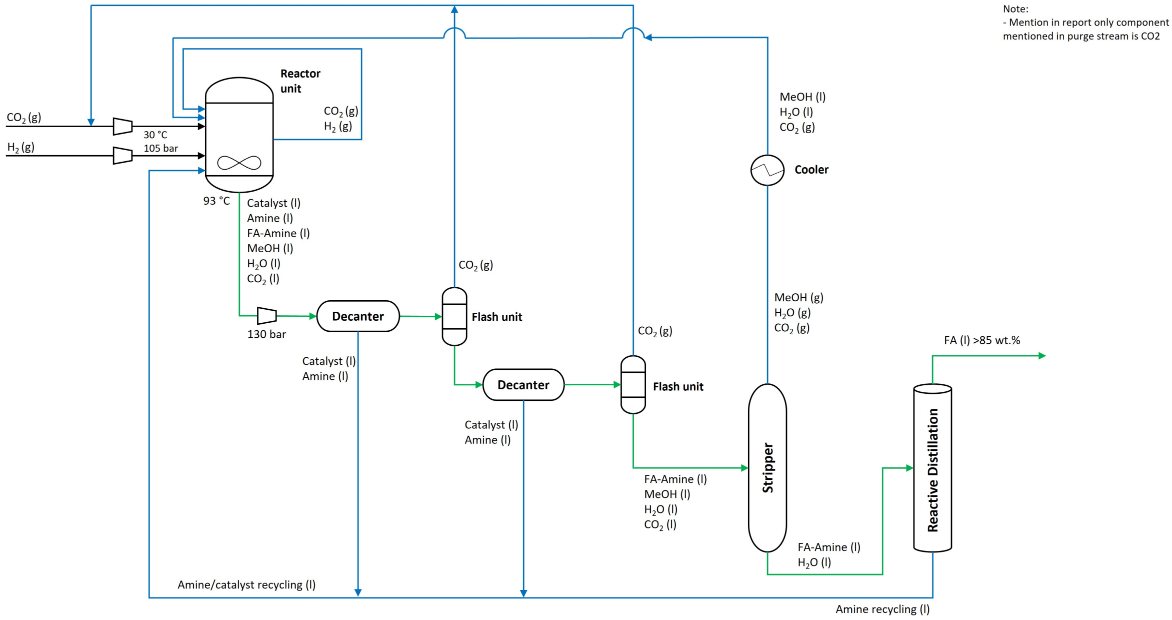


Figure 3.10: Direct CO_2 hydrogenation for FA production using catalyst and stabilizing base inside ionic liquid [100]

The process is designed to produce formic acid with a purity of ≥ 85%. The design consists of a reactor-, catalyst recovery-, methanol recovery- and product purification-stage. For this design the decision is made to use the same conditions as mentioned by Pérez-Fortes et al. [49] and are confirmed using the ranges stated in the patent by Schaub et al. [99]. The base case operation conditions are mentioned in table 3.6. The reactor operates at elevated pressures and an increased temperature, 105 bar and 93 °C respectively. The catalyst use in the process are homogeneous ruthenium- and phosphino-based catalysts. The reactor design, catalysts and components selections are based on different state-of-the-art laboratory studies [101][100][102]. A schematic overview of a continuous-flow hydrogenation process under presence of a catalyst is visualized in figure 3.10 [100].



Note:
- Mention in report only component mentioned in purge stream is CO2

Figure 3.11: Process design thermocatalytical formic acid production

The H_2 and CO_2 feed streams are compressed and enter the reactor, where they are mixed with an tertiary amine and a mixture of methanol and water (polar solvent). Inside the reactor, a chemical reaction between the two feed streams and amine occurs and an amine-FA adduct is generated (equation 3.10). A two-phase flow is formed inside the reactor existing of a gaseous mixture of unreacted CO_2 and H_2 and a liquid flow containing the desired product. The gaseous mixture leaving the reactor is recycled back to the inlet of the reactor. The liquid product stream leaving the reactor consists of two liquid layers, a heavy layer containing the product adduct and polar solvent, and a light layer existing of the tertiary amine and solved catalyst. The catalyst and amine are recovered and recycled back into the reactor via two stages of a decanter. After both decanters, flash vessels are placed to separate formed light gases from the liquid solution via a purge stream. Only formation of gaseous CO_2 is reported by Pérez-Fortes. Therefore, it is assumed the purge stream only exists of CO_2. Next, the product stream containing the amine-FA adduct, MeOH, water and dissolved CO_2 are fed into a stripper column. A mixture of MeOH, water and CO_2 leaves at the top of the column and is condensed before it is fed back to the reactor. The bottom stream leaving the stripper column consists of water and the amine-FA adduct and is fed into a reactive distillation column to obtain the final product. Inside the distillation column, the amine-FA adduct is dissociated thermally into FA and free amine (equation 3.11). The free FA is removed by distillation and the free tertiary amine collected in the bottom of the column being recycled back to the hydrogenation reactor. The FA product is obtained as an aqueous mixture comprising about 85 wt.% [99]. This process design suggests a 100% catalyst, amine and methanol recovery. However, in practice this is not possible and for the economic analysis degradation and costs of renewing components should be accounted for. This will be discussed in more detail in the economical analysis together with the assumptions made.

$$CO_2 + H_2 + C_{18}H_{39}N \rightarrow C_{18}H_{39}N - HCOOH \tag{3.10}$$

$$C_{18}H_{39}N - HCOOH \rightarrow C_{18}H_{39}N + HCOOH \tag{3.11}$$

		Base	Reference
CO_2 selectivity towards FA	%	81%	[49]
CO_2 utilization degree	%	98%	[49]
H_2 selectivity towards CO	%	63%	[49]
H_2 utilization degree	%	19%	[49]

Table 3.6: Base case operation conditions and performances TC FA production

3.3.6. Low Temperature Electrolysis Oxalic Acid

The last molecule analyzed as CO_2R product is oxalic acid. Oxalic acid (OA) is the simplest dicarboxylic acid. Oxalic acid's main uses are for textile finishing and cleaning, metal and equipment treatment and could serve as chemical intermediate for other oxalates [103]. Oxalic acid is an organic compound found in plants, but can also be produced via synthesis. In this study, a process design for the LTE pathway from CO_2 towards OA is made and analyzed based on its performance. LTE production of OA is an immature technology and therefore studies and reports found on this technology are limited. LTE conversion towards OA is only demonstrated on laboratory scale at a maximum of TRL 3, therefore assumptions on the scaling and DSP must be made.

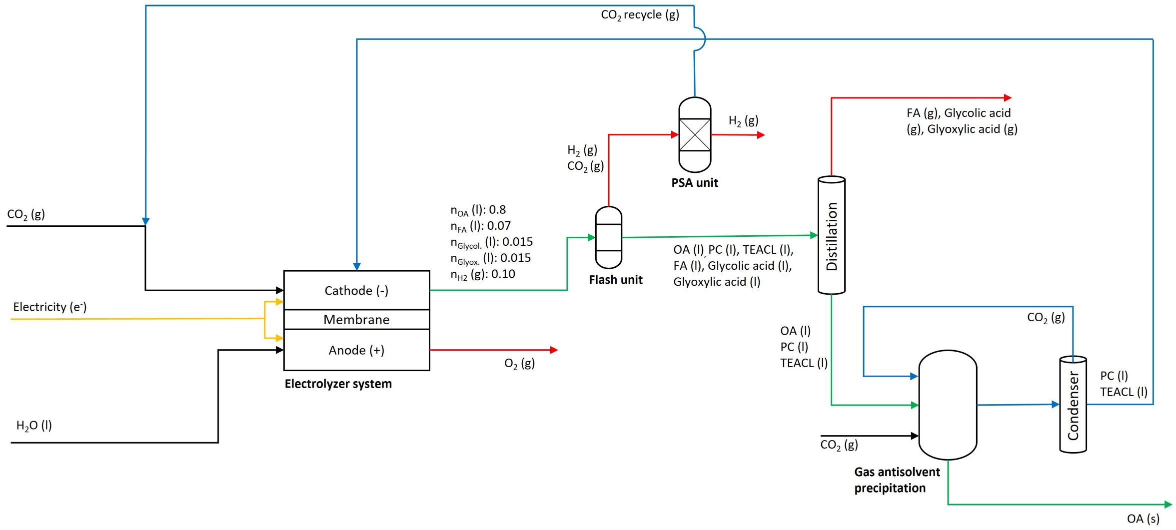


Figure 3.12: Process design low temperature electrolysis oxalic acid production

In figure 3.12 the schematic process design for the LTE production of OA is visualized. Since electrochemical production of OA is only tested on laboratory scale, decisions and assumptions on cell design and DSP are more rough than for other processes. The cell design is based on experimental setups designed by Ikeda et al. [104] and Boor et al. [105]. Electrochemical production of OA is in somewhat more complex than the production of other products such as CO. The product formed depends on the type of electrolyte and electrode material used in the cell. Oxalic acid is obtained in non-aqueous solvents on lead, thalium and mercury electrodes [104]. The design is a 2-compartment cell using a Pt anode and Pb cathode separated by a cation exchange membrane (CEM). For the most efficient conversion towards OA, the selected electrode materials were used and 0.5M H2SO4 as anolyte and 0.7M tetraethylammoniumchloride (TEACl) in propylene carbonate (PC) as catholyte in combination with a cation exchange membrane [104][105]. The metrics of performance were adapted from experiments reported by Boor et al. and listed in table 3.7.

The anolyte is pumped through the anodic compartment. It is not reported what reactions occur inside the anodic compartment. However, it is stated that H^+ ions are generated and migrate through the membrane. The CO_2 is fed to the cathode compartment, where it is in solution with the TEACl and PC. Under influence of the applied current the CO_2 is reduced to CO_2^- and reacts towards oxalate ($C_2O_4^2-$). This reaction mechanism is visualized in figure 3.13. The oxalate then reacts with the H^+ ions towards oxalic acid in liquid phase. Due to the complex conversion process, multiple unwanted by-products are produced. The production of unwanted products decreases the faradaic efficiency towards oxalic acid. This is due to the migration of H_2O via the membrane towards the catholyte overtime. By-products observed in the cathode compartment were formic acid, glycolic acid and glyoxylic acid in liquid phase and H_2 in gaseous phase together with unreacted gaseous CO_2. Separation of the gaseous stream can easily be done using existing technologies.

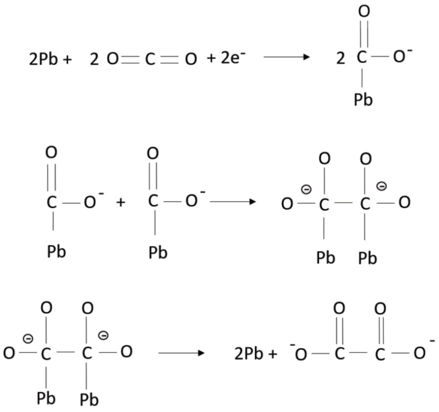


Figure 3.13: Reaction mechanism of the generation of oxalate on Pb surface as described by Eneau-Innocent [106]

The oxalic acid is formed in a non-aqueous solution with TEACl and PC together with the by-products and unreacted gaseous CO_2 and H_2. The product stream consists of liquid and gaseous components. Table 3.8 lists the properties related to the separation of the liquid stream and gives fundamentals for the design of the DSP process. For the product stream leaving the cathodic compartment, a flash unit is used to separate the gaseous H_2 and CO_2 from the liquid product stream. Followed by a PSA unit using zeolites as adsorbent to separate the unconverted CO_2 from the H_2 and recycle it. A similar PSA unit is used as in previous process designs, described by Wiheeb et al. [79] and Wilson et al. [98]. Current studies performed on LTE production of OA, have not reported successful methods for separation of OA and its byproducts. Therefore, the design of the DSP is incomplete and based on multiple assumptions. Recent studies have shown results for recovering PC and purifying oxalic acid from a mixture of OA in solution with PC [105]. This separation method is adapted into the current process design for LTE OA production and estimated at a maximum TRL of 2. The solvent is recovered from the mixture via gas antisolvent precipitation (GAP). For this process, pressurized CO_2 is fed to the mixture in order to expand the solution. This causes the OA to crystallize and form a solid product at the bottom of the unit. According to the report, supported by a similar experiment by Shishikura et al. [107], GAP effectively purifies OA to a solid product and recovers PC to be recycled into the process. However, more extensive research is required to better understand and be able to scale up the separation process. This study did not mention the presence of TEACL in the solution. For the separation of TEACl from the mixture, experimental research must be conducted. It is assumed the TEACL leaves the GAP unit in a liquid stream together with the PC.

		Base	Reference
Cell voltage	V	4	[105]
Current density	A/m^2	1000	[105]
OA faradaic efficiency	%	80%	[105]
CO_2 utilization degree	%	60%	[105]
Specific Energy Consumption	kWh/kg	2.98	Eq. 2.12
Installed capacity	MW	3013	Calculated
Required electrode area	m^2	781.45	Eq. 3.14

Table 3.7: Base case operation conditions and performances LTE OA production

No reports were found on processing the undesired by-products. Based on the chemical properties and boiling point, the selection for distillation is made to separate the boiling point. The heat of evaporation for OA and PC is higher than the by-products. However, no proven research or reports on this method are found. Since there is no scientific data available on the liquid mixture formed, it is impossible to ensure that any azeotrope is formed. For this design, it is assumed that no azeotrope is formed and that, based on the boiling points mentioned in the properties table 3.8, distillation would be a suitable technique of separation. A mixture of liquid OA, PC and TEACL leaves the bottom of the distillation column and is fed into the GAP unit. Further research must be conducted on which separation processes are suitable and what units are required. Additionally, improvements on the cell design could prevent undesired side-reactions by preventing the catholyte from becoming aqueous due to water migration. This could be achieved via adjusted operation conditions or utilizing selective membranes [105]. However, for now the process design is far from complete. All assumptions and design decisions are made with the objective of being able to estimate the capital and operational costs of the production process.

Properties	**Unit**	**OA**	**TEACl**	**PC**	**FA**	**Glyc. Acid**	**Glyox. Acid**
Chemical formula		$H_2C_2O_4$	C_8H_20ClN	$C_4H_6O_3$	HCOOH	$C_2H_4O_3$	$C_2H_2O_3$
Molecular weight	g/mol	90	165,7	102	46,025	76,05	74,04
Boiling point	°C	160 (subl.)	n.a.	242	101	100	111
Density	g/cm3	1,9	1,08	1,2	1,22	4,49	1,34
Solubility in water	g/L	90-100	very soluble	240	477	600	224

Table 3.8: Chemical properties of compounds involved in the product stream of electrolyzer

3.4. Design and Costing Analysis Methodology

Using the process designs made in previous section, the levelized production costs for each process are determined using equations for the costs and scaling of conversion and separation units adapted from scientific reports. The costs of production are divided into a range of contributing categories. These categories include:

- *Operational costs*
- *CAPEX conversion unit*
- *CAPEX DSP units*
- *Stack/reactor replacement cost*
- *Operating and maintenance*

In this section, the design and costing analysis methodology is discussed and assumptions on costing of the process are made. The main costs drivers behind the costing categories are discussed. The assumptions for the general costs contributors are discussed. These include the conversion units and generic DSP units. Besides the operation units, also additional costing factors will be accounted and discussed. The costs contributors discussed in this section are general and applicable to most processes.

Some processes contain more specific units or complex sequences. These specific units/sequences are not discussed in the methodology due to their unique approach. Assumptions made for the non-generic capital and operational costs are mentioned in appendix B.

3.4.1. Low Temperature CO_2 Electrolyzers Costs

For the electrochemical pathways, one of the most important unit in the process design is the electrolyzer. The design of the electrolyzer should incorporate state-of-the-art technologies and performances for carbon dioxide electrolysis. Currently, no standard design for CO_2 electrolyzers is industrial available and many different cell configurations are reported. To be able to make an estimation for the capital costs of the electrolyzer system, water electrolysis systems are used as reference. Non-precious metals can be used as catalyst in the electrochemical reduction of CO_2, making the assumed comparison to water electrolysis suitable [30]. Commercial CO_2 electrolyzers are expected to be comparable in design to the current PEM water electrolyzers [108]. For low temperature CO_2 electrolysis, a PEM water electrolyzer configuration was used as reference. The performances of commercialized water electrolysis stated by Ionomr Innovations [109] and Hydrogen Europe [110] are listed in table 3.9. The investment costs per kWh mentioned are considered to be uninstalled costs. Meaning the investment costs mentioned, refer to the material costs required for the electrolyzer system. Installed costs are determined by applying a factor to the uninstalled costs, including the subcontracted costs, associated direct labor costs and material needed for the installation of the electrolyzer system [111]. The installation factor differs per conversion technology. For low temperature CO_2 electrolyzer systems the installation factor is assumed to be 80% of the uninstalled investment costs based on a previous model by TNO.

Parameter	**Unit**	**Current**	**Near-term**	**Optimistic**	**Reference**
Investment costs	€(2020)/kWh	1050	700	500	[109] [110]
Current Density	A/cm^2	1.8	2.4	3.5	[110]
Cell Voltage	V	1.9	1.8	1.5	[110]
Faradaic efficiency	%	99%	100%	100%	[110]

Table 3.9: Current and future costs and performance for PEM water electrolysis

The reference values mentioned in table 3.9 are used to calculate the capital expenditure (CAPEX) for the CO_2 electrolyzer system. The breakdown of a PEM electrolysis system are listed in table 3.10. First the cell stack costs per kWh are determined for the reference electrolyzer using the rates stated by Patonia et al. [112]. With this, the reference costs per electrode area can be calculated. Using the required electrode area for the CO_2 electrolyzer, the uninstalled cell stack costs are obtained. Using the breakdown by Patonia et al., the total uninstalled investment costs for the CO_2 electrolyzer system are determined.

Using the equations adapted from Shin et al. [31], the investment costs are calculated for the LTE systems. With equation 3.12 the reference costs per electrode area in €/m^2 is determined. Where *Costs stack* represents the costs of the reference PEM cell stack in €/kWh, *CD* the current density in Ampere/cm^2 and *CV* the cell voltage of the PEM electrolyzer. Equation 3.13 is used to calculate the productivity per electrode area in kg/h.m^2 of the Co_2 electrolyzer. Where *FE* represents the faradaic efficiency in %, *capacity* the installed capacity in MW, ne^- the numbers of electrons transferred and *F* the Faraday constant. Equation 3.14 is used to calculated the total required electrode area of the CO_2 electrolyzer cell stack. Finally, equation 3.15 is used to determine the total uninstalled costs of the CO_2 electrolyzer cell stack. With the breakdown of costs, the total investment costs for the electrolyzer system can be determined.

$$Ref.\, electrolyzer\, cost\, per\, area \,=\, Costs\, stack \,*\, CD \,*\, CV \,*\, \frac{kW}{1000} \tag{3.12}$$

$$Prod.\, per\, area \,=\, (\frac{CD * FE * Capacity}{ne^- * F}) \tag{3.13}$$

$$Area\,required \;=\; \frac{[\frac{kg}{hr}]}{Prod\,per\,area} \tag{3.14}$$

$$Stack\,Costs \;=\; \frac{Area\,req. * Ref.\,costs}{Capacity * 1000} \tag{3.15}$$

The breakdown rates are then used for determining the total uninstalled investment costs of the electrochemical cell. The scaling method is considered to be applicable for each electrochemical pathway evaluated in this study.

	PEM	**SOEC**
Cell Stack	60%	30%
Power electronics	15%	30%
Gas conditioning	10%	6%
Balance of plant	15%	34%

Table 3.10: Costs breakdown of total uninstalled investment costs electrolyzer system for PEM and SOEC water electrolysis in percentage. Numbers adapted from Patonia et al. [112]

3.4.2. High Temperature CO_2 Electrolyzers Costs

Similar to the low temperature electrolysis, the design of the high temperature electrolyzer incorporates state-of-the-art technologies and performances of high temperature carbon dioxide electrolysis. In this study, high temperature electrolysis of CO_2 is only considered for the production of carbon monoxide. For the process design of the HTE system, the solid oxide electrolysis cell (SOEC) design from the study by Küngas et al. is used [13]. For high temperature CO_2 electrolyzers, a solid oxide electrochemical cell for water electrolysis is used as reference. The reference performance of commercialized HTE stated by Hydrogen Europe [110] and Böhm et al, [113] are listed in table 3.11. The costs breakdown of SOEC systems is listed in table 3.10. Capital expenditures and required investment costs per installed kWh are determined using the same calculations performed on LTE, using equations 3.12, 3.13, 3.14 and 3.15.

Parameter	**Unit**	**Current**	**Near-term**	**Optimistic**	**Reference**
Investment costs	€(2020)/kg	2215	1250	520	[113] [110]
Current Density	A/cm^2	0.60	0.85	1.5	[110]
Cell Voltage	V	1.50	1.30	1.30	[110]
Faradaic efficiency	%	99%	100%	100%	[110]

Table 3.11: Current and future costs and performance for SOEC water electrolysis

3.4.3. Thermocatalytical Reactors Costs

Conversion of CO_2 inside a thermocatalytic reactor is achieved using heat and hydrogen under the presence of a catalyst. Unlike the electrochemical process, no reference reactor is used for scaling costs and performances. Feedstock use and catalyst lifetime differ per conversion pathway, thus no generic reference model could be drawn. Capital costs of for TC routes are based on the investment costs of the reactor and catalyst costs. Reactor costs are based on the size and productivity and catalyst costs on activity and degradation. Cost assumptions for the thermocatalytic-reactor are based on the calculations performed by Huang et al. [5] using the relation given by equation 3.16. The CAPEX is calculated as uninstalled costs for the reactor system in Euro. Where X represents the flow of product in unit of million standard cubic feet (MMscf) per hour. The installation factor is for the reactor system adapted from [5] and set to be 160% of the total uninstalled investment costs for the reactor.

$$CAPEX = \left(\frac{X}{12.5}\right)^{0.6} * \$872,300 \tag{3.16}$$

The catalyst costs for the two pathways differ per reactor. RWGS is an established reaction and catalysts used in the process are optimized over time. Therefore, catalyst costs can be considered to be included in the CAPEX calculated using equation 3.16. TC production of FA on the other hand, makes use of a homogeneous catalysts. In the reaction, homogeneous catalysts are depleted and cannot be recovered. Catalysts are replaced each year according the assumed consumption stated by Pérez-Fortes et al., increasing the costs significantly. Costs for catalyst material are obtained from Sigma-Aldrich [114][115].

3.4.4. Product Separation Costs

During the process of CO_2R, not all carbon dioxide is converted towards the desired product. By-products are formed and molecules are not converted and leave the stack or reactor in their original form. To end up with the desired product in a pure stream, downstream separation is required to separate by-products and to recycle unreacted CO_2 from other gaseous products back to the upstream process. [32]. The recycle of CO_2 helps closing the carbon loop, since no carbon emissions leave the system, and lowers the required input feed of raw materials. For the purification and separation of the streams leaving the EC or TC systems, different technologies are used. The most common separation unit for all process designs in this study is the pressure swing adsorption (PSA) unit. This method can be used to separate various gaseous streams, such as a stream combined of CO and CO_2 [116]. The investment costs for downstream PSA can be determined using equation 3.17, adapted from Shin et al. [31]. Using the equation, the CAPEX for the PSA separation unit is determined in euro's. Where the product stream is the mixture of gaseous products entering the PSA unit in cubic meter per hour and the reference capacity is 1000 cubic meter per hour. These capital expenditures are based on existing separation/recycle processes of electrolysis systems deployed in industry. Equation 3.17 can be used to scale the PSA unit to the size required for the process. The PSA utility needs in kWh per kg of product are calculated using equation 3.18. Where X represents the input stream into the PSA in m^3 per hour, 0.25 the kWh required per m^3, and *product per hour* the system production in kg per hour.

$$PSA\,CAPEX \; = 1,794,492\,EUR * \left(\frac{product\ stream}{Ref.\ cap.\ [\frac{m^3}{hr}]}\right)^{0.7} \tag{3.17}$$

$$PSA\,OPEX \; = \; X \; * \; 0.25 * \; (\frac{1}{product\,per\,hour}) \tag{3.18}$$

Besides PSA units, also other units used for separation or recycling are present in the process designs. Examples of these units are H_2O flash, different types of distillation towers, crystallization units, et cetera. These units are dependent of the process design and product, and are part of larger separation system designs. Since these designs are unique for each process, assumptions on their costs calculations are stated in appendix B.

3.4.5. Operating and Maintenance

For the operating and maintenance (O&M) costs an annual rate is applied. For the yearly maintenance costs, a rate of 4% is applied over the total installed costs and levelized to costs per kilogram. This percentage is based on rates used in the PEM water electrolysis industry [117][118][119]. The O&M rate is applied on the installed costs of electrochemical and thermocatalytical processes. For other processes, such as DSP and pre-treatment, the same annual rate was used since previous studies have shown that these units are not a significant part of the total O&M costs [118]. Thus, the assumption of an annual O&M rate of 4% generic for all installed costs encountered in the process design is made.

3.4.6. Replacement Costs

Both, the stack and reactor unit are assumed to be replaced after a lifetime of operation. Catalysts replacement for TC reactor units are not included in these costs, those are handled as separate costs. Using the plant's lifetime, FLH's and the lifetime of the electrolyzer system or TC reactor, the costs of replacement is determined. The electrolyzer/reactor is assumed to be replaced after 65,000 hours of cumulative operation at a costs rate of 30% of the uninstalled costs [120]. The plant life time and FLH's are listed in table 3.13. The contribution of the replacement costs to the total costs of production per kilogram of product in EUR/kg is calculated using equation 3.19. Where *FLH's* represent the full load hours per year, *Plant lifetime* the expected lifetime of the complete production plant in years, *Electrolyzer/Reactor lifetime* the assumed cumulative operational hours before replacement and the *uninstalled costs* the investment costs of the uninstalled reactor or electrolyzer system in EUR/kg of produced product.

$$Replacement\,costs\ = \frac{FLH's\,*\,Plant\,lifetime}{Electrolyzer/Reactor\,lifetime} * 30\% * uninstalled\,costs \tag{3.19}$$

3.4.7. Operational Costs

The operational costs refer to the feedstocks and utilities used for the CCU process. These operational costs include water, H_2, CO_2, electricity and heat use. Hydrogen and CO_2 used for the conversion processes are assumed to be available as input stream. Capturing CO_2 and producing H_2 are considered outside battery limits. Utility costs involved in these processes are therefore not considered. The quantity of feedstocks required is calculated according to reaction stoichiometry and conversion performance. These quantities vary per process. Electricity needs for the conversion process are determined for EC processes using the SEC and for TC processes using literature. Electricity needs for the DSP are determined according the equations on DSP OPEX are stated in appendix B together with calculations on heat and cooling utilities. For the production costs analysis, the base case values for the feedstock and utility prices are used. This was done intentionally to have a range both ways for the sensitivity analysis. The feedstock prices used for the production costs analysis are listed in table 3.12.

Input	**Costs**	**Reference**
CO2	0.05	[5]
H2O	0.001	[5]
H2	2.73	[5]
Electricity	0.03	[5]

Table 3.12: Feedstock and utility prices used for the levelized production costs analysis.

3.5. Techno-economic Analysis

To make a comparison between the different products and conversion pathways, a comparison on technical and economical performances is performed. To perform the analysis, several assumptions were made and general parameters were set for all pathways. The assumptions and parameters are mentioned in the sections on the Battery Limits, Use Case and Design Analysis Methodology assessed at the beginning of this chapter. To estimate the financial performance of each pathway, and thereby the feasibility of producing the product, a model is developed to calculate the production costs per kilogram of each product and technology of production. The costs of production were calculated as the investment costs for the electrolyzer system or hydrogenation reactor, downstream processing costs, operational expenditures for the complete system, replacement costs and operation and maintenance costs. Using this model a comparison was made between the levelized production costs of the different products. To take into account the uncertainties in the production parameters and how those affect the system performance, sensitivity analyses are performed. After that, an analysis is performed on the expected future performance of each system. Hereby assumptions are used to determine what possible future performance could be and how those would affect the economic feasibility of the system.

3.6. Production Costs Analysis

The production costs per kilogram for each product per conversion technology, using base case data and assumptions are visualized in figure 3.14. The costs are broken down into different segments contributing to the total costs of production. The CAPEX includes the total investment costs for the conversion process and DSP, annualized and levelized to costs per kilogram of product produced by the system. The OPEX includes the variable costs of raw material required for the production of one kilogram of desired product. Heating/cooling of streams is done by the use of e-boilers where an efficiency of 95% is applied and is expressed in $[\frac{kWh}{kg}]$. Further, costs are included for the replacement of the cell stack or reactor used in the process design.

For the calculation of the total production costs, several rates are applied to cope with several factors affecting the economics such as depreciation, operating and maintenance and owner costs. Table 3.13 gives an overview of base case rates applied. The discount rate is and the plant lifetime are used to calculate the capital recovery factor (CRF). The CRF is a ratio used to determine the present value of a series of equal annual cash payments which is used to annualize the capital expenditure costs and determine its contribution to the total investment costs per kilogram produced. The CAPEX owner costs is used to determine the total costs of ownership for the capital expenditures and is applied on top of the total investment costs (TIC). Finally, the stack/reactor replacement costs are calculated using the plant life time, full load hours (FLH's) and the lifetime of the stack/reactor. For the life time a generic value is chosen for both conversion types, electrochemical and thermocatalytical. By assessing all investment-, feedstock-, operational- and factors affecting the overall-costs, the costs for each conversion pathway are determined using the assumptions and methodology described in sections 3.1, 3.2 and 3.4.

Factor	**Unit**	**Base**
Discount rate	%	10
CAPEX owner costs	% of TIC	10
CAPEX installation factor	% of uninstalled costs	80
O&M	% of TIC	4
Plant life time	years	20
FLHs	hours/yr	8000
Stack/reactor lifetime	hours	65000

Table 3.13: Factors and rates used in calculating the production price per kilogram

3.6.1. Results

The total production costs per kilogram of product at base case conditions are given in figure 3.14. The bar chart clearly indicates by the colored blocks, all contributing expenses and their influence on the total production price. The total costs are indicated on top of the bar chart and all contributing factors are mentioned in the legend.At the base case conditions and the state-of-the-art scenario, LTE is the least performing technology. Whereas other technologies for similar molecules seem to perform better. This is mainly due to the high capital costs for the cell stack. Due to relative low cell performances for LTE CO_2 cell stacks compared to those of PEM water electrolysis (for CO 3.00 V & 2000 A/m^2 vs. 1.9 V & 18000 A/m^2 respectively) the required electrode area is significant larger compared to HTE (1.75 V & 7500 A/m^2 vs. 1.30 V & 8500 A/m^2) and the relatively mature TC technologies. The high performance of a PEM water electrolysis cell per area of electrode results in a high electrolyzer costs per area. Calculating the costs per area using equation 3.12, result in 19053 $[\frac{€}{m^2}]$ and 5980 $[\frac{€}{m^2}]$ for LTE and HTE systems respectively. The large required electrode area and high costs per electrode area for LTE causes the high capital investment costs. The costs of production, deviation from market price and noticeable contributors are listed in table 3.14. Costs for EC pathways are dominated by cell stack investment costs. Contribution of captured CO_2 or electricity costs are less dominant than expected. In general, it is noticeable from the graph that DSP costs are no major contributor to the overall costs. HTE CO production shows the most potential to be competitive with the current market price. Based on the analysis, it is observed that for HTE CO production, which tend to be closer to commercialization, the costs contribution of captured CO_2 and electricity is more significant.

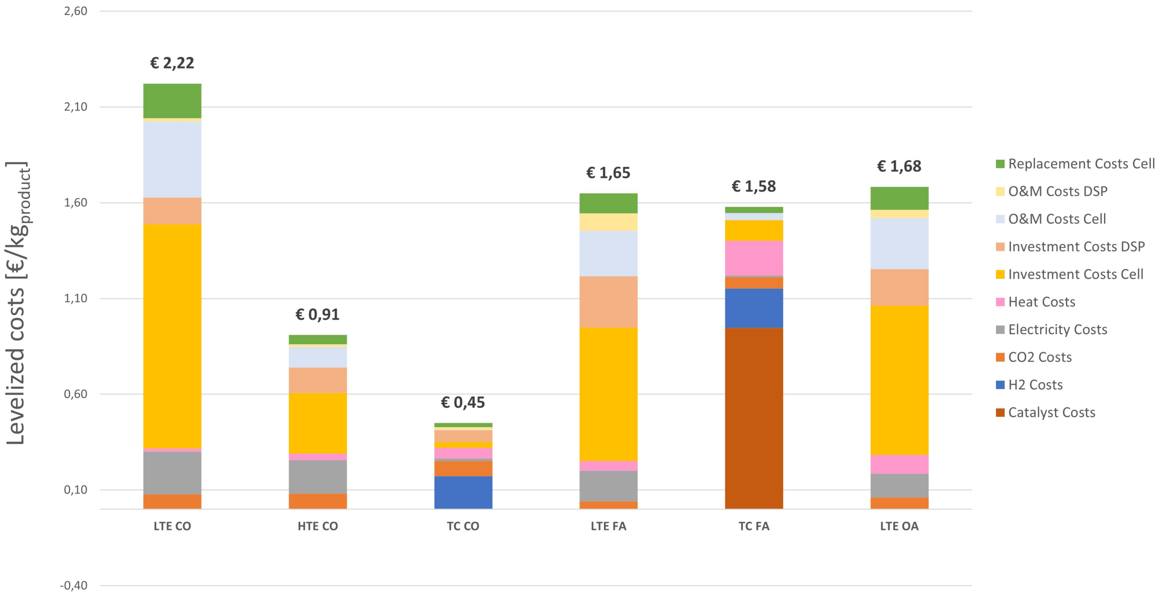


Figure 3.14: Production costs per kilogram for each production pathway for a production capacity of 1000 kg of product per hour for 8000 hours per year. Base case conditions applied for calculations as listed in table3.13.

Product	Market price $[\frac{e}{kg}]$	Prod. costs $[\frac{e}{kg}]$	Deviation	EC system [%]	CO_2 [%]	Electricity [%]
LTE CO	0.53	2.22	319%	53%	4%	10%
HTE CO	0.53	0.91	72%	41%	9%	20%
LTE FA	0.62	1.65	166%	42%	3%	10%
LTE OA	0.47	1.68	257%	46%	5%	13%

Table 3.14: Production costs CO_2 electrolysis products and deviation from current market price, together with contribution of cell stack-, CO_2- and electricity costs in percentage of total production costs. Based on results visualized in figure 3.14.

For the electrochemical pathways, the breakdown of investment costs is visualized in figure 3.15. The graph is visualized to give a better understanding of what costs are included in the CAPEX. It indicates what investments and efforts it would take to set up the process designs. Consistent with figure 3.14, the majority of the costs are costs related to the electrolyzer system. Noticeable is the impact of installation costs. In case of realization of a EC process plant, installation costs and its factor must be taken into account very thoughtfully. The owner costs indicated in the graph account for both the electrolyzer system and the DSP. For the TC process no detailed CAPEX breakdown is constructed. This was done intentionally due to the fact that no generic cost calculation was made for either process. A generic comparison is therefore not possible.

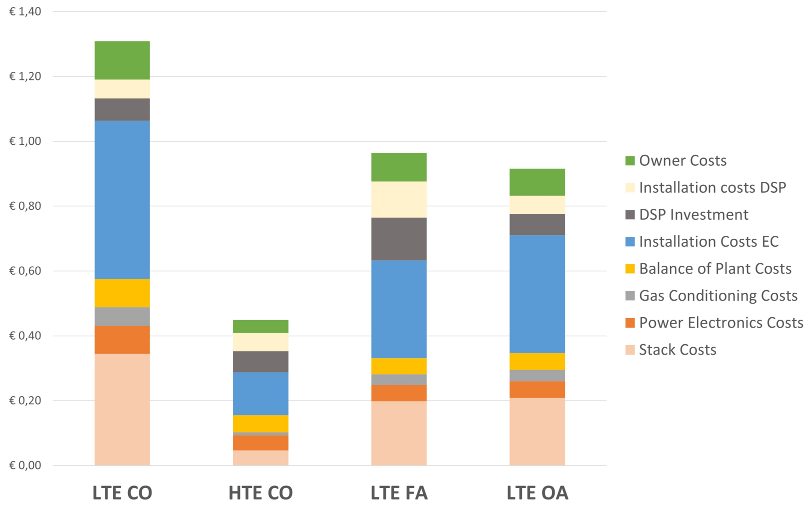


Figure 3.15: CAPEX breakdown of levelized costs per kilogram for each electrochemical pathway. Distinction made between CAPEX related to EC system and DSP.

Investment costs for the thermocatalysis are determined using reactor scaling relation mentioned in section 3.4 on thermocatalyic reactors. Reactor investment costs are no major contributor to the overall costs due to the maturity of the technology. The production production prices for the CO_2 thermocatalysis products, their deviation from market price and the contribution of noticeable components are listed in table 3.15. For both chemicals, CO and FA, the costs of hydrogen converted are one of the largest contributors. The results visualized in figure 3.14 and listed in table 3.15 suggest that TC production of CO already outperforms convenient production methods. These results are remarkable, it is unlikely that a new emerging technology outperforms the convenient method of production. FA on the other hand, is far above the market price and will not be able to compete with the market price. The catalyst costs for the thermocatalytic production of FA is a major expense component of the overall costs. The reactor described by Pérez-Fortes et al. [49] uses homogeneous catalysts. Homogeneous catalyst are often irrecoverable and require replacement after depletion. The reference costs for the catalyst reported in the article are obtained from Sigma-Aldrich [114][115], which is a commercial chemical company. It must be noted that therefore, the costs are relatively high. Since the catalyst for RWGS-CL is not that an investment and is not consumed by the reaction, catalysts costs are minimum and included in the reactor investment, as mentioned in the costing methodology. For both TC produced products no investment costs are major contributors to the overall costs. The costs are primarily driven up by the input materials, especially by H_2 if the costs for catalysts are not included.

Product	**Market price [$\frac{e}{kg}$]**	**CO_2R price [$\frac{e}{kg}$]**	**Deviation [%]**	**Reactor [%]**	**H_2 [%]**	**Heat**
TC CO	0.53	0.45	-15%	7%	38%	13%
TC FA	0.62	1.58	155%	7%	13%	11%

Table 3.15: Production costs CO_2 thermocatalysis products and deviation from current market price, together with contribution of reactor-, H_2- and heat costs in percentage of total production costs. Based on results visualized in figure 3.14.

In general, investment costs for downstream processing differ on how complex the separation process is and how much separation units are necessary. The highest investment costs for separation and purification of product streams are for formic acid. This is due to the challenging distillation sequences for both conversion technologies. Several distillation columns are required including additional heating and compression units, contributing to increased DSP investment costs and more required heat consumption. The complex sequence of processing units requires more heat input, increasing costs of production. Noteworthy is the low contribution of the costs of CO_2 for all pathways. This is due to the recycling of the unconverted CO_2 molecules to the cell stack or reactor. Thereby no CO_2 will be left unused, minimizing the needed CO_2 per produced kg. Similar observations are obtained for H_2, the costs of hydrogen input is not affected by conversion rates. However, conversion rates do affect the DSP costs since unreacted molecules increase the volume of the product streams and need for purification and thereby the size of DSP units. Observed by the analysis of the process designs, is a difference in required CO_2 per technology within the same desired product. The required CO_2 for LTE formic acid production is 0.81 $[\frac{kg}{kg_{product}}]$ compared to 1.16 $[\frac{kg}{kg_{product}}]$ for TC formic acid production. This due to the conversion yield towards the desired product and by-products. In the TC process, carbon selectivity towards FA is lower than in the LTE process, increasing the needed kg of FA for the conversion process.

3.6.2. Discussion

Based on the results visualized in figure 3.14 it can be concluded that at current base case conditions, electrochemical reduction of CO_2 towards valuable chemicals is the least attractive method and not in range of commercial application. This implies that CO_2 electrolysis, especially at low temperatures, is too immature for commercial applications yet. Significantly higher investment costs for the conversion technology are the main reason for this. This is caused by the relative low performance of low temperature CO_2 electrolysis. To improve economic feasibility, cell performance must be improved. This will consequently also improve feedstock efficiency and reduce electricity and CO_2 costs. It is also observed that system performance and capital costs of thermocatalytical conversion systems outperform the electrolysis pathways. This is due to the maturity of the TC technology compared to CO_2 electrolysis. TC production of CO is suggested to outperform convenient production methods. This result is highly unlikely and probably is due to underestimation of capital investment costs, based on the model by Huang et al., and the overestimated market price of CO. Capital investment costs for the thermocatalytical reactor are based on a generic equation for scaling reactors. Novelty of the RWGS-CL technology is not included in this scaling relation and might therefore be underestimated. The market price used for analysis, adapted from multiple reports, is in practice much lower. Therefore the system performance is probably over-estimated. The economical feasibility of TC FA production is killed by the costs of the homogeneous catalyst. Therefore, homogeneous catalyst are not desirable for industrial scale applications since the costs of replacement can be crucial for the economic viability of the process. To reduce the high catalyst costs, extensive research must be performed to find more durable, preferable heterogeneous, catalyst.

3.7. Sensitivity Analyses

To understand the sensitivity of the costs segments affecting the overall production price, a sensitivity analysis is performed. A selection of costs parameters is made for which a range of values was set. Three scenario's were selected for the analysis, an optimal-, a base- and a worst-case scenario. Some of the selected parameters depend on the conversion technology used (e.g. 'H_2 price' is only relevant for TC pathways). Table 3.16 lists all values for each scenario examined in the analysis. The sensitivity analysis is performed using the model used for calculating the production price combined with a What-If analysis on the selected parameters.

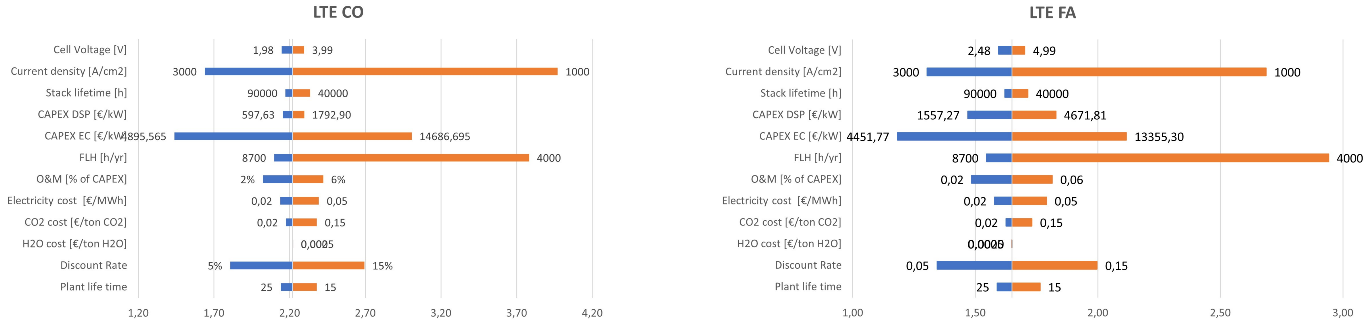
Parameter	**Unit**	**Optimal**	**Base**	**Worst**
Plant lifetime	years	25	20	15
Discount rate	%	5	10	15
H_2O Costs	€/kg	0,005	0,001	0,002
H_2 Costs	€/kg	1,8	2,5	3,91
CO_2 costs	€/kg	0,02	0,05	0,15
Electricity costs	€/kWh	0,02	0,03	0,05
Catalyst degradation	$kg/kg_{product}$	-33%	-	+33%
Operating and maintenance	%	2	4	6
Full load hours	hours/year	8700	8000	4000
Investment costs - Conversion unit	€/kg	-50%	-	+50%
Investment costs - DSP	€/kg	-50%	-	+50%
Conversion unit lifetime	hours	90000	65000	40000
Current density	mA/m^2	+50%	-	-50%
Cell voltage	V	-33%	-	+33%
Faradaic Efficiency	%	100-95	-	-
H_2 Yield	%	+50%	-	-50%

Table 3.16: Range of values parameters selected for sensitivity analysis. Values for optimal-, base-, and worst case scenario. Range of values selected based on recent studies performing similar sensitivity analyses [5][30][32][31].

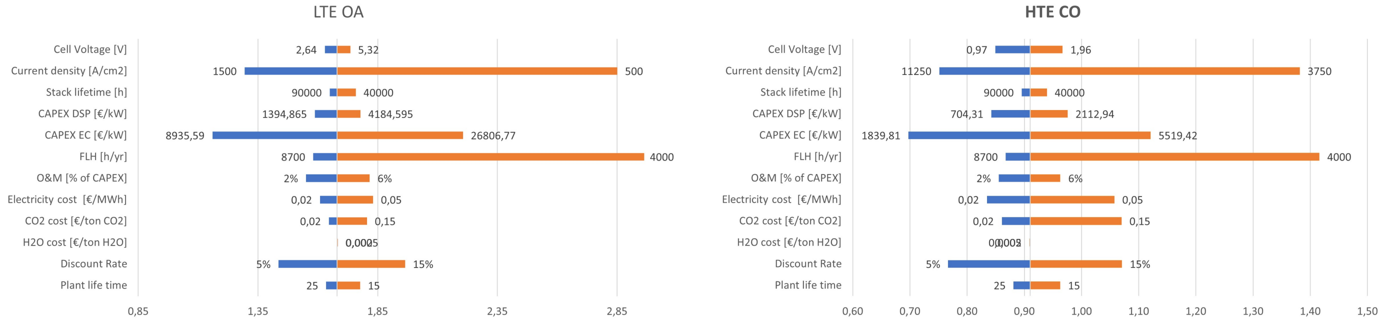
3.7.1. Results

The results of the sensitivity analysis are visualized using horizontal bar charts indicating the change in production price affected by the varying parameters, figure 3.16 and 3.17. The base-case scenario is represented by a vertical midline through the center of the bar chart. This midline corresponds to the production price values visualized in figure 3.14. The absolute change in production price in $[\frac{€}{kg}]$ is shown for optimistic- (blue bars) and worst-case scenario (orange bars). Parameter values used for the analysis are indicated as labels next to the bars inside the chart.

The first sensitivity analyses are performed on the production costs for the electrochemical pathways. A visualization of the results is given by the bar charts in figure 3.16. Distinctive parameters for those pathways are current density and the cell voltage. For the electrochemical pathways in general, it can be noted that the price of production is most sensitive to change in current density and uninstalled CAPEX of the cell stack. This does not include the effect of FLH's, which will be addressed later. It is observed that in a range of 50% and 150% of the original CAPEX value, a price variation of -33% to +33% relative to the base line can be achieved. A worst case scenario of a 50% decrease of current density could increase the production price over 80%. For an equivalent increase in current density, only a 27% decrease is observed. This observation is confirmed by the report by Jouny et al. [30] mentioned in the literature, that influence of current density becomes minimal after it reaches a certain range. Performance of the cell is related to the required electrode area, thus sensitivity towards CD was expected. An inverse relationship is observed between current density and uninstalled CAPEX. Since the investment costs are directly related to the required electrode area, a decrease in costs is observed as the current density improves. An increase of +50% leads to a reduction of uninstalled CAPEX costs of -33%, while reducing the CD by -50% results in a doubling.



(a) Results for low temperature electrolysis towards CO **(b)** Results for low temperature electrolysis towards FA

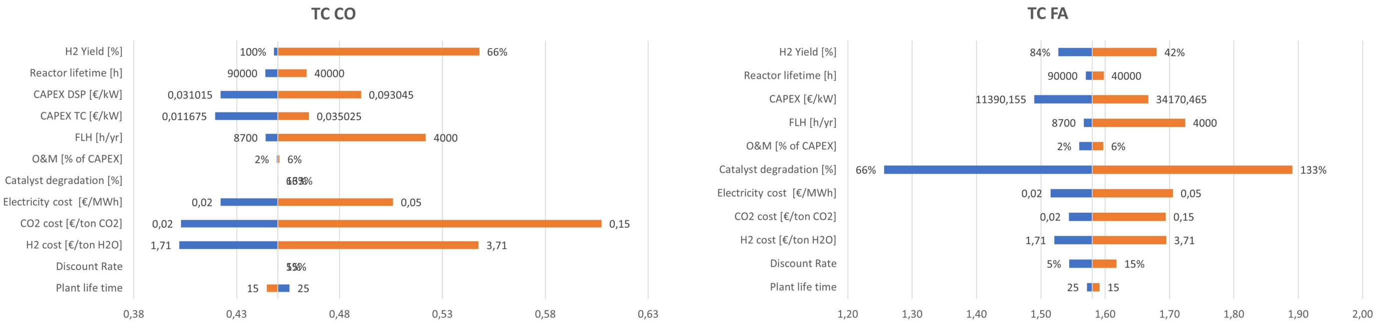


(c) Results for low temperature electrolysis towards OA **(d)** Results for high temperature electrolysis towards OA

Figure 3.16: Sensitivity analysis on absolute change in production price $[\frac{€}{kg}]$ by varying selected parameters for electrochemical production pathways

All electrochemical pathways show a similar pattern on the sensitivity analysis, regardless high- or low temperature. However, for low temperature FA and high temperature CO the influence of operational parameters and downstream processing are more of influence compared to the the other conversion pathways. Varying CAPEX for those pathways result to be less influential on production price. These observations could emphasize that when system performance increase and CAPEX is less influential, operational costs will become more influential for the economics. However, difference between sensitivities are minimal. The sensitivity analysis on the electrochemical pathways show that these systems are CAPEX dominant. Trends on improving technical performance and effects will be observed in future analysis.

Subsequently, the sensitivity analyses are performed on the production costs for the thermocatalytical pathways. A visualization is given by the bar charts in figure 3.17. Distinctive parameters for these sensitivity analyses are H_2 yield towards the desired product and catalyst degradation. Catalyst degradation is introduced due to the effect it has on the production costs of thermocatalytical produced FA. As expected, within the range of catalyst degradation over the different scenario's, significant price variance is observed compared to the influence of other parameters. Within a range of -33% and +33% of the base-case catalyst use, a price variation of -23% to +23% is achieved. The influence of the variance in CAPEX is less due to the maturity of the technology. Similar to the observations for the electrochemical pathways, when the influence of CAPEX is less dominant, the magnitude of the impact of operational costs will become more influential. The analysis shows the sensitivity to hydrogen costs and CO_2 costs for thermocatalytical processes. Especially for the production of carbon monoxide, produced via relative mature RWGS technology, the deviation from the baseline is significant for the costs of H_2 and CO_2. H_2 yield towards CO is at state-of-the-art already near 100%, thus no price reduction is observed in the sensitivity analysis.



(a) Results for thermocatalytic conversion towards CO

(b) Results for thermocatalytic conversion towards FA

Figure 3.17: Sensitivity analysis on absolute change in production price $[\frac{€}{kg}]$ by varying selected parameters for thermocatalytical production pathways

In general, it is observed that capital costs are dominant for the electrochemical production routes and less of influence for the thermocatalytical routes. This is also observed by the varying of the parameters regarding FLH's, discount rate, and plant lifetime. Full load hours are set for base-case scenario at 8000 hours of operation per year. This number is defined in the Use Case section. Increasing the FLH's would lead to increased annual production and thus relative less capital costs per kilogram produced. At a base-case load of 8000 hours per year, the production plant is nearly non-stop operational. Therefore, sensitivity analysis is performed on a range from 4000 to 8700 hours per annum. A total of 4000 FLH's per year suggest a downtime of 50% compared to the base case. Although this is a high figure, it has to be considered, especially given the irregularities in the generation of renewable electricity used in the process. Discount rate and plant lifetime are both parameters related to the capital costs. Consequently, ranging these parameters also affect the variance in production costs of electrochemical processes greater than thermocatalytical processes where capital costs are a less prominent part of the production costs.

3.7.2. Discussion

The sensitivity analyses are performed to gain understanding of the sensitivity of the costs parameters. The most influential parameters for the electrochemical processes were current density and the CAPEX of the cell stack, operational parameters are less of influence. Ranging the current density affects the the price more negatively than it offers improvements. Implying that past a certain value the improvement becomes minimal. Results from the sensitivity analysis on EC parameters confirm that to move more towards commercialization, electrochemical cell performance require improvement on technology and especially on current density. Results on the sensitivity analysis on TC parameters imply that the opportunities for thermocatalysis lie within improvement of the market related parameters. As technologies are more advanced and move towards commercialization, market parameters will become more significant as observed from the analyses. To become more market competitive, production of hydrogen and capture of CO_2 must become more cost effective.

3.8. Future performance

Performance and economics for CCU technologies are expected to be dramatically improve for the near term future. Technical performance will develop over the coming years, and materials used during the process will improve and become less costs intensive to utilize. For the analysis of the future performance of the selected CCU pathways, an outlook is reported for the current base-case performances versus the expected near-term future and optimistic future performance. Near term future refers to a time span of five years. Near-term future performances are the expected performance conversion technologies will reach in five years. Optimistic future performance is on the long term. Performances are not expected to be achieved within five years, but within ten or more. Analysis is performed to gain insights and guidance what future costs drivers could be and where possibilities and opportunities lie for R&D. Assumptions based on expected improvements of parameters are used and obtained from recent reports on CCU technologies. Future scenario's for the operational costs, such as electricity and feedstock price, are similar to the scenario's used in the marginal costs analysis. Using the same model as for the production price analysis, the expected future production prices are determined. Based on those results, improvements are evaluated and potential opportunities are identified. The expected values of performance used for the analysis are listed in table 3.17.

			Current	Near-term	Optimistic	Reference
H2O Electrolysis						
	PEM electrolysis					
	Cell Voltage	V	1.9	1.8	1.8	[110]
	Current Density	mA/cm2	1800	2400	3500	[110]
	Faradaic Efficiency	%	98	100	100	[5]
	SOEC electrolysis					
	Cell Voltage	V	1.5	1.285	1.285	[110]
	Current Density	mA/cm2	600	850	1500	[110]
	Faradaic Efficiency	%	99	100	100	[5]
CO2 Electrolysis						
	PEM electrolysis					
	Cell Voltage	V	-	2.5	2	[74]
	Current Density	mA/cm2	-	500	1000	[74]
	Faradaic Efficiency	%	-	99	100	[74]
	SOEC electrolysis					
	Cell Voltage	V	-	1.47	1.33	[121]
	Current Density	mA/cm2	-	1500	3000	[121]
	Faradaic Efficiency	%	-	99	100	[5]
CO2 Thermocatalysis						
	CO2 conversion	%	-	90	100	[5]
	Selectivity	%	-	90-100	100	[5]
	Yield	%	-	90-100	100	[5]
Operational Costs						
	H2O	€/kg	0.002	0.001	0.0005	
	H2	€/kg	3.71	2.37	1.71	
	CO2	€/kg	0.15	0.05	0.02	
	Electricity	€/kWh	0.05	0.03	0.02	

Table 3.17: Assumed expected values for future performance of CCU pathways. Future technical performances adapted from reported literature. Future operational costs correspond to values used in marginal costs analysis listed in table 2.4

For the future performance analysis, three different types of factors are identified to be relevant for the CCU pathways. These factors are the technical factors (KPI's defined in literature study), economical factors (feedstock costs) and the electricity factor (energy mix and prices). Energy mix refers to the combination of electricity sources and how they are distributed over the total electricity generation. The energy mix is currently dominated by coal, however a trend towards renewables is occurring. The energy mix won't be relevant for the future performance analysis but the electricity price will. Future performance analysis can be performed by varying the performance for each of the three factors individually, resulting in 27 different possible scenario's. To not overly complicate the analysis, the analysis will be performed on today's performance and future performance whereby all three factors (KPI's, economy and electricity prices) are considered. With these scenario's selected, a comparison is made between current scenario and the most optimistic future performances for all three factors.

3.8.1. Results

In figure 3.18 a visualization is given for the future performance analysis on the production costs per CCU pathway. The figure gives the production costs per kilogram for each scenario per CCU pathway. In each pathway category, the most left bar represents the current scenario, the middle bar the performance for the near-term future, and the most right bar represent the most optimistic future scenario. In general, it can be noted that nearly every cost component is reduced as the performance increase. However, the effect of improvement differs per product and conversion technology. A clear distinction can be made between the improvements for electrochemical pathways and thermocatalytical pathways.

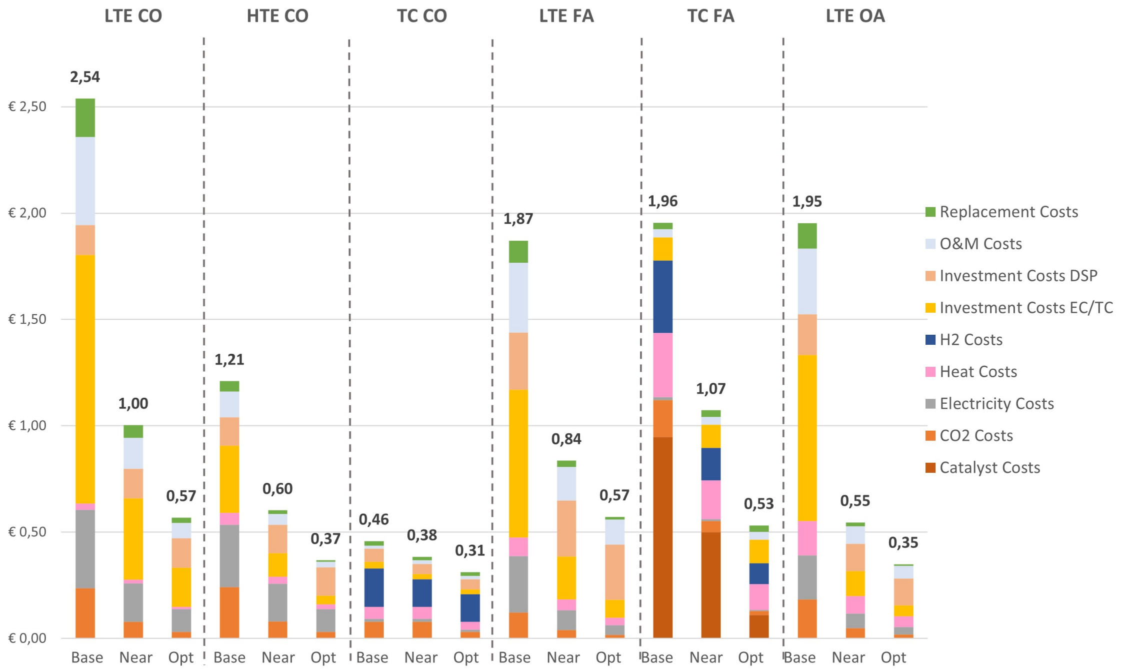


Figure 3.18: Production costs per CCU pathway for current conditions, near term future conditions and optimistic future conditions

TC pathways have the benefit of years of research, deployment and infrastructure investments for the syngas industry [5]. This conversion technology has been around for years and process designs and their affiliated costs have been optimized throughout the years. TC production of CO for example, is performed via a variant of reversed water gas shift, which is a phenomena known for centuries. For those conversion technologies, improvements on production costs are mainly driven by market parameters. The economical- and electricity factors are therefore the most contributing to the reduction in production price over the future scenarios. For the TC processes, a reduction of 47-49% could be achieved for the near-term future scenario and a 57-60% reduction for the optimistic future scenario. Within those improvements, H_2 and CO_2 cost reduction play a significant role. For TC FA production, also the improvement on catalyst degradation is a significant contributor. The greatest potential for technical improvements of CCU via hydrogenation would be R&D efforts on catalyst improvement. Assuming 50% of initial catalyst depletion on near-term and 10% for optimistic future scenario. The costs of using homogeneous catalysts could be killing for the economic viability of CCU via hydrogenation and is unlikely to be viable in the future. Luckily, not all TC processes involve the use of homogeneous catalysts. Consequently, the greatest potential for improving the economics of TC processes besides the conversion technology is via R&D efforts on green H_2 production and CO_2 capture. For TC pathways, the most near-term potential lies within improvement of the economic factors. Figure 3.19 visualizes the potential production costs reduction for near term future. Indicating the potential reductions due to technical or market parameter improvements. TC production of CO confirms the influence of the contribution due to economical/market factors. For TC FA production, improvements of catalyst consumption is considered as technical parameter, therefore influence of market parameters seems to be of less influence.

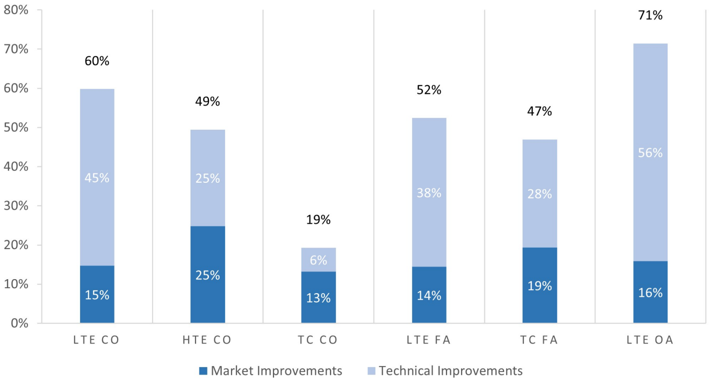


Figure 3.19: Percentage reduction in production costs moving from current scenario towards near-term future scenario. Distinction made between reduction due to technical (light blue) and market (dark blue) parameters.

Due to relative low TRL, electrochemical pathways are mostly affected by improvements on the technical parameters. Technologies regarding EC CCU pathways are not as developed compared to TC technologies, with a significant cost contribution of production cost per kg. In general, production costs for EC pathways are potentially reduced by over 50% and up to 75% for the near-term future scenario. For the optimistic future scenario, a production price reduction up to 85% can potentially be achieved, visualized in figure B.1. To increase the TRL for EC CCU pathways, opportunities lie within extensive R&D on the conversion technologies. Insights on fields of focus for the R&D are gained with the sensitivity analysis performed in previous section, visualized in figure 3.16. For the LTE and HTE pathways, current density is observed to have the greatest influence on the production costs. CO_2 electrolysis SOTA technologies operate at low current densities. Moderate improvements on current density already have significant effects on the cell stack performance electrode are required, reducing investment costs. At current scenario, investment costs for the LTE cell stacks contribute for ± 44% of the total costs. Improvement of current density to 500 mA/cm^2 and 1000 mA/cm^2 for LTE have a big impact and lead to contribution of the cell stack investment costs of ± 29% and ± 21% of the total production costs for near-term and optimistic future scenarios. Moving from current scenario of 100-200 mA/cm^2 to near-term future scenario of 500 mA/cm^2, shows the biggest influence on the total production price. Supporting the suggestion by Huang et al. that beyond a certain current density, improvements become less influential. Improvements of HTE cell performance is of less influence since cell stack investment costs are already less contributing to the production costs (± 25% of total production costs). Considering the impact of current density on investment costs and thus production costs, it must be the first primary field of focus for potential R&D investments.

In figure 3.20 the deviation of the production price from the reported market prices in percentage is given for the three scenario's observed in this analysis. Under current conditions (orange squares), none of the CCU pathways is cost competitive to the current market prices of the selected chemicals, besides TC produced CO. After applying the potential parameter improvements for the near-term future scenario (blue squares), production prices drop by an average of 54% for all pathways. Resulting in TC produced CO falling further below the market price, and EC produced OA leveling the market price. This suggests that under a near-term future scenario those two pathways being potentially market competitive. Under the optimistic future scenario, only LTE produced CO remains above the market price. Unfortunately, this implies that LTE produced CO will not be potentially market competitive even for the optimistic future scenario in which improvements for all three factors (technical, economic and energy mix) are accounted. However, it should be noticed that for all CCU pathways the parameter improvements are based on assumptions. Real life improvements could deviate and outperform the expected performances. Additionally, in the analysis the market price for the selected chemicals is assumed to be stable and that it will not change over the scenario's. However, in future scenario's penalties could be set on carbon emissions for conventional chemical production processes, affecting the market prices.

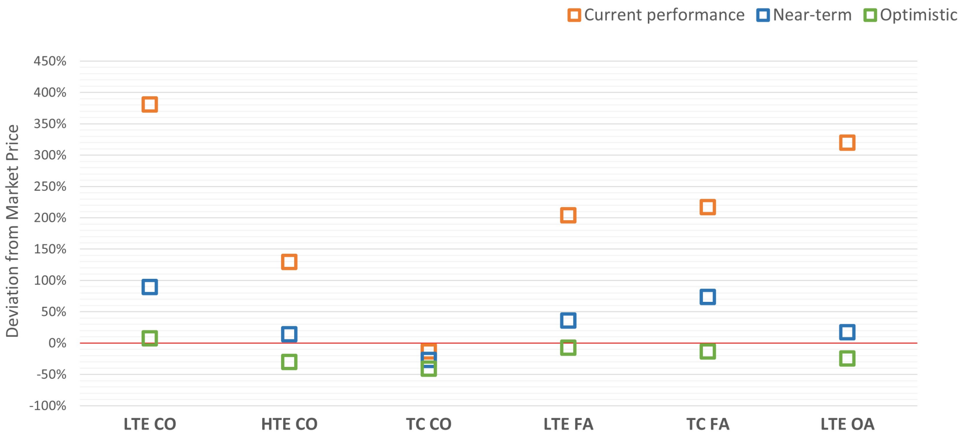


Figure 3.20: Deviation production costs from reported market prices in percentage for selected chemicals in current, near-term future and optimistic future scenario

3.8.2. Discussion

The analysis was performed to gain insights and guidance for future investments and developments. From the results of the future performance analysis can be concluded that thermocatalytical processes could be market competitive on a short term. For TC conversion to become economic viable and reliable, investment must be made in optimization of feedstock production, renewable electricity generation and supply. TC production of FA is unlikely to compete with conventional production technologies. The use of homogeneous catalysts is killing for the process and economic feasibility would be impossible if no serious improvements are made. In the future analysis progressive assumptions are made on catalyst material improvement. There seems to be a possible feasibility in it, but that is no certainty. Opportunities for EC processes lie within extensive R&D on the conversion technologies. Future analysis show great opportunities for electrochemical CO_2 reduction, however investment in cell performance are necessary. Current CO_2 electrolyzers, LTE and HTE, operate at too moderate conditions. According to the expected future improvements, especially current density must be improved and costs per area of electrode need to be drastically reduced, especially for LTE. Due to relative low TRL, there is more potential improvement on technical performance. As the analysis shows, significant improvements are achieved by minimum improvements.

3.9. Results from other works

A few reported works have performed similar comparable TEA's on the production of valuable chemicals via CCU. In table 3.18 the results of those comparable TEA's are listed. The production costs per kilogram of product are listed together with the KPI's used for the analysis. The results of this work are also mentioned in the table, to be able to make a comparison between the different results and to validate the research. The reference used are the reports by Huang et al. [5], De Luna et al. [34], Shin et al. [31] and Jouny et al. [30]. Not all reports have the same products covered in their work, those are left blank in the table. Unfortunately no comparable TEA including TC FA was found in literature. For the validating of our results for TC FA, the article by Pérez-Fortes can be used.

Looking at the table, it is observed that the costs of this study are significantly higher than reported in the other TEAs conducted. To identify the causes of these differences, the KPIs used for the analyses have been evaluated. Using the differences in KPI's reported and the price breakdown per product, conclusions can be drawn on the inconsistency between the results. The technical parameters for LTE conversion pathways used by Jouny et al. and Shin et al. are very optimistic. Current densities of 500 mA/cm^2 are used which has a significant effect on the investment costs and thereby costs of production. As observed in our sensitivity and future performance analyses, modest improvements on current densities have major effects. Current densities of 500 mA/cm^2 for low temperature CO_2 electrolysis are unrealistic for state-of-the art technologies. Breakdowns of the production costs for LTE CO and FA by Shin et al. and Jouny et al. are dominated by electricity and CO_2 costs [30][31]. Capital investments on the electrolyzer system contribute for approximately 10-20% of the total production costs. Compared to the 36-49% calculated in this work (table 3.14). KPI's mentioned for all pathways by Huang et al. are equivalent to performance used in this work and their results are approaching those of this work. Contribution of electrolyzer CAPEX is comparable to the results of this work. The DSP, on the contrary, was estimated to be significantly lower, namely 1% of the total production cost, resulting in lower overall costs. Noticeable is the performance of the LTE OA pathway. KPI's used in this analysis for the CO_2 electrolyzer producing OA are reasonably higher compared to the performance by Huang et al., which result in less capital investment costs. The biggest difference is most likely caused is the contribution of the electricity cost. The conversion technique analyzed in this work is performing better, thus less electricity is needed. In the report by Huang et al. electricity costs contribute 34%, compared to 12% in this work. The production costs for thermocatalytical produced FA reported by Pérez-Fortes et al. [49] is €1.52 per kg FA. Which is remarkably close to the costs from the production cost analysis. This is in line with the expectations, since much of the process design matches that of Pérez-Fortes et al. [49].

Product	Parameter	Unit	Huang et al. [5]	De Luna et al. [33]	Shin et al. [31]	Jouny et al. [30]	This work
	CO_2 costs	$\frac{\text{€}(2020)}{kg}$	0.04	0.03		0.04	0.05
	Electricity costs	$\frac{\text{€}(2020)}{kWh}$	0.06	0.04	0.03	0.03	0.03
	H_2 costs	$\frac{\text{€}(2020)}{kg}$	3.71				2.37
CO LTE	Current density	mA/cm^2	200	500	500	200	200
	Cell voltage	V	3	3.15	2.6	2.3	3
	Faradaic efficiency	%	98	90	95	90	98
	Prod. Costs	$\frac{\text{€}}{kg}$	**1.40**	**0.20**	**0.44**	$<$ **0.60**	**2.22**
CO HTE	Current density	mA/cm^2	772				750
	Cell voltage	V	1.41				1.47
	Faradaic efficiency	%	99.5				99
	Prod. Costs	$\frac{\text{€}}{kg}$	**0.38**				**0.91**
CO TC	Selectivity	%	100				100
	Carbon yield	%	68				64
	CO2 utilization	%	68				64
	Prod. Costs	$\frac{\text{€}}{kg}$	**0.45**				**0.45**
FA LTE	Current density	mA/cm^2	140	500	200	200	200
	Cell voltage	V	3.5	3.3	3.5	2.3	3.75
	Faradaic efficiency	%	94	90	85	90	82
	Prod. Costs	$\frac{\text{€}}{kg}$	**1.36**	**0.11**	**0.59**	**<0.70**	**1.65**
FA TC	Selectivity	%					81
	Carbon yield	%					0.79
	CO2 utilization	%					98
	Prod. Costs	$\frac{\text{€}}{kg}$					**1.58**
OA LTE	Current density	mA/cm^2	75				100
	Cell voltage	V	6.5				4
	Faradaic efficiency	%	60				80
	Prod. Costs	$\frac{\text{€}}{kg}$	**2.23**				**1.51**

Table 3.18: Production costs per kilogram for each CCU pathway according to comparable TEA's. Production costs per kilogram of product is stated together with the KPI's used in the analysis. At top of graph used feedstock costs used per report are listed.

In general, it can be noted that this research is based more on present state-of-the-art technologies and realistic system performance. Resulting in less optimistic production prices and a more realistic representation of the current state of technology. Recycle streams of CO_2 and re-usable components are integrated in the DSP to be able to evaluate the process design at system level. It is uncertain how the process designs used in the reference reports are structured. It is therefore hard to come with a fair comparison between the results of the TEA's. Conclusions are based on the similarities between the reports, which are the conversion technologies. The sensitivity analysis by Huang et al. reports similar findings as the analysis performed in this work. For electrochemical reactions the CD and CAPEX are significantly and operational related parameters less. For the thermocatalytical processes also a similar effect is reported: the production costs are most sensitive to varying H_2 and CO_2 costs. Sensitivity analyses reported by De Luna et al., Shin et al. and Jouny et al. show the most sensitivity towards CO_2 and electricity price. This is a consequence of the overestimated technical performance. The difference in sensitivity to varying parameters between the reports confirms the observation that the production costs of more mature technologies are less CAPEX driven.

4

Environmental Analysis

The goal of CCU is to offer an emission reduction solution that reduces the carbon concentration in the atmosphere and prevent future emissions by replacing conventional production methods. To measure the emission reduction achieved by the selected CCU pathways, and analysis is performed on their environmental impact. The analysis on the environmental impact is performed by means of a life cycle analysis (LCA). Throughout the process, interaction with the environment takes place in terms of feedstock consumption and emission of pollutants. The LCA is a quantitative method to examine the process and its interactions on their environmental impact. The analysis for the selected pathways is performed on a gate-to-gate basis. The result of the analysis is an overview of the global warming impact (GWI) per product pathway compared to the conventional production method of the selected chemical. The global warming impact is expressed in the unit of kilograms CO_2 equivalent per kilogram of product $[\frac{kg.CO_2-eq}{kg_{product}}]$. The LCA is performed according to the methodology described by Müller et al. [122] and standardized by the international standardization organization (ISO) in ISO 14040 and 14044 [123].

4.1. Approach

According to the standardized LCA methodology, the analysis is divided into four phases. The four phases are distinctive but all related to each other. Often not all information for the phases is known or available. The four different phases are divided into (1) goal and scope definition, (2) life cycle inventory analysis, (3) life cycle impact assessment and (4) interpretation. In this study, the four phases are used as guidelines to help determine the environmental impact. The LCA performed in this report is a preliminary study on the environmental impact of the CCU pathways. A complete LCA from cradle-to-grave would be a whole study in it self. Therefore, not all phases will be covered in as much detail. Figure 4.1 gives a schematic overview of the gate-to-gate approach for the LCA.

4.1.1. Goal and definition

The specific goal of the LCA is to determine the global warming impact of the routes and to determine the benefits of the renewable pathways over the conventional production methods. For the selected chemicals, performance of conventional routes are adapted from reported studies and numbers. The GWI of all pathways is quantified in terms of emissions of CO_2 per produced product. For all chemicals, the unit for GWI was measured in 1.0 kilogram of desired product. The boundaries of the analysis are set to gate-to-gate. A gate-to-gate approach includes the production process starting from the receiving of the raw materials to the completion of the final product. The raw materials entering the system are CO_2, H_2O, electricity and materials used for the conventional production methods (e.g. CO for conventional FA production). The CO_2 is assumed to be captured direct from the air or point-source and thus has a negative effect on the GWI since CO_2 is reduced from the atmosphere. Electricity is assumed to be produced according to the energy mix composition according to PBL Netherlands

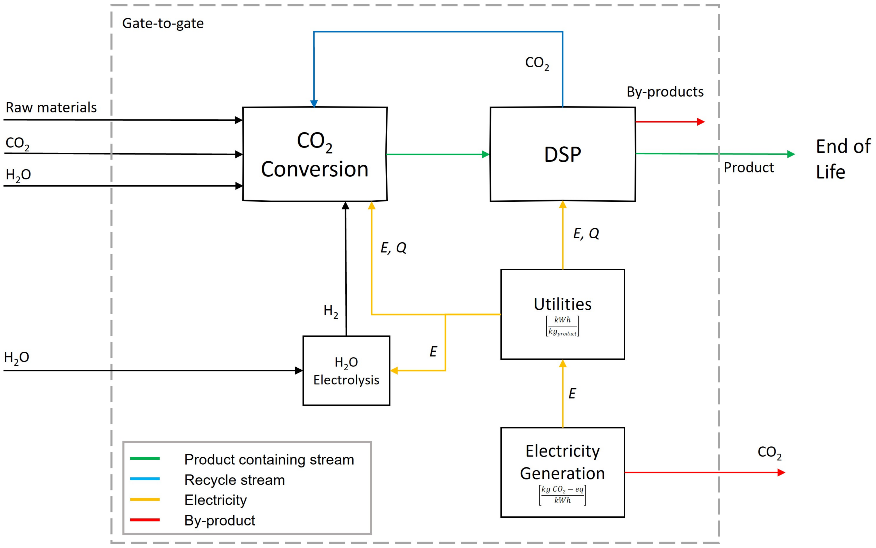


Figure 4.1: Process life cycle analysis overview: schematic drawing gate-to-gate approach. Input-, product- and output streams indicated. Electricity flow indicated by E and heat flow indicated by Q.

Environmental Assessment Agency [124]. H_2 is assumed to be produced inside the system boundaries.

4.1.2. Life Cycle Inventory Analysis

In the inventory analysis phase it is determined how data is gathered and processed in the LCA. The inventory analysis is based on the data available on the flow of materials and utilities into the systems. For the gate-to-gate approach, only the impact of those streams are considered. Installation of plants, transportation, maintenance etc. are not considered. For the CCU pathways, the impact of inlet streams are considered to be contributing. Since the processes are designed to recycle unreacted products, no emissions are released. Inventory analysis for the CCU pathways are based on the process designs made in previous chapter. Materials and utilities used in the LCA are adapted from that chapter. For the conventional routes, raw materials used in reported production methods are considered. The materials used for each process will be discussed in the analysis per product. For some chemicals, very little inventory data is available. For those assumptions are made based on reaction stoichiometry or processes of similar products.

4.1.3. Life Cycle Impact Assessment

For the LCA performed in this study, the global warming impact is considered. The GWI for CCU and conventional pathways are evaluated using the kilogram CO_2 equivalent per kilogram of product. The impact assessment is performed based on input streams, utilities used and emissions produced during the production process. The GWI of input material streams is determined using the standard CO_2 emission factors reported by the Netherlands Enterprise Agency [125]. The emission factors used and their values are reported per product analysis. The composition of the energy mix used for the conversion processes is adapted from reports by PBL Netherlands Environmental Assessment Agency [124]. Assigning the GWI per contributing generation technique, values are used reported in the EU reference scenario 2050 on energy, transport and GHG emissions [126]. An overview of the contribution per electricity source and the total GWI of the energy mix for current and future scenarios is given in table 4.1.

Electricity Source	**2020**	**2030**	**2050**
Nuclear	0.003	0.002	0.001
Solids (coal)	0.115	0.066	0.000
Gaseous fuels (NG)	0.093	0.074	0.064
Biomass	0.014	0.012	0.014
Hydropower	0.003	0.003	0.003
Wind	0.002	0.003	0.004
Solar	0.003	0.006	0.009
Total	0.232	0.165	0.095

Table 4.1: Overview of GWI contribution per electricity source and total GWI of energy mix for current- and future scenarios in kg CO_2 equivalent per produced kg of product. Values adapted from the EU reference scenario 2020 on energy, transport and GHG emissions [126].

The H_2 is considered to be produced inside the system boundaries. Therefore, the electricity needs for H_2 production are calculated in terms of KWh/kg. This is done by using the lower heating value of H_2 and the efficiency for PEM water electrolysis for current and future scenarios. According to the report published by IRENA on green hydrogen production [127], the lower heating value of hydrogen is 33.32 kWh/kg of H_2. Using the reported efficiencies, the electricity needs for the production of 1 kg H_2 are calculated and listed in table 4.2.

		2020	**2030**	**2050**
Efficiency PEM		65%	68%	71%
Electricity needs	[kWh/kg]	51.27	49.00	46.93

Table 4.2: Conversion efficiency PEM water electrolysis [127] and electricity needs for H_2 production for current and future scenarios

4.2. Results and Discussion

The global warming impact for the CCU pathways compared conventional methods is analyzed using input streams, utilities and emissions for all products and production pathways as defined in previous sections. All numbers were converted to match the output of 1 kilogram of product. In this section, for each product all utilities, input- and output streams needed per pathway are obtained and the GWI is calculated. Based on the results, the environmental impact of CCU compared to conventional routes is determined.

4.2.1. Carbon Monoxide

Carbon monoxide is produced via various production methods. On commercial scale, carbon monoxide is generated by the oxidation of hydrocarbon gases, such as natural gas, via the production of syngas [128]. The CO content in the product stream is highly dependent on the C/H atoms concentration in the feedstock gas. Alternatively, carbon monoxide can be produced via the gasification of coal and coke [129]. Industrial production of CO can thus be performed via various methods. Therefore, for this analysis no general production route is established containing input stream and utilities used. The global warming impact of the conventional process is adapted from the list of fuels and standard CO_2 emission factors published by the Netherlands Enterprise Agency [125]. The generic GWI for conventional CO production is reported to be 1.57 $\frac{kg.CO_2-eq}{kg_{product}}$. For the CCU pathways and input of CO_2, H_2O and electricity is required. The input and output for each process is listed in table 4.3.

	Input Material [kg]			**Utilities [kWh]**			**Output [kg]**		
Method	**H2**	**CO2**	**H2O**	**Electricity**	**Heat**	**Cooling**	**CO2**	**H2O**	**O2**
Conventional							1.57		
LTE		1.57	0.13	7.40	0.57				0.56
HTE		1.57		2.84	3.68	0.47			0.57
TC	0.07	1.57		0.49				0.22	

Table 4.3: Input-output balance for all carbon monoxide production processes

The input of H_2 is considered to be produced inside the system boundaries. The electricity needs per kilogram of H_2 is given in table 4.2. With this, the input of H_2 can be put in terms of kWh per kilogram. With all input streams and utilities gathered, the GWI for all production pathways is determined, visualized in figure 4.2. The LTE pathway is dominated by the electricity use, being the largest contributor to the impact on the environment. A small fraction of the total goes to the heat utilities used in the downstream processing. The GWI for the HTE pathway is relative evenly distributed. Less electricity is required for the conversion process, however since it operates at elevated temperatures, significant more heat is required. The TC pathway is the only of the three CCU technologies that has a negative GWI, meaning it consumes more CO_2 than is produced during the complete process. The hydrogen production accounts for the most CO_2 emissions during the process. In terms of net CO_2 emissions, the CCU pathways have a significant lower impact compared to the conventional CO production. The direct conversion of CO_2 leads to a serious decrease in GWI. In the conversion process, more CO_2 is utilized than is emitted during electricity, heat and hydrogen production. Without the utilization of CO_2 in the processes, the LTE pathway would be emitting more than the conventional method due to the high electricity use for the electrochemical process.

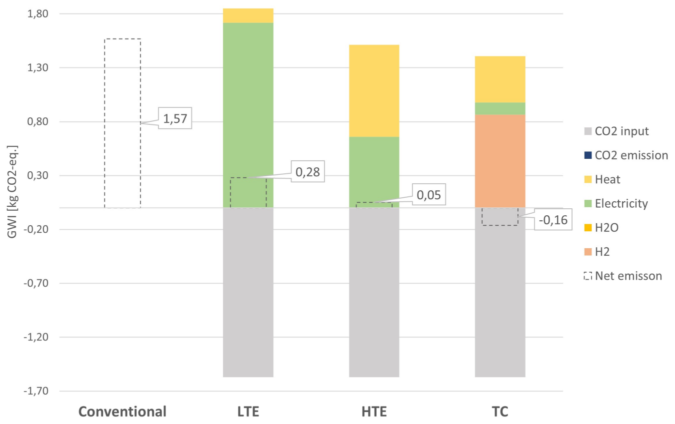


Figure 4.2: Global warming impacts for conventional and CCU production pathways for CO production

4.2.2. Formic Acid

Conventional synthesis of formic acid is done via hydrolysis of methyl formate, which is obtained from carbonylation of methanol [130]. The production process consists of two following stages; (1) carbonylation of methanol into methyl formate by the incorporation of carbon monoxide into the methanol molecule, and (2) hydrolysis of methyl formate into formic acid. The process used as reference is carried out globally on industrial scale for many years by BASF. Part of the process design DSP is similar to the process design of the LTE CCU pathway. The input streams, utilities and emissions are adapted from Sutter et al. [131]. The process requires CO, MeOH and significant heating for the production of 1 kg FA. Values for the process, along with those for CCU pathways, are listed in table 4.4. The CCU pathways both use CO_2 as their feedstock but the reaction mechanisms require different utilities to perform the reaction. The EC pathway primarily requires electricity as utility, whereas the TC method requires mostly heat. The GWI for the CO and MeOH used in the conventional process are adapted from the list provided by the Netherlands Enterprise Agency [125] and are 1.57 and 0.3 $\frac{kg.CO_2-eq}{kg_{product}}$ respectively. The impact values for CO_2, H_2O and electricity used are similar to the values used for CO. Again, the H_2 needed produced and expressed in terms of kWh/kg using table 4.2.

	Input Material [kg]					**Utilities [kWh]**		**Output [kg]**			
Method	**H2**	**CO2**	**CO**	**MeOH**	**H2O**	**Electricity**	**Heat**	**CO2**	**CO**	**H2O**	**O2**
Conventional			0.61	0.04		0.13	5.35	0.01	0.01		
LTE		0.81			0.68	5.33	1.72			0.15	0.36
TC	0.09	1.16				0.30	6.05				

Table 4.4: Input-output balance for all formic acid production processes

Based on all input streams, utilities and emissions the GWI per production route is determined and visualized in figure 4.3. For the conventional process, the GWI is dominated by emissions corresponding to the CO required CO and the heat required for the process. The breakdown of GWI for the LTE and TC pathways are similar as for the production of CO. EC is dominated by emissions from electricity generation and TC by emissions caused by H_2 generation and heat production. Unfortunately, none of the CCU pathways has a net negative CO_2 emission per kg of product for the current conditions. This is due to the environmental of the current electricity mix. The GWI of the energy mix has a significant influence on the process since the utilities and H_2 production are put to numbers in means of kWh/kg. Compared to the production of CO, less captured CO_2 is converted during the process, due to the relative high molar mass of FA. An equal amount of carbon atoms are involved per produced molecule, but FA contains one more oxygen and two more hydrogen atoms. Less captured CO_2 is put into the process, resulting in less emission reduction from carbon capture. As observed earlier, TC conversion requires more captured CO_2 into the process due to the lower carbon selectivity towards FA. Also, significantly more utilities are required compared to EC, resulting in higher net emissions.

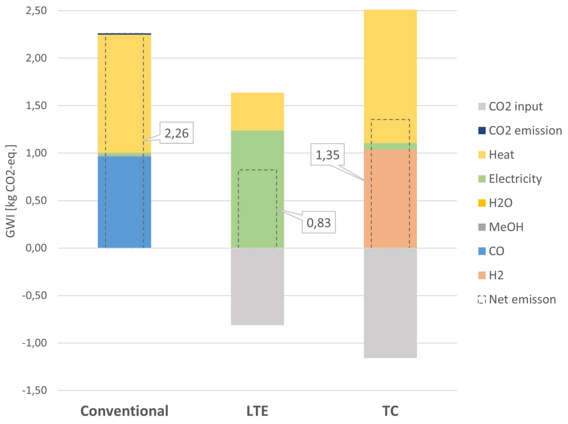


Figure 4.3: Global warming impacts for conventional and CCU production pathways for FA production

4.2.3. Oxalic Acid

Oxalic acid has various industrial processes for production, all carried out by a large number of companies on industrial scale. The processes are based around the starting materials used. At this day, generally three classes of starting materials are used for the synthesis of OA. These classes are: (1) carbonhydrates, (2) olefins and (3) carbon monoxide [132]. The most recent synthesis method applied on industrial scale is the oxidation of carbon monoxide (Boudouard reaction). This relative new technique has the advantage of inexpensive starting material (CO), and no nitrogen oxides are emitted during the process. Which happens during the oxidation of carbonnhydrates and olefins. Nitrogen oxide is produced during the process, however it is converted back to its initial alkyl nitrite form and subsequently hydrolyzed to an alcohol which can be easily separated [133]. Due to those advantages, the oxidation of

	Input Material			Utilities		Output
Method	**CO2**	**CO**	**H2O**	**Electricity**	**Heat**	**CO2 emission**
Conventional		0.78	0.2			0.20
LTE	1.22	0	0.20	2.98	1.16	

Table 4.5: Input-output balance for all oxalic acid production processes

CO for OA synthesis will be considered in this study as the conventional production route and will be compared to the CCU pathway. Using reported conversion reactions, reported efficiencies and literature based assumption, an estimation of the GWI of carbon monoxide oxidation towards OA is made. The desired reaction mechanism for OA synthesis via carbon monoxide is given by equations 4.1 and 4.2. Unfortunately, little data on industrial OA synthesis performance is available. Assumptions are made to determine the GWI for the conventional production method. The following assumptions were made: (1) the required input is based on the reaction stoichiometry from equation 4.1 and 4.2, (2) the CO yield to OA is 80% [134], (3) the only by-product is CO_2 (Boudouard reaction) and (4) the needed utilities are similar to conventional FA production. With these assumptions, a safe estimate can be made on the GWI om the OA synthesis. In practice, the GWI would possibly higher due to the production of more unwanted by-products, more complicated DSP, higher utility needs and unwanted nitrogen oxide forming. The values for the input streams, utilities and emissions for conventional OA synthesis and LTE production are listed in table 4.5.

$$2CO + 2ROH + \frac{1}{2}O_2 \rightarrow 2(COOR) + H_2O \qquad \Delta H = -52.8\,kJ/mol \tag{4.1}$$

$$2(COOR) + 2H_2O \rightarrow C_2H_2O_4 + 2ROH \tag{4.2}$$

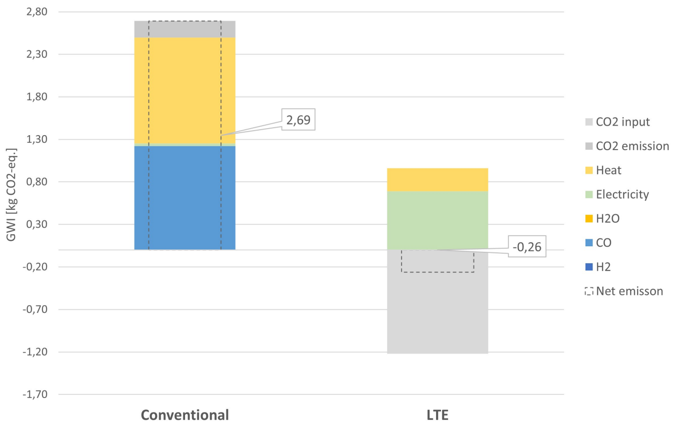


Figure 4.4: Global warming impacts for conventional and CCU production pathways for FA production

Again, the same emission factors are used to determine the overall GWI of the processes. For both OA conversion methods, conventional and LTE, the environmental impact is calculated and visualized in figure 4.4. The emissions produced in the conventional OA synthesis are mainly influenced by the converted CO and heat used required. The CO_2 emissions are relatively high compared to other processes. This is due to the fact that during the production, formed CO_2 is released to favor the reaction dynamics towards the product [132]. Similarly to the other LTE processes, the GWI for the CCU pathway is significantly influence by the electricity needs. In combination with the negative GWI factors for the CO_2 input, the LTE production of OA utilizes more CO_2 than is emitted. Analysis on future performance using the expected future energy mix must be performed to determine the improved the environmental impact of the processes. It should be noted, for both technologies, that the LCA performed is very basic and extremely simplified. Because of the lack of process data and the simplified process design made for the CCU pathway, rough assumptions are made. Despite the missing data and assumptions made, LTE production of OA comes out of the analysis well and promises an improvement over its current processes.

4.2.4. Discussion

The LCA is performed to study the environmental feasibility of CCU pathways and to compare them with current state-of-the-art production methods. The LCA was performed for one environmental factor, which is the global warming impact. Results are quantified using data reported in literature. For some processes, a minimum quantity of data was available. This made it necessary for assumptions or estimations to be made. The major environmental contributors were identified for each production method and produced chemical. The results provide useful insights on different environmental drivers and how the GWI could be improved for future performance. The results show that all CCU production methods show potential to reduce GHG emissions and reduce fossil resource use by utilizing captured CO_2. In the electrochemical processes, the main drivers are electricity and heat demand. Improving KPI's of the electrolyzer stacks reduces the electricity needs and could lower the emissions produced. For that, investments must be made on R&D regarding cell optimization to improve electrode material, catalyst use and thereby electricity needs. In the TC processes, the main environmental driver is the electricity need for H_2 production. R&D on improving H_2O electrolysis should be made. Improvements on PEM cell stacks reduce the required electricity per kg of H_2 and would benefit the environmental impact. In all strategies, utilities are largely affected by the energy mix used. Switching to a more renewable energy mix, all strategies would benefit. Including the conventional methods. Future scenario's include a bigger contribution of renewable electricity generation in the energy mix. For the near-term future- and optimistic future scenario a reduction of 29% and 59% on the kg CO_2-eq per kWh is expected, using the emission factors for future energy mixes listed in table **??**.

5

Conclusions

In the work presented, several chemicals were studied in depth on possible CCU strategies involving electrochemical and thermocatalytical conversion technologies. In a literature study, a selection of possible CCU product was evaluated and a selection was made for which conceptual process designs would be developed. The processes were designed and evaluated at system level. Subsequently each system was individually modelled and evaluated on its costs of production, parameter sensitivity and possible future performance. Finally, a life-cycle assessment was performed to determine the global warming impact of each CCU pathways compared to their convenient production methods. These results were subsequently translated into a techno-economic and environmental assessment to identify the potential and opportunities of the designed processes. The sub-questions stated in Chapter 1, served as step-by-step tools to answer the main research question:

- *What are the most relevant pathways for the valorization and utilization of carbon dioxide based on their techno-economical and environmental performance?*

Based on the studied literature, it has been decided to perform the parametric analysis on single-step CCU products. This is due to the broad range of possible products and to focus on feasibility of CCU to deliver a product instead of directly using the chemicals as intermediates. The parametric analysis suggested that potential for CCU is mostly determined by the molecule of interest instead of conversion technology. It is observed that more oxygenated molecules tend to perform better in conversion processes due to the yield to mass efficiency. The products selected to be analyzed in this study were carbon monoxide (LTE, HTE and TC), formic acid (LTE and TC) and oxalic acid (LTE). All processes are designed at a capacity of 1000 kg CO_2R product per hour, with being operational for 8000 hours per year. Utilizing scaling equations and reference conversion units for the reaction mechanism, processes were designed. Observed was varying complexity in process design, depending on the complexity of the molecule, phase it leaves the system and TRL of technology. FA leaves the reactor/electrolyzer in liquid phase, increasing complexity significantly. OA exits the electrolyzer as liquid and the process is extremely low TRL, therefore the system is designed based on assumptions. During the design of the processes, assumptions and rough estimations had to be made, but they provide a tool for further analyses on technical and economical performances.

Subsequently, the techno-economic performance of the conceptual processes was determined. A model was created to simulate the CCU systems and to calculate their performances at state-of-the-art operation conditions. Looking at the current production costs analysis, electrochemical pathways towards CO_2 are the the least attractive CCU pathways. Analysis shows that EC pathways are too immature for commercial application. Up to 53% of the costs are investment costs for the electrolyzer system. Indicating necessary investments for improvements on cell stack development. Thermocatalytical systems are more influenced by hydrogen and heat costs due to maturity of the technology. For TC FA production, the economic feasibility is killed due to extreme catalysts costs. Homogeneous catalyst are therefore not applicable for commercial industrial scale production processes. The economic feasibility of TC CO production is probably due to the underestimated capital investment costs of the reactor and due to the high assumed market price. The market price obtained from multiple reports [30][5][31], ranges from 0.53 to 0.80. In practice these market prices will be significant lower, having a negative effect on the business case for CCU production of CO. Based on the parameter sensitivity analysis, state-of-the-art EC systems show to be dominated by current density and CAPEX, which are inverse related. Processes which are less mature are more sensitive to varying of technical- (CAPEX driven), and less to market parameters. TC pathways are more advanced towards commercialization and more sensitive for varying of market parameters. Both processes are prone to the full load hours. This shows the importance for all CCU pathways to operate at constant load and to have a stable supply of captured CO_2, green H_2 and renewable electricity. Potential future performances show significant improvement for electrochemical pathways. Opportunities for EC improvements lie especially in CAPEX driven improvements. Only LTE CO production will not be feasible for future scenario's according to the analysis. At current scenario, none of the electrochemical pathways are economically feasible. Significant costs reduction in electrolyzer costs must be realized. Opportunities lie within focusing R&D investments on improving current densities and overall cell performances. Thermocatalytical pathways show promising improvements for future performance. However, both analyses have their limitations. TC CO has limitations on its underestimated investment costs and overestimated market price and TC FA on assumptions regarding improvement catalysts degradation. Pathways suggested to become economic feasible in the near-term future are HTE CO and LTE OA as the CO_2 electrolyzer cell performance improve as expected. For the optimistic future scenario, only LTE CO is unlikely to be economic feasibly.

The environmental impact of the process designs is put into terms of GWI by a performed LCA at a gate-to-gate principle based on the state-of-the-art system performances. The most significant reduction on GWI can be achieved for CO and OA. TC produced CO and LTE OA both utilize more kg CO_2 per kg of product than is emitted during the process, at a gate-to-gate perspective. The conversion technologies have a GWI reduction potential of 1.73 and 2.71 $\frac{kgCO_2-eq}{kg}$ compared to convenient production methods. GWI reduction for formic acid CCU pathways is minimal due to emissions of significant required utilities compared to negative emissions due to capture CO_2. Emissions due to utilities are largely affected by the energy mix used. Future scenarios will include a bigger contribution of renewable electricity. For the near-term future- and optimistic future scenario a reduction of 29% and 59% on the kg CO2-eq per kg of product is expected.

The aim of this study was to evaluate the possible CCU pathways for valorization and utilization of CO_2 and identify the most relevant strategy based on their techno-economic and environmental performance. Overall it can be said that CCU pathways are currently not economical viable to show compatibility with the convenient industry. Technical performance are yet too moderate, catalyst too expensive, and renewable utilities and feedstocks too expensive. Despite the current poor performance, significant improvements can be achieved in parameter optimization of EC systems. R&D opportunities lie within cell performance developments, catalyst improvements and reducing H_2 production and CO_2 capture costs. Near term feasibility is achieved for HTE- and TC CO and LTE OA production. CCU towards FA should be achieved via electrochemical conversion, due to rising improvements of electrochemical performance. The TC route relies on homogeneous catalysts that have been shown to hinder economic feasibility. The environmental impact differs per product and method of production. Oxalic acid has the most GWI reduction potential, reducing the CO_2 equivalent to below zero for a gate-to-gate analysis.

6

Recommendations

The process designs and findings of this research gave many insights on CCU pathways and their techno-economic performances and environmental impact. Possibilities and opportunities have been identified as well as challenges and focus for future development is examined. With this, the main research question has been answered, but more importantly, directions for future researches can be defined which will be discussed in this section.

As briefly discussed during the production costs analysis, the current market price of CO is estimated at a value of €0.53 per kilogram. In practice, the market price for CO is significant lower. Carbon monoxide is often produced in as syngas and reports on market prices of CO are scarce, which makes it hard adapt a representative price for the analysis. A method to effectively estimate the price of CO, for future research and analyses, is using the kg CO_2 equivalent for the convenient production and linking it to a possible CO_2 tax or penalty assigned to emissions. This method could be applied for all chemicals assessed in this research. Briefly, to obtain a more realistic price indication for carbon monoxide costs, more research must be conducted. Furthermore, market prices used in this study are taken as constant for all scenarios. Future price developments were not considered in this study. Follow-up research could consider how the market prices of the selected fossil-based chemicals develop. At the moment many developments are taking place regarding the cost of fossil products, which may have a positive effect on the business case for CCU products. In future scenarios, products such as methanol or ethylene glycol may make more sense to produce via CCU when market prices change towards market stimulating fossil-free produced products.

Another focus for future research is more detailed process designs. In this study the process designs were evaluated at conceptual level to perform analysis on their technical and economical performance. For further research, if a pathway is selected for a detailed analysis, a more extensive process design is required. Material flows, conversion performance and utilities used need to be modulated using a professional chemical process simulation program, such as Aspen Plus. Most of the process designs have been worked out in experimental studies and in some cases in scaled-up pilots, where the methods and technologies have been validated. However, some design decisions were based made on assumptions due to lack of available data or low TRL. In particular, oxalic acid is a basic conceptual model. Formation of by-products is uncertain and there is no long term stability reported yet. Additionally, DSP for this OA reaction is only examined for an OA-PC mixture. On further separation of the formed by-products no data is available. Thus, the process design for LTE OA is very pre-mature and research on stabilizing the cell stack and improving DSP should be focus for future research.

Finally, the life cycle assessment performed is a preliminary on the environmental impact of the CCU pathways. The four phases identified according the standardized LCA methodology were used as guidelines to determine the GWI. Future research could focus on a more complete and comprehensive analysis on the environmental impact. To do so, a detailed and simulated process design is required. A complete environmental analysis would be a study on its own. Thus, it will be an interesting follow-up research for a selected CCU pathway which will be analyzed in more detail.

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A

Appendix A: Literature Phase

A.1. CCU pathways

Patway	Product	References
EC		
	Carbon Monoxide	[13] [82]
	Methanol	[35] [135] [136]
	Methane	[39] [37] [48]
	Formic Cid	[35] [34] [7]
	Formaldehyde	[41]
	Ethylene	[68] [42] [30]
	Ehtanol	[37] [137] [138]
	Oxalic Acid	[44] [45]
	Ethylene Glyclol	[46]
	Acetic Acid	[30]
	Glyoxylic Acid	[139]
	Glycolic	[139]
	n-propanol	[140] [141]
TC		
	Methanol	[49] [52] [142]
	Carbon Monoxide	[50] [88] [86]
	Methane	[49] [52]
	Formic Acid	[102]
	Dimethyl Ether	[59] [58] [57] [143]
	Ethylene	[56] [144]
	Ethanol	[72] [60] [145]
	Ethane	[146] [147]
	Acetic Acid	[148] [149]
	Acetaldehyde	[150]
	Methyl Formate	[49] [151]
	Glyoxylic Acid	[139]
	Ethylene Glycol	[139]
	Formaldehyde	[152]

Table A.1: Possible CCU products via electrochemical and thermocatalytical production

A.2. Market price for studied CO$_2$R products

Product	**Price [$/kg]**	**Price [/kg]**	**Annual Production (Mtonne)**	**References**
Carbon Monoxide	0.60	0.53	150	[30]
Methanol	0.37	0.33	100.90	[30][9]
Methane	0.17	0.15	2336	[30][9]
Formic Acid	0.74	0.65	0.60	[30][9]
Formaldehyde	0.50	0.44	45.60	[9]
Ethylene	1.00	0.88	148	[34][30][9]
Ethanol	1.00	0.88	83.30	[34][30][9]
Oxalic Acid	0.66	0.58	2.70	[65]
Ethylene Glycol	0.93	0.82	18.30	[9]
Dimethyl Ether	0.64	0.57	3.70	[58][9]

Table A.2: Carbon Product Prices in Euro per Kilogram and Annual Global Production in Mtonnes per annum

EC Product	**FE [%]**			**CV [V]**			**Ref**
	SOTA	**Near**	**Opt.**	**SOTA**	**Near**	**Opt.**	
carbon monoxide	95	99	100	3	2.5	2	[5] [13] [34]
carbon monoxide (HTE)	99.5	99.5	100	1.41	1.15	0.96	[5] [13] [47]
methanol	77.6	90	100	2.67	2	1.5	[35] [36]
methane	48	90	100	2.94	2.5	2	[37] [38] [39]
formic acid	95	99	100	3.5	2.5	2	[35] [7] [34]
formaldehyde	74	85	100	2.5	2	1.8	[41]
ethylene	70	85	100	2.4	2	1.8	[5] [42] [43] [34]
ethanol	52	85	100	2.21	2	1.5	[37] [34]
oxalic acid	51	85	100	3	2.5	2	[44] [45] [5]
Ethylene Glycol	80	90	100	3	2.5	2	[46]

TC Products	**CO2 Ut. [%]**			**Selectivity [%]**			**Yield [%]**			
	SOTA	**Near**	**Opt.**	**SOTA**	**Near**	**Opt.**	**SOTA**	**Near**	**Opt.**	
carbon monoxide	68	68	68	100	100	100	68	68	68	[49] [50]
methanol	27	27	27	68	90	100	18	24	27	[52] [51]
methane	80	84	85	99	100	100	80	84	84	[53] [54]
formic acid	81		85	40	40	40	16	90	95	[49] [55]
ethylene	20	30	50	90	95	100	35	40	50	[56]
dimethyl ether	31	34	34	85	90	100	73	80	80	[57] [58] [59]
Ethanol	56.5	60	60	98	100	100	55.37	60	60	[60]

Table A.3: Reported performance KPI's per product and conversion technology according to references. Estimations on expected future performance KPI's estimated using reported references and general estimations by Huang et al. [5] and Norksov et al.[74]

B

Appendix B: Design Phase

B.1. Capital and Operating costs assumptions

Parameter	**Assumption**	**IF**$^{(1)}$	**Justification and reference**
Capital Costs			
Pressure Swing Adsorption	1,794,492 * $(X/1000)^{0.7}$	0.85	(X in unit of m3 per hour) [31]
Flash unit	1,794,492 * $(X/1000)^{0.7}$	0.85	(X in unit of m3 per hour) [31]
Distillation Column (LTE OA)	$(X/22700)^{0.60}$*(6008000)	2.1	(X in unit of kg per hour) [5]
GAP unit (LTE OA)	2.144*$(X/1000)^{0.7}$	0.85	(In M(2020), X in unit of kg/hr) [153]
BASF costs (LTE FA)	7.64 M(2020) per 1000 kg/hr		(For 85wt.% purity) [97]
DSP process TC FA	1.44 M(2020) per 1500 kg/hr		(HEX, pumps, DSP) [49]
Operating Costs			
Pressure Swing Adsorption	X * 0.25 * (1/1000)		(X in unit of M3 per hour) [31]
Flash unit	X * 0.25 * (1/1000)		(X in unit of M3 per hour) [31]
Distillation column (LTE OA)	6750 * 0.000293071 in kWh/kg		(Rewritten from Btu/kg to kWh/kg) [5]
BASF (LTE FA)	1461 kW for 1000 kg/hr		[97]
Heating TC FA	2.783 * (1/eff. Boiler)		(Heating in kWh per kg FA) [49]
Cooling TC FA	2.962 * (1/eff. Cooler)		(Cooling in kWh per kg FA) [49]
Utilities HEX	Q = Cp * m * dT		NIST [154][155]

Table B.1: Costs assumptions for downstream processing. First part of graph contains capital costs assumptions, second part assumptions on operating costs of DSP units. (1) IF = Installation Factor

B.1.1. Heating/Cooling streams

In some processes heating and cooling of streams is required. To determine the duty required for this process, the specific heat, mass flow and change in temperature are required. Each component has its own specific heat. Most of them are reported in databases such as NIST. Components of which the specific heat is not mentioned, can be calculated using equation B.1. The heat capacity is calculated in

$\frac{J}{mol\,K}$. t represents the temperature in $\frac{T\,(K)}{1000}$, and each capital letter represents a factor which differs per component. In table B.2 the factors for the components CO_2 and H_2 are listed obtained from NIST [154][155]. Heat capacities for other products were available, no calculations were required.

$$Heat\,Capacity \;=\; A + (B * t) + (C * t^2) + (D * t^3) + (E/t^2) \tag{B.1}$$

	CO2	**H2**
A	25	33.06618
B	55	-11.3634
C	-33.6914	11.43282
D	7.948387	-2.77287
E	-0.13664	-0.15856
Reference	[154]	[155]

Table B.2: Factor for determining heat capacity per component of gaseous stream.

B.2. Costs breakdown analysis

B.2.1. Low temperature electrolysis carbon monoxide

	Unit	**Base**	**Near-term**	**Optimistic**
Cell Performance				
Current Density	$\frac{A}{cm^2}$	2000	5000	10000
Cell Voltage	V	3	2.5	2
faradaic Efficiency	%	0.97	0.99	1
SEC	$\frac{kWh}{kg}$	5.92	4.83	3.83
Stack power density	$\frac{W}{m^2}$	6000	12500	20000
Productivity per installed capacity	$\frac{kg}{h\,MW}$	168.96	206.93	261.27
Installed Capacity	MW	6.21	5.07	4.02
Total Electrode area required	m^2	1035.77	405.94	200.94
Costs Breakdown				
H_2O	$\frac{e}{kg}$	0.00	0.00	0.00
CO_2	$\frac{e}{kg}$	0.24	0.08	0.03
Electricity	$\frac{e}{kg}$	0.37	0.18	0.11
Heat	$\frac{e}{kg}$	0.03	0.02	0.01
Annualized CAPEX Cell	$\frac{e}{kg}$	1.17	0.38	0.18
Annualized CAPEX DSP	$\frac{e}{kg}$	0.14	0.14	0.14
Stack replacement costs	$\frac{e}{kg}$	0.18	0.06	0.03
Total O&M costs	$\frac{e}{kg}$	0.41	0.15	0.07
Total	$\frac{e}{kg}$	2.54	1.00	0.57

Table B.3: Performance and costs breakdown of low temperature electrochemical carbon monoxide production. Technical performance and calculated costs for current-, near term-, and optimistic scenarios reported.

B.2.2. High temperature electrolysis carbon monoixde

	Unit	Base	Near-term	Optimistic
Cell Performance				
Current Density	$\frac{A}{cm^2}$	7500	15000	30000
Cell Voltage	V	1.47	1.47	1.33
faradaic Efficiency	%	0.99	1	1
SEC	$\frac{kWh}{kg}$	2.84	2.81	2.55
Stack power density	$\frac{W}{m^2}$	11025	22050	39900
Productivity per installed capacity	$\frac{kg}{h\,MW}$	351.92	355.47	392.89
Installed Capacity	MW	2.98	2.95	2.67
Total Electrode area required	m^2	270.63	133.96	66.98
Costs Breakdown				
H2O / H2	$\frac{e}{kg}$	0.00	0.00	0.00
CO2	$\frac{e}{kg}$	0.24	0.08	0.03
Electricity	$\frac{e}{kg}$	0.29	0.18	0.11
Heat	$\frac{e}{kg}$	0.06	0.03	0.02
Annualized CAPEX Cell	$\frac{e}{kg}$	0.32	0.11	0.04
Annualized CAPEX DSP	$\frac{e}{kg}$	0.13	0.13	0.13
Stack replacement costs	$\frac{e}{kg}$	0.05	0.02	0.01
Total O&M costs	$\frac{e}{kg}$	0.12	0.05	0.03
Total	$\frac{e}{kg}$	1.21	0.60	0.37

Table B.4: Performance and costs breakdown of high temperature electrochemical carbon monoxide production. Technical performance and calculated costs for current-, near term-, and optimistic scenarios reported.

B.2.3. Thermocatalysis carbon monoxide

	Unit	Base	Near-term	Optimistic
Reactor Performance				
Product yield CO_2	%	100	100	100
CO2 Conversion	%	64	90	100
Product yield H_2	%	99	300	100
H2 conversion	%	38	90	100
Costs Breakdown				
H_2	$\frac{e}{kg}$	0.18	0.13	0.13
CO_2	$\frac{e}{kg}$	0.08	0.08	0.03
Electricity	$\frac{e}{kg}$	0.01	0.01	0.01
Heat	$\frac{e}{kg}$	0.06	0.06	0.04
Catalyst	$\frac{e}{kg}$	0.00	0.00	0.00
Annualized CAPEX Cell	$\frac{e}{kg}$	0.03	0.02	0.02
Annualized CAPEX DSP	$\frac{e}{kg}$	0.06	0.05	0.05
Stack replacement costs	$\frac{e}{kg}$	0.02	0.02	0.02
Total O&M costs	$\frac{e}{kg}$	0.01	0.02	0.02
Total	$\frac{e}{kg}$	0.46	0.38	0.31

Table B.5: Performance and costs breakdown of thermocatalytic carbon monoxide production. Technical performance and calculated costs for current-, near term-, and optimistic scenarios reported.

B.2.4. Low temperature electrolysis formic acid

	Unit	Base	Near-term	Optimistic
Cell Performance				
Current Density	$\frac{A}{cm^2}$	2000	5000	10000
Cell Voltage	V	3.75	2.5	2
faradaic Efficiency	%	0.82	0.95	0.99
SEC	$\frac{kWh}{kg}$	4.53	2.60	2.00
Stack power density	$\frac{W}{m^2}$	7500	12500	20000
Productivity per installed capacity	$\frac{kg}{h\,MW}$	1.66	4.80	10.00
Installed Capacity	MW	4.75	2.74	2.10
Total Electrode area required	m^2	633.74	218.81	104.98
Costs Breakdown				
H2O / H2	$\frac{e}{kg}$	0.00	0.00	0.00
CO2	$\frac{e}{kg}$	0.12	0.04	0.02
Electricity	$\frac{e}{kg}$	0.27	0.09	0.05
Heat	$\frac{e}{kg}$	0.09	0.05	0.03
Annualized CAPEX Cell	$\frac{e}{kg}$	0.70	0.20	0.08
Annualized CAPEX DSP	$\frac{e}{kg}$	0.27	0.26	0.26
Stack replacement costs	$\frac{e}{kg}$	0.10	0.03	0.01
Total O&M costs	$\frac{e}{kg}$	0.33	0.16	0.12
Total	$\frac{e}{kg}$	1.87	0.84	0.57

Table B.6: Performance and costs breakdown of low temperature electrochemical formic acid production. Technical performance and calculated costs for current-, near term-, and optimistic scenarios reported.

B.2.5. Thermocatalysis formic acid

	Unit	Base	Near-term	Optimistic
Reactor Performance				
Product yield CO_2	%	81	90	100
CO2 Conversion	%	98	100	100
Product yield H_2	%	63	90	100
H2 conversion	%	19	90	100
Costs Breakdown				
H_2	$\frac{e}{kg}$	0.34	0.15	0.10
CO_2	$\frac{e}{kg}$	0.17	0.05	0.02
Electricity	$\frac{e}{kg}$	0.01	0.01	0.01
Heat	$\frac{e}{kg}$	0.30	0.18	0.12
Catalyst	$\frac{e}{kg}$	0.95	0.50	0.11
Annualized CAPEX Cell	$\frac{e}{kg}$	0.11	0.11	0.11
Annualized CAPEX DSP	$\frac{e}{kg}$			
Stack replacement costs	$\frac{e}{kg}$	0.03	0.03	0.03
Total O&M costs	$\frac{e}{kg}$	0.04	0.04	0.04
Total	$\frac{e}{kg}$	1.96	1.07	0.53

Table B.7: Performance and costs breakdown of thermocatalytic formic acid production. Technical performance and calculated costs for current-, near term-, and optimistic scenarios reported.

B.2.6. Low temperature electrolysis oxalic acid

	Unit	Base	Near-term	Optimistic
Cell Performance				
Current Density	$\frac{A}{cm^2}$	1000	5000	10000
Cell Voltage	V	4	2.5	2
faradaic Efficiency	%	0.8	0.9	0.95
SEC	$\frac{kWh}{kg}$			
Stack power density	$\frac{W}{m^2}$	4000	12500	20000
Productivity per installed capacity	$\frac{kg}{h\ MW}$	335.91	604.65	797.80
Installed Capacity	MW	3.13	1.74	1.32
Total Electrode area required	m^2	781.45	138.92	65.81
Costs Breakdown				
H2O / H2	$\frac{e}{kg}$	0.00	0.00	0.00
CO2	$\frac{e}{kg}$	0.18	0.05	0.02
Electricity	$\frac{e}{kg}$	0.21	0.07	0.03
Heat	$\frac{e}{kg}$	0.16	0.08	0.05
Annualized CAPEX Cell	$\frac{e}{kg}$	0.78	0.12	0.05
Annualized CAPEX DSP	$\frac{e}{kg}$	0.19	0.13	0.13
Stack replacement costs	$\frac{e}{kg}$	0.12	0.02	0.01
Total O&M costs	$\frac{e}{kg}$	0.31	0.08	0.06
Total	$\frac{e}{kg}$	1.95	0.55	0.35

Table B.8: Performance and costs breakdown of low temperature electrochemical oxalic acid production. Technical performance and calculated costs for current-, near term-, and optimistic scenarios reported.

B.2.7. Future performance analysis

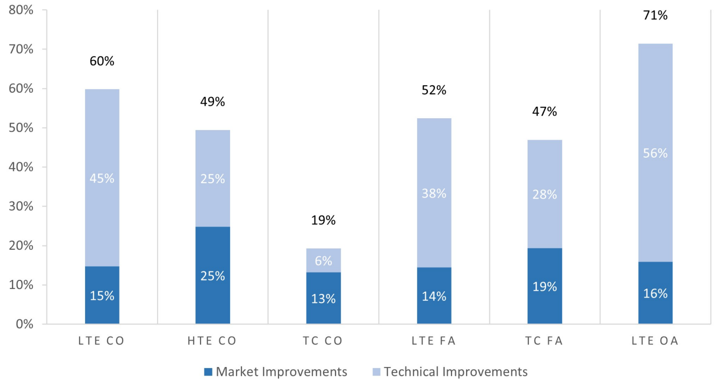

Figure B.1: Percentage reduction in production costs moving from current scenario towards optimistic future scenario. Distinction made between reduction due to technical (light blue) and market (dark blue) parameters.

B.3. Life Cycle Assessment

B.3.1. Electricity Mix

Electricity Source	**2020**	**2030**	**2050**	**Reference**
Nuclear	0.003	0.002	0.001	[126]
Solids (coal)	0.115	0.066	0.000	[126]
Gaseous fuels (NG)	0.093	0.074	0.064	[126]
Biomass	0.014	0.012	0.014	[126]
Hydropower	0.003	0.003	0.003	[126]
Wind	0.002	0.003	0.004	[126]
Solar	0.003	0.006	0.009	[126]
Total	**0.232**	**0.165**	**0.095**	

Table B.9: Kilogram CO_2-equivalent per produced kWh of produced electricity for energy mix of 2020, 2030 and 2050. Numbers adapted from EU Reference Scenario 2020 [126].

B.3.2. Breakdown GWI per product

Product	**H2**	**CO2**	**CO**	**MeOH**	**Electricity**	**Heat**	**CO2 emission [kg]**	**GWI [kg CO2-eq/kg]**
Formic Acid								
Conventional	0,00	0,00	0,96	0,01	0,03	1,24	0,01	2,26
LTE		-0,81	0,00	0,00	1,24	0,40	0,00	0,83
TC	1,04	-1,16	0,00	0,00	0,07	1,41	0,00	1,35
Carbon Monoxide								
Conventional								1,57
LTE		-1,57	0,00	0,00	1,72	0,13		0,28
HTE		-1,57	0,00	0,00	0,66	0,96		0,05
TC	0,87	-1,57	0,00	0,00	0,11	0,43		-0,16
Oxalic Acid								0,00
Conventional			1,22		0,03	1,24	0,20	2,69
LTE	0,00	-1,22	0,00	0,00	0,69	0,27		-0,26

Table B.10: Break down of global warming impact per product for each conversion pathway. Numbers in graph represent emission factors in kg CO_2-eq per kilogram of product. Each column is indicates contributing factor to the total GWI. Most right column is the total global warming impact per pathway.