Performance Assessment of Industrial-scale *n*-Caproate Production utilizing CO_2 as Feedstock

A comparitive study between different n-caproate production pathways at the Port of Rotterdam

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by

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Abstract

The Port of Rotterdam is one of the largest CO_2 emitters of the Netherlands. One method to reduce its emissions is by implementing carbon capture and utilization (CCU) technologies. In this research two different CCU routes for industrial-scale *n*-caproate production are compared. The first route utilizes microbial electrosynthesis (direct route). The second route uses syngas formation via electro-reduction combined with syngas fermentation (indirect route).

Based on the European Union's technology readiness level, the maturity of both routes is ranked as 3 to 4. This indicates that both routes are in the demonstration phase. In this phase scientists play an important role, as the focus is on researching the technology's overall feasibility. It is also the phase in which financial barriers are the most pressing. Early-stage investors can help overcome these barriers, by allocating (financial) resources. Nonetheless, an assessment method taking both scientists' as well as early-stage investors' perspectives into account is missing. This research contributes to filling this knowledge gap.

The methodology applied is bricolage, using a mixture of literature research, simulation data and interviews. Data of the direct route is retrieved from literature research. To obtain data of the indirect route, a simulation is made in Aspen Plus v12. An overview of important assessment parameters are acquired via the conducted interviews.

In total 15 participants are interviewed, of which; 8 scientists working on CCU technologies, 5 early-stage investors, 1 governmental policy executing party and 1 NGO. These interviews, combined with metrics found in literature research, led to an overview of parameters to be assessed for a performance analysis.

Overall, 10 metrics are selected and used for the performance assessment. These include technical, economic, environmental and strategic metrics. The technical assessment showed that the indirect route has a significantly higher energy consumption compared to the direct route (0.35 $GJ/kg_{caproate}$ compared to 0.1 $GJ/kg_{caproate}$). However, the indirect route has a higher production selectivity towards *n*-caproate. The economic performance assessment resulted in a lower CAPEX and OPEX for the direct route. Still, for both routes, the minimum *n*-caproate selling price is below the current *n*-caproate market price. The net carbon footprint of the indirect route is 7.3 $kg_{CO_2}/kg_{caproate}$, indicating that a significant amount of CO_2 is being emitted during its production.

While an analysis at this maturity stage of the production routes comes with uncertainties, it gives a first sound indication of its performance and bottlenecks. For the indirect route, the energy consumption is dominated by the two electrolyzers used and the downstream processing. This energy consumption is also the main contributor to the OPEX (47%) and the carbon footprint (79%). Another factor largely responsible for the carbon footprint are the emissions during fermentation (19%). The main cost item of the equipment cost is the H_2O alkaline electrolyzer (42% of total cost).

To conclude, the indirect route shows the potential of industrial-scale *n*-caproate production with a high selectivity. Nonetheless, it is key to reduce its energy consumption and implement more efficient off-gas recycling to improve its techno-economic and environmental performance.

Nomenclature

General Abbreviations

AEA	Aspen Energy Analyzer v12
APEA	Aspen Process Economic Analyzer v12
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
EA	Environmental Analysis
ESG	Environmental Social and Governance
ETS	Emission Trading System
GHG	Greenhouse Gas
II-grid	Influence-Interest grid
IPCC	Intergovernmental Panel on Climate Change
IPR	Intellectual Property Rights
KPI	Key Performance Indicator
MOB	Mobilization for the Environment
NGO	Non-Governmental Organization
RVO	Rijksdienst voor Ondernemend Nederland
TEA	Techno-economic Assessment
TIS	Technological Innovation System
TRL	Technology Readiness Level

Economic Abbreviations

BA	Business Angel
CAGR	Compound Annual Growth Rate
CAPEX	Capital Expenditures
CF	Cash Flow
DCF	Discounted cash flow
ESI	Early-stage Investor
FCI	Fixed Capital Investment
FO	Family Office
IA	Information Asymmetry
IPO	Initial Public Offering
IRR	Internal rate of return
MCSP	Minimum Caproate Selling Price
NPV	Net Present Value
OPEX	Operational Expenditures
PE	Private Equity
VC	Venture Capital
WCI	Working Capital Investment

Technical Abbreviations

AEL	Alkaline Electrolyzer
CEM	Cation Exchange Membrane
DO	Direct Oxidation
DSP	Downstream Processing
EPC	Electric Power Consumption
FGD	Flue gas desulfurization
ISPR	*In-situ* Product Recovery
LLE	Liquid-Liquid Extraction
LSM	$La_{1\text{-}x}Sr_xMnO_{3\pm\delta}$
MES	Microbial Electrosynthesis
MOEC	Molten Carbonate Electrolysis Cells

PEMEL	Proton Exchange Membrane
RBO	Reverse β-oxidation Pathway
SOEC	Solid Oxide Electrolysis Cells
TOA	Trioctylamine
WLP	Wood-Ljungdahl Pathway
YSZ	Yttria-Stabilized Zirconia

Definitions

Definition (**Business Angel**)**.** A high net worth individual who invest his/her own money, along with time and expertise, directly in unquoted companies in which they have no family connection, in the hope of financial gain *(Harrison et al. 2015)*.

Definition (**Capital Expenditures**)**.** The total amount of money needed to supply the necessary plant and manufacturing facilities, plus the amount of money required as working capital for operation of the facilities. Consists of direct cost, indirect cost and working capital *(Peters et al. 2003)*.

Definition (**Cleantech**)**.** Any product, service or process that delivers value using limited or zero non-renewable resources and/or creates significantly less waste than conventional offerings *(Gray and Caprotti 2011)*.

Definition (**Early-stage Investors**)**.** Financing parties helping to overcome the Valley of Death. The parties can be publicly or privately funded. They include business angels, family offices, venture capital, private equity and crowdfunding.

Definition (**Family Offices**)**.** Organizations that manage the wealth of business families by taking actions (i.e., investments) to sustain and grow their wealth *(Block et al. 2019)*.

Definition (**Hard & Soft Institutions**)**.** Formal institutional mechanisms, such as laws, intellectual property rights and industry standards (hard). Norms and values (soft) *(Vroon et al. 2021), (Woolthuis et al. 2005)*.

Definition (**Influence**)**.** The power to have an effect on people or things, or a person or thing that is able to do this *(*Cambridge Dictionary *2022)*.

Definition (**Infrastructure**)**.** The availability of finance for innovation in the form of venture capital, funds, subsidies or programs *(O'Sullivan 2005)*.

Definition (**Interest**)**.** The feeling of wanting to give your attention to something or of wanting to be involved with and to discover more about something *(*Cambridge Dictionary *2022)*.

Definition (**Interview Guide**)**.** A list of questions which directs conversation towards the research topic during the interview *(Kallio et al. 2016)*.

Definition (**Network**)**.** Cooperative relationships and links between actors *(Wieczorek and Hekkert 2012)*.

Definition (**Operational Expenditures**)**.** Consists of the variable production cost, fixed production cost and the overhead cost *(Peters et al. 2003)*.

Definition (**Private Equity**)**.** The provision of capital and management expertise given to companies to create value and, consequently, generate [big] capital gains after the deal *(Caselli and Negri 2021)*.

Definition (**Stakeholder(s)**)**.** Individuals or groups who have an interest or some aspect of rights or ownership in the project, and can contribute to, or be impacted by, either the work or the outcomes of the project *(Walker et al. 2008)*.

Definition (**Technological Innovation System [TIS]**)**.** A network of agents interacting in the economic/industrial area under a particular institutional infrastructure and involved in the generation, diffusion, and utilization of technology *(Vroon et al. 2021)*.

Definition (**Valley of Death**)**.** The middle part between government-funded R&D and self-sustaining funding from customers. The phase in which innovative technology firms struggle most *(Bürer and Wüstenhagen 2009)*.

Definition (**Venture Capital**)**.** A high-risk financial capital provision for innovative ventures, which offers the potential for financial returns *(Randjelovic et al. 2003)*.

Contents

Chapter 1

Introduction

"It has been clear for decades that the Earth's climate is changing, and the role of human influence on the climate system is undisputed" Valérie Masson-Delmotte, co-chair IPCC.

The Intergovernmental Panel on Climate Change (IPCC) states that human activities are responsible for a global temperature increase of approximately 1.1 ℃ in between 1850 to 2021 (IPCC 2021). If this increase surpasses 1.5 ℃, heat extremes with a devastating effect on agriculture and human health will occur more often (IPCC 2021). To limit global warming to 1.5 ℃ , carbon emissions need to be reduced by 49% in 2030, compared to the level in 2017 (Tollefson 2018). Even though several air pollutants enhance global warming, the main driver of climate change is CO_2 (IPCC 2021) (ElMekawy et al. 2016).

1.1 CO_2 as a Resource for *n*-Caproate Production

The accumulation of CO_2 highlights the importance of reshaping our economic system. Changing it from a linear economy to a circular economy can be seen as part of the solution of overcoming (harmful) waste generation (Jourdin et al. 2020). In a circular economy, CO_2 can be used as a resource for the production of renewable materials. Technologies that seek to not only reduce CO_2 emissions, but also to obtain a benefit through the use of it, are called 'Carbon Capture and Utilization (CCU)' technologies. CCU utilizes CO_2 in different types of industrial processes to replace conventional raw materials (Aresta 2010) (Baena-Moreno et al. 2019). CCU technologies can be seen as examples of 'clean technologies' ('cleantech'). This term refers to *"any product, service or process that delivers value using limited or zero nonrenewable resources and/or creates significantly less waste than conventional offerings"* (Gray and Caprotti 2011) (Georgeson et al. 2014). Solely implementing CCU techniques will not be enough to solve the issue of climate change, but producing carbon emission free/limited renewables is seen as an essential step to mitigate the problem (Baena-Moreno et al. 2019).

Multiple chemical compounds can be produced with CO_2 as feedstock. A main category of these chemicals are carboxylic acids/carboxylates. Carboxylic acids are organic compounds with a general structure of R-COOH, carboxylates are the dissociated form (Senboku and Katayama 2017). In specific the carboxylate *n*-caproate ($C_5H_{11}COOH$) is targeted as it has several advantages over other carboxylates (Wood et al. 2021). Firstly, it has multiple industrial usages and can be used as platform chemical. Some of its applications are as an antimicrobial agent, an additive in animal feed, a flavor additive, a lubricant and as a precursor for drop-in fuels and bio-plastics (de Araújo Cavalcante et al. 2017) (Urban et al. 2017) (Jourdin et al. 2020) (Lambrecht et al. 2019) (Kaitwade 2021). Secondly, preliminary techno-economic reviews state *n*-caproate as the only chemical that can be produced completely renewable at a market-competitive price via the technologies this research focuses on (Wood et al. 2021) (Jourdin et al. 2020). Thirdly, *n*-caproate has a process advantage. It has a relative ease of extraction due to its low solubility in water (Wood et al. 2021) (W. Chen et al. 2017).

Thus, *n*-caproate is a promising carboxylate to target for CO_2 valorization in the context of this research.

1.1.1 *n*-Caproate Market Outlook

n-Caproate is currently made as a by-product of palm oil refining. The main production bases are in Malaysia and Indonesia (Nebraska 2022). Malaysia is the world's largest producer and exporter of palm oil. It contributes to about 47% of the total world's supply (Haslenda and Jamaludin 2011). Global major companies producing *n*-caproate and palm oil include Braido, Oleon NV, Vigon International and Arizona Chemicals (Expresswire 2022). In general, *n*-caproate is being sold at a purity of 98% or above (Expresswire 2022). In this research, a purity of 99% is targeted. *n*-Caproate from this purity has a current market price in between €4.4 per kg and €55 per kg, depending on the quantity ordered (Merck 2022) (TCI-Chemicals 2022) (Jourdin et al. 2020). Orders in size from above a tonne are reported to be priced around €4400 per tonne (Jourdin et al. 2020).

The annual global production of *n*-caproate is around 25-30 kilo-tonne (Jourdin et al. 2020) (Wood et al. 2021) (Zacharof and Lovitt 2013). In 2020, it had a global market value of €162.15 million. In the period of 2020 to 2027, it is expected to grow with a compound annual growth rate (CAGR) of 5.6%, reaching a market size of €237.63 million by 2027. Growth is especially expected in China (CAGR of 9.1%), Canada (CAGR of 4.5%) and Germany (CAGR of 3.9%) (Research and Markets 2021). The growth in China is expected to be caused by the increasing demand for personal care products. The growth in North America and Europe is anticipated to be caused by the growth of polymer processing industries (Kaitwade 2021). The variety of usages and the expected market growth highlight the market potential of sustainable *n*-caproate production.

1.1.2 Different Routes for *n*-Caproate Production

As stated above, the conventional route of *n*-caproate production is via fractional distillation of palm or coconut oil (de Araújo Cavalcante et al. 2017) (Jourdin et al. 2020). However, solely 1% of these oils consist of *n*-caproate, making the production process inefficient (Wood et al. 2021). Moreover, the recent expansions of palm and coconut oil plantations in Asia have caused concerns about the potential negative environmental impacts. These expansions are reported to cause a decline in biodiversity and an increase in greenhouse gas emissions, air pollution and peatland draining (Meijaard et al. 2020). Thus, a more sustainable production process of *n*-caproate would be desired.

n-Caproate can also be produced via two different CCU pathways. As first option, it can be achieved via microbial electrosynthesis (MES). Here, CO_2 , (renewable) energy and microorganisms are used to produce *n*-caproate (Wood et al. 2021). The second option is to combine syngas formation via electro-reduction with syngas fermentation (Wood et al. 2021). Syngas consists mainly of CO and H_2 , but its precise composition is dependent on the feedstock and process conditions (Wilhelm et al. 2001). In this route, syngas is produced out of CO_2 and H_2O. Subsequently, the produced syngas is converted into *n*-caproate via microbial fermentation (Vasudevan et al. 2014).

The MES route converts CO_2 directly via fermentation into *n*-caproate. Therefore it is referred to as the 'direct' route. The other option utilizes syngas as an intermediate. In the rest of this report, it is referred to as the 'indirect' route. The direct route has been simulated and analyzed previously (Luo et al. 2022). The focus of this research will therefore be on the indirect route and its comparison to the direct route.

A schematic overview of the three production routes can be found in Figure 1.1.

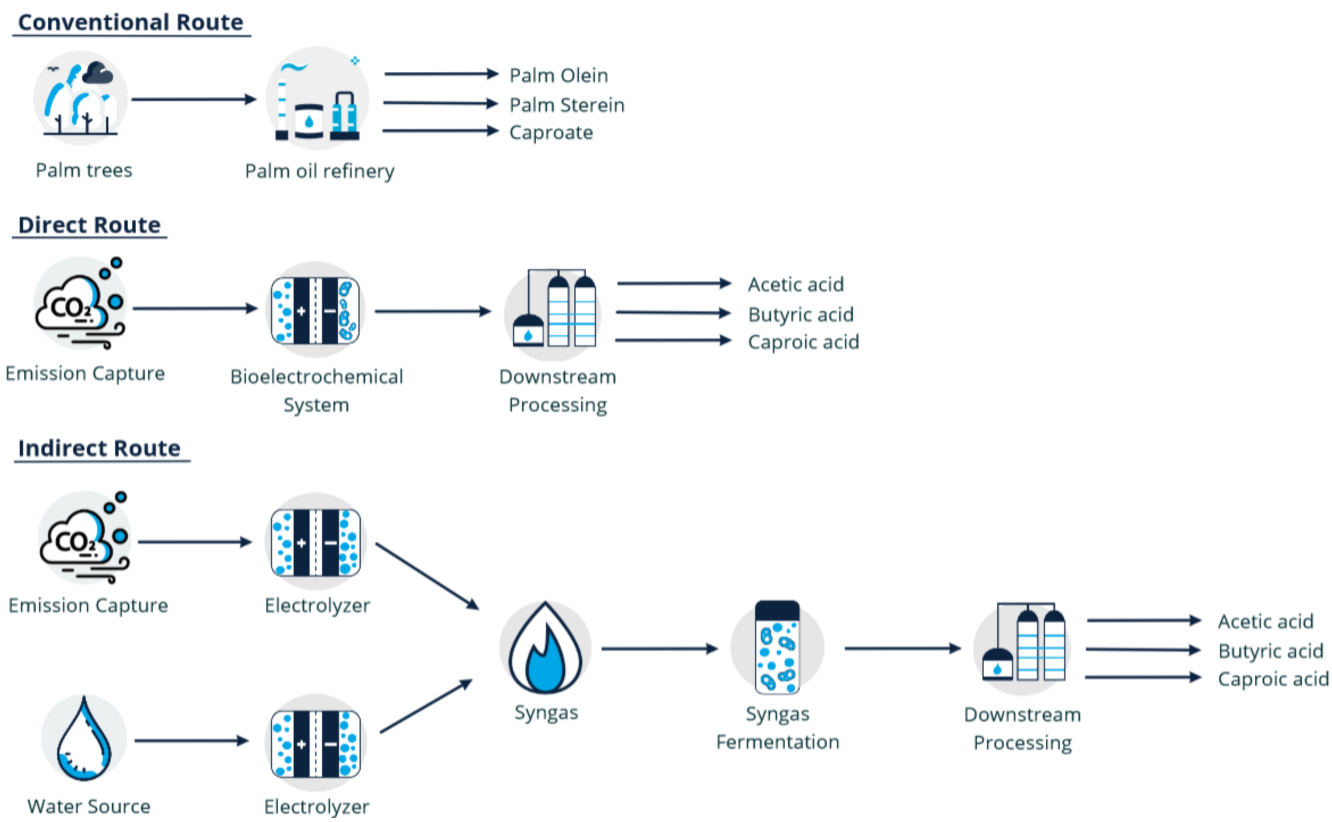

Figure 1.1: Schematic overview of the three *n*-caproate production routes. The conventional route uses palm or coconut trees as a feedstock. The direct and indirect route use CO_2 . In the direct route CO_2 is directly converted by microbial electrosynthesis. The indirect route produces syngas as intermediate. *Based on Mba et al. 2015 and Wood et al. 2021*

1.2 Performance of the Indirect *n*-Caproate Production Route

Using CCU technologies for successful climate change mitigation, would benefit from advancing the technologies with the best performance (Van der Spek, Ramirez, et al. 2017). Hence, it is useful to assess the performance of the indirect route. This would enable a comparison to other CCU routes and, more specifically, to the direct route. The interest is in the performance of both routes on an industrial-scale, but CCU-based *n*-caproate production on such a scale is not yet present. Constructing a detailed, rigorous process model is also difficult, due to limitations in data, time and resources (Van der Spek, Ramirez, et al. 2017).

Nevertheless, even at a very early stage, it is possible to perform an assessment with an acceptable level of reliability. If certain conditions are met, a thrust-worthy future commercial state of the technology can be predicted. These conditions are; 1) the presence of initial estimates for the energy use and, 2) the possibility to draw-up a generic equipment list (Van der Spek, Ramirez, et al. 2017).

The maturity stage of a technology is associated with a specific data availability level and accuracy. This data availability and accuracy affects the approach and robustness of the performance analysis (Rafiaani et al. 2020). Therefore, it is important to firstly analyze the technological maturity level of the (in)direct route. Based on this development stage, an appropriate approach for its performance assessment can be chosen.

1.2.1 Technology Readiness Level (TRL)

A method to track and compare a technology's maturity is by using the Technology Readiness Level (TRL) metric (Zimmermann and Schomäcker 2017). This scale is used by the European Union to position requested projects on the Horizon Europe project (*Horizon Project - Annex G* 2020). An overview of the TRL scale is shown in Figure 1.2.

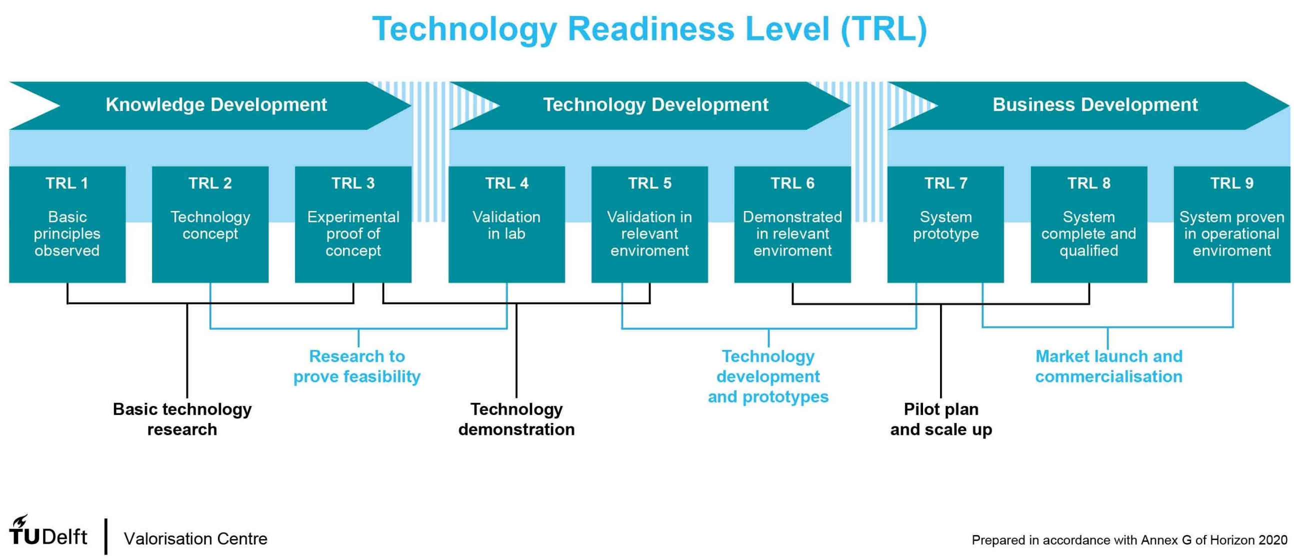

Figure 1.2: Overview of the Technology Readiness Level scale. This scale is used by the European Union to indicate the position of a technology. *Retrieved from: E-refinery 2022.*

When applying the levels described in Figure 1.2, the current n-caproate production route can be set at TRL 9. Considering the direct and indirect route, the level is lower. The direct route uses MES of which different applications are possible. Dependent on the application, the TRL ranges between 2 to 7 (Fruehauf et al. 2020). When looking at the MES process variant that would be used for direct n-caproate production, a TRL of 3 to 4 is appropriate (Fruehauf et al. 2020) (Roy et al. 2022).

The indirect route consists of multiple technologies, namely CO_2 and H_2O electrolysis and syngas fermentation. Different types of electrolyzers and different modes of fermentation are possible to reach n-caproate production. The TRL of the route is dependent on the electrolyzers, fermentation process and downstream processing methods chosen. Nonetheless, the TRL of n-caproate production via the indirect route is expected to be also in the range of 3 to 4 (Fernández-Blanco et al. 2022) (P. Yang et al. 2018).

Development towards a higher TRL

The development and diffusion of CCU technologies, and cleantech in general, is hampered by multiple barriers (Polzin 2017). An overview of the type of barriers present in each development phase is shown in Figure 1.3. Highlighted is the demonstration phase, the phase which encompasses TRL 3-5 (see Figure 1.2). Governmental policies as well as finance instruments and structures can help overcoming barriers in all development phases.

As depicted in Figure 1.3, technologies in the demonstration phase encounter technological, economic, financial, political and transformational barriers. Of these barriers, one of the most salient is the financial one (Polzin 2017) (Polzin et al. 2016), (Iyer et al. 2015). The demonstration phase, combined with the

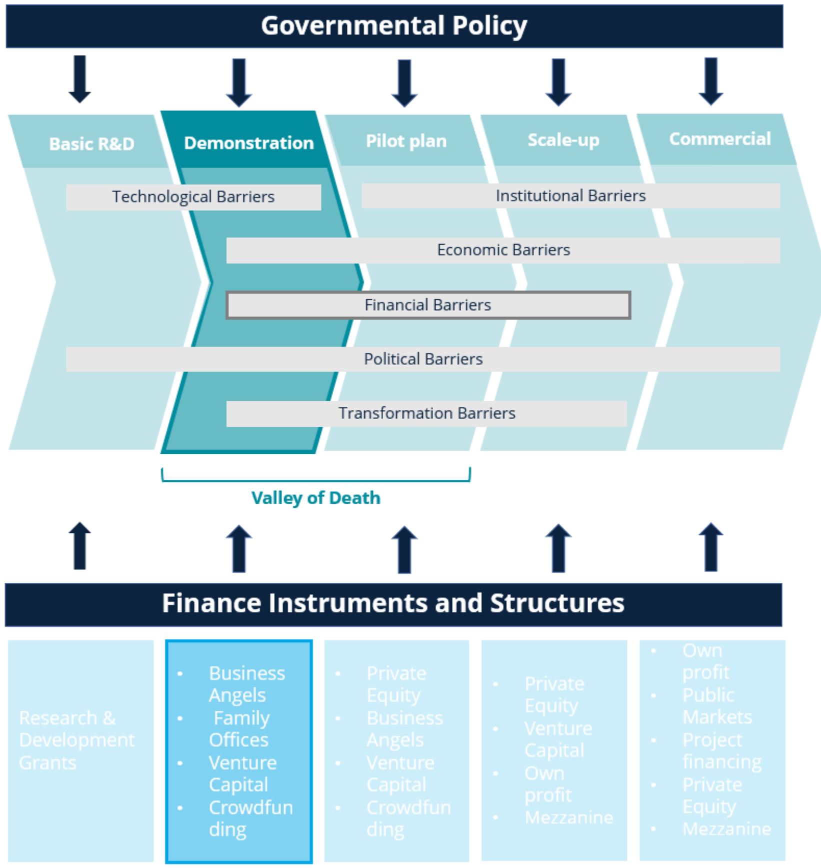

Figure 1.3: Overview of the type of barriers present at each phase of cleantech development. Barriers are not mutually exclusive. Moreover, the common forms of financing per phase are shown. The indirect route is at the start of the demonstration phase. General important financing parties at this phase are business angels, family offices, venture capital and crowdfunding. *Adapted from: Polzin 2017 and Bürer and Wüstenhagen 2009.*

pilot-plan phase, is also known as the 'Valley of Death'. The Valley of Death describes the part between government-funded R&D and self-sustaining funding from customers (Bürer and Wüstenhagen 2009). In these phases, attracting financing is the most difficult and innovative technology firms struggle the most (Bürer and Wüstenhagen 2009).

The financing parties helping to overcome the Valley of Death are mostly; business angels (BA), family offices (FO), venture capital (VC) and private equity (PE) (Polzin 2017) (Bürer and Wüstenhagen 2009). In this research the following definitions are used for these parties. A business angel is *"a high net worth individual who invest his/her own money, along with time and expertise, directly in unquoted companies in which they have no family connection, in the hope of financial gain"* (Harrison et al. 2015). The term family office refers to *"organizations that manage the wealth of business families by taking actions (i.e., investments) to sustain and grow their wealth"* (Block et al. 2019). Private equity indicates *"the provision of not only capital, but also management expertise to companies to create value."* PE obtains capital gains from this deal (Caselli and Negri 2021). Lastly, venture capital refers to *"a high-risk financial capital provision for innovative ventures, which offers the potential for financial returns"* (Randjelovic et al. 2003). All these parties combined are called 'early-stage investors' (ESIs). Mostly BA, FO and VC look into technologies in the demonstration phase. PE looks more into the pilot plan and scale-up phase (Grubb 2004). Nonetheless, most early-stage investors are not limited to one phase and the phases should not be seen as demarcated (Polzin 2017).

Financing can be obtained via governmental funds and/or via early-stage investors. In order to limit global warming, an estimated cleantech investment of 1-2% of the global GDP is necessary (Polzin 2017). This amount surpasses the budgets of governmental funding. As a result, in addition to the governmental funds attracting (private) early-stage investments is of key importance (Polzin 2017). Unfortunately, as widely described in literature, cleantech is generally underfunded (Harrer and Owen 2022) (Owen et al. 2020) (Jensen et al. 2020).

1.2.2 Attracting Financing from Early-Stage Investors

In the period of 2004-2011, cleantech investments have experienced a so-called 'boom and bust'. Since then, the amount of early-stage investments in cleantech have remained constant and low (Gaddy et al. 2017) (Eilperin 2012). This is problematic, as investments in the this stage are seen as an important catalyst to develop sustainable businesses (Bocken 2015). Nevertheless, an opportunity for the recovery in (private) cleantech funding is present (Gaddy et al. 2017). Announcements made at the 2015 Paris Climate Change Conference and by the Breakthrough Energy Coalition (a group of wealthy investors led by Bill Gates) lead to a renewed tailwind (Gaddy et al. 2017). However, it is vital that past mistakes leading to the previous boom and bust are avoided.

Research conducted by Bocken 2015 draws lessons from these past mistakes. Even though it is hard to pinpoint all influences, some factors that contributed to the failure can be found. These include a lack of suitable investors and a short-term investor mind-set. Focusing on ESIs with longer time horizons (>5 years) is advised (Bocken 2015) (Gaddy et al. 2017). These type of ESIs generally include governmental-sponsored investment funds and family offices (Gaddy et al. 2017). Therefore the ESIs discussed in this research are mostly governmental funded or VCs/FOs. All have a long (10+ years) time horizon.

In general, ESIs attempt to carry out exhaustive analyses before they fund a business (Marcus et al. 2013). Nonetheless, the resources to perform these analyses are limited. Typically, only 10% of the business plans coming to an ESI's attention gets a serious look and solely 1% is actually funded (Marcus et al. 2013). Next to the difficulty of obtaining early-stage investments, which is hard for all type of innovations, cleantech faces an additional challenge. As stated by Harrer and Owen 2022, cleantech business cases are in general riskier and more difficult to understand (Gaddy et al. 2017). For example, an investor often has limited detailed knowledge of how the innovation achieves CO_2 emission reduction (Owen et al. 2020). As a result, information asymmetries (IAs) for investors are amplified, hampering funding in cleantech (Harrer and Owen 2022).

The chances of receiving early-stage funding can be enlarged by understanding the factors influencing the relevant ESIs' decision making and reducing IA (Michelfelder et al. 2022) (Harrer and Owen 2022). IAs can be reduced by focusing on effective communication between parties and acknowledging the heterogeneity between early-stage investors (Harrer and Owen 2022) (Clarke et al. 2019). The metrics on which an ESI's decision is based are heterogeneous, investor specific and exceed the aim for financial gains (Bocken 2015). Effective communication refers to, among others, how the value proposition is expressed (Clarke et al. 2019). Even if the value proposition is the same, key actors in early-stage cleantech funding use different performance indicators to communicate it. An analysis of which indicators are preferred by key stakeholders could help improve communicating the business' performance and thus reduce information asymmetries (Harrer and Owen 2022).

1.2.3 Performance Assessment at a low TRL

Different methods to assess a technology's performance at a TRL 3 to 4 are present. One of the possible approaches for the assessment of a technology is to look into key performance indicators (KPIs) (Peterson

2006) (Bortoluzzi et al. 2021). This is a general business method to evaluate and compare a process (Bortoluzzi et al. 2021). According to Peterson 2006, the concept of KPIs tries to present technical data in a 'business-relevant language'. KPIs can be used for assessing environmental, technical and economic performance. It is also used by different stakeholders to communicate a business' value proposition (Harrer and Owen 2022). The usage of these indicators might be widely applied by investors, but their use is limited in performance analyses of processes concerning sustainable development (Schramade 2017).

An approach more commonly used for the assessment of sustainable processes is a technology's full life-cycle cost (Hardisty et al. 2011). It can be argued that without considering a full life-cycle, it is not possible to judge whether a technology is a truly effective option for climate change mitigation (Hardisty et al. 2011). The full life-cycle cost include the total environmental, social and economic benefits, but also its costs and risks (Hardisty et al. 2011). However, taking all these factors into account for a low TRL technology proves to be difficult due to a lack of data (Rafiaani et al. 2020).

At a low TRL an analysis can be made of which KPIs are most important for its assessment. These KPIs can be a starting point for a full life-cycle analysis (Rafiaani et al. 2020). The factors to be analyzed can be obtained and considerately narrowed down by researching those important from an expert point of view. By doing so, it shows an overview of the most and least relevant aspects. This helps prioritizing which parameters should be assessed (Rafiaani et al. 2020).

Considering the TRL of the direct and indirect route and the scope of this research, two groups can be considered experts. Firstly, the scientists working on CCU technologies related to one of the routes. This group is involved in the research to improve the overall feasibility of the technology. The second expert group consists of parties from the finance community. As described in Section 1.2.1, especially governmental-funded ESIs and family offices are of interest.

1.3 Research Gap

Three different methods to produce *n*-caproate are discussed. Of these routes, solely the production via palm oil distillation is currently being operated at commercial scale. The other two routes are an example of carbon capture and utilization. Hence, these routes use CO_2 as feedstock and offer the potential towards a more sustainable production process. However, these routes have a TRL of approximately 3-4. In order to analyze and compare the performance of the low TRL routes, an *ex-ante* performance analysis can be made. Such an analysis is present for the direct *n*-caproate production route, but absent for the indirect route. Not only is such an analysis for this route not yet present, a framework of parameters most important for the assessment and comparison of the different CCU routes is missing.

The parameters for this assessment can be determined by the experts involved in this stage of the technology. In this context, experts refer to the scientists working on technologies related to the (in)direct route and long-term early-stage investors. Due to the heterogeneity of the stakeholders, the perspective of those stakeholders specifically involved for the indirect route should be taken into account. To the best of the author's knowledge, the perspective of both groups regarding either the direct or indirect route has not been considered before. Furthermore, the performance of an industrial-scale indirect route has not yet been assessed on economical, technical and environmental factors. To conclude, the problem present is: *the absence of an ex-ante assessment of industrial-scale n-caproate production via syngas formation and fermentation, taking the perspective of both scientist as well as early-stage investors into account.*

1.4 Research Questions

Based on the previous mentioned problem, the following research question is set: ***How is the ex-ante performance of the indirect route and direct route compared, taking both scientists' as well as early-stage investors' perspectives into account?***

This overall research question can be divided into two sub research questions:

1. *With which performance indicators do scientists and early-stage investors assess the overall performance of a CO_2 utilizing technology?*

    This research question determines the performance indicators used by scientists and early-stage investors to assess the performance of CO_2 utilizing technologies. A particular interest is on the proposed *n*-caproate production routes. Their assessment is summarized as different performance indicators, including technical, environmental, economic and strategic metrics. Based on these parameters, the direct and indirect route can be compared. The two stakeholder groups are chosen as they are considered experts, taking into account the development phase of the routes.

2. *How does the technical, economic and environmental performance of the indirect route compare to the direct route and which improvements can be made to enhance its performance?*

    The *ex-ante* performance of the *n*-caproate production route is evaluated on metrics judged to be most important, as described by the research question above. The parameters used for this evaluation are both qualitative and quantitative. To calculate these parameters initial estimates for the route's energy use and a generic equipment list are required. The obtained parameters enable an *ex-ante* comparison between the direct and indirect route. It also leads to an analysis of the bottlenecks present in the indirect route. Potential focus points for the improvement of the process performance can be analyzed.

1.5 Relevance to Management of Technology

This research is conducted for the partial fulfilment of the requirements for obtaining a Master degree in 'Management of Technology' (MoT) at the TU Delft. In this context, the criteria for this research are the following: the reporting of a scientific study in a technological context, an understanding of technology as a corporate resource and utilization of research methods as put forward in the MoT curriculum.

This research is focused on the evaluation of a novel technology to potentially be implemented on an industrial-scale. It shows the difficulties and uncertainties present for the evaluation of a low TRL CCU technology. It emphasizes the importance of understanding the current placement of the technology in the innovation chain. The research uses this understanding to select which stakeholders should be involved and which criteria are used for its performance assessment.

Moreover, this study shows an understanding of the development of innovation beyond its technical improvements. It acknowledges, among others, the importance of financial support, policy regulations and collaboration between actors. This research assesses the performance of a low TRL production route by looking broader than technical parameters. It analyzes the most important aspects as determined by various relevant actors. Retrieving and analyzing these parameters is done with help of research methods as put forward in the MoT curriculum.

Chapter 2

Methodology

In this chapter the methodology to answer the research questions is explained. An overview of the approach is shown in Figure 2.1.

Overall, the approach used in this research can be seen as an application of bricolage. Bricolage is a method that emphasizes the value of using different methodologies and the exploration of a broad set of different data sources (Steinberg 2017). Moreover, bricolage emphasizes the relationship present between a researcher's information gathering and interpretation, and his/her social location and personal history (Kincheloe 2011). Therefore it is important to consider these aspects and their effect on me, the scientist conducting this research, as well. Some information about my personal background is given in section A.1.

The data sources used in bricolage could be either existing or produced by the researcher. When a literature read is performed, it should preferably come from a wide range of disciplines (Wibberley 2017). The data sources used in this research are; the data banks and assumptions integrated in the simulation software Aspen Plus, scientific papers from various research disciplines and interviews with relevant stakeholders. How this data is retrieved is explained in the coming paragraphs.

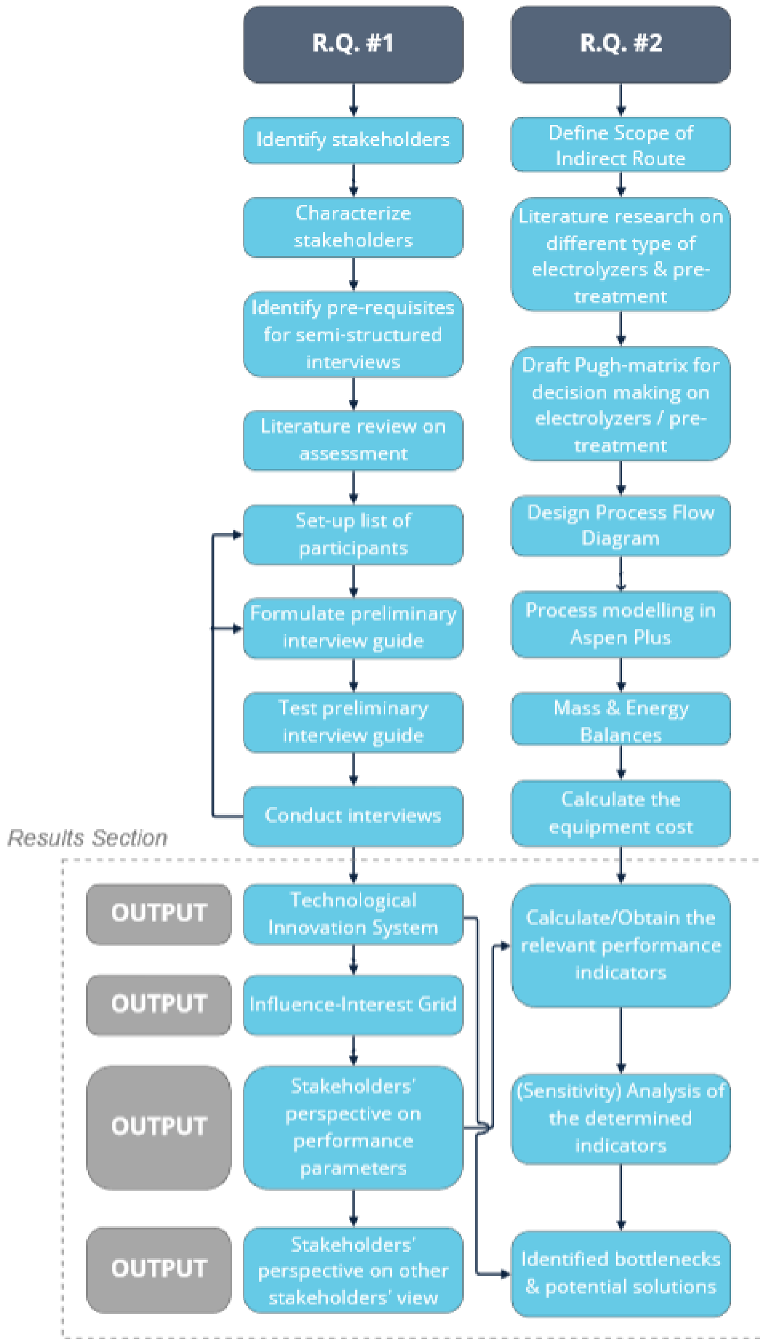

Figure 2.1: Schematic overview of the methodology used to answer the two research questions. The first research question is: *With which performance indicators do scientists and early-stage investors assess the overall performance of a CO_2 utilizing technology?*. The second research question is: *How does the overall performance of the indirect route compare to the direct route and which improvements can be made to enhance its performance?*

2.1 Assessment of Different Stakeholders' Perspective on the Technology's Performance

At the start of this section, it is important to express what is meant by the term 'stakeholder'. Through this report, 'stakeholder' is used to identify *'individuals or groups who have an interest or some aspect of rights or ownership in the project, and can contribute to, or be impacted by, either the work or the outcomes of the project'* (Walker et al. 2008). To clarify, the mentioned groups of 'scientists' and 'early-stage investors' can include multiple stakeholders.

The methodology to assess the perspective of important stakeholders is based on Luyet et al. 2012, Wieczorek and Hekkert 2012. In Luyet's research, a framework is set to engage stakeholders in a sustainable innovation process. It starts with identifying and characterizing the involved stakeholders, before stakeholder participation techniques are chosen. The focus of this research corresponds to these first two steps of Luyet et al. 2012's framework. Stakeholder engagement is not in the scope of this research.

During the stakeholder identification and characterisation, a technological innovation system (TIS) as described by Wieczorek and Hekkert 2012 is drafted. An innovation system is used to explain innovation and technological change (Charles Edquist et al. 1997). If one wants to describe, understand and explain (and maybe influence) processes of innovation, all factors shaping and influencing it should be taken into account (Charles Edquist et al. 1997). These factors include more than the stakeholders. They also consider networks, infrastructures and hard & soft institutions, which are shown in the TIS (Wieczorek and Hekkert 2012). Based on the TIS, bottlenecks hampering the innovation of the indirect route can be found.

Conducting the stakeholder identification, characterization and the drafting of the TIS results in a complete overview of the innovation eco-system of the indirect route. Based on this data, the influence and interest of different stakeholders are retrieved. The stakeholders with the highest influence and interest are interviewed. Interviews are conducted following the guidelines as described by Kallio et al. 2016.

2.1.1 Stakeholder Identification

The stakeholders that are involved in the development of the discussed technologies are identified via the quadruple helix approach, as described by Yan Yang, Holgaard, and Remmen 2012. This approach is an extension of the triple helix methodology developed by Leydesdorff and Etzkowitz 1996.

The triple helix generalizes innovation dynamics to a non-linear interactive and reflective process among the stakeholders (Leydesdorff and Etzkowitz 1996). It stresses the strategic importance of interactions between the following three stakeholder groups; 'Government', 'Academia' and 'Industry' (Leydesdorff and Van den Besselaar 1998) (Yan Yang, Holgaard, and Remmen 2012). These intensive interactions are required to reach innovation in the modern society (Klitkou and Godoe 2013).

The quadruple helix adds the stakeholder group of 'non-governmental organizations (NGOs) & communities' to the previous three stakeholder groups (Yan Yang, Holgaard, and Remmen 2012). This group is seen as important to add, because the innovation in this report has a clear intention to generate not only economic benefits, but also environmental. Environmental protection is viewed as a common benefit. NGOs and (local) communities are, next to the government, the parties representing public' interest. They also have a long-term perspective. Therefore, issues involving the common benefit imply an explicit focus on NGOs and the civil society (Yan Yang, Holgaard, and Remmen 2012). Indeed, it can be seen that public participation has been a part of a wide range of environmental applications (Luyet et al. 2012).

2.1.2 Stakeholder Characterization

The stakeholder identification is followed by their characterization. As described by Luyet et al. 2012, the goal of stakeholder characterization is to understand the power relations between them and the specific interest in the project. By making the power dynamics explicit, it helps to prioritize which stakeholders to engage in a project (Reed et al. 2009). This prioritization contribute to finding a balance in taking a broad range of stakeholders into account, but still yield manageable numbers to work with. Finding this balance is key for conducting research involving stakeholders (Ackermann and Eden 2011).

Stakeholder characterization can be achieved by looking into a variety of criteria (Luyet et al. 2012). There is generally no systematic approach to which of these criteria to choose. Which criteria are fitting is dependent on the project context and objectives (Luyet et al. 2012). In this research, the following two criteria are judged to fit the objective of this research the best. These are the scale of; 1) the stakeholders' influence and 2) of their interest in the project. The ranking of the stakeholders based on these two criteria can be visually shown in an interest-influence grid (II-grid) (Reed et al. 2009). Each stakeholder is given a score of 1 (very low) to 5 (very high) on both criteria. These scores should be seen as a measure to show stakeholders in contrast to each other, not as an absolute value. This mapping is based on desk-research and adapted with information retrieved from stakeholders' interviews (see subsection 2.1.3) (Olander and Landin 2005) (Bryson 2004).

In this research, 'influence' is defined as *'the power to have an effect on people or things, or a person or thing that is able to do this'* (*Cambridge Dictionary* 2022). The definition of 'interest' is *'the feeling of wanting to give your attention to something or of wanting to be involved with and to discover more about something'* (*Cambridge Dictionary* 2022).

It can be argued that a more common type of stakeholder characterization is the power-interest grid (PI-grid). However, it is judged that mapping 'influence' instead of 'power' is more fitting for the TRL at which the discussed CCU technology is. In this stage, a stakeholder might not have the power to carry the innovation from TRL 3 to commercialization. However, this stakeholder might be very influential in reaching other parties who do have this power. This can be via, for example, having a certain credibility and/or (way of) communicating about the technology (Hoosbeek and de Vries 2021).

Technological Innovation System

The understanding of the role of a stakeholder within the technology's development can be deepened by forming a technological innovation system. A technological innovation system (TIS) describes all factors shaping and influencing innovation (Wieczorek and Hekkert 2012). It transcends researching the traditional economic factors and the linear view on innovation (Charles Edquist et al. 1997). A TIS is defined as *'a network of agents interacting in the economic/industrial area under a particular institutional infrastructure and involved in the generation, diffusion, and utilization of technology'* (Vroon et al. 2021). It is a very powerful tool to facilitate understanding of the dynamics of innovation (Charles Edquist et al. 1997). By analyzing a TIS, systemic problems negatively influencing the speed and direction of an innovation can be found. By identifying these problems, suitable measures can be taken to overcome them (Wieczorek and Hekkert 2012).

A TIS is build up of four factors. These factors are; actors, networks, infrastructures and hard & soft institutions (Wieczorek and Hekkert 2012) (Vroon et al. 2021). What each type of these factors encompasses and how they are retrieved in this research are elaborated upon in this paragraph. The first factor is the actors, which corresponds to the stakeholders identified previously (Vroon et al. 2021) (Wieczorek and Hekkert 2012). The actors are placed in the TIS based on the findings of the stakeholder identification. The second factor is networks. A network refers to *'cooperative relationships and links between actors'* (Wieczorek and Hekkert 2012). The networks are identified via the literature research and the conducted interviews.

Thirdly, there is infrastructure. For 'infrastructure', there is no conclusive agreement to what this term covers (Wieczorek and Hekkert 2012). In this research, the definition set by O'Sullivan 2005 is applied. Here, 'infrastructure' describes *'the availability of finance for innovation in the form of venture capital, funds, subsidies or programs'*. Similar to the networks, infrastructures are found via the conducted interviews and desk-research. Lastly, with hard institutions formal institutional mechanisms are meant (Woolthuis et al. 2005). Laws, intellectual property rights and industry standards are examples of formal institutions (Vroon et al. 2021). Soft institutions refer to norms and values (Vroon et al. 2021). Hard and soft institutions are retrieved via literature research.

2.1.3 Data Collection of Stakeholder's Perspective

To obtain the parameters used by the stakeholders for a technology's assessment, direct data collection is required. These data is obtained via face-to-face semi-structured interviewing. This form of data collection is chosen over other methods due to reasons described by Brinkmann 2014, Sekaran and Bougie 2016, Varvasovszky and Brugha 2000. Brinkmann states that it is important to not only receive a set of answers to the questions, but to include an analytic focus on 'the larger set of practices of knowledge production'. An interview, and especially a semi-structured interview, provides space to do so (Brinkmann 2014).

A set of questions was drafted beforehand, but there was space and time in the interview to go in different directions. Moreover the order in which questions are asked shifted depending on the conversation (Brinkmann 2014) (Kallio et al. 2016). This generally leads to an increase in information retrieved (Newcomer et al. 2015).

Guidelines for Conducting Semi-Structured Interviews

For conducting the semi-structured interviews, the framework described by Kallio et al. 2016 is followed. This framework provides five steps, which are:

1. Identifying the pre-requisites for using semi-structured interviews.
2. Retrieving and using previous knowledge.
3. Formulating the preliminary semi-structured interview guide.
4. Pilot testing of the interview guide.
5. Presenting the complete semi-structured interview guide.

The first step is to identify the pre-requisites for using semi-structured interviews. This step aims to review if semi-structured interviewing is an appropriate data collection method to achieve the research goal set (Kallio et al. 2016). For reasons described previously, semi-structured, individual face-to-face interviewing is evaluated as an appropriate method.

Secondly, a literature research is conducted to retrieve previous knowledge. The aim of this literature research is to gain a comprehensive and adequate understanding of the subject. The literature study gives an idea of the parameters that the stakeholders could mention. The literature review can be found in subsection 2.1.4.

As a third step, a preliminary interview guide is set. An interview guide is defined as: *"A list of questions which directs conversation towards the research topic during the interview"* (Kallio et al. 2016). The questions should be, among others, participant-orientated, not leading, single-faceted and open-ended. Moreover questions on two levels are asked. Questions based on main themes and follow-up questions (Kallio et al. 2016). The main theme questions covered the main content of the researched topic and were prepared in advance. The follow-up questions were spontaneous and used to maintain the flow of interview or to clarify

(Rabionet 2011).

The fourth step in the framework is to pilot test the interview guides. Maxwell 2012 states that a small sample of participants who are similar to the actual study participants can be used for pilot testing. This approach is followed. The interview guides set in the previous step are tested on two stakeholders. These stakeholders are a researcher working on a CCU technology and a portfolio manager at an venture capital firm. Based on their experience, the interview guides were modified. No significant changes are made, thus the results are not shown.

Lastly, the interview guides are shown in this report. They can be found in Appendix A. Publishing these guides contributes to the credibility, confirmability and dependability of the study (Kallio et al. 2016). As stated by Shenton 2004, readers can use it to evaluate if the study measures what was intended. It shows which questions were asked and how it connects to the studied phenomena and reported conclusion (Kallio et al. 2016). Publishing the interview guides also adds to the confirmability of the study as the research process is made more transparent. The confirmability is also increased by other steps in the framework, such as the pilot testing and by basing the questions on findings reported in previous literature (Kallio et al. 2016). Finally, presenting the complete guides makes them available as a data collection tool for other researchers. This adds to the dependability of the study (Kallio et al. 2016).

2.1.4 Literature Review on Performance Assessment

A literature study is performed to retrieve existing knowledge on the assessment metrics used by scientists and ESIs. The methodology to find relevant literature is three-fold. Firstly, a list of key terms is drafted (results not shown). Secondly, these key terms are used to find relevant literature via Google Scholar. Lastly, references from the relevant papers are checked to find new papers on this topic ('backwards snowballing' method) (Wohlin 2014).

The performance indicators found in literature are categorized into 'technical', 'economic', 'environmental', 'social' and 'strategic' parameters. Moreover, an analysis is performed to see if some indicators show overlap. For example, indicators such as; 'the levelised costs of chemicals', 'the product price' and 'the production cost per product' are all categorized as 'minimum product selling price'. An overview of the indicators and their grouping can be found in Appendix B. Of these indicators a selection of those most mentioned by a stakeholder group is made.

Parameters used by Scientists for the Viability Assessment

The metrics most mentioned to be used by scientists for a low TRL technology's assessment are shown in Table 2.1. The parameters are used for the assessment in this report.

Parameters used by Early-Stage Investors for the Viability Assessment

Similarly to the analysis above, the perspective of early-stage investors is researched. Here, the focus is not solely on the assessment of low TRL CCU technologies, but broadened to cleantech investment opportunities. 'Cleantech' can be seen as the investment category of which CCU is a part (O'rourke 2009). Broadening the category is chosen as, from an investor's point of view, the indirect route competes not solely with other CCU technologies. The indirect route competes with other cleantech investment opportunities as well (O'rourke 2009). Moreover, the category is broadened to enlarge the literature findings. The main parameters used by early-stage investors are shown in Table 2.2.

Table 2.1: Parameters used to assess a low TRL technology's performance. Given from a scientists' perspective and based on literature research. Solely the most often mentioned parameters are shown. See Appendix B for an overview of all parameters.

Category	Parameter	Times Mentioned	*Sources*
Technical	Energy usage/ consumption	5	*Jourdin et al. 2020* *Verma, B. Kim, et al. 2016* *Jarvis and Samsatli 2018* *Roh et al. 2020* *de Medeiros, Noorman, et al. 2020*
	Energy Efficiency	4	*Jourdin et al. 2020* *Verma, B. Kim, et al. 2016* *Roh et al. 2020* *de Medeiros, Noorman, et al. 2020*
	Substrate Conversion Efficiency	3	*Jourdin et al. 2020* *Roh et al. 2020* *Munasinghe and Khanal 2010*
	Plant Operational Life Time	2	*Wood et al. 2021* *Jarvis and Samsatli 2018*
	Plant Production Capacity	2	*Wood et al. 2021* *Jourdin et al. 2020*
Economic	Min. Prod, Selling Price	8	*Jourdin et al. 2020* *Wood et al. 2021* *Jarvis and Samsatli 2018* *Roh et al. 2020* *Somoza-Tornos et al. 2021* *Munasinghe and Khanal 2010* *B. Sun et al. 2019* *de Medeiros, Noorman, et al. 2020*
	OPEX	5	*Jourdin et al. 2020* *Wood et al. 2021* *Jarvis and Samsatli 2018* *Somoza-Tornos et al. 2021* *de Medeiros, Noorman, et al. 2020*
	CAPEX	4	*Wood et al. 2021* *Jarvis and Samsatli 2018* *Somoza-Tornos et al. 2021* *de Medeiros, Noorman, et al. 2020*
Environmental	GHG Reduction Potential	2	*Roh et al. 2020* *Somoza-Tornos et al. 2021*
	Carbon Footprint	1	*Roh et al. 2020*

Table 2.2: Parameters used by early-stage investors for the assessment of a cleantech investment opportunity.

Category	Parameter	Times Mentioned	*Sources*
Strategic	Preparing for Energy Transition	1	*Hegeman and Sørheim 2021*
	Strategic Returns	1	*Hegeman and Sørheim 2021*
	Widening Client Base	1	*Hegeman and Sørheim 2021*
	Potential for easy liquidation	1	*Hargadon and Kenney 2011*
Technical	Scalability	1	*Hargadon and Kenney 2011*
Economic	Return on Investment	1	*Gaddy et al. 2017*
	Risk on Investment	1	*Gaddy et al. 2017*
	Market Growth Rate	1	*Hargadon and Kenney 2011*
Social	Local Entrepreneurship	1	*Hegeman and Sørheim 2021*
	Local Knowledge Creation	1	*Hegeman and Sørheim 2021*

2.2 Design of the Indirect Route's Process Model

This section discusses the methodology applied to answer the second research question. To conduct the performance assessment of the indirect route, energy balances and a general equipment list are required (Van der Spek, Ramirez, et al. 2017). For the indirect route, these two are obtained by simulating this route on industrial-scale. For the direct route an *ex-ante* assessment of industrial-scale performance is already available (Luo et al. 2022).

For the design of the simulation, the concept of drafting Pugh matrices is used. This is applied to identify and decide upon the electrolyzer and pre-treatment options for the indirect route. Pugh matrices are a systematic method for the quick selection of a 'best' concept. It helps to compare technology candidates, even at a low TRL, when a series of (interwoven) criteria have to be taken into account (Pugh 2009) (Dincan et al. 2017). It is commonly used in engineering decision making as stated by Nixon et al. 2013. See subsection 2.2.1 for more information.

When modeling a process, a suitable modeling method should be selected. The three main types of modeling are; rigorous, shortcut/intermediate or simplified (Van der Spek, Ramirez, et al. 2017) (Van der Spek, Fout, et al. 2020). Based on the objectives and due to limited resources (data, time and skill), a simplified modeling method is chosen. As a software, the simulation software Aspen Plus v12, developed by AspenTech is used. Complementary software for economic and environmental analyses are available (Aspen Energy Analyzer and Aspen Process Economic Analyzer v12). The usage of Aspen Plus is explained in detail in subsection 2.2.3.

2.2.1 Decision Making on the Design

Pugh matrices are drafted based on the steps as described by Madke and Jaybhaye 2016 and Guerrieri et al. 2017. In a Pugh matrix, comparisons between design candidates against a number of criteria are set. The first step is to identify and define the knock-out criteria. If one of these criteria is fulfilled by a technology, it is 'knocked-out' as an option. Secondly, selection criteria on a first and second level are set. The first level of criteria considers categories. Four categories are determined, namely; 'Risk', 'Process Properties', 'Economics' and 'Sustainability'. The second level is more detailed. These are the criteria at which the design options are ranked. The criteria are retrieved from reviews published by Küngas 2020 and Endrodi et al. 2019. The third step is to rank and compare the design options to each other. The score is on a scale of 1-3, at which 1 is the best and 3 the worst (compared to the other technology options). Fourthly, weightings are assigned to the criteria. These weightings are allocated to the importance of a category from the researcher's point of view (Mia et al. 2018). Lastly, the weighted average of each option is calculated. The lowest score is considered the 'best' option and chosen to be used in the indirect route.

An overview of the knock-out and selection criteria set for each category can be found in section G.1 and section G.2. The category 'process properties' has given an overall weight of 40% in the decision making, while the other categories weight 20% each.

2.2.2 General Assumptions in the Process Flow Diagram

While simulating the indirect route in Aspen, several assumptions are made. The general assumptions are listed below. Assumptions made specific for a process unit will be discussed in the section explaining the modeling of this specific unit. These sections are 3.2 for the pre-treatment modeling and the modeling of the electrolyzers, 3.3 for the fermentation processes and 3.4 for the downstream processing.

The assumptions used in the simulation are listed below. These are in line with the VICI Project guidelines (Ramírez 2022).

- The temperature and pressure of in-going streams are based on industrial values. If these conditions are not specified, ambient conditions are assumed. Ambient conditions are; a temperature of 15 ℃ and a pressure of 1.02 bar.
- Process air is composed of the following molar fractions: 0.777 N_2, 0.209 O_2, 0.0093 Ar, 0.0044 H_2O, 0.0003 CO_2 .
- Compressors have an isentropic efficiency of 85%.
- Turbines have an isentropic efficiency of 90%.
- Pressure drops are not taken into consideration.
- Fermentations are modeled as a black-box, utilizing the reaction stoichiometry and product yields. Factors such as mass transfer, kinetics and hydrodynamics are not taken into account.

2.2.3 Property Methods Applied in Aspen Plus

Aspen Plus v12 contains several build-in models to determine physical property specifications. The parameters of the compounds in Aspen's Database are retrieved from, and calculated based on, the data in the Dortmund Databank (AspenTech 2019). Each of the property sets contains assumptions and application limits, which influence the calculations of the mass and energy balances. The property methods used in this research are; 'Non-Random Two-Liquid and Hayden-O'Connell Equation-of-State' (*NRTL-HOC*), 'Peng-Robinson Equation-of-State' (*PENG-ROB*), 'UNIFAC and Hayden-O'Connell Equation-of-State' (*UNIF-HOC*) and 'Electrolyte Non-Random Two-Liquid' (*ELECNRTL*). The underlying assumptions of each method are described in Appendix E.

2.3 Determination and Calculation of the Parameters for the Techno-Economic Assessment and Environmental Analysis

For CCU technologies it can be challenging to make decisions concerning research, development and deployment (Zimmermann, Wunderlich, et al. 2020). In order to be able to compare CCU technologies fairly to each other, a techno-economic assessment (TEA) and an environmental analysis (EA) can help. Well established methods are present for TEA analysis of (near) commercial energy technologies. However, using these methods for low TRL technologies can be challenging and leading to inaccurate results (Van der Spek, Ramirez, et al. 2017). Therefore, the TEA and EA will be performed using metrics found in the literature review and interviews, see subsection 2.1.3 and subsection 2.1.4. The parameters discussed in this section are those retrieved from the literature review. Later on, parameters might be added or altered, based on the interview results. After the assessment of the parameters, a sensitivity analysis is performed to evaluate the uncertainties of the results.

2.3.1 Framework for Techno-Economic Analysis

The metrics used for the TEA of the indirect route are shown below. The boundaries of the analyses are gate-to-gate.

Technical Parameters

The technical parameters used for the assessment of the indirect route are the following. These parameters are retrieved from the literature research (see subsection 2.1.4):

- **CO_2 Conversion Efficiency**

  The conversion rate of the substrate is the percentage of in-going CO_2 converted into products (Jourdin et al. 2020). These products include medium-chain fatty acids, short-chain fatty acids and biomass. The values are retrieved from the mass balances generated by the flowsheet simulation.

- **Specific Primary Energy Consumption**

  Specific primary energy consumption reflects the net primary energy input, with primary energy referring to non-renewable energy use (Posada et al. 2016). The usage can be retrieved from the energy balances provided by the Aspen Plus simulation. The specific primary energy consumption puts the primary energy usage in perspective to the energy output (Roh et al. 2020).

Economic Parameters

The economic parameters retrieved from the literature study are shown below. The calculation methods of these parameters are described by Van der Spek, Ramirez, et al. 2017, Perry et al. 1997 Peters et al. 2003 and Benalcázar et al. 2017. The parameters are:

- **Capital Expenditure (CAPEX)**

  The capital costs are calculated via the direct bottom-up method (Van der Spek, Ramirez, et al. 2017). Here the costs of building a plant are directly calculated from the list of equipment used by the plant. These costs are obtained using the Aspen capital cost estimator v12. Based on the equipment cost other costs such as the yard improvements required are estimated (Peters et al. 2003).

- **Operational Expenditure (OPEX)**

  The operational costs includes the following factors; variable costs, fixed costs and overhead costs (Van der Spek, Ramirez, et al. 2017). The variable costs consist of various factors including the raw materials, utilities and cost of waste treatment. These expenses are retrieved from the Aspen simulation. The fixed costs are based on payments for patents, local taxes and property insurance. Thirdly, the overhead cost are estimated based on the variable and fixed costs (Peters et al. 2003).

- **Minimum Caproate Selling Price (MCSP)**

  The minimum caproate selling price is defined as the selling price that would bring the net present value (NPV) to zero within a given time-period. This definition is retrieved from Benalcázar et al. 2017. Here, this time-period is set at 30 years, as this is considered the lifetime of the plant. This lifetime period is based on Jourdin et al. 2020.

2.3.2 Framework for Environmental Analysis

The environmental analysis considers the carbon footprint and the greenhouse gas (GHG) emission reduction of the new technology. A description of these parameters is given below.

- **Carbon Footprint**

  The carbon footprint refers to the CO_2 emission caused by the production of the product. This is calculated following the IPCC's methodology (IPCC 2019). The carbon footprint is retrieved by multiplying all in- and outlet streams with its corresponding CO_2 equivalent emission factor. These factors are retrieved from database's such as EcoInvent (EcoInvent 2022). For the CO_2 equivalent emission factors of the utilities, the Aspen Energy Analyzer is used.

- **Greenhouse Gas Reduction Potential**

  The GHG reduction potential puts the reduction achieved by the new technology in perspective to the market size of the produced product. It is calculated by looking at the GHG emissions that are mitigated per product unit by the new process, compared to the reference process. This value is multiplied by the market demand of the product (Roh et al. 2020).

2.3.3 Sensitivity Analysis

After the TEA and EA, the obtained metrics are analysed. Part of this analysis is the sensitivity analysis to show the robustness of the results. It also helps to identify opportunities for further improvement (Fernández-Dacosta et al. 2015). The most critical variables of the economic and environmental analysis are looked into, similar to Fernández-Dacosta et al. 2015. For the economic assessment these variables are; 1) the equipment cost of the alkaline electrolyzer, 2) the electricity price and 3) the industrial oxygen price. Parameters most critical for the environmental assessment are; 1) direct CO_2 emission during the pre-treatment, 2) electricity usage, 3) cold utility usage and 4) hot utility usage. The economical parameters are varied by $\pm$ 33%, based on the price range given by Taibi et al. 2020. The environmental parameters are varied $\pm$ 100%. This range is based on the aim of the Dutch Government to supply carbon neutral utilities in 2050 (Rijksverheid 2022).

Chapter 3

Process Design of *n*-Caproate Production Route

In this chapter the process design for *n*-caproate production via syngas formation and fermentation is described. This route is referred to as the 'indirect route'. The scope of the design is limited to a gate-to-gate design. This indicates that solely the operational phases are modeled (Nguyen et al. 2020). Other components, such as the product distribution, the electricity source and the transportation of the feedstock will not be considered. Hence, all energy is thus assumed to be purchased from the Dutch energy grid, with natural gas as primary source. The CO_2 emissions caused by the usage of natural gas and electricity are accounted for in the environmental assessment. As stated by Van der Spek, Ramirez, et al. 2017, taking the CO_2 source into account is required to ensure that reliable conclusions can be drawn on the feasibility of the technology. However, overtime the Dutch energy mix will substitute non-renewable energy sources for renewable sources, such as solar and wind energy (European Commission 2017). Therefore, the CO_2 emissions originating from utility usage in this report show a conservative estimate. It is likely that their carbon footprint is lower in the time-frame at which the plant would theoretically operate.

The scope of the project is schematically shown in Figure 3.1.

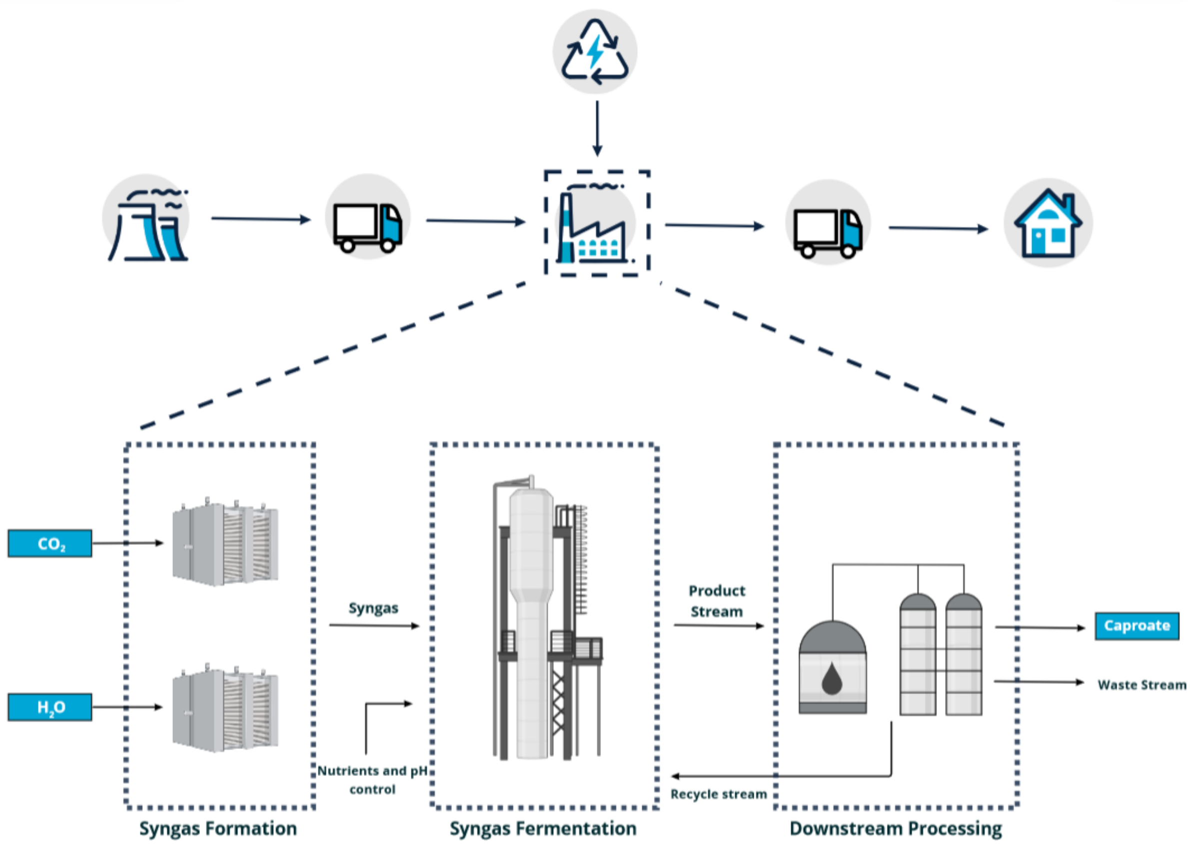

Figure 3.1: Schematic Overview of the scope of the process design and performance assessment. The scope is limited to a gate-to-gate design, excluding feedstock production and transportation, (renewable) electricity production and product distribution. Within the scope of this research are; pre-treatment of the feedstream, syngas formation via electroreduction of CO_2 and H_2O , *n*-caproate production via syngas fermentation and downstream processing.

3.1 Basis of Design

3.1.1 Production Scale and Product Purity

The aim is to produce 10 kt of *n*-caproate per year, with a purity of $\geq$ 99%. The annual plant operating time consists of 8000 hours and its overall lifetime is assumed to be 30 years. The plant's lifetime is based on the analyses made by De Luna et al. 2019 and Jourdin et al. 2020. The production aim is set to be similar to the direct *n*-caproate production route (Luo et al. 2022). An annual production of 10 kt on a global market of 25-30 kt can be seen as substantial and changes on a macroeconomic level can be expected. However, the macroeconomic impact of this additional supply is out of scope of this research. It is assumed that the impact of the additional supply on the market dynamics will be negligible.

3.1.2 Plant Location

The location of the plant is the Port of Rotterdam. This location is chosen as this research is part of Prof. A. Ramírez' VICI project. This project is being applied to the petrochemical energy cluster around the port of Rotterdam (Ramírez 2019).

Another reason for this location is the expressed ambition of the Port's Authority to reduce their carbon emissions. They aim to achieve 49% reduction by 2030 relative to 2019 (The Port of Rotterdam Authority 2021). In order to reach the reduction aim, technologies such as carbon capture and storage (CCS) and CCU are (among others) required. The Port of Rotterdam is for example investing in the production of green hydrogen, sustainable aviation fuel, wind energy and bio-based chemicals (The Port of Rotterdam Authority 2021) (van Dooren 2022) (Klimaattafel 2020). They explicitly state that their focus will be on *'the valorisation of waste flows through their transformation into alternative raw materials (...) to produce secondary chemicals and fuels with a smaller carbon footprint'* (Port of Rotterdam 2019). This indicates their willingness to support and invest in technologies contributing to the sustainability of the Port.

Thirdly, the Port of Rotterdam also has the space and the infrastructure to locate a biochemical plant. Over 100 hectare is currently available for companies to settle (Distripark Maasvlakte West) (Port of Rotterdam 2022a). In this area, over 45 chemical production companies and refineries are present. Due to their presence, the area is suitable for the supply and distribution of (hazardous) chemical products (Port of Rotterdam 2022a).

3.1.3 Feedstock Source

The feedstock sources for syngas formation via electroreduction are CO_2 and H_2O . For both feedstock sources it is researched if and how these are available at the Port of Rotterdam.

Carbon Dioxide Source

Transportation of flue gases should be minimal, due to economic aspects (Ravi et al. 2017). Therefore it would be beneficial if the CO_2 source plant is also present at the Port of Rotterdam. This will limit the transportation distance, and thus the costs, of the CO_2 source. As the Port emitted 2.908 Mton of CO_2 in 2019, it is assumed that sufficient CO_2 feedstock is available (Rijksoverheid 2022).

Not only is enough CO_2 available at the Port, it can also be captured. By 2024, a CCS infrastructure is finished. This project, named 'Porthos', includes the collection of CO_2 from several companies, the compression of the CO_2 and the storage into the North Sea (Porthos 2022b). The companies themselves are responsible for the carbon capturing and for supplying it to the Porthos' CO_2 infrastructure. Moreover they pay a processing fee per tonne of CO_2 . This processing fee is initially set at €60 per ton CO_2 , but is expected to be lowered once the Porthos' project is in full operation (Lamboo and Lensink 2020). On the other hand, the price could also be increased, depending on the price set by the European Union on carbon emissions. This pricing is very volatile and fluctuated between €33 and €89 per tonne CO_2 in 2021 (TradeEconomics 2022). In this report a value of €60 per tonne CO_2 is taken as a benchmark price. This has the same order of magnitude as the techno-economic assessment performed by Jourdin et al. 2020.

The CCS infrastructure can handle 2.5 Mton per year. After 15 years, the storage unit in the North Sea will be full (Porthos 2022a). In this research it is assumed that the Porthos infrastructure can be partly used for capturing and transporting CO_2 to the *n*-caproate production plant. The characteristics of the CO_2 stream leaving the Porthos' compressor will be used as CO_2 feedstock stream in this design. The CO_2 stream leaves the compressor at a maximum of 120 bar and at 80 ℃ (Port of Rotterdam, EBN, Gasunie 2019) (Geerts 2019).

Water Source

It is assumed that the water required for the production plant can be obtained via the water grid present at the Port of Rotterdam. Water provided to (chemical) industries at the Port is retrieved from three sources, making its supply robust (van Zaanen 2021). In 2019, the Dutch water price for the industrial sector is €0.80 per m^3. On top of this comes an annual fixed price of €4770 (Waternet 2019).

3.1.4 Utilities

The utilities are based on those generally used within the VICI project. Heating is achieved by using various types of steam (very low pressure up to very high pressure steam), hot oil or fired heat. These utilities are generated by using natural gas. The industrial price for natural gas in 2019 was €6.76 per GJ (Statline 2022a). Cooling is achieved by using steam generation, cooling water or chilling water. Cooling down streams up to 150 ℃ is achieved by steam generation. If possible, the generated steam is used for heating in the indirect route. It is assumed that the remaining generated steam can be sold to other plants at the Port. To cool down a streams of 150 ℃ or lower, cooling and/or chilling water is used. For both heating and cooling utilities Aspen default prices are used (2019 price levels). The required electricity is purchased from the electricity grid present at the Port of Rotterdam. In 2019, the Dutch industrial electricity price was €0.11 per kWh (Statline 2022a).

It should be noted that a two- to four-fold increase in (green) electricity demand in the Port is expected for the coming decades (Brouwers 2019). This forecast is based on the key roles that renewable electric power and green hydrogen play to achieve the goals set in the Paris Agreement on Climate Change. Currently, the capacity of the existing power grids and connections in the Port does not suffice the expected increase (Brouwers 2019). Therefore, the possibility to buy (sustainable) electricity from the Port's power grid at the current price, is dependent on the future expansion of the energy grid.

Carbon Footprint of the Utilities

The carbon footprint of the heating and cooling utilities is calculated on the assumption that all originate from natural gas. The efficiency of the production of the heating, cooling and electric utilities out of natural gas is assumed to be 100%.

The carbon footprint of the electricity usage is based on the Dutch electricity mix in 2019. In this period, electricity originated for 76% of fossil-based sources and 24% of renewable sources (Statline 2022b).

A summary of the identified plant location, feedstock sources, product properties and utilities is schematically shown in Figure 3.2.

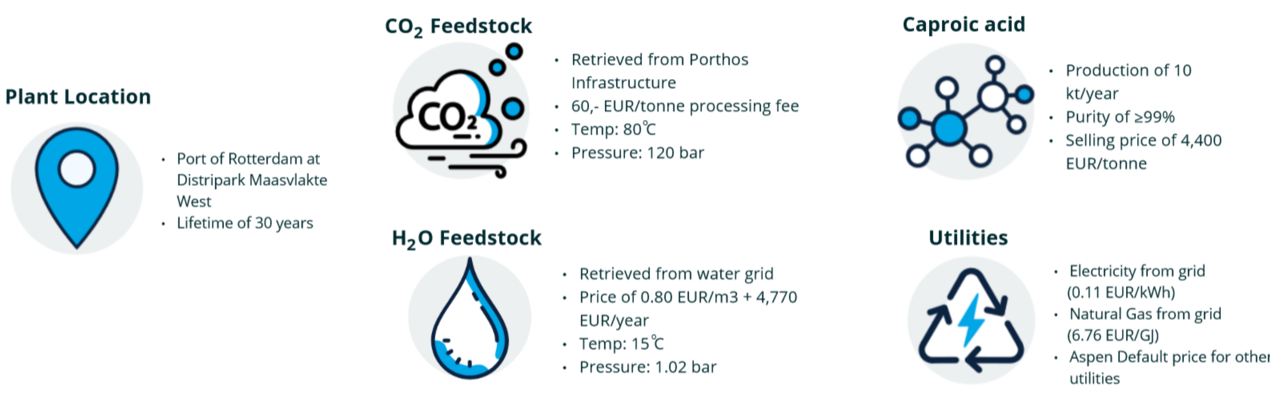

Figure 3.2: Schematic summary of the identified plant location, feedstock sources, product properties and utilities.

3.2 Syngas Formation

The first steps in the indirect route are the formation of syngas, as schematically shown in Figure 3.3. This is achieved by electroreduction of CO_2 and H_2O. This section discusses their design and consists of the following parts. Firstly, the electrolysis of CO_2 for the formation of carbon mono-oxide (CO) is discussed (subsection 3.2.1). The second part discusses the pre-treatment of the CO_2 feed-stream (subsection 3.2.2). It is dependent on the CO_2 electrolyzer chosen and the impurities in the Porthos stream. The last part of this chapter focuses on H_2O electrolysis (subsection 3.2.3). Based on the H_2O electrolyzer chosen, pre-treatment of the water stream is not necessary.

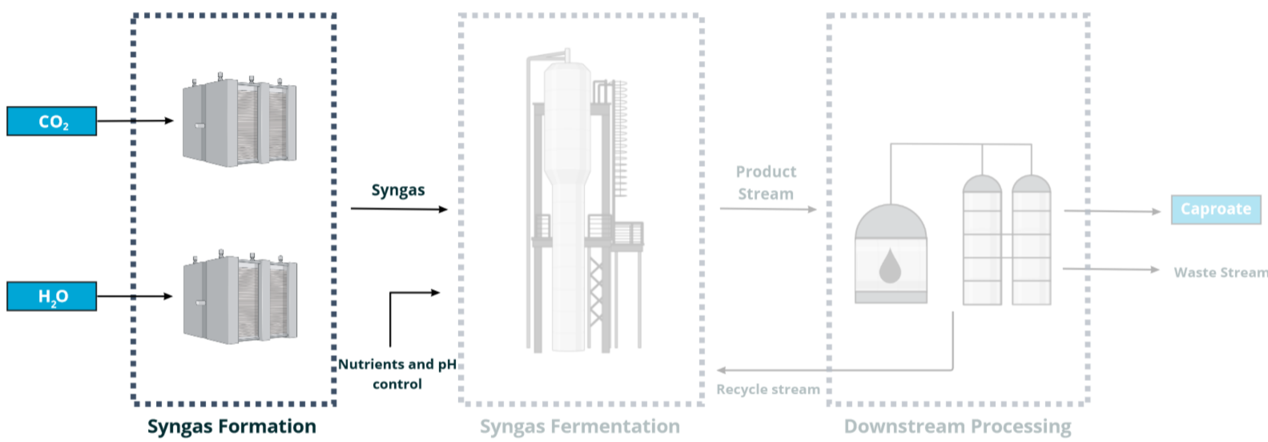

Figure 3.3: Schematic overview of the focus areas of section 3.2. These focus areas are the CO_2 electrolysis, the H_2O electrolysis and the pre-treatment of the Porthos stream.

3.2.1 CO_2 Electrolysis

The process design of CO_2 electrolysis consists of the following steps. It starts with the selection of a CO_2 electrolyzer by drafting a Pugh matrix. This is followed by an explanation of the characteristics of the chosen electrolyzer. Lastly, the modeling of this electrolyzer in Aspen Plus is described.

Selection CO_2 Electrolyzer

Different type of electrolyzers can be used to achieve CO_2 electroreduction. The electrolyzers analyzed for the design of the *n*-caproate production process are low-temperature electrolyzers, molten carbonate electrolysis cells (MOEC) and solide oxide electrolysis cells (SOEC). All three electrolyzers are ranked on their technology risk, their process performance, their economic performance and their environmental sustainability. An overview of the quantitative values can be found in section G.1. From this data, a Pugh matrix is drafted (see Figure 3.4). The electrolyzers are ranked based on best (indicated with 1) to worst (indicated with 3) performance. Based on this matrix, solid oxide electrolysis is decided to be the best choice for CO_2 electrolysis. The characteristics of the SOEC used in this report will be based on research conducted by Küngas 2020. A similar modeling approach as described by Ali et al. 2020 and Kamkeng and M. Wang 2022 is taken.

Category	Criterium	Weight	Low-Temperature	Molten Carbonate	Solid Oxide Electrolysis Cell
Risk	*Technology Readiness Level*	10%	3	2	1
	Proven Durability	10%	2	3	1
Process Properties	*Operation Temperature*	5%	1	2	3
	Faradaic Efficiency	7.5%	3	1	1
	Partial Current Density	7.5%	3	2	1
	Operating cell voltage	7.5%	3	2	1
	Conversion Efficiency	7.5%	3	1	2
	Tolerance to impurities	5%	3	1	2
Economics	*CAPEX*	20%	2	1	1
Sustainability	*Catalyst Material*	10%	3	2	1
	Electric Power Consumption	10%	3	2	1
SCORE			2.6	1.7	1.2

Figure 3.4: Pugh matrix to decide on which CO_2 electrolyzer is used. The Pugh matrix is based on the quantitative data shown in Appendix G.1. Each electrolyzer is scored from 1 to 3, at which 1 indicates the best performance and 3 the worst, compared to the other options. The weighted average of this score shows the best outcome (score of 1.2) for the SOEC.

Characteristics of a CO_2 Solid Oxide Electrolyzer Cell

A simplified schematic overview of the working principle of a SOEC is shown in Figure 3.5.

The following reactions take place at the cathode (reaction 3.1) and anode (reaction 3.2) of the electrolyzer (Y. Jiang et al. 2021):

$$CO_2 + 2e^- \rightleftarrows CO + O^{2-} \tag{3.1}$$

$$O^{2-} \rightleftarrows 2e^- + \frac{1}{2}O_2 \tag{3.2}$$

These reactions combined lead to the overall reaction shown in Equation 3.3:

$$CO_2 \rightleftarrows CO + \frac{1}{2}O_2 \tag{3.3}$$

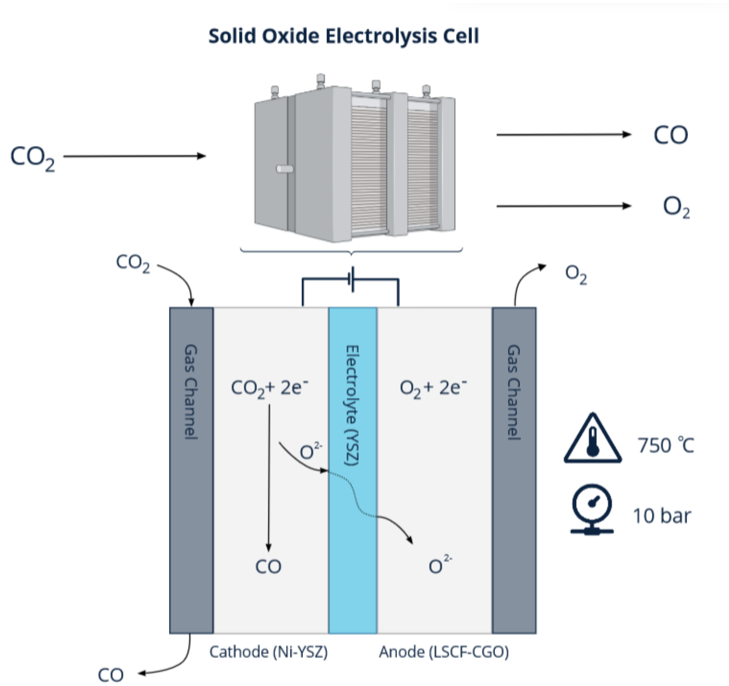

Figure 3.5: Schematic overview of the working principle of a solid oxide electrolyzer cell (SOEC). At the cathode CO_2 is converted into CO. At the anode an oxygen atom reacts to form oxygen (O_2).

The electrolyte of a SOEC is a solid ceramic material. This material conducts oxide ions at a high temperature ($\geq$ 600 °C) without being permeable to oxygen and electrons (Küngas 2020). SOEC's are typically operated between 700 °C and 900 °C (Küngas 2020). The most commonly used electrolyte is Yttria-stabilized Zirconia (YSZ) due to its excellent redox stability, high mechanical strength, relative low cost, oxygen ionic conductivity and abundance (Song et al. 2019) (Hauch et al. 2020). As a cathode Nickel-YSZ is used, which has a proven good electrochemical performance and high stability for CO_2 electrolysis (Song et al. 2019) (Küngas 2020). The anode for SOEC can consist of either noble metals or electron-conducting oxides. Due to the high cost and scarcity, noble metals are discarded. The anode material selected in this research is the commonly used lanthanum strontium cobalt ferrite combined with cerium gadolinium oxide (LSCF-CGO) (Küngas 2020). This type of SOEC electrolyzer is commercially available and known as eCOs™, manufactured by Haldor-Topsoe (Küngas et al. 2017).

Modeling of the CO_2 Solid Oxide Electrolyzer Cell in Aspen Plus

Aspen Plus does not contain a build-in electrolyzer. In this research the SOEC electrolyzer is modeled with an RSTOIC reactor followed by a separator. Both their property method is set to Peng-Robinson (Kamkeng and M. Wang 2022). For the type of SOEC used, a conversion efficiency of 80% to 90% is reported (Küngas 2020) (Ebbesen and Mogensen 2009). The average, a conversion efficiency of 85%, is set in the simulation. It is assumed that no oxygen or CO cross-over occurs (Kamkeng and M. Wang 2022). Therefore, the separator shows 100% separation of O_2 and CO. The described modeling approach is based on Ali et al. 2020. By using an RSTOIC reactor, kinetic changes and pressure losses in the electrolyzer are not taken into account. For the design of the SOEC in this research, a thermoneutral mode of operation is assumed. This means that the heat caused by the overpotential is equal to that required for the CO_2 splitting (L. Wang et al. 2018). As a result, no external heat source is required during the operation of the SOEC.

The CO_2 stream retrieved from Porthos has a temperature of 80 °C and a pressure of 120 bar (Port of

Rotterdam, EBN, Gasunie 2019) (Geerts 2019). The stream is pre-treated to be purified and to reach the operating conditions (750 ℃ and 10 bar) of the SOEC (Küngas 2020). Having the SOEC operated at this relatively high temperature offers a great opportunity for heat integration with the downstream processing (L. Wang et al. 2018). Nevertheless, in a real life situation, reaching this high operating temperature in an efficient and reliable way is challenging (Ali et al. 2020) (L. Wang et al. 2018).

After electrolysis the CO is further processed into syngas. The produced oxygen is upgraded and sold as industrial oxygen (described in Appendix F). An overview of the SOEC Aspen flowsheet is shown in Appendix J, Figure J.2.

3.2.2 Pre-treatment of the Porthos Stream

The impurity tolerances of SOEC's and the relevant impurities present in the Porthos stream are shown in Figure 3.6. It can be seen that the concentration of sulphur compounds in the feedstream transcend the impurity tolerance levels. Both the level of H_2S and SO_2 should be lowered. Therefore, pre-treatment of the Porthos stream is required.

Compound	Concentration in Feedstock	Tolerance of SOEC	*Source*
Methane	< 1%	Fuel	*Kushi et al. (2017)*
Aliphatic hydrocarbons	< 1200 ppm	Fuel	*Allegue et al. (2012)*
H_2S	< 5 ppm	< 1 ppm	*Wasajja et al. (2020)*
SO_2	< 15 ppm	< 0.5 ppm	*Jeanmonod et al. (2020)*
Ammonia	< 3 ppm	< 5000 ppm	*Allegue et al. (2012)*
Halogens	X	< 1 ppm	*Allegue et al. (2012)*

Figure 3.6: Overview of the impurity tolerance of a solid-oxide electrolysis cell (SOEC) and the impurities present in the CO_2 feedstream. It can be seen that pre-treatment for sulphur removal is required. *Based on: Jeanmonod et al. 2020, Kushi 2017, Allegue et al. 2012, Wasajja et al. 2020, Porthos 2019.*

Sulphur concentrations higher than the reported tolerance levels will negatively impact the performance of the SOEC (Jeanmonod et al. 2020) (Wasajja et al. 2020). The catalytic and electrochemical reactions of Ni-YSZ based SOEC's are reported to be negatively influenced by a SO_2 concentration of above 0.5 ppmv (Jeanmonod et al. 2020). Also the presence of other sulphur compounds, such as H_2S, C_4H_4S and COS may decrease its performance (Jeanmonod et al. 2020) (Kushi 2017) (Wasajja et al. 2020). As stated by Wasajja et al. 2020, these concentrations should not exceed 1 ppmv to prevent damaging the SOEC's performance.

Next to the negative impact on SOEC's, sulphur is also reported to affect syngas fermentation. By a syngas fermentation with *C. ljungdahlii*, a H_2S concentration of 0.1 g L^{-1} leads to less biomass formation, a delayed acetate production and no alcohol formation (Oliveira et al. 2022).

H_2S Removal

Removal of sulphur compounds can be achieved via several technologies. According to Allegue et al. 2012, the most common H_2S removal technologies are adsorption, absorption and gas-gas separation. Another approach is to convert H_2S into SO_2 and remove this in the subsequent step (done with a process called CrystaSulf®). The different options are shown and compared in Appendix I. Based on this analysis, the first part of the hybrid CrystaSulf® process is chosen for the removal of H_2S. Generally this process consists of a direct oxidation (DO) reactor unit followed by the CrystaSulf reactor. The DO reactor uses air and a catalyst to oxide the present H_2S into SO_2. Subsequently this is converted into elemental sulfur in the CrystaSulf unit (Meyer 2010). As discussed in Appendix I, the sulfur load in the Porthos stream is too low to be economically viable to upgrade into elemental sulfur. Therefore, solely the DO reactor of the hybrid CrystaSulf® technology is implemented.

This reactor oxidizes H_2S following Equation 3.4 and Equation 3.5 (Dalrymple 2004).

$$2\ H_2S + 3\ O_2 \rightleftarrows 2\ SO_2 + 2\ H_2O \tag{3.4}$$

$$2\ H_2S + O_2 \rightleftarrows 2\ S + 2\ H_2O \tag{3.5}$$

The formed SO_2 will be removed in the next step, but elemental sulfur not. Hence, it is important to favor Equation 3.4 over Equation 3.5. This can be achieved by providing air with a ratio of 1.5 mole O_2 to 1 mole H_2S (Dalrymple 2004). The produced elemental sulfur when operating at this ratio is negligible. The process is modeled in Aspen by using the reactor REquil with Peng-Robinson as property method. Operation conditions are 200 ℃ and 20.7 bar (Dalrymple 2004). The simulation approach is similar to that of Quevedo 2021.

SO_2 Removal

When the SO_2 concentration is relatively low, it is generally recommended to neutralize it with a once-through sorbent (Hanif et al. 2020). Considering all the indirect route's characteristics, scrubbing with Na_2SO_3 in a rotary packed bed column is chosen as the SO_2 cleaning method (B. Sun et al. 2019). The solvent with a concentration of 7.5 wt% Na_2SO_3 enters the column. Its flow is set to reach the required purity of 0.5 ppmv SO_2. Both SO_2 and NO_2 are absorbed by the solvent. This process is modeled in Aspen by using a RadFrac column with property method ELECNRTL.

An overview of the pre-treatment modeling can be found in the SOEC Aspen flowsheet (Appendix J, Figure J.2).

3.2.3 Water Electrolysis

The process design of H_2O electrolysis follows a similar approach as for CO_2 electrolysis. An electrolyzer is chosen with help of a Pugh matrix. This is followed by a description of its specific characteristics and the modeling approach in Aspen Plus.

Selection H_2O electrolyzer

The electrolyzers that are considered are alkaline (AEL), proton exchange membrane (PEMEL) and solid-oxide electrolyzer cells (SOECs). Similar criteria as used for CO_2 electrolyzers are used to rank the H_2O electrolyzers. The specific parameters and their value for each type of the proposed options is shown in Appendix G.2. This data is used to draft a Pugh matrix as described in subsection 2.2.1. An overview of this matrix is shown in Figure 3.7.

Category	Criterium	Weight	Alkaline	Polymer Electrolyte Membrane	Solid Oxide Electrolysis
Risk	*Technology Readiness Level*	10%	1	1	2
	Proven Durability	10%	1	1	2
Process Properties	*Operation Temperature*	2.5%	1	2	3
	Pressure	2.5%	1	2	1
	Faradaic Efficiency	7.5%	1	1	1
	Partial Current Density	7.5%	3	1	2
	Operating cell voltage	7.5%	2	2	1
	Conversion Efficiency	7.5%	1	1	1
	Tolerance to impurities	5%	1	1	2
Economics	*CAPEX*	20%	1	2	3
Sustainability	*Catalyst Material*	10%	1	2	1
	Electric Power Consumption	10%	2	2	1
SCORE			**1.3**	**1.5**	**1.8**

Figure 3.7: Pugh matrix to decide which H_2O electrolyzer is used. The Pugh matrix is based on the data reported in Appendix G.2. Each electrolyzer is scored from 1 to 3, at which 1 indicates the best performance and 3 the worst, compared to the other options. The weighted average of this score shows the best outcome (score of 1.3) for the alkaline electrolyzer. Note, the conversion efficiency of a SOEC could not be determined under the circumstances mentioned. Therefore, all electrolyzers are ranked equally on this criterium. In terms of faradaic efficiency, all electrolyzers score equally.

As can be seen in Figure 3.7, the alkaline electrolyzer is the best choice regarding the parameters taken into account. Therefore, this type of electrolyzer is used to model H_2O electrolysis. This model is based on the design presented by Sanchez et al. 2020 and adapted with estimations made by Taibi et al. 2020.

Characteristics of an Alkaline electrolyzer

A simplified schematic overview of the alkaline electrolyzer is shown in Figure 3.8.

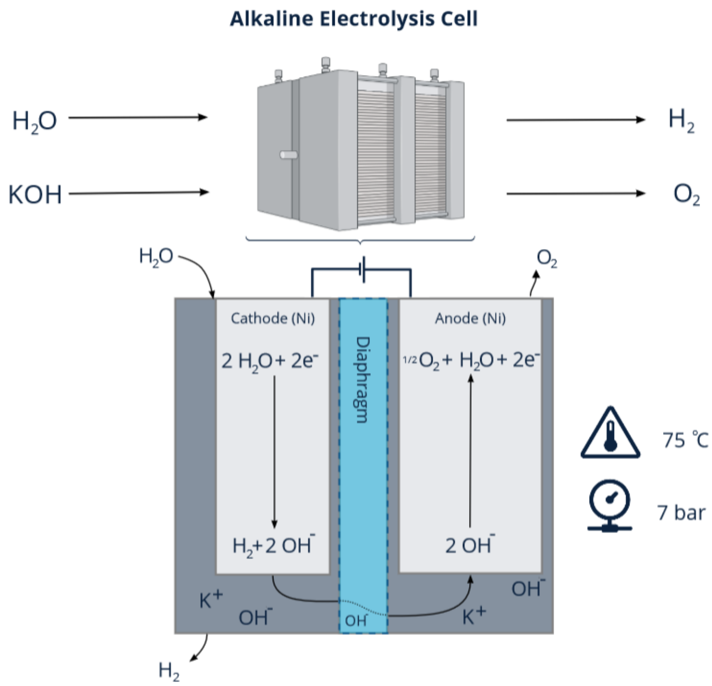

Figure 3.8: Schematic overview of the working principle of an alkaline electrolyzer. At the cathode H_2O is converted into H_2. At the anode OH^- react to O_2 and water. 35 wt% aqueous potassium hydroxide (KOH) is used as liquid electrolyte.

The following reactions take place in the cathode (reaction 3.6) and anode (reaction 3.7) (Mulder and Geerlings 2021):

$$2\,H_2O\ + 2e^- \rightleftarrows H_2 + 2\,OH^- \tag{3.6}$$

$$2\,OH^- \rightleftarrows \frac{1}{2}\,O_2 + H_2O\ + 2e^- \tag{3.7}$$

These reactions combined lead to the overall reaction shown in Equation 3.8:

$$2\,H_2O\ \rightleftarrows O_2 + 2\,H_2 \tag{3.8}$$

Commonly, an AEL consists of electrodes made out of nickel and an electrolyte of 35% KOH and 65% H_2O (Sanchez et al. 2020). Nickel is advantageous to use since it is cost effective and stable in the KOH solution. KOH is a good electrolyte as it has a high conductivity (Mulder and Geerlings 2021). The operating temperatures of a AEL are in the range of 60 ℃ to 90 ℃ and the pressure below 30 bar (Sanchez et al. 2020).

Modeling of the H_2O Alkaline Electrolyzer in Aspen Plus

The alkaline electrolyzer is modeled as an RSTOIC reactor followed by several separator vessels. For all units containing liquid the property method ELECNRTL is used. Gases are modeled with PENG-ROB. The operating conditions are 7 bar and 75 ℃ (Sanchez et al. 2020). The crossover of the oxygen to the hydrogen side is approximately 0.1% to 0.5% (Janssen et al. 2004). For the modeling in Aspen, the effects of crossover from either side is assumed to be negligible. The electrolyte is evenly distributed between both products and 100% efficiently recycled back to the RSTOIC reactor. A water trap is set to limit the amount of condensate water in the hydrogen stream.

An overview of the Aspen flowsheet of the AEL is shown in Appendix J, Figure J.3.

3.3 Syngas Fermentation

The next step in the process design is syngas fermentation to produce *n*-caproate. See Figure 3.9 for a schematic overview of the focus of this section. This section consists of two parts. Firstly, the fundamental steps of syngas fermentation are explained (subsection 3.3.1). The second part of this chapter discusses the design approach selected for syngas fermentation (subsection 3.3.2).

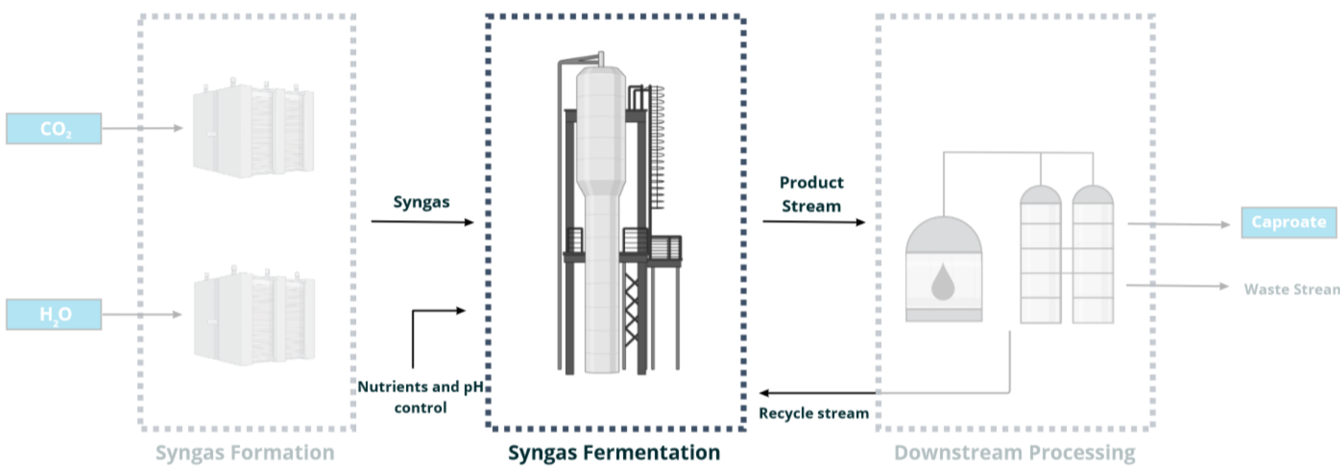

Figure 3.9: Schematic overview of the focus areas of section 3.3. These focus areas are the required composition of syngas, the fermentation routes possible and their *n*-caproate yields.

3.3.1 Fermentation of Syngas to *n*-Caproate

Syngas fermentation into *n*-caproate occurs in two general steps. The formation of acetate (CH_3COOH) and ethanol (C_2H_5OH) out of syngas is performed by acetogenic bacteria, called 'acetogens' (de Medeiros, Posada, et al. 2019) (Bertsch and V. Müller 2015). Subsequently, the produced acetate and ethanol are the substrate for chain-elongation. During chain-elongation, medium-chain fatty acids are produced. The main medium-chain fatty acids produced are *n*-butyrate (C_3H_7COOH) and *n*-caproate ($C_5H_{11}COOH$) (Fernández-Blanco et al. 2022). Acetogenesis and chain-elongation are performed by different type of microorganisms, utilizing different metabolic routes (Fernández-Blanco et al. 2022). Therefore, this can be seen as separate steps in the fermentation process.

Acetate and Ethanol formation by Acetogens

Syngas fermentation is performed by acetogens (de Medeiros, Posada, et al. 2019) (Bertsch and V. Müller 2015). The metabolic route utilized by these bacteria is the Wood-Ljungdahl Pathway (WLP). Here, syngas is converted into Acetyl-CoA. Once Acetyl-CoA is produced, it can be used as a precursor for the formation of acetate, ethanol or biomass (de Medeiros, Posada, et al. 2019) (Bertsch and V. Müller 2015). A schematic overview of the Wood-Ljungdahl Pathway is shown in the upper half of Figure 3.10.

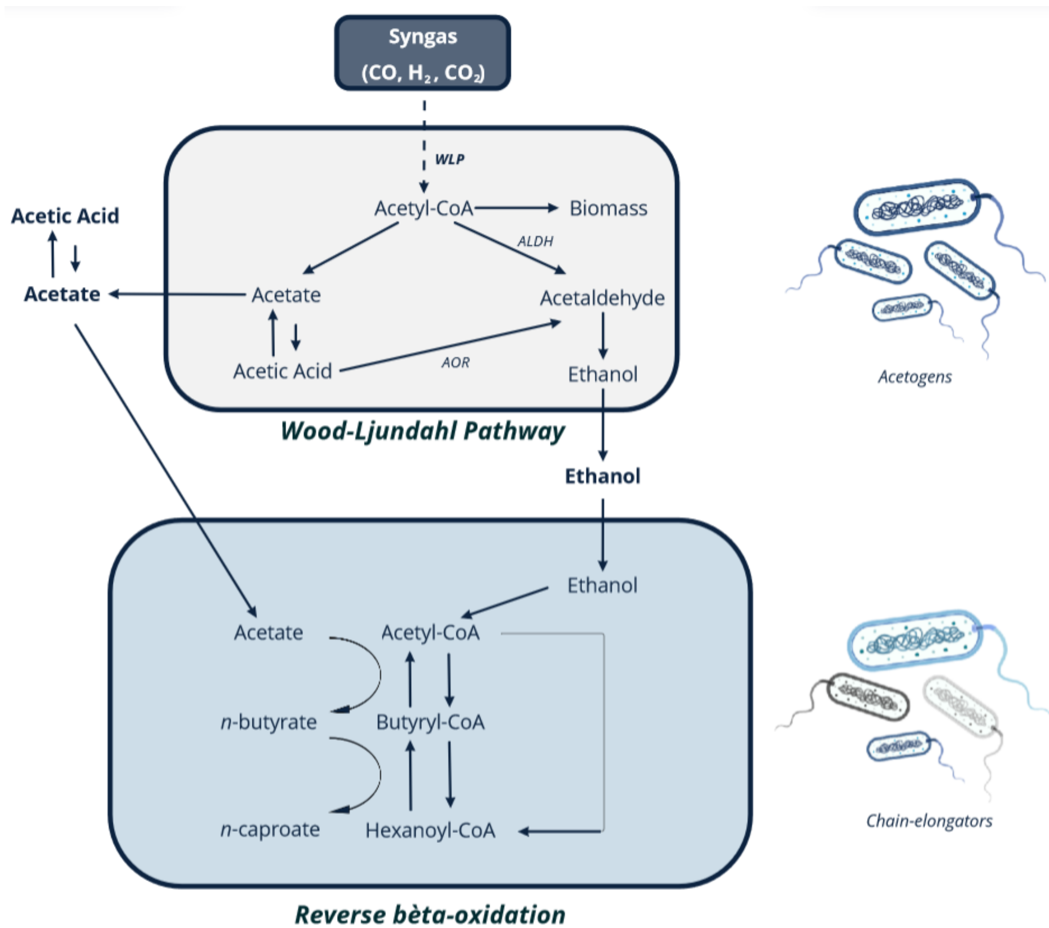

Figure 3.10: Schematic overview of the metabolic pathways used for: 1) syngas conversion into acetate and ethanol and 2) acetate and ethanol fermentation into medium-chain fatty acids (n-butyrate and n-caproate). Conversion 1 occurs via the Wood-Ljungdahl Pathway and 2 via reverse β-oxidation cycle *(Fernández-Blanco et al. 2022)*.

The stoichiometry of the relevant metabolic reactions of the WLP are summarized below. Equation 3.9 and 3.10 show the steps for acetate production and Equation 3.11 and 3.12 for ethanol production (Bertsch and V. Müller 2015) (de Medeiros, Posada, et al. 2019) (Phillips et al. 1993).

$$4\,CO + 2\,H_2O \rightarrow C_2H_3O^- + H^+ + 2\,CO_2 \tag{3.9}$$

$$2\,CO_2 + 4\,H_2 \rightarrow C_2H_3O^- + H^+ + 2\,H_2O \tag{3.10}$$

$$6\,CO + 3\,H_2O \rightarrow C_2H_5OH + 4\,CO_2 \tag{3.11}$$

$$2\ CO_2 + 6\ H_2 \rightarrow C_2H_5OH + 3\ H_2O \tag{3.12}$$

To retrieve the stoichiometric reaction required for biomass formation, a general bacterial biomass composition is assumed. This composition is $CH_{1.8}O_{0.5}N_{0.2}$, following Wooley and Putsche 1996. Furthermore ammonia ($NH_4{}^+$) is assumed to be the sole nitrogen source. Taking the aforementioned assumptions into account, Equation 3.13 shows the reaction of biomass formation.

$$5\ CO + NH_4^+ + 5\ H_2 \rightarrow 5\ CH_{1.8}O_{0.5}N_{0.2} + 2.5\ H_2O \tag{3.13}$$

The product distribution is dependent on several factors, such as the syngas composition, the pH, the microorganisms present and the product concentration (de Medeiros, Posada, et al. 2019). One should be aware of the influence of these factors when comparing different syngas fermentation studies. Therefore, research conducted by the research group of de Medeiros *et al.* (de Medeiros, Noorman, et al. 2020, de Medeiros, Posada, et al. 2019, de Medeiros, Noorman, et al. 2021), is the main source used for obtaining process conditions and estimating yields. De Medeiros *et al.* use the experimental data from Phillips et al. 1993, Gaddy et al. 2017 and Maddipati et al. 2011 as basis for their metabolic model.

According to de Medeiros, Noorman, et al. 2020, an economic optimum for syngas fermentation is present at an ethanol productivity of 4.5 g L^{-1} h^{-1}. Assuming a high mass transfer, this indicates a CO conversion of approximately 90% (de Medeiros, Noorman, et al. 2020). These results are based on utilizing *Clostridium ljungdahlii* as acetogen. However acetogens are inhibited by high ethanol concentrations (Ramió-Pujol et al. 2018). *C. ljungdahlii* is reported to show the downsides of ethanol inhibition starting from an ethanol concentration of 35 g/L (Phillips et al. 1993).

n-Butyrate and *n*-Caproate formation by Chain-Elongators

The formation of *n*-butyrate and *n*-caproate is performed by chain-elongating microorganisms. Chain-elongation is often achieved by using an open-culture fermentation. This indicates that multiple genera of bacteria are present (Spirito et al. 2014). The usage of an open-culture instead of a pure or defined-mixed culture shows multiple advantages, as discussed by Spirito et al. 2014. The abundant metabolic pathway present in this type of microbiome is the (reverse) β-oxidation pathway (RBO) (Spirito et al. 2014). This is a reversible pathway that elongates ethanol and acetate into *n*-butyrate and *n*-caproate. A schematic overview of the reverse β-oxidation pathway is shown in Figure 3.10.

The relevant metabolic reactions in the RBO are shown below. Equation 3.14 shows the overall *n*-butyrate reaction and Equation 3.15 the *n*-caproate formation.

$$6\ C_2H_5OH + 4\ C_2H_3O^- \rightarrow 5\ C_3H_7COO^- + H^+ + 2\ H_2 + 4\ H_2O \tag{3.14}$$

$$6\ C_2H_5OH + 5\ C_3H_7COOH \rightarrow 5\ C_5H_{11}COO^- + C_2H_3O^- + H^+ + 2\ H_2 + 4\ H_2O \tag{3.15}$$

For the stoichiometric reaction for biomass formation, a universal biomass structure of $CH_{1.8}O_{0.5}N_{0.2}$ is assumed (Wooley and Putsche 1996). The overall reaction is shown in Equation 3.16.

$$4\ CO_2 + HCO_3^- + 10.5\ H_2 + NH_4^+ \rightarrow 5\ CH_{1.8}O_{0.5}N_{0.2} + 8.5\ H_2O \tag{3.16}$$

The simulation of chain-elongation in this report is based on the research published by P. Yang et al. 2018. In this research n-caproate and biomass formation occurred in a molar ratio of 1:0.08. These rates are achieved in a batch-fermentation with operating conditions of pH 7 and 37 ℃ (P. Yang et al. 2018). The final concentrations achieved are 32.6 ± 0.8 mM caproic acid and 15.4 ± 0.55 mM butyric acid. The achieved n-caproate concentration is in the same order of magnitude as research published by Roghair et al. 2018 and Baleeiro et al. 2021.

The presence of n-caproate and n-butyrate can damage the cell membrane of the chain-elongators. Thus, a high concentration of these compounds is toxic to the micro-organisms (Roghair et al. 2018). The chain-elongation microbiome used by Roghair et al. 2018 showed to be proportionally inhibited to 45% at an n-caproate concentration of 172 mM. It is assumed that the inhibitory and toxic effects of n-caproate at a concentration of ≈ 32.6 mM are negligible.

Modeling of Syngas Fermentation in Aspen Plus

For the fermentation hierarchy, the property method NRTL-HOC is used. Syngas consists of a ≈ 1:1 molar ratio of CO_2 and H_2 , similar to the composition described by de Medeiros, Noorman, et al. 2020. The fermentation is modeled with two RSTOIC reactors. The yields of the reactions are calculated based on the product yields obtained by de Medeiros, Noorman, et al. 2020 and P. Yang et al. 2018. Based on the overall conversion rate of the components and the product yields, the missing biomass formation is derived. The yields for each reaction can be seen in Table 3.1.

Table 3.1: Overview of the stoichiometric reactions taking place at the fermentations. The conversion of each reaction is shown as the fractional conversion of the compounds CO, H_2, ethanol or NH_4Cl

Reaction	Fractional Conv.	Component	Reaction	Fractional Conv.	Component
Equation 3.9	0.035	CO	Equation 3.14	0.60	Ethanol
Equation 3.10	0.031	H_2	Equation 3.15	0.41	Ethanol
Equation 3.11	0.65	CO	Equation 3.16	0.95	NH_4Cl
Equation 3.12	0.58	H_2			
Equation 3.13	0.21	CO			

The nutrient composition can be found in Appendix H. Potential nutrient limitations are circumvented by ensuring a residual nutrient fraction of 0.05%. For the second fermentation additional acetate is supplied to increase the final n-caproate yield (P. Yang et al. 2018).

Biomass is modeled as a solid. The chemical properties of biomass and its particle size distribution are retrieved from the data published by Wooley and Putsche 1996. The cells and the products are separated via micro-filtration (Zacharof and Lovitt 2013). 90% of the biomass is collected in the permeate. This stream is recycled back into the fermentor, which is in line with the process described by Phillips et al. 1993. The same recycling ratio is used for chain-elongation.

An overview of the fermentation in the Aspen Flowsheet is shown in Appendix J, Figure J.4 and Figure J.5.

3.4 Downstream Processing

The last step in the *n*-caproate production process is the downstream processing (DSP). See Figure 3.11 for an overview. In many microbial production processes, the separation of the target product from the fermentate is often the most expensive and environmentally burdensome set of unit operations (Saboe et al. 2018). Thus, the DSP approach chosen can significantly impact the overall performance of the process. The DSP consists of several steps. Firstly, the pH of the fermentation broth is adjusted. Secondly, solid waste is separated from the broth. Thirdly, *in-situ* product recovery (ISPR) coupled distillation combined with azeotrophic distillation is used. This approach is suggested by Saboe et al. 2018 and also employed for the DSP of the direct route (Luo et al. 2022).

This section explains the working principle of all DSP steps. Especially, the filtration of the fermentation broth, the pH adjustment, the liquid-liquid extraction and the different distillations are discussed. Per DSP step the modeling of this step in Aspen Plus is elaborated on.

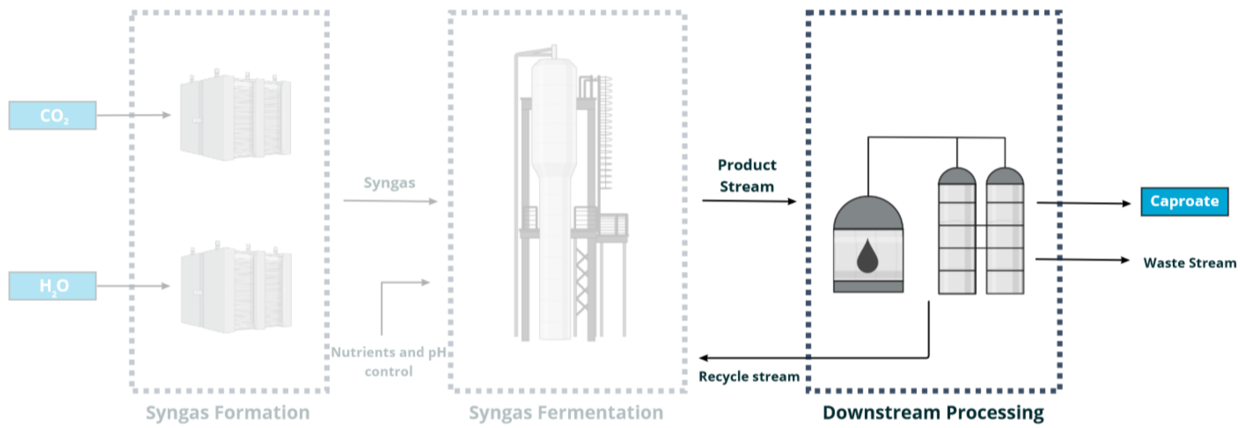

Figure 3.11: Schematic overview of the focus areas of section 3.4. These focus areas are the pH adjustment of the fermentation broth and reaching a *n*-caproate concentration of 99% in the product stream.

3.4.1 pH Adjustments of the Fermentation Broth

Firstly, the fermentation broth is filtered by micro-filtration. Here 90% of the biomass is recycled to the reactor. This is explained in section 3.3. The retentate of the micro-filtration contains the products acetate, butyrate and *n*-caproate. The pH of this stream is adapted to shift the carboxylates into their acidic form. This is achieved by adding a H_3PO_4 solution. The protons present in this solution react to form acids. As an example, this reaction for acetate is given (see Equation 3.17). The remaining HPO_4^{2-} is precipitated by adding $CaCl_2$. The resulting reaction equation is shown in Equation 3.18. The precipitated salt and remaining biomass is removed from the product stream.

$$CH_3COO^- + H^+ \rightarrow CH_3COOH \tag{3.17}$$

$$HPO_4^{2-} + Ca^{2+} \rightarrow CaHPO_4(s) \tag{3.18}$$

Modeling in Aspen Plus
The property method NRTL-HOC is used. The pH adjustment is done by mixing the H_3PO_4 and $CaCl_2$ with the retentate. This mixing occurs in an RSTOIC Reactor. The amount of H_3PO_4 and $CaCl_2$ added is calculated based on the amount of carboxylates present. Their stream flow is set with calculator blocks. After the pH adjustment, the solids (biomass and $CaHPO_4$) are removed via a separator.

3.4.2 *In-situ* Product Recovery coupled Distillation

In-situ product recovery (ISPR) coupled distillation is chosen to retrieve the *n*-caproate from the fermentation broth (see Saboe et al. 2018). This DSP method is also applied for the direct route of *n*-caproate production, easing comparison between those routes. Furthermore, ISPR coupled distillation enables continuous product removal, which has two main advantages over batch processing. Firstly, an increased microorganism productivity and yield can be achieved due to a decrease in product inhibition. Secondly, the pH of the bioreactor can be regulated without the equimolar addition of base (Saboe et al. 2018). Overall, this results in a better economic performance (Van Hecke et al. 2014) (Nelson et al. 2017).

The ISPR coupled distillation applied in this research consists of three main steps after fermentation. Firstly, liquid-liquid extraction (LLE) is performed to recover the organic products from the water phase. The product stream from the fermentation consists for $\geq 97\%$ of water. Water and *n*-caproate form an azeotrope, hampering successful separation (Saboe et al. 2018). As mentioned by Saboe et al. 2018, decreasing the water fraction can significantly decrease the distillation OPEX. LLE enables the movement of *n*-caproate into a different solvent, which eases distillation. Secondly, the organic phase is passed into a distillation column. Here, acid vaporization takes place. The steps of LLE followed by distillation are performed twice. After the second distillation, the mass fraction of *n*-caproate is $\geq 50\%$. As a last step, a final distillation is implemented to separate *n*-caproate from the other fatty acids and H_2O .

An overview of the Aspen Flowsheet can be found in Appendix J Figure J.6.

Liquid-Liquid Extraction (LLE) of the Organic Phase

Solvent Selection
Liquid-liquid extraction is based on the addition of a liquid solvent phase to the original liquid. The components of interest will be distributed among both liquid phases in a certain ratio (E. Müller et al. 2000). The equilibrium constant of this ratio is dependent on the type of liquid extractant used (Towler and Sinnott 2013). Thus, the extractant influences the concentration of *n*-caproate concentration in the organic phase (Saboe et al. 2018). As a result, it is beneficial to select a solvent with a high equilibrium constant of *n*-caproate for the organic phase. Next to this, the step after LLE should be taken into account. After the LLE, distillation is performed. In order to enable the acid to be recovered as a distillate, the volatility of the solvent should be low (Saboe et al. 2018). A solvent fulfilling both requirements, which is also available in Aspen, is trioctylamine (TOA). TOA has a high equilibrium constant for *n*-caproate (69.1 $\pm$ 32) and a low volatility (Saboe et al. 2018). Thus, TOA is chosen as extractant in LLE.

Modeling in Aspen Plus
For LLE *UNIF-HOC* is set as property method. The LLE is modeled with a 10-stage extractor. Here the organic acids move to the TOA phase. The amount of TOA added to the extractor is based on the H_2O present in the feedstream. For the first LLE, a molar feed of $\approx 0.02 \times$ the water feed is taken. The second LLE uses a ratio of $\approx 0.016 \times$ the water feed. These values are determined by considering the maximal *n*-caproate extraction versus minimizing the TOA usage and utility costs.

Vacuum Distillation of the Organic Phase

After the LLE, the *n*-caproate is extracted from TOA via vacuum distillation. These distillations are performed at a pressure of 0.05 bar (Saboe et al. 2018). The pressure was lowered to lower the liquid boiling points and prevent auto-oxidation of the organic phase (Brimberg 1993). *n*-Caproate leaves both distillation in the distillate fraction. TOA leaves at the bottoms and $\geq$ 99% is recycled.

Modeling in Aspen Plus
Vacuum distillation is modeled with RadFrac and the property method *NRTL-HOC*. The required pressure of 0.05 bar is achieved by using an ejector-nozzle system. This system is simplified and modeled as pumps in Aspen Plus. The first distillation consists of 5 stages. Using 5 stages enables significant *n*-caproate and TOA separation without adding unnecessary stages. *n*-Caproate is set to have a mass recovery of 99.95%. The feedstream has an *n*-caproate mass fraction of 0.01 and the distillate has a mass fraction of 0.32. The distillate moves towards a second LLE, as described above. When leaving the LLE, it enters a second vacuum distillation. This column contains 6 stages. A similar operation as for the first LLE + distillation is taken.

Important to note is that the second distillation is the final step that enables TOA removal. TOA has a molecular weight of 353.7 g/mol, which is significantly higher than the molecular weight of the other compounds present. The presence of TOA will thus have a serious impact on the final *n*-caproate purity. Therefore, its presence in the product stream should be limited. A mass purity of $\approx 1.49 \times 10^{-4}$ is taken as design specification. Next to this it is ensured that the *n*-caproate recovery in the distillate is $\geq$ 99.95%. The mass fraction of *n*-caproate in the distillate of the second distillation is $\approx$ 0.54.

3.4.3 Azeotropic distillation of *n*-Caproate

The final step is a distillation to separate *n*-caproate from H_2O and the shorter-chained fatty acids. *n*-Caproate is recovered as the heavy key and *n*-butyrate as the light key. The bottom product contains 99% pure *n*-caproate. The remaining 1% consists of trace amounts of TOA, H_2O , *n*-butyrate and acetate.

Modeling in Aspen Plus
For the modeling of this distillation column a RadFrac model specified as 'azeotropic distillation' is taken. Its property is set to *NRTL-HOC*. Specified are a mass fraction of 99% *n*-caproate as heavy key. Moreover the bottom flow is 1250 kg/hr. This flow is set to ensure that the annual production aim of 10 kt is reached. The distillate consists mainly of butyrate ($\geq$ 70%) and water ($\geq$ 20%). This stream is assumed to be distributed to a neighbouring chemical plant.

Chapter 4

Results & Discussion

This chapter shows and discusses the results of the performed analyses and simulation. It starts with the stakeholder identification and characterisation (section 4.1, 4.2 and 4.3). The stakeholders are visualized in a quadruple helix, technological innovation system (TIS) and influence-interest grid (II-grid). The TIS shows the dynamics of the innovation. It enables the identification of failures present in this system. The II-grid helps to prioritize which stakeholders to interview.

Secondly, an overview of the parameters retrieved from the interviewed stakeholders are shown (section 4.4). Parameters that are often mentioned are compared to the parameters retrieved from literature analysis. This is followed by a comparison of the viewpoint of the interviewed scientists and that of the ESIs on the technology's assessment. This section closes with a reflection on the relevance of interviewing the selected stakeholders.

Thirdly, an overview of the mass and energy balances is given (section 4.5). These balances are retrieved from the simulation made in Aspen Plus. The electricity demand of the electrolyzers is calculated separately of Aspen. The obtained results are compared to the yields and flows described in literature.

Lastly, the performance of both routes is assessed (section 4.6). This assessment contains technical, economic, environmental and strategical metrics. The final parameters considered for the comparison are; CO_2 conversion efficiency, specific primary energy consumption, product selectivity, TRL, CAPEX, OPEX, MCSP, carbon footprint, GHG reduction potential and its competitive advantage.

4.1 Stakeholder Identification via the Quadruple Helix

The identified stakeholders are shown in Figure 4.1. The stakeholders are placed in four groups; 'Academia', 'Industry', 'Government' and 'NGOs & Communities'. The stakeholders in academia are the scientists working on MES, syngas fermentation and sustainable *n*-caproate production.

The stakeholders from the industry are the industrial partners from Porthos, the JDA Partners. These include Air Liquide, Air Products, Exxonmobil and Shell (Porthos 2022a). These four parties are international incumbent refineries/ chemical firms. Other industrial parties involved are early-stage investors and Porthos. Porthos is a collaboration between the Authority of the Port of Rotterdam, GasUnie and EBN (Porthos 2022a).

The governmental stakeholders are the Ministry of Economic Affairs & Climate Policy, the European Union, the Rijksdienst voor Ondernemend Nederland (RVO) and DCMR Milieudienst Rijnmond (DCMR). RVO is the executing party of the policy set by the Ministry. Their goal is to enhance Dutch economic growth and sustainability (RVO 2022a). DCMR Milieudienst Rijnmond is a joint environmental service of the Province of South Holland and fifteen municipalities in the Rijnmond region. They draw up environmental regulations for the region and monitor compliance of these regulations (and other laws). They also have the task to supervise so-called high-risk companies, such as refineries and chemical plants (DCMR 2022). The Port of Rotterdam is located in the Rijnmond region and many of the present industries are subject to DCMR's checks. Furthermore DCMR is the party that can grant companies environmental permits (DCMR 2022).

The NGOs consist of the association formed by the industries at the Port and NGOs involved in mitigating climate change. The association representing 95% of the logistic, ports and industrial enterprises in the mainport Rotterdam is called Deltalinqs. Their goal is to strengthen the Port's competitiveness, sustainable growth and social and political acceptability (Deltalinqs 2022). Next to Deltalinqs, NGOs involved with tackling climate change as their main goal are present. These NGOs' focus area can be divided into a regional, national and European level. The NGO on the regional level is 'Natuur- en milieufederatie Zuid-Holland'. On a national level 'Milieudefensie' and 'Mobilization for the Environment' (MOB) are present. On a European level 'Transport & Environment' is the NGO concerned with the sustainability of the Port of Rotterdam.

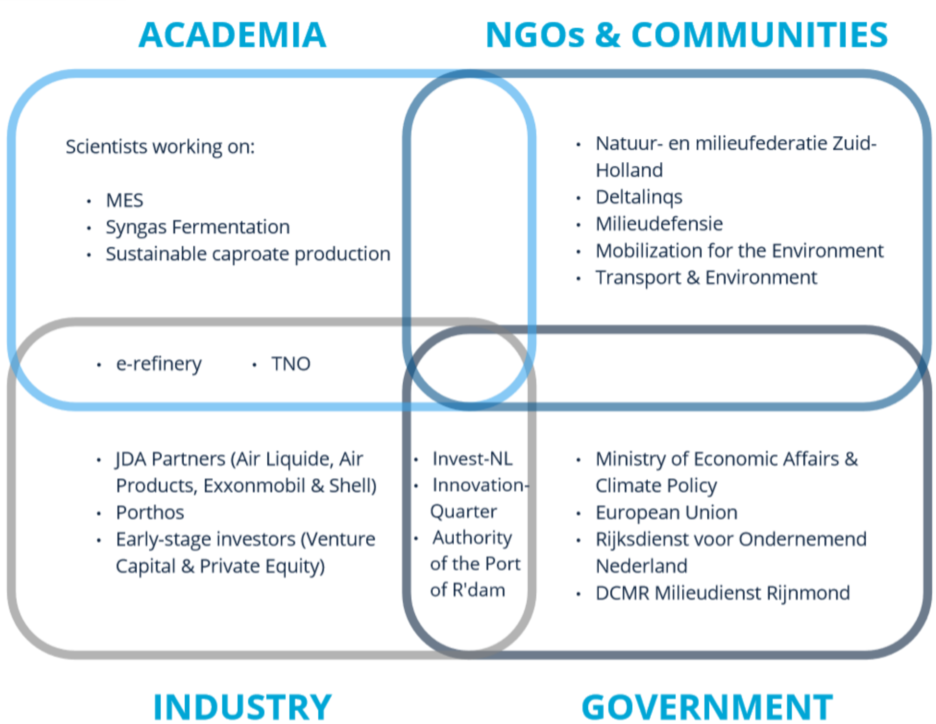

Figure 4.1: Overview of the stakeholders involved. They are identified and grouped via the quadruple helix approach. The categories are; government, industry, academia and NGOs & communities.

Five stakeholders could not be specifically categorized in one of the four stakeholder groups. They are rather an overlap between either 'academia and industry' or 'government and industry'. These stakeholders are; the e-refinery group, TNO, Invest-NL, InnovationQuarter and the Authority of the Port of Rotterdam. The e-refinery institute is a collaboration of research and industry. Their goal is to develop the technologies required for the energy transition, but also its implementation (E-Refinery 2022). TNO is a research institute which frequently collaborates with and is hired by companies, public-sector bodies and other type of organisations. TNO is an institute independent of academia, industry and the government (TNO 2022). The stakeholders Invest-NL and InnovationQuarter are impact investors. However, their capital source originates from the government. They are dependent on other, non-governmental, investors to join a project and cannot fund a project fully on their own (Invest-NL 2022) (InnovationQuarter 2020). The Authority of the Port of Rotterdam is the owner, exploiter and developer of the Port of Rotterdam. It has a company structure with a profit target. However, all company shares are owned by the regional and national government (70% and 30% respectively) (Port of Rotterdam 2022b).

4.2 The Technological Innovation System for CCU at the Port of Rotterdam

An overview of the technological innovation system for n-caproate production of the indirect route at the Port of Rotterdam is shown in Figure 4.2. A TIS framework is a tool to understand the dynamics of innovation (Charles Edquist et al. 1997). It helps to pinpoint both technical as well as social problems hampering the diffusion of the innovation (Vroon et al. 2021). In this research, it is used to give the environment in which the stakeholders are acting (Negro et al. 2012). Furthermore, it is used to analyze how the performance of the innovation can be improved.

A TIS shows that multiple types of failures can be present by the development, diffusion and implementation of a technology (Negro et al. 2012). It transcends the neoclassical view of 'market failure'. Market failure is often mentioned as issue to describe the hampering of sustainable innovation (Cumming et al. 2016). The view of market failure states that a below-optimal rate of innovation can be solved by (financial) resource relocation (Arrow 1962) (Negro et al. 2012). To speed-up the innovation path of sustainable technologies, the private under-investment in this sector is to be compensated by subsidies and taxes (Negro et al. 2012). The impact of increased public support are expected to be beneficial for the development of cleantech. This is expressed in various bodies of literature (Negro et al. 2012) and by the interviewed stakeholders in Appendix D. But, which type of subsidies are required and which budget should go where? Using a TIS is believed to have a more elaborated view than the neoclassical approach. It has a greater potential for identifying areas of systematically weak performance. These areas could be strengthened by public support (K. Smith 2000) (Alkemade et al. 2011).

As explained in subsection 2.1.2, a TIS consists of four factors, namely actors, networks, infrastructures and hard & soft institutions (Wieczorek and Hekkert 2012) (Vroon et al. 2021). Each of these factors in the context of CCU technologies at the Port of Rotterdam will be elaborated on below.

Outside of the TIS, four other sustainability projects present at the Port of Rotterdam are depicted. It includes the production of sustainable methanol, renewable bio-diesel and sustainable aviation fuel. These projects are part of the Port's key pillar to replace fossil-fuels (van Dooren 2022). The fourth depicted project is 'MAGPIE'. This is a collaboration between several European ports to accomplish green, sustainable ports of the future (MAGPIE 2022). These four projects are shown, since they are part of the network of sustainable bio-technologies present at the port and/or the link to other European ports. Each of these projects has a TIS, which is connected to the TIS shown in Figure 4.2. To prevent this TIS from being cluttered, these projects are shown outside of it.

4.2.1 Actors in the Technological Innovation System

Similar to Vroon et al. 2021, the previously performed stakeholder analyses and the interviews conducted are used to set the actors in the context of the TIS. The findings of these performed analyses can be found in section 4.3 and Appendix D.

In the TIS, the quadruple helix categories can be recognized. Obviously the NGOs discussed in this report can be found under 'Non-Governmental Organisations'. An exception is the branch organisation 'Deltalinqs'. This is categorized as 'Support Organization', as it represents the interests of the Port's industrial cluster

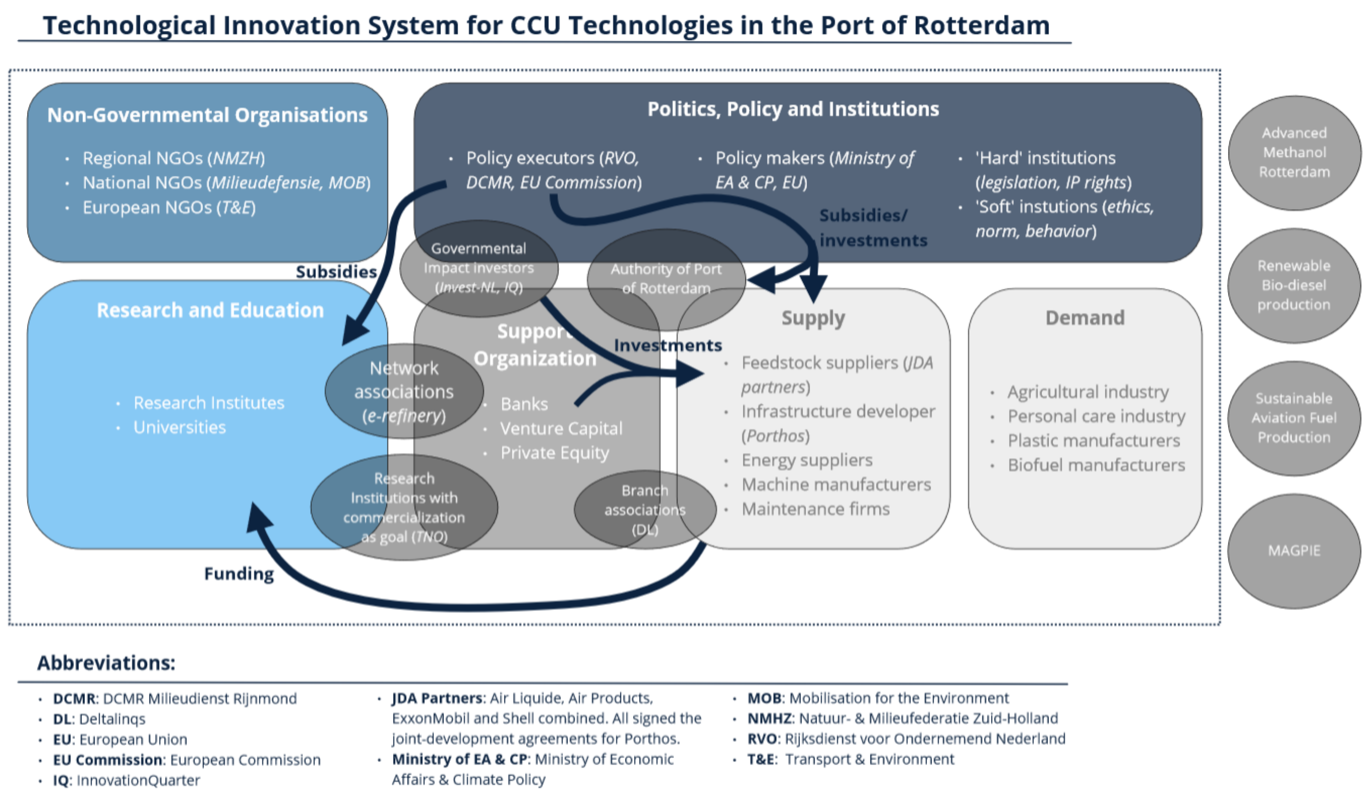

Figure 4.2: Overview of the innovation ecosystem. The group of 'industry' is divided into support organizations, the supply side and the demand side. Arrows indicate subsidy and investment flows. Next to the parties shown in this innovation ecosystem, a notion of other CCU projects and consortia present at the Port of Rotterdam are given. These projects include the production of sustainable methanol (named 'Advanced Methanol Rotterdam'), renewable bio-diesel, sustainable aviation fuel and the MAGPIE consortium. The MAGPIE consortium is a European collaboration to create smart green ports. *Structuring of the innovation ecosystem is based on: Vroon et al. 2021.*

(Deltalinqs 2022). The stakeholders identified in the group 'Academia' are placed at 'Research and Education'. Similarly stakeholders from the group 'Government' are part of 'Politics, Policy and Institutions'. The stakeholders identified as industrial stakeholders are separated between support organizations, supply and demand. Stakeholders with an overlap between multiple of the categories of the quadruple helix are shown with overlap between the TIS groups.

Actor Failures

As indicated by Wieczorek and Hekkert 2012, two types of problems related to the actors can be present. These can either be the absence of actors or their insufficient capabilities. As can be seen in Figure 4.2, for each category, multiple actors are present. Parties that show an overlap between different categories are also existent and play a significant role. Therefore, it is expected that there is no problem related to missing actors (Wieczorek and Hekkert 2012).

In terms of insufficient capabilities, this does play a role in the TIS for CCU at the Port. In the interviews with the ESIs (Appendix D), all three privately-funded parties state that they are having an increased interest in cleantech and sustainability. However, they indicate that a lack of resources to fully understand these type of technologies and its sustainability impact is present. This results in a hesitance to invest, as they cannot properly estimate the risk of the technology. The personal view on this topic of the second governmental investor confirms this finding. This investor states that other investors mainly look at the technology as a 'black box'. This 'black box' approach is not sufficient to fully value an investment. A proposed way to overcome this issue is for FOs, VCs and PEs to enlarge their teams with employees with an engineering background (see interview with *GOV.INV #2* in Appendix D).

4.2.2 Networks in the Technological Innovation System

The specific interactions present between the different stakeholders are not visualized in the TIS. This would lead to a complex and cluttered scheme. This is a common risk when mapping a large amount of stakeholders with complex interactions (Varvasovszky and Brugha 2000). The importance of collaboration between all stakeholder groups to reach innovation is also implied by the quadruple helix (Yan Yang, Holgaard, and Remmen 2012). Common issues present for this factor are the absence of networks or the type of connections within it. As stated by Wieczorek and Hekkert 2012, the connections between actors should not be too weak or too strong.

Strong Connections

Strong connections are caused by networks that are too close. The actors become reluctant to exit the group and it is difficult for new parties to enter (Negro et al. 2012). This results in missing developments outside of the network (Woolthuis et al. 2005). The TIS discussed in this research has connections to various outside projects, such as MAGPIE and bio-fuel production. Furthermore, the supply and demand parties use alternative technologies at the moment and have not committed to CCU. Thus, it is expected that the impact of strong network failures is negligible.

Weak Connections

Weak connections lead to network failures causing poor cycles of learning. As a result, adaptation to new technological developments are prevented (Negro et al. 2012). A weak network failure is caused when the connectivity among complementary technologies and actors is poor (Woolthuis et al. 2005). To see if weak connections are present, the connection between each group is analyzed in more detail below.

Firstly, a look at the network of NGOs is given. As indicated in Appendix D, a close collaboration between different NGOs is present. Furthermore, extensive consultations between these NGOs, Deltalinqs, governmental parties, research funds and the Authority of the Port happen. The connection of the NGO with research groups and financial support organizations is less. Specifically, as stated by the interviewed participant *NGO #1*, they would like to improve their interaction and collaboration with research groups, such as the 'Energy & Industry' group at the TU Delft.

Secondly, a couple of interactions are present in the network of 'Research and Education'. In general universities and several industries present at the Port have close contacts. Network associations such as the e-refinery are enhancing this connection. A party like TNO bridges scientific novelty with industrial application, stimulating interaction between the research field, industry and politics. However, the research and education parties might have minimal contact with NGOs and (financial) support organizations. An exception is one of the governmental impact investors. As can be seen in Appendix D, *GOV.INV #2* indicates a close connection to the universities in order to track the technological development for a longer period of time. This interviewed participant highlights the importance of understanding a technology. (S)he states that the connection between private early-stage investors and scientists is minimal/absent.

Thirdly, the connections of 'politics, policy and institutions' are analyzed. The policy makers and executors have extensive contact with financial support organizations and branch associations (NVP 2022). As described previously, consultations between NGOs and politicians are also present. The Dutch government stimulates collaboration between research institutes/universities, industry and governmental parties. This is stimulated by financing public research institutes and by promoting and enabling contact between academia and industry (*Publiek-privaat onderzoek* 2022).

Fourthly, the network of the support organizations is analyzed. The support organizations include network associations, branch associations, governmental funded investors and privately funded investors. The network associations and branch associations enhance connectivity between the group that they represent and other actors. Deltalinqs can be shown as example. This organisation enhances interactions with parties such as NGOs and the government. Other stakeholders can approach Deltalinqs to discuss several topics instead of having to reach out separately to over 700 companies at the Port (Deltalinqs 2022). This significantly smoothens stakeholder interaction.

The governmental funded investors have a close connection to private investors, as they always co-invest with this party. Privately funded investors have intensive contact between other investment parties. Nevertheless, these investors seem to have a minimal connection to the universities and NGOs (see interviews in Appendix D).

To summarize, network failures due to weak connections are present between three stakeholder groups, namely scientists, NGOs and private early-stage investors. From the interviewed NGO's perspective, especially the link between NGOs and scientists would be beneficial to improve. Since this NGO has an advising role in funding distribution and the energy transition at the Port, it seems beneficial for both parties to enhance collaboration. As stated in the interview, this NGO does have some connection to research institutes, but is willing to collaborate more extensively with the TU Delft.

When looking at the perspective of private VC, weak connections with NGOs and scientists are present. However, the private VCs interviewed, indicated a lack of skills to fully assess and understand the sustainability and technology from cleantech investment opportunities. Collaborating with NGOs and scientists could enhance this understanding resulting in a decreased uncertainty about these type of investments. The improvement of the ties between NGOs, scientists and private early-stage investors can result in fruitful learning cycles, creation of new ideas and a shared vision of future technology developments (Woolthuis et al. 2005) (Negro et al. 2012).

4.2.3 Infrastructures in the Technological Innovation System

The infrastructure shows the availability of finance for innovation. The focus is on financing in the form of venture capital, funds or subsidies (O'Sullivan 2005). The funds, subsidy and investment streams are shown in Figure 4.2. Their flow is depicted as arrows.

Funding flows from incumbent CO_2 producing firms to research groups are present. For example, the Royal Dutch Shell has a history of funding research groups at the TU Delft (Jongeneel 2019). Governmental subsidies for sustainable innovations are present for four phases; fundamental research, research & development, demonstration and up-scaling & market introduction (RVO 2022b). CCU can obtain subsidies in these four phases, except for the demonstration phase due to European legislation (see Appendix D). Subsidies are given towards research and education actors and suppliers at the Port of Rotterdam.

In the cleantech sector, VC is generally invested in the demonstration phase and the pre-commercial phase. Note, that subsidies for the demonstration phase of CCU are minimal due to European legislation. Therefore, it can be argued that the presence of VC in this phase is of additional importance. In the pre-commercial phase, PE investors join in as well. This actor also invests at the start of commercialization (Bürer and Wüstenhagen 2009). However, the boundaries between VC and PE are not very strict. As stated by the interviewed participant ESI.#1: *'We invest in several stages, from seed funding up until series E, or maybe even F. For seed funding to series B, we invest on our 'own'. For larger series, we invest via a fund.'*. This indicates that this company is involved in the full range of seed funding up to IPO. However, *how* they are involved differs.

Underinvestment in Cleantech and in the Wrong Stage

Overall, the activity of VC in the Netherlands has increased from an average of €250.000 in 2012 to 1.9 million in 2021 (PwC 2022). Especially the funding size in seed and later-stage venture has increased (PwC 2022). Also, the presence of governmental funded investors has had a positive impact on the overall funding that enterprises receive (Brander et al. 2015). In particular the mixture of governmental funded and privately funded capitalists influences the financing available to a company and its success (Brander et al. 2015). Between 2012 and 2021, the sectors 'Energy & Industry' and 'Chemical Products and Materials' both received a significant increase in VC. For 'Energy & Industry' the budget rose ten-fold and for 'Chemical Products and Materials' a doubling was present (PwC 2022). When looking at PE, such a trend was not present. Here both sectors had a one-year increase, but the other years showed no significant difference. Nonetheless, even with increasing funding sources, it should be noted that this does not necessarily result in more cleantech investments. Let alone investments in CCU. Furthermore, are these increased investment streams enough?

It can be stated that VC investments in the energy and chemical industry are in general underrepresented (van de Vrande et al. 2020). This is caused by the capital intensiveness of these industries (van de Vrande et al. 2020). Research conducted by van de Vrande et al. 2020 looked into a Flemish-Dutch collaboration that accelerates the transition to a clean process and manufacturing industry. The interviewed stakeholders of that research identified the access to funding as their largest issue. They state that the issue is not only the lack of funding, but also the stage and duration of it.

To conclude, financial infrastructure failure is present at the TIS for CCU technologies at the Port of Rotterdam. This failure is two-fold. Firstly, cleantech is in general a sector in which under-invested is present due to its capital intensiveness. However, a change might be present as the VC budgets and subsidy budgets in the energy and chemical sector are increasing. Action should be taken to ensure that cleantech also profits from this trend. Secondly, the stage and duration in which these fundings are available are not sufficient, as indicated by van de Vrande et al. 2020. It is found that sufficient support up to TRL 6 is present. Once up-scaling starts, long and capital intensive development cycles are present. Here lies a funding problem (van de Vrande et al. 2020). Furthermore, funding should be available for various components, not only for R&D. As example, financing marketing to gain credibility from incumbent firms is mentioned to be of importance as well (van de Vrande et al. 2020).

4.2.4 Hard & Soft Institutions in the Technological Innovation System

Formal and soft institutions are a key element in the TIS. They are seen as a defining and structuring element in the system (Negro et al. 2012). When looking at the VC decision making in cleantech, these institutions can play a significant role. For example, they can reduce the transaction costs and opportunity costs that VCs face (Cumming et al. 2016). Moreover, soft institutions can provide an increased incentive for the provision of sustainability (Cumming et al. 2016).

Hard Institutions

Hard institutions indicate formal institutional mechanisms (Woolthuis et al. 2005). One of the most important mechanisms of hard institutions related to innovation is protection via intellectual property rights (IPR) (Charles Edquist et al. 1997). IPR are often well defined for high-tech companies, but not for cleantech (Hegeman and Sørheim 2021). The reason behind this lays in the external benefits reached by cleantech (Hegeman and Sørheim 2021). Cleantech enhances sustainability, but it is difficult to capture the value it brings (Yan Yang, Holgaard, and Remmen 2012). The external benefits make value protection in the form of IPR difficult. The importance of IPR and technology protection are also mentioned in the interviews with the early-stage investors (Appendix D). As a result, a certain level of hard institutional failure is present as the current IPR framework does not protect the full value of cleantech, decreasing the likelihood for financial investments in this sector.

Next to the above mentioned failure, another aspect of hard institutional failure is identified. This is the low level of standardization methods for the assessment of CCU technologies (Zimmermann and Schomäcker 2017). The allocation of funding for cleantech should be based on a rational assessment, making it possible to compare technologies from different disciplines. A systematic method to find advantages and challenges of the technologies should be used (Zimmermann and Schomäcker 2017). Such methods could also help to identify new research goals (Zimmermann and Schomäcker 2017). As can be seen in the conducted interviews and the literature review in subsection 2.1.4, each stakeholder mentions different metrics and approaches. The mentioned metrics do have overlap or dependency on each other, but it illustrates the lack of a common framework.

Soft Institutions

Soft institutions are informal and show the norms and values present. It takes into account factors such as the culture present within a TIS, the willingness to share resources and the legitimacy of the new technology (Negro et al. 2012). As a note, legitimacy is not given, but rather formed through conscious actions by various actors (Bergek et al. 2008). The assessment of the culture present within the CCU is out of scope for this research. This holds also for the legitimacy of the CCU technologies, such as syngas formation and fermentation.

A summary of the found failures present in the TIS is shown in Table 4.1.

Table 4.1: Overview of the failures currently present at the TIS of CCU Technology at the Port of Rotterdam

Factors	Type of Failure	Present?
Actors	Absence	
	Insufficient Capabilities	X
Networks	Absence	
	Weak Connections	X
	Strong Connections	
Infrastructure	Lack of Funding	X
	Duration of Funding	X
Hard & Soft Institutions	IPR Protection	X
	Standardization methods	X

4.2.5 Shortcomings of the Technological Innovation System

It should be noted that the concept of TIS also holds two main shortcomings. Firstly, the framework mainly focuses on the role of institutions, thus looking at a macro level. However, as stated by C. Edquist 2001, innovation is both an individual and a collective act. The TIS minimizes the role of the individual (micro level), even though this is also a driving force for innovation (Hekkert et al. 2007).

Next to the focus on the macro level, a TIS is also centred on a specific (emerging) technology, such as CCU implementation at the Port of Rotterdam. As a result, it does not fully tackle the wider transformative change required, which can be described as 'transformation of the industrial cluster' (Weber and Rohracher 2012).

4.3 Influence and Interest of the Stakeholders

The influence and interest that these stakeholders have is shown in Figure 4.3. Note, the n-caproate production technology discussed in this report has a technology readiness level of 3, as discussed in subsection 1.2.1. Therefore, influence and interest of the stakeholders are defined and assessed in the context of the current

TRL. It is also important to keep in mind that, even though based on the interviews and literature research, an II-grid is eventually made from the researchers own perspective (see subsection 2.1.2).

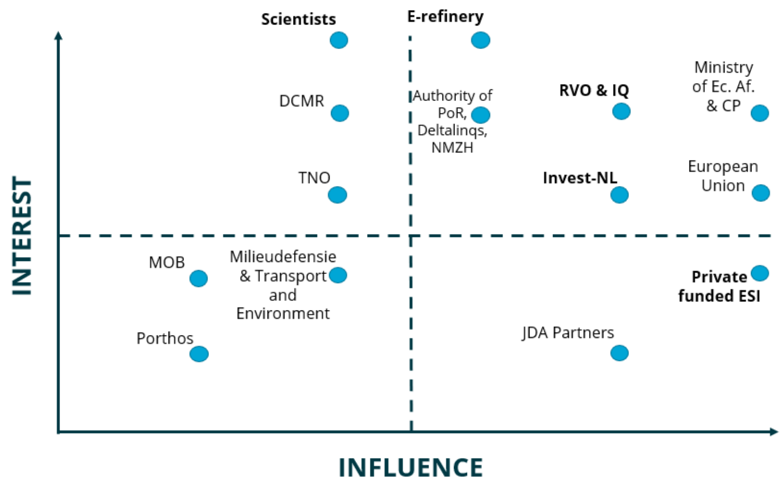

Figure 4.3: Current status of the influence and interest of stakeholders involved in developing CCU technologies at the Port of Rotterdam. The ranking indicates the influence and interest of a stakeholder in comparison to another stakeholder. Stakeholders shown in bold are interviewed. Policy makers are not interviewed as they are out of the scope of this research.

4.3.1 Stakeholders with a High Influence

As can be seen in Figure 4.3, the policy makers and early-stage investors have a high influence at this phase of the technology. At a TRL of 3-5, the funding for CCU technologies comes mostly from governmental parties, venture capital funds and private equity (Cumming et al. 2016). Bürer and Wüstenhagen 2009 underlines the high influence of VC and PE in the technology development. The JDA Partners are also classified as having a high influence, as they can steer the future valuation of the technology. As mentioned by Hargadon and Kenney 2011 and Vinig and De Haan 2002 (and confirmed by interviewed stakeholders), the exit strategy for investors is an important metric. Large incumbent firms, such as the JDA Partners, could increase their change on a profitable 'exit' and thus influence these stakeholders. They can do so by communicating their interests in a technology and provide it credibility (Steen and Weaver 2017). The same holds, for a lesser extend, for the Authority of the Port of Rotterdam, Deltalinqs and NMZH. The communication and attitude of the Port and Deltalinqs can impact other stakeholders as well. If these parties state that they would like to implement CCU, it leads to a certain credibility and less risky exit strategy. NMZH is regarded to have a similar influence, as they have an important advising function concerning the energy transition at the Port. Moreover, they are embedded in a strong network with different actors. Therefore, they are regarded to have a significant influence on other powerful parties.

The JDA partners have a high influence, but a low interest at the moment. This is because they can be viewed as 'locked-in' in a technological trajectory (Geels et al. 2016). Next to this, it is stated by Ortt and van der Duin 2008 that Shell develops radical innovations with partners and not in their in-house R&D. For Exxonmobil it is stated that their functional R&D program focuses on technologies that are scalable and provide the company a competitive advantage (Jacobs 2012). These finding are in line with what is described by Cumming et al. 2016. His research states that funding sources such as mergers & acquisitions start playing a role when the focus becomes on manufacturing and rolling-out of the technology (TRL 6-9).

4.3.2 Stakeholders with a High Interest

The parties with a high interest in the technology are mostly the researchers involved, governmental parties and regional NGOs. The researchers working on (one of) the technologies involved in the indirect route are ranked as having the highest interest. This ranking is based on the fact that their career is focused around these technologies. It fits the definition of 'interest' very well, since they want to give their attention to it, be involved with it and discover more about it (*Cambridge Dictionary* 2022).

The governmental parties have a high interest as well. DCMR Milieudienst Rijnmond is interested as they monitor regional environmental and safety regulations. They are involved in the industrial developments at the Port of Rotterdam as a regulating party. The other governmental parties with a high interest are the Ministry of Economic Affairs & Climate Policy and RVO. The Dutch government has set the goal of being energy neutral in 2050 (Ouden 2020). The guidelines and subsidy budgets to achieve this are set by the Ministry of Economic Affairs & Climate Policy. RVO is the executing party of the policy. Both parties are interested in CCU and which role it can play in the energy transition.

InnovationQuarter focuses on high-risk sustainable investments in the South-Holland region. They actively collaborate with universities and governmental parties to be involved with innovations at a very early TRL stage (see Appendix D). Moreover, they have to comply with the goals set by the Ministry, which indicates that their interest is partly formed by the governmental interest. Therefore, they are indicated to have a similar interest in CCU as RVO and the Ministry.

The Authority of the Port of Rotterdam is another industrial partner, strongly linked to the Dutch government. All the Port's shareholders are governmental actors (Port of Rotterdam 2022b). They state that they are focused on the valorizing of waste flows into secondary chemicals, to decrease their carbon footprint (Port of Rotterdam 2019). Their interest is therefore also ranked similar to that of other government (owned) parties.

The regional NGOs also are ranked as having a high interest. These NGOs focus on the impact of the Port of Rotterdam on the regional environment, but also acknowledge the its economic and logistic importance. NMZH collaborates with several stakeholders, including the Authority of the Port, to achieve its sustainable development. Their two main focus points are decarbonisation and the quality of the (regional) environment (Milieufederatie 2022). Deltalinqs is another regional NGO, representing the different industrial partners present at the Port. NMZH's interest on CCU is more from a sustainability perspective, while Deltalinqs looks at CCU from the presepctive to enhance innovation and the harbour's competitiveness (Deltalinqs 2022).

4.3.3 Expected Changes in Stakeholders' Interest and Influence over time

In general, interest and influence of stakeholders is subject to change over time. It is thus important to emphasize that their position on the II-grid is in constant motion (Varvasovszky and Brugha 2000). Parties that are expected to increase their influence and interest include, but are not necessarily limited to, the NGOs, the early-stage investors, Porthos and the JDA Partners. These trends are represented in Figure 4.4.

Rise in Influence and Interest for NGOs

The influence and interest of 'Milieudefensie', 'Mobilization for the Environment' (MOB) and 'Transport & Environment' is expected to rise when the technology reaches higher TRLs. This is expected, since these NGOs do have expressed an interest in the Porthos project and/or the CO_2 emissions of the JDA Partners earlier on. Each of these parties is elaborated upon below.
In 2019, Milieudefensie has successfully sued JDA Parter Shell for its CO_2 emissions. As a result, Shell has the juridical obligation to reduce its CO_2 emissions (Milieudefensie 2022b). Milieudefensie has also investigated the climate action plans of, among others, Shell and Exxonmobil (Mooldijk et al. 2022) (FD 2022a).

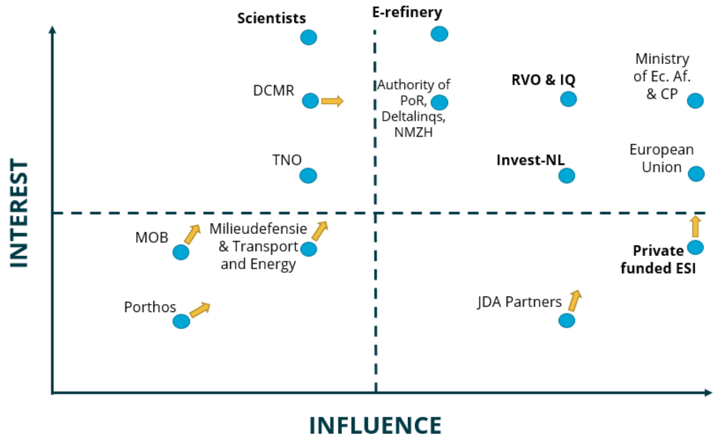

Figure 4.4: Expected motions in the influence-interest grid of the stakeholders involved in developing CCU technologies at the Port of Rotterdam. The ranking indicates the influence and interest of a stakeholder in comparison to another stakeholder. An expected motion is depicted by a yellow arrow.

Their climate action plans are judged to be insufficient to mitigate and are even accelerating climate change. Milieudefensie advocates to stop all governmental funding for sustainability related projects of these companies, including Porthos (Milieudefensie 2022a). During a conversation with Milieudefensie, they expressed that their interest is not in a low TRL technology. Nevertheless, they would become interested when it comes closer to application.

Another national NGO, MOB, has also expressed critique on the subsidy policy of the Dutch government. MOB has started a legal case against the Ministry of Economic Affairs & Climate Policy because of their approval for the building of the Porthos infrastructure. Furthermore, MOB has criticised the €2 billion of subsidies that Porthos has received from the Dutch government, asking out loud why the polluting parties are being paid (FD 2022b) (van Heel 2022). This party is led by Johan Vollenbroek. He is a famous and awarded figure in the Dutch nitrogen discussion (Hakkenes 2019). It is highly expected that his interest in a CCU technology at the Port of Rotterdam will increase once implementation comes closer. Furthermore, as has been shown in the nitrogen discussion, he has significant influence if he is against a project.

Thirdly, the European NGO Transport & Environment is an NGO focusing on the sustainability of different modes of transportation and the energy sector. It has ranked the Port of Rotterdam as the most polluting port in Europe (Transport&Environment 2022). However, it also ranks the Netherlands third of the European countries in the speed at which sustainability in the maritime sector is implemented. Furthermore it states the high influence that the Netherlands can have on other European countries (Mackor 2022). Therefore, it is expected that the interest of this NGO will increase when implementation of a CCU technology in the Port of Rotterdam becomes a reality.

Rise in Influence for Governmental Stakeholders

When the technology comes closer to implementation, the influence of DCMR becomes higher. As stated previously, DCMR has the power to grant permits for industrial plants at the Rijnmond region. Moreover, they monitor the safety of hazardous chemical plants. If the (pilot) plant does not comply with their regulations, it will not be built.

Rise in Interest for Industry Stakeholders

The industry stakeholders include the private early-stage investors, the JDA partners and Porthos. Private equity and venture capital are often funding at a TRL of 3-5 (Cumming et al. 2016). Since this technology is still at TRL 3, it is expected that the influence and interest of the PE and VC will increase when the technology develops further. The emergence of the cleantech sector is market-driven and provides a tangible expression of the trend towards a 'green economy' (Georgeson et al. 2014). The interviewed investors all have a 10 years+ investment horizon for these type of investments. This is longer than the time horizon reserved for 'conventional' investments. This corresponds to the finding reported by Mathews et al. 2010, that long-term financing is key for these type of projects. The longer timeframe can be seen as in indication that these investors see the long-term potential of cleantech projects. Once the technology develops further, their interest will probably also increase.

It is expected that the JDA partners and Porthos will become more interested when the technology is in the scale-up phase. The first reason for this, is that then a partnership might be set, similar to the JDA partners and the Porthos project. The JDA Partners can collaborate with other firms to reduce their CO_2 emissions, which Air Liquide has already done (Laperche and Picard 2013). A second reason why the JDA Partner firms become more interested at a higher TRL is the following. When the focus becomes on manufacturing and rolling-out the technology (TRL 6-9), funding sources such as a mergers & acquisitions start playing a role (Cumming et al. 2016). The acquisition of sustainable energy start-ups by an incumbent non-sustainable firm can have many positive effects. Some of these are; reducing environmental costs, absorbing practical technologies and announcing the firm's green innovation (Kwon et al. 2018).

At a lower TRL, these companies do have some interest and involvement in the CCU technology, but their interest is more focused on partnerships and consortia. For example, Shell has (financially) contributed to the e-refinery consortium (Herder 2019). The internal R&D programs are mostly based on incremental innovations and technologies ready for scale-up (Ortt and van der Duin 2008) (Jacobs 2012).

4.4 Important indicators for the assessment of a CCU Technology from Different Stakeholders' Perspectives

4.4.1 Participant Selection

The participants of the interviews are selected from the II-grid shown in Figure 4.3. Approached scientists are researchers working on CCU, syngas formation or syngas fermentation. Some of these researchers are part of the e-refinery consortium. Approached early-stage investors are either governmental funded or privately funded. Governmental funded investments include both subsidies as well as investments. Privately funded investments can be family offices, venture capital or private equity. For a privately funded ESI to be invited for the interview, two additional requirements had to be met. Firstly, the company had to had invested in at least one cleantech investment. Secondly, a potential time horizon of over 10 years had to be present. The first requirement is set to ensure that the party has experience in conducting cleantech investments and is willing to do so. The second requirement is set based on the 'typical' cycle of VC investments. This cycle consists of approximately 5-10 years, requiring an exit around year 10 (Gaddy et al. 2017). However, cleantech innovation, especially in the chemical industry, is subject to longer time horizons (Giorgis et al. 2022).

Next to the ESIs and scientists, an NGO is interviewed as well. Several factors attributed to involving them in this research. As can be seen in the II-grid (Figure 4.3), this party has a high interest and influence in respect to the energy transition at the Port of Rotterdam. They also play a significant network role between different parties involved with this transition and have an advisory role towards subsidy for research into novel technologies. On top of that, it is expected that the interest and influence of other NGOs will rise once the technology develops further (see Figure 4.4). In general, NGOs can contribute signficantly to eco-innovation. They can play important roles as external expert knowledge provides, mediators and supporters (Yan Yang and Holgaard 2012). On the other hand, if a degree of discontent develops, action and mobilization can occur to influence the focal party (Rowley and Moldoveanu 2003).

An overview of the (semi-anonymous) interviewees can be found in Appendix C. For early-stage investors and NGOs the job function of the participant is listed. Furthermore, ranges of the overall budget available for cleantech and their average ticket size is given. For scientists their career moment is stated instead of their job function. This is done to ensure their privacy.

Note, the impact of policy making on cleantech research and investments should not be neglected (Bjornali and Ellingsen 2014) (Georgeson et al. 2014) (Bürer and Wüstenhagen 2009) (Cumming et al. 2016) (interviewed investors). However, the role of these actors are out of scope in this research.

4.4.2 Assessment from a Scientists' Perspective

The summaries of the interviewed scientists can be found in Appendix D. Based on these interviews, the parameters indicated as important by the participants are retrieved. An overview of these parameters can be found in Table 4.2.

The interviewed scientists emphasized the use of technical and environmental parameters. Most interviewed participants have a strong intrinsic motivation to contribute to sustainability. This intrinsic motivation can be seen in their extensive view on a technology's environmental assessment. All participants mentioned the energy usage and the energy source of a technology as important to assess. All but one also mentioned the carbon footprint, or its potential to reduce the carbon footprint, compared to the current production route. Participant *SCI #2* did not explicitly mention this, but does emphasize that a fully circular system should be designed. This implies no netto CO_2 emissions. Other factors that are important are the use of hazardous chemicals, scarce materials and water.

Note that some participants focus on using a renewable energy source for the process from an environmental perspective. Others already assume that all future energy sources will be fully sustainable. Taking this as starting point, they want to limit energy usage from an economic perspective, or to limit the land use required for this renewable energy generation.

Looking at the technical parameters, especially the substrate (CO_2) conversion efficiency and the production rate are mentioned to be important. Next to this, four of the eight interviewed scientists explicitly mentioned the downstream processing and its effect on the overall process. This parameter is mentioned as it is, according to the interviewees, one of the biggest bottlenecks hampering profitability of both the direct and indirect route. This is partly caused by the low n-caproate concentration in the product stream and thus partly related to the production rate and substrate conversion efficiency.

The interviewed scientists also utilize economic parameters to benchmark a process. All interviewed participants acknowledged the importance to reach a profitable business case. Parameters to assess the potential for a process' profitability are its minimum product selling price, the CAPEX & OPEX and the product market's characteristics.

Aspects that are minimally focused on by the interviewed researcher are the social impact of the technology and the influence of strategical matters. Solely participant *SCI#5* mentioned local employment as important to consider. For strategical issues, participant *SCI #8* speaks about the difficulty of forming industrial partnerships between sectors that are not collaborating at the moment. Other social or strategical factors are not discussed.

Table 4.2: Overview of the parameters for the assessment of cleantech/CCU based on the conducted interviews. The parameters are retrieved from the interviewed scientists. When a parameter is mentioned to be important it is shown with a '++' (very important) or '+' (important). When a parameter is not mentioned, the box remains blank.

Category	Parameter	SCI#1	SCI#2	SCI#3	SCI#4	SCI#5	SCI#6	SCI#7	SCI#8
ORGANISATIONAL / STRATEGICAL	Network / Partnerships								++
TECHNICAL	TRL		++						
	Product Diversification / Application		+	+			+		++
	Scalability	+	++						
	Production Rate / Selectivity	++		++	++		++		
	Substrate Conversion Efficiency	++		++	++	++	++		++
	Mass Transfer							++	
	Type of microorganism	+						++	
	Separation Process	++			+		+		+
ECONOMIC	IRR / NPV / DCF								
	Min Prod. Selling Price	+				++			
	CAPEX & OPEX		++		++			+	
	Positive Cash Flow								
	Market characteristics / Competitive Advantage		++			++	++		++
ENVIRONMENTAL / SOCIAL	Carbon Footprint / Reduction Potential	+		++	++	++	++	++	++
	Energy usage / Source	++	+	++	++	++	+	++	+
	Use of Hazardous Chemicals/reactions	+					+		
	Use of scarce materials	+						+	+
	(Local) Employment					+			
	Land use		+						
	Water Usage	++			++				

4.4.3 Assessment from an Early-Stage Investors' Perspective

The parameters indicated as important by early-stage investors (ESIs) are shown in Table 4.2. It is important to highlight the difference between early-stage investors, the governmental party (*GOV #1*) and the interviewed NGO (*NGO #1*).

As shown in Table 4.4.3. the main focus of both governmental as well as private early-stage investors is on organisational/strategical aspects. One of the first parameters that is mentioned by each of these parties is the character of the team involved in the innovation, which is in line with the results found by Bachher and Guild 1996. This includes not only their expertise and experience, but also more subjective factors such as a 'feeling of trust' and 'getting along with the people' (interviewee *ESI #1 and ESI #2*). Especially at a lower TRL, the (management) team becomes more important. As stated by *ESI #1*: *'in a very early phase, the people behind it give the numbers credibility'*.

Next to this, the track record of the company and/or the entrepreneur also play an important role for private ESIs. They use this track record to predict the changes of success. A company's track record gives information about the likeliness that they will deliver on their promises.

Thirdly, all interviewed ESIs showed interest in who the other financing parties are and if the investment opportunity came through via their network. For the governmental funded parties, this is an important metric as they can only finance up to 50% of an investment. They are dependent on joining private investors for both the other 50% and the terms of the investment. For the private ESIs, all showed to be (or open to be) influenced by their network for investment decisions (see the interviews with *ESI #2* and *ESI #3*).

The metric 'network' has another dimension as well. It does not only apply to a network of other early-stage investors. It is also between producers, suppliers and customers. The majority of the interviewed participants (*GOV.INV #1*, *GOV.INV #2*, *ESI #2*) explicitly stated that contracts with customers are a big advantage. It limits the risks as you already know the price and amount of product that you can sell.

A fourth organisational/strategical factor that plays a role is the presence of intellectual property rights. As indicated by *GOV.INV #1* and *GOV.INV #2*, this is one of the metrics to determine the risk of the investment. *ESI #2* mentions that having IP(R) can be seen as a competitive advantage. The importance and difficulty of obtaining IPRs in cleantech are discussed in section 4.2.

In terms of technical parameters, most investors are not looking closely into these, except for the TRL. The TRL is used as an indication for the technology's risk. Participant *GOV.INV #2* states that: *'The potential of a technology should be bigger at an earlier TRL in order to get the same valuation as other investments.'*.

The economic parameters differ per investor. Some prefer using IRR, some the minimum product selling price. There is not one overall universally used metric. The main economic parameter that almost all use are to look into the market characteristics of the product produced. They are interested to see if there is a market for the product and how the market is developing. The importance of market size and growth for VCs is also mentioned by Hargadon and Kenney 2011 and Bachher and Guild 1996.

In terms of environmental parameters, the main focus of the investors is on the carbon footprint of a business case. Participant *ESI #1* looks additionally into nitrogen emissions (if applicable) and the use of hazardous chemicals. Also the energy usage is important, but merely from the perspective of the accompanying CO_2 emissions. *ESI #3* mentions that each investment opportunity has to pass their ESG check. For *ESI #2* cleantech is an interesting investment sector merely from an economic point of view. (S)he expects cleantech to become economically viable and indicates that it has a *'strong tailwind behind it'*. This is mostly driven by higher oil prices and governmental support.

A difference can be seen between governmental funded investors and private investors. The former shows, in addition to the CO_2 footprint, interest in the impact on the local environment. This metric describes factors such as air and noise pollution. Furthermore the influence of the investment on the national employment is also an important metric. Their interest in these metrics is driven by the KPIs set by the Dutch National Government.

Assessment from a governmental and NGO's perspective

As expected the governmental party and the NGO interviewed are not concerned about organizational/strategical parameters. Their main focus is on the environmental. As can be seen in Table 4.4.3, their main interest for the assessment of a novel technology is in the CO_2 reduction that will be achieved and the energy usage. Furthermore, a focus on the local environment or employment is present. The interviewed NGO also values the nitrogen emissions and the use of hazardous/polluting chemicals. This includes for example the presence of PFAS.

Both parties mention the potential for product diversification or the specific *n*-caproate application as important. In the case of these parties, this metric is looked at from a sustainability point of view. They emphasize the current debate about the 'true' sustainability of CCU. Both parties highlight the importance of keeping the captured CO_2 out of the atmosphere for a long time-period. Thus, producing bio-fuels out of (fossil-fuel retrieved) captured CO_2 might not be sustainable. The application of the product has a high impact on the sustainability assessment. As mentioned by *GOV #1*: *'A problem with CCU is that no clear CO_2 reduction 'amount' has been set for it'*. It is not sure if CCU is eventually needed to reach a circular economy.

Table 4.3: Overview of the parameters for the assessment of cleantech/CCU based on the conducted interviews. The parameters are retrieved from the interviewed early-stage investors, governmental party and NGO. When a parameter is mentioned to be important it is shown with a '++' (very important) or '+' (important). When a parameter is not mentioned, the box remains blank.

Category	Parameter	ESI#1	ESI#2	ESI#3	GOV.INV#1	GOV.INV#2	GOV #1	NGO#1
ORGANISATIONAL / STRATEGICAL	Character of Team involved	++	++	++	++	++		
	Track Record Company	++	+	++				
	Other financing parties / Network	+	+	+	++	++		
	IPR		+		++	++		
	Exit Strategy	+						
TECHNICAL	TRL	+			++	+	++	
	Product Diversification / Application						+	+
	Scalability				++			
ECONOMIC	IRR / NPV / DCF	+	++					
	Min Prod. Selling Price	++						
	CAPEX & OPEX	+						
	Positive Cashflow			++				
	Market characteristics / Competitive Advantage	++	++		++	++		
ENVIRONMENTAL / SOCIAL	ESG			+	++			
	Carbon Footprint \ Reduction Potential	++		+	++	++	++	++
	Energy usage	+		+			++	++
	Nitrogen Emissions	+						++
	Use of Hazardous Chemicals	+			+	+		++
	Use of scarce materials					+		
	Local Environment				+	+		+
	(Local) Employment				+	+	++	

4.4.4 Differences between Stakeholders' Assessment

The type of parameters mentioned by the scientists and ESIs are compared. An analysis is made of the average amount and type of parameters find important by either a scientists or an ESI. The result is shown in Figure 4.5. Here, it can be clearly seen that scientists focus more on technical parameters and ESIs on strategic parameters.

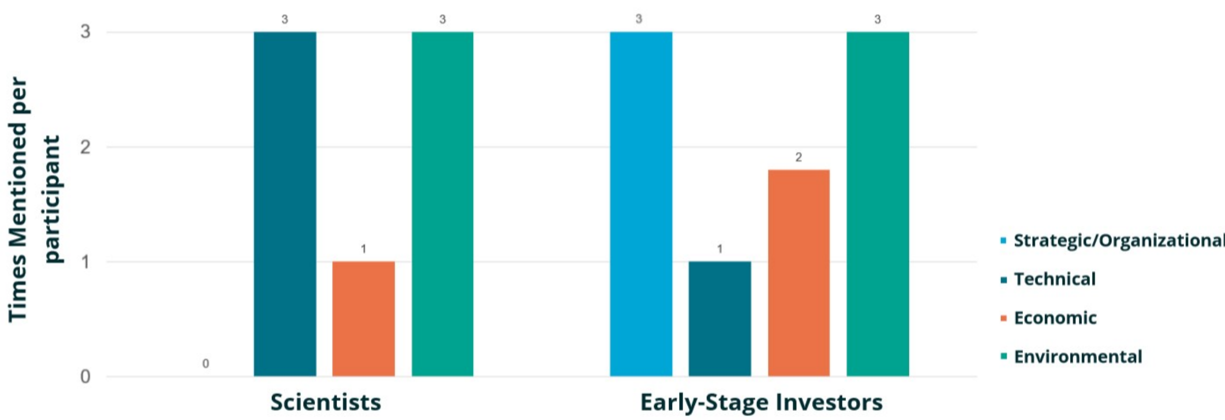

Figure 4.5: Overview of the category of metrics mentioned by either the scientists or ESIs. On average, scientists mention 0 strategic parameters, 3 technical, 1 economic and 3 environmental. ESIs mention 3 strategic, 1 technical, 2 economic and 3 environmental parameters.

When comparing the metrics mentioned by the different stakeholders four main differences can be identified. The differences are based on the interviews conducted and Table 4.2, Table 4.3 and Figure 4.5 that follow from this data.

Firstly, the influence of organisational/strategical factors on investment decisions is often overlooked by scientists. Secondly, scientists use a more extensive technical framework to assess a technology's performance compared to ESIs. Thirdly, all parties value sustainability, but its assessment of ESIs is mostly limited to CO_2 emissions. Lastly, the interviewed scientists and privately funded ESIs have a minimal focus on social factors. Solely one interviewed scientist (*SCI #5*) mentions this aspect. The governmental funded investors, governmental parties and the interviewed NGO do take some of these factors into account.

Organisational and Strategical Factors

Firstly, the investment parties value organisational and strategical parameters highly. Especially the character and track record of the (management) team and the company are important. The importance of the entrepreneur is also described by Bachher and Guild 1996 and Vinig and De Haan 2002. The people in the business give credibility to the forecasts they present. This becomes even more important at a lower TRL, as no clear track record of the company is present.

Moreover, if a business case reaches the investors via their network, it influences the view of stakeholders on the investment opportunity. It even makes them consider cases that they would otherwise not look into. This phenomenon is in line with findings reported by Vinig and De Haan 2002 and Marcus et al. 2013. According to them, VCs view non-network originated business plans as lower quality and thus they get less attention. The so-called entry point of a business case is of importance as not all business plans are equally intensive analyzed. It is simply too labor intensive to analyze them all (Vinig and De Haan 2002) (Marcus et al. 2013). This can already be partly seen by the statements of *ESI #1*. (S)he works at a relatively small firm and indicates that not enough FTE is available for quantitative sustainability assessments. For governmental investors their network is also important for another reason. These investors are dependent on these other financing parties for at least 50% of the total investment. These private parties are also able to set the investment terms, which the governmental investors will likely follow.

Even though these factors clearly have a significant importance for the investing parties, none of these metrics are mentioned by the other stakeholders. Solely *SCI #8* indicates that collaboration between different firms should be set up. However, this is a different type of partnerships than those between financing networks.

Technical Parameters

A second finding of this research is the contrast between the variety of technical parameters mentioned by scientists compared to the scarce metrics used by the other parties. The scientists mention process specific technical metrics such as the substrate conversion efficiency. The other stakeholders are merely interested in the TRL level in order to assess the risk that the technology brings.

As stated by *GOV.INV #2*, most investors view the technology as a black-box. The findings reported here are in line with this interviewee's observation. Most investors mainly focus on the overall production cost and the product's price. A risk of approaching a novel technology this way, is that bottlenecks inherent to the process are overlooked by investors. Interviewed scientists *SCI #1* mentions that, if he was an investor, he would want to know if 'fundamental bottlenecks' in the technology are present. As an example, (s)he mentions the characteristics of the microorganisms. This is an example of the type of factors that are not mentioned by neither the ESIs, governmental party or NGO. This black-box viewing can result in a completely miscalculated risk estimate of the technology (see *GOV.INV #2*'s interview).

Nevertheless, it should not be concluded from the above mentioned results that ESIs, governmental parties and NGOs do not care about technology specific parameters. The difference in technical parameters mentioned could also result from the difference in technology understanding between the scientists and other stakeholders. Some stakeholders might work with a black-box model, but for example *ESI #2* states that (s)he requires time to get acquainted with the technology they are investing in. This insinuates the wish to deepen the knowledge about it, before a subsequent larger investment is made.

Another interesting finding related to the technological assessment is the following. The majority of the interviewed scientists mention their focus on reaching high substrate conversions and production rates. Contrary, private ESIs have explained that their focus is not per se on efficiency, but more on the costs to reach this efficiency.

Environmental Assessments

From the results shown in Table 4.2 and Table 4.3, it can be concluded that (almost) all participants value environmental sustainability. Nevertheless, the environmental assessment from a scientists' perspective entails a broader view. The carbon footprint, energy, water and scarce material' usage are mentioned. For ESIs, the focus is mainly on CO_2 emissions. Important to note here, is that CO_2 footprint could entail energy usage. As mentioned by *ESI #1*, CO_2 usage includes the energy usage. These two parameters are viewed separately by scientists, as they generally assume a sustainable energy source.

The early-stage investors and NGO show their interest in which (hazardous) chemicals are used. On top of this, some of them state that the nitrogen emissions accompanying the implementation of the technology play an important role as well. Both interviewees (*ESI #1* and *NGO #1*), state that this parameter is quite 'new' and caused by the current NO_x debate within the Netherlands.

Social Parameters

Lastly, the governmental funded investors, the governmental party and the NGO interviewed, mention social parameters to be of importance. These parameters are the impact of the innovation on local employment and the local environment. The importance of the local employment is solely mentioned by one scientist. The private investment parties and the other scientists do not mention this parameter or a parameter that is related to this topic.

4.4.5 Additional Parameters for the Assessment of the Indirect Route

Based on the metrics mentioned by the interviewees, the framework for the techno-economic and environmental assessment can be extended. The additional metrics are selected based on the summation of '+' in Table 4.2 and Table 4.3. The metrics that are added to the performance assessment are:

- Product Selectivity (8)
- Technology Readiness Level (8)
- Competitive Advantage within the current market (8)

Next to these metrics, the organisational/strategic factors are very important as well. Nevertheless, due to the current development phase of the technology, these factors are not yet analyzed. It would require mostly assumptions, which is judged to lead to too much speculation. Nevertheless, these factors should be taken into account for further TRL phases.

4.4.6 View of Stakeholders' on each others Perspective

The following section focuses mostly on the stakeholder group 'scientists' and 'early-stage investors'. The governmental party *GOV. #1* and the NGO *NGO #1* are not considered, as a sample size of 1 is considered not robust enough to draw conclusions from.

The motivation of each stakeholder group is mentioned. Furthermore, the view of scientists on early-stage investors' perspective on cleantech and vice versa is discussed.

Stakeholders Motivation

The conducted interviews with the scientists show a clear motivation to mitigate climate change. All participants stated their focus on contributing to a (bio-based) sustainable society. This drive is expressed by the majority of the scientists during their personal introduction at the start of the interview. A few do not state it explicitly, but do emphasize environmental parameters as (the most) important for the assessment of the technology. A second core driver of the scientists is their interest in conducting research. They state that they like this activity, even if they did not expect this at first. The intertwining of both factors resulted in their decision to have the job they have at the moment.

The interviewed early-stage investors are driven by accelerating (sustainable) innovation and implementing these innovations. For the governmental funded investors this motivation is clearly linked to reaching a more sustainable economy. The private ESIs do not have this connection to sustainability very clearly. The motivation for the private ESIs is to look for portfolio diversification with technology start-ups. This can be due to a personal interest in these type of innovations or because they feel like cleantech has a strong tailwind behind it.

Different Stakeholders' Perspective on each others View

In general the participants highlighted that they do not have much contact with the other stakeholder group. They find it difficult to assess what the other party values.

From the Scientists' Perspective
Nevertheless, the scientists mention the following two points the most when asked about ESIs technology

assessment parameters. Firstly, the scientists state the importance of economic returns to the ESIs. These can be quantified by looking at the internal rate of return, payback time, net present value et cetera. It is stated that these economic parameters mainly influence an investors decision making. Secondly, they state that ESIs value sustainability, but mostly the story-line around it and not its quantitative assessment. Some also state that the interest from ESIs into sustainability is mainly from an economic point of view.

When comparing these two prejudices to the parameters that ESIs mentioned, two interesting conclusions can be drawn. Firstly, the impact of organisational and strategic factors on ESIs decision making is overlooked by the interviewed scientists. Secondly, the majority of the interviewed investors do value quantitative assessments of sustainability parameters. However, they do not have the resources or technical background to perform such an elaborate analysis. Potentially, the same holds true for technical parameters. You cannot name extensive parameters if you do not understand the technology on that level of detail.

From the ESI's Perspective

The ESIs interviewed mention that, from their point of view, scientists might be focusing too much on discovering novelties. They might not have the implementation of the researched technology enough in mind. As stated by *ESI #2*: *'What is the point of developing something mind-blowing if you cannot roll it out to the general public?'*. Interviewee *ESI #1* also states that scientists might focus too much on reaching high conversions, neglecting the costs that accompany these high conversions. In general, differences between experimental conditions and 'real life' situation result in certain risks that are not accounted for by scientists.

When looking at the parameters mentioned by scientists, an awareness of the importance of economic profitability is present. The interviewed researchers do show a focus on implementing sustainable technologies in society. Nonetheless, one of the most mentioned technical parameters by scientists' is the substrate conversion efficiency, something that investors care less about. From an investor's point of view, there is a difference between optimizing a business case and optimizing a technology. The latter impacts the former, but is not the same. Scientists may be less aware of this difference.

Next to this, all interviewed investors value the risk-assessment of the technology highly. In their opinion, scientists might not consider the risks that the technology brings enough. When analyzing the metrics which scientist mention, they do evaluate the risk of a technology. However, they valuate it mostly from a technical perspective. To illustrate, they consider the robustness of the microorganism or scale impacts on the mass transfer. For ESIs, risk has a different meaning. Risks are valuated by factors such as the risk of competitors copying the technology or the structure of the product's market. It can be argued that the risk inherent to the technology is summarized into the metric 'TRL'. For both parties it is valuable to be aware of each others risk assessment and perception, since it plays a large role in the assessment of a novel technology.

The main findings are schematically summarized in Figure 4.6.

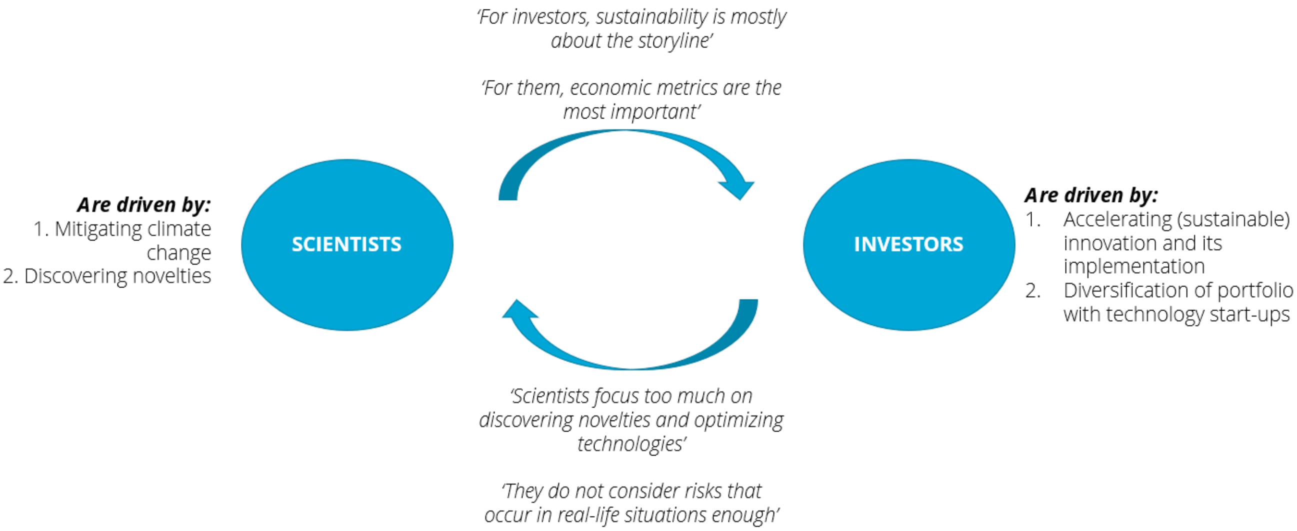

Figure 4.6: Schematic overview of the view of the stakeholders on each others perspective. It shows the motivation of both scientists and early-stage investors to work in their sector. Furthermore their view on the other stakeholders' perspective is shown in parentheses.

4.4.7 Relevance of the Stakeholder Interviews

The conducted interviews have value for both the current TRL and for more mature phases. From the interviews multiple metrics additional to those from the literature research were found to be of importance. Of these metrics, three are already significant to assess at a TRL of 3 (product selectivity, TRL and competitive advantage). These are therefore included in the performance assessment conducted in this research.

On top of these three, additional (mostly strategic) parameters are mentioned. These parameters are not necessarily relevant at the current TRL. However, they do become increasingly important when the technology matures. These include topics such as the potential of product diversification, IPR and the presence of buyers contracts (see Appendix D, Table 4.2 and Table 4.3). Overall most parameters can be related to a way of measuring 'risk'. From ESIs perspective two questions are important: what is the gain and what is the risk? In general, scientists might overlook the importance of the risk, which transcends risks linked to the technology. Being aware of these aspects in advance can positively influence the decisions that have to be made at higher TRLs.

The following advise is given towards ESIs and scientists.

Early-stage Investors

- Invest time and resources to understand the technology

  Even though resources are limited, it is advised to shift some of the focus towards understanding the technology on a more detailed level. This can be done by keeping in touch with a technology's development over a certain time period, before investments are required. This approach is taken by *GOV. INV#2* and is stated as having a positive effect on their decision making.

Scientists

- Consider the strategical perspective

Strategical parameters are mostly overlooked by scientists. Even though these parameters might not be extremely relevant at a low TRL, they can still change decisions. Before a decision is made on which product to target or which technology to use, one is advised to analyze strategical parameters. Look into the current market characteristics, potential buyers, potential partnerships, IPR, etc.

- Clear Communication about (technological) risks

  In the interviews conducted, the ESIs emphasize the importance of being able to assess an innovation's risk. Of all aspects of risk, they find it most difficult to assess the technology's risk due to a lack of resources. As a result, the technology is often looked at as a 'black-box' and technology-intensive investments are underfunded (Gaddy et al. 2017) (Appendix D). Here, scientists can play a role as they have a better understanding of risks that accompany a (clean) technology. It is advised to be aware of its importance and the difficulty that some ESIs face for its assessment. clearly communicating about the (technology's) risk is thus advised.

Next to the above mentioned topics, the interviews conducted led to another insight. As stated by the governmental party *GOV. #1*, the sustainability of CCU is debated. The interviewed NGO also expressed its concerns about its true environmental sustainability. The time period at which CO_2 remains fixed when using the indirect route might be relatively short. This debate shows the in-consensus on the sustainability assessment and the importance of considering the use of the end-product.

Impact of the Interviews on the Design of the Indirect Route

This section discusses if and when interviewing stakeholders to retrieve assessment metrics is beneficial. This paragraph uses the impact it had on my research and is thus drawn from my own experience. Conducting the interviews led to the general advise given in subsection 4.4.7. When looking specifically at the design of the indirect route, it altered my research in three ways. Firstly, it made me minimize the risks in the route. This can be seen by considering the risks of the electrolyzers in the Pugh matrix. Nonetheless, especially at a low TRL, a certain degree of risk remains present. Secondly, based on the results from the interviews I choose to assess the competitive advantage and product selectivity of both routes. Thirdly, the interviews with the ESIs and NGO resulted in new collaboration opportunities. Several parties expressed their interest to remain involved in the research and to help developing the indirect route. This can be seen as a start of stakeholder engagement (Luyet et al. 2012). Engaging the stakeholder from an early stage is advised, as it can lead to a better understanding of the project's issues and more trust in the final design. However, it is also a time-consuming process (Luyet et al. 2012).

To conclude, interviewing stakeholders has several advantages, but is also time-consuming (Luyet et al. 2012). A trade-off should be made, which is specific to each researcher. Nonetheless, the ESI's, governmental and NGO's parameters shown in this research can be generalized for the assessment of other cleantech routes at the Port of Rotterdam and the Netherlands in general. The scientists perspective is specific to the (in)direct route. When cleantech at the Port has to be assessed, the framework presented in this research can thus be used.

However, due to the heterogeneity of the stakeholders, the results in this study cannot be fully generalized to other TIS frameworks (Clarke et al. 2019) (Bocken 2015). This holds especially when the geographical location switches. Research taking place outside of the TIS is advised to identify which stakeholders are relevant and to assess their perspective. An approach as described in this report can be followed. If overlap between the stakeholders in this research is present, the metrics shown here can be used.

4.5 Mass and Energy Balances of the Indirect Route

This section shows the mass and energy balances of the indirect route. Both balances should meet the principle of mass and energy conservation. According to this principle, the total mass and energy in a closed system is always conserved (Beck 2020). Due to the scope of this research, the boundaries of the closed system are set at the syngas formation, fermentations and downstream processing. Obtained yields and conversions should match experimental results (Roh et al. 2020). A detailed overview of the Aspen flowsheets complementing the shown mass and energy balances can be found in Appendix J.

4.5.1 Mass Balances

The mass balances show the total in- and outflow of mass in the system. An overview of the mass balances is shown in Figure 4.7. The in- and outflows for the different technology blocks of the indirect route are given. A detailed overview of the mass flows and their compositions can be found in Appendix K.

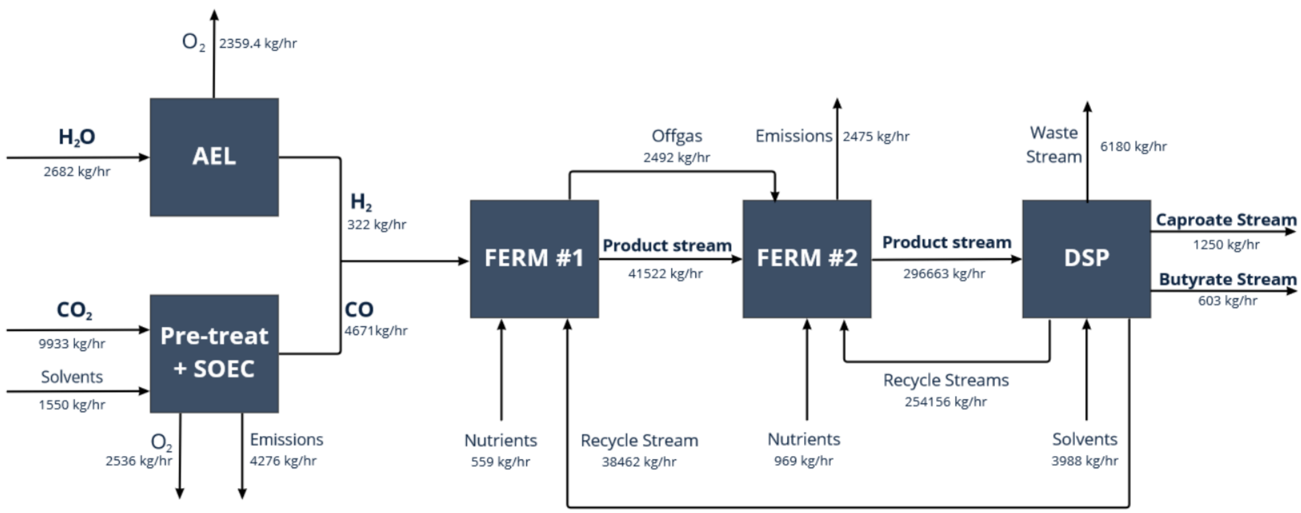

Figure 4.7: Mass balances of the indirect route.

Alkaline Electrolyzer

The water feedstream is mixed with 45 wt% potassium hydroxide. In total a mixture of 2928 kg/hr of H_2O and 1577 kg/hr KOH enters the AEL. This is in line with the 35 wt% KOH as described by Sanchez et al. 2020. Of this stream 90.5% of the water is converted into H_2 and O_2.

Oxygen and hydrogen are 100% separated at the outlet of the AEL (EL-SP1) (Sanchez et al. 2020). The remaining electrolyte mixture of KOH and H_2O is evenly distributed between these outgoing streams. This is followed by a gas-liquid separation of either electrolyte and oxygen and electrolyte and hydrogen (EL-D1 and EL-D3).

For the oxygen stream, the next step is passing a water trap (EL-D4). This trap eliminates the maximum amount of condensate water (Sanchez et al. 2020). After the water trap, the gas and liquid phase are separated by a flash column (EL-D4). A similar approach is used for the separation of H_2 and the liquid phase.

An additional stream of H_2O (1697 kg/hr) is added to recover the original electrolyte composition of 45 wt%. As a result, all electrolyte can be recycled. It is assumed that no net electrolyte inflow or outflow is required

(Sanchez et al. 2020). Water recovered from the flash drums and electrolyte are recycled back to the AEL. The produced hydrogen stream contains 25.56 kg H_2O per hour and the produced oxygen 6.4 kg H_2O per hour. This results in a total water usage of $(0.905 \times 2928) + 25.56 + 6.4 = 2681.8$ kg/hr, which corresponds to the inlet shown in Figure 4.7.

Solid Oxide Electrolyzer

This block contains both the pre-treatment and the SOEC. A total flow of 9933 kg/hr of the Porthos stream enters the system. For the pre-treatment a total of 1550 kg/hr of solvents are added. A stream of 0.23 kg/hr of air is used to oxidize H_2S into SO_2 (EC-R1). After this step 1550 kg/hr of 7.5 wt% Na_2SO_3 solvent is added to remove the SO_2 (PT-T1) (B. Sun et al. 2019). A gas to liquid ratio of 155 is found to be required to reach an SO_2 level of below 1 ppm. This ratio is in line with the range reported by B. Sun et al. 2019 to achieve an SO_2 removal of over 98% (G/L ratio of 90 to 200 for the solvent used). The pre-treatment results in a waste stream of 4276 kg/hr. This waste stream mainly consists of CO_2 (64 wt%) and H_2O (33 wt%).

The purified CO_2 enters the SOEC. A single-pass conversion of 85% is present (Küngas 2020). CO and oxygen are produced (Küngas 2020). Similar to the AEL, no crossover of the products and/or contaminants is assumed to be present. A CO product stream of 4671 kg/hr leaves the SOEC. Moreover a stream of 2536 O_2 is present. This stream is upgraded with multi-stage compression (EC-C8) to be sold as industrial oxygen.

Fermentation

The feed entering the bubble column (F1-R1) has a molar fraction of 50% CO and 47% H_2. The remaining 3% are impurities such as H_2O (0.5%), N_2 (1.7%), CH_4 (0.5%), Ar (0.3%) and trace elements. The syngas fermentation described by de Medeiros, Noorman, et al. 2020 mentions molar fractions of 50% CO and 50% H_2. No impurities are present in their feedstream. Nevertheless, the presence of the remaining impurities are expected to have a negligible effect on the performance of the fermentation.

Next to the feedstream a total of 559 kg/hr of additional nutrients are added. The composition of this nutrient stream can be found in Appendix K and Appendix H. An additional 38,462 kg/hr is recycled between the first and second fermentation. This stream mainly consists of H_2O ($\geq$ 99%). The reactions and yields of the bubble column (F1-R1) are previously described in Equation 3.3.1. Overall a CO conversion of: $\frac{F_{in,CO} - F_{out,CO}}{F_{out,CO}} = \frac{(4444-444)}{4444} = 0.9$ is present. For H_2, a conversion of $\frac{F_{in,H_2O} - F_{out,H_2O}}{F_{out,H_2O}} = \frac{(300-41.7)}{300} = 0.86$ occurs. Research conducted by de Medeiros, Noorman, et al. 2020 shows a CO conversion of $\approx$ 85%-95% and a H_2 conversion of $\approx$ 72%-88%. The conversions in the indirect route match these ranges.

The product stream of the first fermentation has a flow of 41,522 kg/hr. It contains an ethanol concentration of $\frac{1{,}615{,}870\ g/hr}{53{,}489\ L/hr} = 30.21\ g/L$, This is below the threshold of 34 g/L, so no inhibitory effects are expected to occur (Phillips et al. 1993). Biomass is produced with a rate of 837 kg/hr. Microfiltration (F1-F1) is used to separate the biomass from the product stream. A total of 90% of the biomass is separated from the product stream and recycled back to the bubble column (Phillips et al. 1993).

For the second fermentation a nutrient flow of 969 kg/hr is added. A composition of the nutrient stream can be found in Appendix H. This stream also contains acetate to prevent limiting *n*-caproate production. In total an acetate concentration of $\frac{10.34\ kmol/hr}{345761\ L/hr} \approx 30 mM$ is present in the CSTR (F2-R1). This is in line with conditions mentioned by P. Yang et al. 2018. Furthermore a stream of 254,156 kg/hr ($\geq$ 99% H_2O) is recycled from the downstream processing.

In line with the product profile reported by P. Yang et al. 2018, 100% of the ethanol is used to form butyrate and *n*-caproate. The product stream contains a butyric acid concentration of $\frac{c_{C4ATE}}{Flowrate} = \frac{5{,}550{,}000\ mmol/hr}{345761\ L/hr} = 16.05\ mM$. This is slightly exceeding the range of the concentration described by P. Yang et al. 2018 (namely

15.4 ± 0.55 mM). The caproic acid concentration is $\frac{c_{C6ATE}}{Flowrate} = \frac{11{,}830{,}000\ mmol/hr}{345761\ L/hr} = 34.2\ mM$. This is also higher than the reported 32.6 ± 0.8 mM of P. Yang et al. 2018, but still in a non-limiting range (Roghair et al. 2018). The higher concentrations can be explained by the presence of recycle streams. The research conducted by P. Yang et al. 2018 used a batch experiment. Moreover, a biomass production of 0.08 times the molar production of *n*-caproate is reported by P. Yang et al. 2018. The biomass produced during chain-elongation equals $(Biomass_{out} - Biomass_{in}) = 349.44 - 348.50 = 0.94\ kmol/hr$. The produced *n*-caproate is 11.83 kmol/hr. A molar ratio of $\frac{0.94}{11.83} = 0.08$ is thus reached.

Downstream Processing

The biomass formed during the fermentation is removed with microfiltration (F1-F1 and F2-F1). For both syngas fermentation and chain-elongation 90% of the biomass is recycled. Next the pH of the product stream is adjusted by adding H_3PO_4 (DSP-R1). As a result, the carboxylates react to acids. Additionally $CaCl_2$ is added to precipitate the now formed anion HPO_4^{2-}. Both biomass and $CaHPO_4$ are removed by a separator (DSP-SP1). This waste stream has a total mass of 3021 kg/hr. The HCl mixture is recovered by separating the ions (H^+ and Cl^-) from the product stream. This results in a waste stream of 3021 kg/hr.

The remaining DSP shows the *in-situ* product recovery (ISPR) coupled distillation as proposed by Saboe et al. 2018. Liquid-liquid extraction (DSP-T1) is used to extract the organic phase from H_2O . The solvent TOA is added with a molar feed of 1/50 times the amount of H_2O present in the product stream. The water phase is recycled to the syngas fermentation (291061 kg/hr). From this stream, 0.5% is assumed to be discarded as waste (1463 kg/hr). The carboxylic acids solved in TOA enter a vacuum distillation column (DSP-T2). The distillation is performed with a molar reflux ratio of 0.25 and a mass bottom to feed ratio of 0.75. Operating the distillation under these conditions ensures a *n*-caproate mass recovery of 99.95% and a corresponding TOA mass purity of 0.0002351. The majority of the bottom stream consists of TOA (≥ 99.99%) and is reused for LLE. The distillate of DSP-T2 consists of 36 wt% *n*-caproate.

The distillate leaving DSP-T2 cannot be directly purified with an azeotropic distillation. Therefore, a second LLE (DSP-T3) combined with vacuum distillation (DSP-T4) are implemented. For LLE again a molar solvent feed of 1/50 times the amount of H_2O is added. This corresponds to a total of 535 kg/hr of TOA. The outgoing waste stream of the second extraction consists of 96% H_2O . Of this stream, 0.5% is discarded as waste, the remaining is sent back to the fermentation (1,557 kg/hr). For the second vacuum distillation an *n*-caproate mass recovery of 99.99% is set. Moreover, the fraction of TOA in the distillate should be minimized. Namely, the TOA fraction leaving the distillate of DSP-T4 will remain in the final product stream. Similar to the previous vacuum distillation, the solvent in the bottoms' rate is recycled for LLE. The distillate stream consists of 67 wt% *n*-caproate.

The final DSP step is azeotropic distillation (DSP-T5). *n*-caproate is recovered in the bottoms flow with a mass purity of 99 wt% and a total flow of 1250 kg/hr. The distillate has a total flow of 603 kg/hr and consists of 70 wt% of butyric acid, 28 wt% of H_2O and 2 wt% of acetic acid. This stream is not pure enough to be sold as butyric acid on the global market. Nevertheless, it is assumed that this stream can be used in a different process within the chemical cluster at Rotterdam. Butyric acid namely has a wide variety of applications, even at a lower mass purity (L. Jiang et al. 2018).

4.5.2 Energy Balances

The energy balances show the total in- and outflow of energy streams in the system. It consists of the energy of the in- and outgoing streams and the utilities used. It is important to gain an understanding of the overall energy requirements of the system. These requirements influence, among others, the production costs and CO_2 emissions. As stated previously, heat integration in this design is minimal, as it is beyond the scope of this research. Nevertheless, implementation of heat integration would potentially decrease the energy requirements (L. Wang et al. 2018).

The energy of each in- or outgoing stream are retrieved from the Aspen simulation. Next to this, a suitable utility for all equipment units of the indirect route is selected. This is done in the Aspen Flowsheet. The choices of each utility allocated to their corresponding equipment unit are based on the guidelines set by the VICI project (Ramírez 2022). It is ensured that the maximum temperature differences between the utility and the corresponding stream remain. After matching each equipment unit to an appropriate utility, the amount of energy required by each utility is calculated and retrieved from Aspen Energy Analyzer (AEA). An exception on this approach is made for the electrolyzers. Since Aspen does not contain a built-in electrolyzer, the electricity demand of those is calculated separately. See the sections below for details.

An overview of the utilities is shown in Table 4.4 and 4.5. Note, that the hot and cold utilities shown in subsection 4.5.2 show an overview of the total requirements. Hence, the steam generating is shown as a cooling requirement. Contrary, when e.g. utility costs are calculated, steam generation is subtracted from the corresponding heating utilities.

Table 4.4: Overview of the heating and cooling utilities used by the indirect route.

Heating Utilities	
Stream Type	Energy (GJ/hr)
LLP Steam	57.0
LP Steam	20.1
MP Steam	0.01
HP Steam	44.8
VHP Steam	3.7
Hot Oil	59.6
Fired Heat	6.9
Total	**211.1**

Cooling Utilities	
Stream Type	Energy (GJ/hr)
Chilling water	149.4
Cooling water	8.5
LLP Steam Gen.	0.2
LP Steam Gen.	19.7
MP Steam Gen.	14.09
Total	**191.8**

Table 4.5: Overview of the electricity usage by the indirect route. Retrieved from the Aspen Flowsheet. *The duty of the electrolyzers is calculated based on: 1 kW = 0.0036 GJ/hr.

Electricity		
Type	Power (kW)	Duty (GJ/hr)
Solid oxide Electrolyzer	8886.5	32.0*
Alkaline Electrolyzer	16943.5	61.0*
Miscellaneous	2020	7.3
Total	**27850**	**100.3**

Electricity usage SOEC

A measure to define the performance of an electrolyzer is its electric power consumption (EPC). It describes the amount of electric energy that is required for the production of 1 Nm^3 of product gas (Küngas 2020). EPC is calculated following Equation 4.1.

$$EPC = \frac{(E \times z \times F)}{(\eta_F \times V_m)} \tag{4.1}$$

EPC	Electric Power Consumption (kWh)
E	Cell Voltage (1.1 V)
z	Electrons tranferred per ion (2)
F	Faraday constant (96,485 C/mol)
η_F	Faradaic Efficiency (100%)
V_m	Molar Volume of Ideal Gas (22.4 L/mol)

As described by Küngas 2020, the operating cell voltage of an eCO is 1.1 V with a complementing faradaic efficiency of 100%. The amount of electrons transferred during CO_2 reduction is 2 ((Ganji et al. 2020) and see Equation 3.1). The molar volume of CO under normal conditions is 22.4 L/mol. Using the conversion of 1 joule is 2.78×10^{-7} kWh, this results in an EPC of:

$$EPC = \frac{(1.1 \times 2 \times 96,485)}{(1 \times 22.4 \times 10^{-3})} \times 2.78 \times 10^{-7} = 2.5 \, \frac{kWh}{Nm^3}$$

This EPC corresponds to the value described by Haldor-Topsoe (2.5 kWh per Nm^3) (Küngas et al. 2017). Other research conducted into CO_2 reduction via SOEC reported a EPC of 2.4 kWh per Nm^3 (Ebbesen and Mogensen 2009) (Küngas 2020).

The CO production at the SOEC consists of 158.687 kmol per hour. Assuming an ideal gas, this corresponds to an overall power consumption of:

$$Power_{cons} = EPC \times n \times V_m$$
$$Power_{cons} = 2.5 \times 158,687 \times 22.4 \times 10^{-3} = 8886.5 \, kW.$$

Electricity usage AEL

The calculation of the electricity usage of the AEL is similarly calculated as the SOEC. The EPC is calculated following Equation 4.1, as shown previously.
The faradaic efficiency and cell voltage of the AEL are calculated in Appendix L. The retrieved values are an η_F of 95% and a cell voltage of 2.04 V. During the redox reactions a total of 2 electrons per ion are transferred (see Equation 3.7).

$$EPC = \frac{(2.04 \times 2 \times 96,485)}{(0.95 \times 22.4 \times 10^{-3})} \times 2.78 \times 10^{-7} = 5.14 \, \frac{kWh}{Nm^3}$$

A total of 147,083 mol H_2 per hour is produced by the AEL.

$$Power_{cons} = 5.14 \times 147,083 \times 22.4 \times 10^{-3} = 16943.5 \, kW.$$

The obtained values are compared to the general H_2 AEL' performance as indicated by the International Renewable Energy Agency (Taibi et al. 2020). Current alkaline electrolyzers have a nominal current density of 0.2-0.8 A/cm^2. The current density of the AEL of the indirect route is 0.45 A/cm^2. The voltage limits are 1.4-3 V, a range where the calculated voltage of 2.04 V falls in. The electrical efficiency of the system is in between 50-78 kWh/kg_{H2}. The calculated 16943.5 kW for 147,083 mol H_2 corresponds to $\frac{Power_{cons}}{Prod_{mol} \times MW_{H2}} = \frac{16943.5}{147,083 \times 10^{-3} \times 2.016} = 57$ kWh/kg. Based on these results the performance of the AEL is judged to be realistic.

4.6 Determination and Quantification of the Relevant Performance Indicators

In this section, the techno-economic and environmental analysis of the indirect route is performed. The parameters considered are based on literature research and the conducted interviews (see Appendix B and Appendix D). These parameters are: 1) CO_2 conversion efficiency, 2) specific primary energy consumption, 3) product selectivity, 4) technology readiness level, 5) CAPEX, 6) OPEX, 7) minimum *n*-caproate selling price, 8) carbon footprint, 9) greenhouse gas reduction potential and 10) competitive advantage within the current market. An explanation of each parameter retrieved from literature research is described in chapter 2. The parameters retrieved from the interviews are explained in this section.

If applicable, these parameters are compared to the results of the direct route. This comparison is mainly based on the techno-economic assessment (TEA) of MES published by Jourdin et al. 2020 and Luo et al. 2022. Note, the TEA of the direct route is based on an annual operation of 8760 hours and did not include pre-treatment of the CO_2 feedstream. In order to ensure a fair comparison of some parameters, the value of the total process, but also of the process without pre-treatment is given. A summary of all retrieved parameters can be found in Table 4.6.

Table 4.6: Overview of the technical, economic and environmental assessment of both the direct and indirect route. An explanation of each parameter is described in the sections below. Note that the direct route is excluding pre-treatment. Therefore, the indirect route is also subdivided into pre-treatment and the rest of the process if relevant. *Based on; 1) Luo et al. 2022, 2) Jourdin et al. 2020, 3) Roy et al. 2022.*

		Indirect Route				Direct Route
		Pre-treatment	**Production**	**DSP**	**Total**	**Total**
TECHNICAL	*CO_2 Conversion efficiency*	72%	75%	-	54%	94%[1]
	Specific Primary Energy Cons.	0.005 GJ/kg_{Cap}	0.180 GJ/kg_{Cap}	0.166 GJ/kg_{Cap}	0.351 GJ/kg_{Cap}	0.1 GJ/kg_{Cap}[1]
	Product Selectivity	-	Caproate (1 kg/kg) Acetate (0 kg/kg) Butyrate (1.23 kg/kg) Biomass (0.69 kg/kg)	-	Caproate (1 kg/kg) Acetate (0 kg/kg) Butyrate (1.23 kg/kg) Biomass (0.69 kg/kg)	Caproate (1 kg/kg[2]) Acetate (7.40 kg/kg) Butyrate (2.71 kg/kg) Biomass (- kg/kg)
	TRL	9	3	4	3	3-4[3]
ECONOMIC	*CAPEX*	-	-	-	e 166,298	e 93,100,000[1]
	OPEX	-	-	-	e 58,725,000	e 34,000,000[1]
	Min. Caproate. Selling Price	-	-	-	€3924 per tonne	€3584 per tonne
ENVIRONMENTAL	*Carbon Footprint*	-	-	-	7.3 kg_{CO_2} /$kg_{Caproate}$	N/A

4.6.1 Technical Assessment

For the technical assessment the CO_2 conversion efficiency, primary energy usage and product selectivity are researched.

CO_2 Conversion Efficiency

The CO_2 conversion efficiency refers to the percentage of in-going CO_2 which is converted into products (Jourdin et al. 2020). Products include *n*-caproate, *n*-butyrate, acetate and biomass. The mass flows are retrieved from the mass balances, as shown in Appendix K. The CO_2 conversion efficiency is calculated with Equation 4.2. The initial in-going CO_2 stream is 9694 kg/hr.

$$\eta_{CO_2 conv.} = \frac{(CO_{2,in} - CO_{2,out})}{CO_{2,in}} \tag{4.2}$$

For the indirect route, two main CO_2 waste streams are present. The first one is during the purification of the Porthos stream. This stream results from the SO_2 removal and has a flow of 2717.8 kg/hr CO_2 . The second waste stream of CO_2 is generated during the syngas fermentation. This stream consists of 1754.4 kg/hr of CO_2 . The origin of this CO_2 is the acetate and ethanol formation via the Wood-Ljungdahl Pathway (see Equation 3.9 and Equation 3.11).

As a result, the following CO_2 conversion efficiencies are found for both the pre-treatment and the syngas formation & fermentation:

$$\eta_{CO_2 conv.,pre-treatment} = \frac{(9694 - 2717.8)}{9694} = 0.72$$

$$\eta_{CO_2 conv.,process} = \frac{(6976 - 1754)}{6976} = 0.75$$

The downstream processing does not have any CO_2 in- or outflow. Combining the CO_2 conversion efficiency of both the pre-treatment and the production process, the overall process has an efficiency of $0.72 \times 0.75 = 0.54$.

The CO_2 conversion efficiency for *n*-caproate production via microbial electrosynthesis (MES) is reported to be 94% (Luo et al. 2022). However, the reported direct route did not include pre-treatment of the CO_2 stream. A feedstream $\geq$ 99.9% pure CO_2 stream is assumed. Even comparing the CO_2 conversion efficiency of the direct route to the efficiency of the process without pre-treatment should be done with caution. The CO_2 source and pre-treatment method will likely impact the mode of operation and the design of an MES plant. A different mode of operation can alter the CO_2 conversion achieved (Jourdin et al. 2020) (Bakonyi et al. 2020).

The CO_2 conversion could potentially be lowered by a different type of CO_2 electrolyzer. An electrolyzer that can handle higher levels of impurities, such as a molten carbonate electrolyzer, is expected to have different, less-demanding, pre-treatment requirements (Küngas 2020). This could potentially limit the CO_2 loss caused by the pre-treatment. Furthermore, if the electrolyzer is able to handle gas with a lower CO_2 purity, the fermentor's off-gas can potentially be recycled to it. The electrolyzer will then convert the CO_2 produced during fermentation into CO. This would also lead to a decrease in CO_2 emissions.

Another method to limit the CO_2 emission is to optimize the syngas composition for the fermentation. During fermentation some reactions utilize CO_2 while others produce it (see chapter 3). A different ratio of H_2 and CO influences which metabolic reactions occur at which rate (Jack et al. 2019). This could potentially be used to limit the CO_2 forming reactions.

Specific Primary Energy Consumption

The specific primary energy consumption shows the energy use compared to the produced product (Roh et al. 2020). This parameter is seen as a technical parameter, as it describes the energy efficiency of the system. It is also related to the environmental performance of the production route as energy usage is often related to CO_2 emissions.

The specific energy consumption is calculated following Equation 4.3 (Roh et al. 2020).

$$Specific\ Primary\ Energy\ Consumption = \frac{net\ primary\ energy\ input}{Functional\ Unit} \tag{4.3}$$

'Functional unit' refers to 1 kilogram of n-caproate. The primary energy input is retrieved from Aspen Energy Analyzer (AEA). The results discussed in subsection 4.5.2 are used for this analysis. An overview of the relevant energy streams are shown in Table 4.7.

Table 4.7: Overview of the utility' streams break-down over pre-treatment, production process and downstream processing. For each part the specific primary energy consumption, normalized per kg of n-caproate produced is shown. The hourly n-caproate production is 1237.5 kg/hr.

	Pre-treatment	Process	DSP	Total
Electricity Usage (GJ/hr)	1.6	98.6	0.04	100.3
Hot & Cold Utilities (GJ/hr)	4.4	124.0	205.8	334.2
Prim. Energy Use (GJ/kg_{Cap})	0.005	0.180	0.166	0.351

Table 4.7 shows several results. Firstly, the process and downstream processing utilize significantly more energy than the pre-treatment. When looking at the production process, both the electricity and the hot & cold utility usage are significantly large. The main cause of these high requirements are the SOEC and AEL. The two electrolyzers account for 93 GJ/hr of the electricity demand. They are also responsible for 86.8 GJ/hr of the hot utilities, to reach their operating temperature. In terms of specific energy consumption, the SOEC and AEL have a consumption of $\frac{(93+86.8)}{1237.5} = 0.15$ GJ/kg_{Cap}.

For the DSP, this usage is dominated by the hot and cold utilities. the main contributor to the energy used is the pH adjustment of the fermentation broth (DSP-R1). In this step, the carboxylates are converted into carboxylic acids. Cooling down the reactor requires 106 GJ/hr. The second unit that has a significant contribution to the utility usage is the first vacuum distillation (DSP-T2). Here, a total of 52 GJ/hr is utilized. Both steps combined have a specific energy consumption of $\frac{(106+52)}{1237.5} = 0.13$ GJ/kg_{Cap}.

The direct route has an energy requirement of 0.1 GJ/$kg_{Caproate}$ (Luo et al. 2022). This is significantly lower than 0.35 GJ/$kg_{Caproate}$ required for the indirect route. One of the main factors causing the higher energy usage is the electricity demands of the electrolyzers. The direct route contains a bio-electrochemical system, which can also be seen as a type of electrolyzer. Nevertheless, due to a lower operating temperature and pressure its energy usage is lower (Jourdin et al. 2020).

Furthermore, the energy consumption at the DSP is for the indirect route significantly larger then for the direct route. This can be explained by looking at the volume flow of the system. The fermentation at the direct route reaches a concentration of ≈ 60 mM, while those at the indirect route reaches 34.2 mM (Luo et al. 2022) (P. Yang et al. 2018). Moreover, the direct route operates 8760 hours a year, while for the indirect route the conventional 8000 hours is used. Both factors contribute to a higher flow rate for the indirect route. As a result the energy demand of, e.g. distillation is higher.

It is expected that the energy usage of the indirect route can be decreased by considering the following. Firstly, heat integration in this design is minimal. The electrolyzer operate at a relatively high temperature, the fermentation at ambient temperatures and the DSP at a high temperature. These fluctuations in the temperature require a lot of heating followed by cooling. By implementing an optimal heat integration, it is expected that the energy usage becomes more efficient.

A second option to decrease the utility usage is to use the produced biomass as a fuel. At the moment the biomass is discarded as waste. Future research could analyze a scenario in which the produced biomass is used to produce bio-gas.

Thirdly, both the solid oxide electrolyzer and the alkaline electrolyzer are currently under development. As described by Taibi et al. 2020 and Küngas 2020, the energy efficiency of both is expected to be increased over the years. Due to the large contribution of the electrolyzers to the overall energy usage, this is expected to decrease the energy demand.

Product Selectivity

The interviews with the stakeholders showed the importance of assessing the product selectivity (see section 4.4). The product selectivity gives insight into the distribution of the substrate and energy over the product spectrum. For the indirect route the product spectrum consists of n-caproate, butyrate and biomass. When utilizing the direct route, the products are n-caproate, butyrate and acetate. The product selectivity is calculated by Equation 4.4:

$$Selectivity_{prod,A} = \frac{Amount\ product\ A\ produced\ (kg/hr)}{Caproate\ produced\ (kg/hr)} \tag{4.4}$$

The market price of n-caproate is higher than those of acetate and butyrate. Pushing the product spectrum towards n-caproate would ensure the 'highest price per carbon' (as shown in Table 4.8). Furthermore, recovering a large variety of products also leads to a more extensive DSP, increasing process complexity. For MES, enhancing the product selectivity towards n-caproate is stated to be the key to economic viability (Jourdin et al. 2020).

Table 4.8: Products of the direct and/or indirect route and the calculated price per carbon atom. n-Caproate has not only the highest market price, but also the highest price per carbon atom. *1) Prices are retrieved from Jourdin et al. 2020.*

	Cmol per mole	MW (kg/kmol)	Market Price[1] (EUR/tonne)	Market Price[1] (EUR/kmol)	Market Price (EUR/Cmol)
Acetate	2	60.05	650	0.011	0.0055
Butyrate	4	88.11	2000	0.023	0.0058
Caproate	6	116.16	4400	0.0379	0.0063
Biomass	1	24.61	0	0	

The production rates of the indirect route and direct route are shown in Table 4.9. The rates of the indirect route are retrieved from the Aspen simulation designed in this research. The data of the direct route is retrieved from Jourdin et al. 2020. Note that his research considers an annual production of 0.091 ton, while the indirect route produces 10 kton. For the comparison between the routes, it is assumed that the product distribution of the direct route is remained during up-scaling. The same assumption was made when designing the indirect route, see chapter 3.

As can be seen in Table 4.9, the indirect route has, in terms of mass, less side-products being produced per kilogram of n-caproate production. This is considered beneficial, as explained above. The downside of the indirect route is the presence of an additional compound, namely biomass. For the direct route, the biomass is grown as a biofilm. Biomass is still produced, but the amount present in suspension is considered negligible (Jourdin et al. 2020). This would ease the downstream processing, as no micro filtration would be required.

Table 4.9: Product selectivity of the direct and indirect route. The production rate of each product is shown. This amount is put in the perspective to the amount of *n*-caproate produced. Note that the overall production scale of the direct route is significantly lower than that of the indirect route. The data for the indirect route is drawn from the simulation discussed in this report. Data of the direct route is retrieved from *1)*: Jourdin et al. 2020.

	Indirect Route		Direct Route [1]	
	Production rate (kg/hr)	Product Selectivity (kg/kg_{Cap})	Production rate (kg/hr)	Product Selectivity (kg/kg_{Cap})
Acetate	0.0	0.0	0.077	7.40
Butyrate	1523	1.23	0.028	2.71
Caproate	1,238	1.00	0.010	1
Biomass	860	0.69	-	-

TRL of the Indirect Route

The process design of the indirect route consists of several technological parts. The TRL of these technologies vary between 2 and 9. There is no main method to determine the TRL of a system of technologies. Moreover, the interpretation of the 'readiness' of a technology is subjective (Tomaschek et al. 2016). However, TRL is a metric often used by academics and investors to benchmark technologies (as discussed by Webster and Gardner 2019 and the Horizon 2020 Project of the European Union (*Horizon Project - Annex G* 2020)). Therefore, it is still valuable to use the TRL scale to give an indication at which level the indirect route is. It is proposed to use the technology with the lowest TRL to reflect the TRL of the overall innovation (Tomaschek et al. 2016).

For the indirect route, the technology with the lowest TRL is chain-elongation. The concept of chain-elongation is known and there is an experimental proof of concept. However, the feasibility of this technology still has to be researched. At the moment, it is unknown which feedstock composition and which operation conditions enable the optimal *n*-caproate production (P. Yang et al. 2018). Therefore, for this technology the focus is on so-called knowledge development. When looking at the TRL metric shown in the introduction (Figure 1.2), this corresponds to a TRL of 3. As a result, the overall indirect route is judged to have a maturity level of TRL 3.

System Readiness Level

As discussed by Sauser et al. 2006 and Tomaschek et al. 2016, using the TRL metric to indicate the maturity of a system is flawed. The reason behind this is the fact that a system is a sum greater than the parts of the individual technologies. A multilateral causality between the subsystems and the environment is present. Moreover, there is a flow of information between the components, which also should be accounted for (Sauser et al. 2006). Overall, TRL does not account for integration readiness (Tomaschek et al. 2016). Indices that might be better suited to benchmark the maturity of a system are the 'System Readiness Level' (SRL) and/or the 'Integration Readiness Level' (IRL) (Sauser et al. 2006).

The SRL index can be compared to the TRL (Sauser et al. 2006). One phase in the SRL includes several TRL levels. When benchmarking the indirect *n*-caproate route on the SRL, it would be in the phase of 'concept refinement', as the initial concept is being refined with a focus on the development strategy (Sauser et al. 2006). This corresponds to a TRL of 2-4. To conclude, the maturity level of the indirect route is set at a TRL of 3, but this value should not be seen as a demarcated scale, but merely as gradual.

4.6.2 Economic Assessment

For the economic assessment the capital expenditure (CAPEX) and operational expenditure (OPEX) are calculated. These calculations are performed by using Aspen Process Economic Analyzer (APEA) adapted with manual calculations. The APEA template is set as EU based. As a default, Rotterdam is used as location. Additional information about sizing and equipment material is obtained from the manual AspenTech 2021 v12.

Capital Expenditure

A study estimate is made to gain insight into the CAPEX of the indirect route (Peters et al. 2003). CAPEX is defined as *'the total amount of money needed to supply the necessary plant and manufacturing facilities, plus the amount of money required as working capital for operation of the facilities'.* (Peters et al. 2003). The method to obtain the CAPEX is the direct bottom-up approach (Van der Spek, Ramirez, et al. 2017). This method uses the total installed equipment cost as starting point. Based on these cost and its ratio to other cost, the CAPEX can be estimated. The CAPEX consists of the fixed-capital investment (FCI) (80%-90%) and the working capital (10%-20%). The FCI entails the direct (65%-85%) and indirect (15%-35%) cost. The direct costs include *'material and labor involved in actual installation of complete facility'*. The indirect costs are *'expenses which are not directly involved with the direct costs'* (Peters et al. 2003). An overview of the build-up of the CAPEX is shown in Figure 4.8.

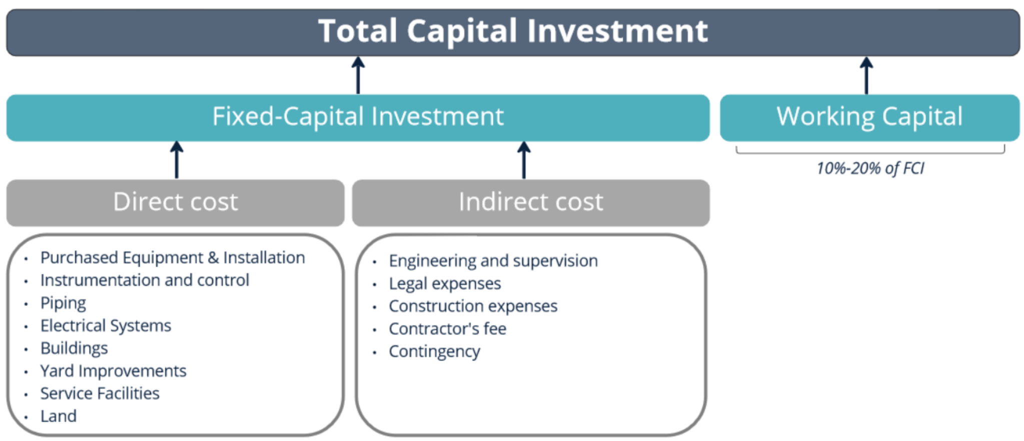

Figure 4.8: Schematic overview of the bottom-up approach. The total capital investment is calculated by retrieving the direct and indirect costs from Aspen Process Economic Analyzer. Based on these costs, the fixed capital investment (FCI) is retrieved. The working capital investment is 10%-20% of the FCI. Combined they form the total capital investment.

Equipment Cost

The direct and indirect cost components can be retrieved from APEA v12. Nevertheless, not all equipment, such as the electrolyzers, is correctly represented in Aspen. Therefore, the results from APEA do not represent the actual cost estimated. In order to obtain a correct estimation, the following steps are taken. Firstly, the direct and indirect costs are derived via APEA v12. Next, these costs are used to derive the percentage of each factor to the build-up of the fixed-capital investment. If a specific factor could not be obtained, the percentage as proposed by Peters et al. 2003 Chapter 6 is used. Thirdly, an estimation of the equipment cost for units not represented in APEA is made. These include the direct oxidation (EC-R1 + EC-C5), SOEC (EC-R2 + EC-SP1), AEL (EL-R1 + EL-SP1) and the two membrane separators (DSP-T1 and DSP-T3). The equipment cost of these items is shown in Table 4.10. The retrieving of these costs are explained in section M.1. Furthermore, the build-up of the equipment cost can be seen in Graph 4.9. Lastly, the now calculated equipment costs and the retrieved percentage of each component is used to calculate the direct and indirect cost. The results are shown in Table 4.11.

As can be seen in Figure 4.9, the alkaline electrolyzer (AEL) has a significant contribution to the overall equipment cost. Moreover, the price of H_2O alkaline electrolyzers ranges in between 500-1000 USD/kW in 2020, but are also expected to drop to $\leq$ 200 USD/kW in 2050 (Taibi et al. 2020). Due to its impact on the

Table 4.10: Overview of the equipment units whose price is manually calculated. Calculations are explained in section M.1

Item	Flowsheet ID	Estimated cost (EUR)
Direct oxidation	EC-R1 + EC-C5	578,767
SOEC	EC-R2 + EC-SP1	2,090,530
AEL	EL-R1 + EL-SP1	11,945,168
Membrane Separation #1	DSP-T1	1,591,200
Membrane Separation #2	DSP-T3	1,591,200

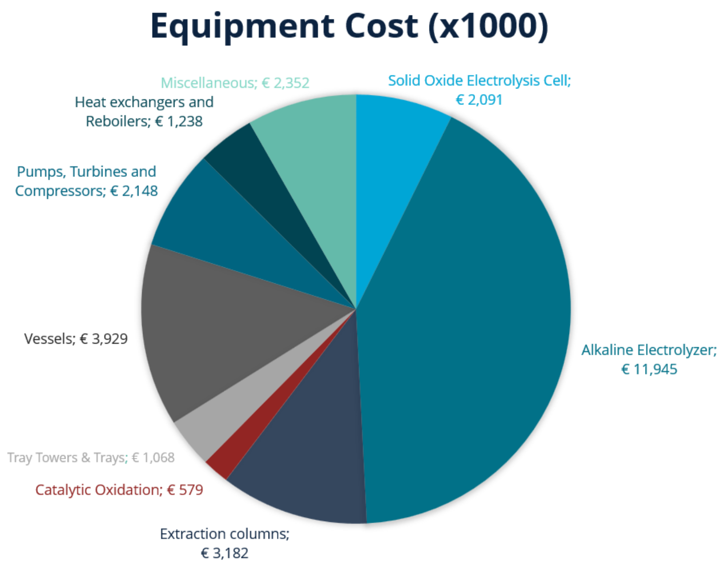

Figure 4.9: Component breakdown of the equipment cost. Cost are retrieved from the Aspen Process Economic Analyzer or manually calculated as explained previously. The costs are shown in x €1000. The total equipment cost are € 28.53 million and dominated by the alkaline electrolyzer of €11.95 million.

overall equipment cost and the price uncertainty, a sensitivity analysis on the AEL price is performed. This analysis can be found in Appendix O.

Total Capital Investment
Based on the equipment cost obtained via manual calculation and APEA, the total CAPEX is build-up. The results can be seen in Table 4.11. It shows that the installed capital cost are the largest contributor to the FCI ($\approx$ 20%). Nevertheless, this cost is slightly below the range given by Peters et al. 2003 (21%-54%). When comparing the obtained percentages to the percent ranges given by Peters et al. 2003 Chapter 6, all other components fit within. The build-up of the CAPEX is in line with the expectation.

Operational Expenditure

The operational expenditure (OPEX) consists of the variable production cost, fixed production cost and the overhead cost. The build-up of the OPEX is based on Peters et al. 2003 and can be seen in Table 4.12. The raw material usage, waste disposal and utility cost are calculated manually as shown in Table M.2. Their cost are based on the price and flow rate of each material (see section M.2). The other components are retrieved from the APEA analysis or based on the cost distribution as described by Peters et al. 2003.

As can be seen in Table 4.12, the OPEX are dominated by the electricity usage ($\approx$ 40%). Based on the energy analysis described previously, this is not surprising. Nevertheless, an average chemical plant has 10%-20%

Table 4.11: Overview of the Fixed capital cost of the indirect route. *These components' percentage contribution to the CAPEX are estimated based on the percentages retrieved from Peters et al. 2003 Chapter 6.

Capital Expenditure			
	Components	% of total	x1000 EUR
DIRECT	Installed capital cost	19.7%	28,532
	Instrumentation	9.8%	14,119
	Piping	10.6%	15,338
	Electrical	3.9%	5,681
	Buildings*	3.0%	4,338
	Yard improvements*	3.5%	5,061
	Service facilities*	14.0%	20,245
	Land*	1.7%	2,494
INDIRECT	Engineering and supervision	12.4%	17,981
	Construction expenses	5.8%	8,356
	Contractor's fee	2.6%	3,740
	Contingency	13.0%	18,720
Fixed Capital Investment (FCI)		100.0%	144,607
Working Capital Investment* (WCI)		15% of FCI	21,691
Total Capital Investment (CAPEX)			**€ 166,298**

Table 4.12: Overview of the operational expenditure of the indirect route. *These components' percentage contribution to the OPEX are estimated based on the percentage retrieved from Peters et al. 2003. Other components are manually calculated, see Table M.2.

Operational Expenditure (OPEX)			
	Components	% of total	x1000 EUR/yr
Variable Costs of Production	Raw materials	12.6%	€ 7,399
	Waste Disposal	6.6%	€ 3,858
	Operating labor	5.9%	€ 3,454
	Operating Supervision and Clerical Assistance*	0.9%	€ 518
	Utilities - Total	47.6%	€ 27,941
	Electricity		€ 23,784
	Hot utilities		€ 4,424
	Cold utilities		-€ 267
	Maintenance and repairs*	5.3%	€ 3,139
	Operating supplies*	0.8%	€ 471
	Laboratory charges*	0.9%	€ 518
Fixed Costs of Production	Patents and Royalties*	4.7%	€ 2,766
	Local Taxes*	7.4%	€ 4,338
	Property insurance*	0.1%	€ 55
Overhead Costs	Overhead Costs*	7.3%	€ 4,266
Total Operating Cost (OPEX)			**€ 58,725**

of its total production cost allocated to utility usage. This indicates that the utility usage for the indirect route is large compared to other chemical plants. The impact of the electricity price on the economic performance of the indirect route is assessed by a sensitivity analysis. This analysis can be viewed in Appendix O.

The second largest contributing factor is the raw material cost. This accounts for ≈ 13% of the OPEX, which can be seen as quite low (Peters et al. 2003). Note, its percent contribution will change if the process would become less energy demanding. The rest of the components are based on and thus in line with estimations provided by Peters et al. 2003.

Minimum n-Caproate Selling Price

The minimum n-caproate selling price (MCSP) indicates the n-caproate price required to reach a net present value (NPV) of 0. The MCSP and NPV are calculated following Equation 4.5 and Equation 4.6.

$$MCSP = \frac{NPV}{\sum_{n=1}^{n=t} \frac{M_{cap}}{(1+i)^n}} \tag{4.5}$$

$$NPV = \sum_{n=1}^{n=t} \times \frac{CF}{(1+i)^n} \tag{4.6}$$

$$CF_{t=n} = Revenue_{t=n} - OPEX_{t=n} - Depreciation_{t=n} \tag{4.7}$$

$MCSP$	Minimum caproate selling price (EUR/kg)
NPV	Net Present Value
t	Years of operation (30 years + 1 year construction)
M_{Cap}	Annual n-caproate production (10 kton)
i	Discount Rate (8%)
$CF_{t=n}$	Cash Flow in year n (€/yr)
$Revenue$	Dependent on MCSP.
$OPEX$	€ 58,725,000 per year
$Depreciation$	€ 951,000 per year

For the calculations, the following assumptions are used:

- Construction of the plant starts in 2025.
- All equipment cost are made upfront, in 2025.
- n-Caproate production starts in 2026.
- The plant operational life is 30 years (so 2026 to 2056).
- The discount rate is 8%.
- All equipment has a lifetime of 30 years.
- Depreciation is calculated with the straight-line method (Peters et al. 2003). This results in an annual depreciation of $\frac{28{,}532{,}124}{30} = €951,000$.

The revenue is generated by selling the n-caproate and the industrial oxygen. Computing the n-caproate price at which the NPV is zero, results in a MCSP of €3924 per tonne. The current market price of n-caproate is €4400 per tonne (described in subsection 1.1.1). Therefore, in terms of economics, the n-caproate production could be feasible.

However, it is important to note that 51% of the revenue is generated by selling industrial oxygen. Industrial oxygen is produced with an annual production of 108,000 m^3 and has a selling price of €376 per m^3 (Made-in-China 2022). This results in a revenue of €40.6 million. A breakdown of the revenue at an n-caproate selling price of 3924 is shown in Table 4.13.

If the revenue would be solely generated by selling n-caproate, a MCSP of €7,985 per tonne is calculated. This price is, unsurprisingly, significantly larger. It is also larger than the current market price. Hence, the profitability of the indirect route is significantly influenced by the revenue generated by the upgrading of oxygen. The sensitivity of the MCSP to the oxygen price is calculated in Appendix O. Therefore, if this

Table 4.13: Breakdown of the revenue generated. The revenue is generated by selling *n*-caproate and industrial oxygen. *Minimal *n*-caproate selling price, as determined for a NPV of 0.

Product Stream	Annual Production	Price (EUR)	Revenue (x € 10^6)
Caproate	10,000 tonne	3924 per tonne*	39.2
Industrial Oxygen	108,000 m^3	376 per m^3	40.6
Total			79.8

process is to be implemented on industrial scale, an analysis on the industrial oxygen market is recommended.

For the direct route an MCSP of €3,584 per tonne is calculated (Luo et al. 2022). This route also produces industrial oxygen. In this route, the annual oxygen production is 257,970 m^3. When comparing the MCSP of the two routes, it can be seen that the MCSP of the indirect route is higher. The difference in MCSP is influenced by three factors; revenue, OPEX and depreciation.

When looking at the revenue of both routes, the direct route has a higher revenue stream. Both routes produce 10 kton of *n*-caproate annually. However, the flow of industrial oxygen produced is higher for the direct route. As a result, the overall generated revenue is higher. Secondly, in the current design, the energy demand of the direct route is lower. This influences the OPEX significantly, as previously described. The OPEX of the indirect route is about 1.7 times as large. The third factor is the depreciation. The depreciation is dictated by the equipment cost. Since the CAPEX of the direct route is lower, it is assumed that the equipment cost are also lower. As a result, less depreciation cost are annually made. To conclude, with the current design the direct route generates a higher revenue and has a lower OPEX and CAPEX.

4.6.3 Environmental Assessment

The environmental analysis consists of the calculation of the indirect route's carbon footprint, GHG reduction and its reduction potential. The GHG reduction compares the carbon footprint of the indirect route to the current production process. The GHG reduction potential also accounts for the market size of the product (Roh et al. 2020) (see also chapter 2).

Both the conventional route and the indirect route produce multiple products. Therefore, mass allocation is used to distribute the GHG emissions (Moncada et al. 2018). This is done following Equation 4.8.

$$AF_i = \frac{m_i}{\sum_{j=1}^{n} m_j} \tag{4.8}$$

AF	Allocation Factor
m	Product Flowrates
i, j	Counters for the Products

For the conventional route the products for mass allocation are palm oil and *n*-caproate. The indirect route has industrial oxygen, the final butyrate-rich stream and *n*-caproate as products.

Carbon Footprint of the Indirect Route

The carbon footprint of the production process is determined by calculating the carbon footprint of the raw materials, utilities and waste streams. The computation of the carbon footprint is done with the methodology developed by the IPCC (IPCC 2022). Here, the CO_2 equivalent emission factor of each material/utility is multiplied by its flow. An overview of the CO_2 equivalent emissions and the CO_2 calculation is shown in Appendix N. The indirect route has an annual CO_2 emission of ≈ 250 ktonne. The contribution of the raw materials, waste streams and each utility is depicted in Figure 4.10.

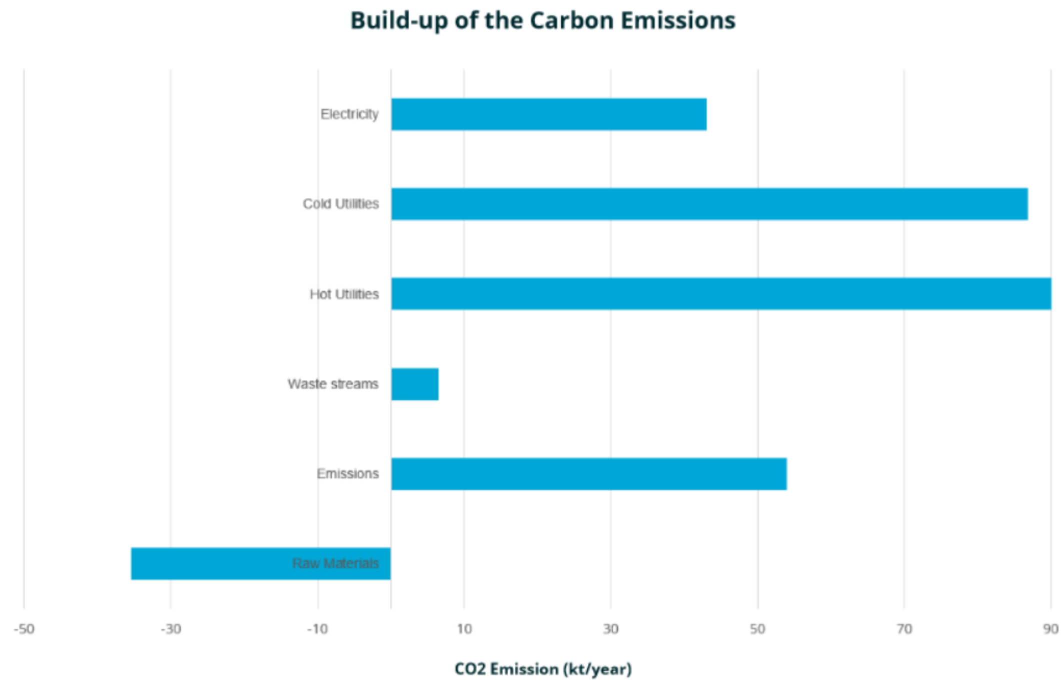

Figure 4.10: Overview of the contribution of the raw materials, waste streams, emissions and utilities to the total annual carbon emissions of the indirect route. The raw material input shows a negative carbon emissions, since it is dominated by the Porthos stream. Utilizing this CO_2 stream has a carbon emission factor of -1 $kg_{CO_2\text{, emitted}}/kg_{CO_2}$.

The build-up of the CO_2 emissions shows that these emissions are dominated by the direct CO_2 emissions and the utility usage. The direct CO_2 emissions are generated during the pre-treatment of the Porthos stream ($\approx$ 50% of the total emission) and during the fermentation ($\approx$ 50% of the total emission). Pre-treatment of the Porthos stream is required to remove sulfur components, which shorten the lifetime of the SOEC electrolyzer (Kushi 2017). Even though pre-treatment results in a longer lifetime of the SOEC, it also has a significant contribution to the carbon footprint. Therefore, it is recommended to perform an in-depth techno-economic and environmental assessment of alternatives for the SOEC. Another option is to perform the indirect route without pre-treatment and a shorter lifetime of the SOEC.

All three utilities have a significant contribution on the carbon emissions, but the heating and cooling requirements are dominant. This is in line with the expectation, since the energy usage of the indirect route is relatively large. The electrolyzers operate at a high pressure and temperature, resulting in a high energy usage. Furthermore, the down-stream processing also requires a significant amount of energy (see 4.6.1). Nevertheless, it is expected that the utility usage can be improved due to two factors. Firstly, heat integration in this study is minimal. Both hot and cold utility requirements are high. Optimal heat integration is expected to limit the usage of both (L. Wang et al. 2018). Secondly, the heating and cooling utilities are currently retrieved from natural gas usage. However, the energy mix of the Netherlands will shift towards 100% renewable in 2050 (Rijksverheid 2022). It is expected that the carbon footprint of each utility will therefore drop in the coming years.

The impact of the CO_2 emissions and utility usage is assessed in a sensitivity analysis (see Appendix O).

The carbon footprint of the produced *n*-caproate is calculated via mass allocation of the total annual emission. The product flow and corresponding allocation factor is shown in Table 4.14. Using an allocation factor of 0.29, the carbon footprint of the *n*-caproate is calculated following Equation 4.6.3.

$$\frac{AF_{Cap} \times annual\ CO_2\ \ emission}{Annual\ caproate\ production} \tag{4.9}$$

$$\frac{0.29 \times 250}{10} = 7.3\ kg_{CO_2}/kg_{caproate}$$

Table 4.14: Overview of the mass allocation factors of the indirect route.

Product	Flow (kt/yr)	Allocation Factor
Caproate	10	0.29
Industrial Oxygen	20	0.57
Butyrate-rich stream	5	0.14
TOTAL	**35**	**1**

Greenhouse Gas Reduction and its Reduction Potential

The current production process of n-caproate is via a palm oil refinery. which main product is refined palm kernel oil. On average, about 80% of the crude palm oil is upgraded to refined palm kernel oil (P. P. Kumar and Krishna 2014) (Tan and Nehdi 2012). The concentration of n-caproate in crude palm oil is $\approx$ 1% (Tan and Nehdi 2012). An overview of the allocation factors and the corresponding emission are shown in Table 4.15.

Table 4.15: Overview of the mass allocation factors of the conventional route.

Product	Allocation Factor	Carbon Footprint (kg_{CO_2} / $kg_{product}$)
Caproate	0.01	0.07
Refined palm oil	0.80	5.8
Other products	0.19	1.4

The carbon footprint of refined palm oil is around 5.8 kg_{CO_2} -eq/$kg_{\text{refined palm oil}}$ (J. Schmidt and De Rosa 2020). This carbon footprint encompasses, the stages of oil palm cultivation, milling and the refinery. The downstream life cycle stages, such as the usage of palm oil are excluded. Based on this CF, the emission allocated to n-caproate is calculated. The CF calculation shows the generally low CO_2 emissions allocated to n-caproate production via palm oil refineries.
From an investors' perspective it is interesting to see the GHG reduction potential as it shows the impact that the innovation can make (see Appendix D). Nonetheless, this comparison should be made with caution. Firstly, it is unlikely that the indirect route will substitute the conventional route. Solely 1% of the conventional route's production consists of n-caproate (J. Schmidt and De Rosa 2020). The focus of the indirect route is on reducing CO_2 emissions. Comparing both GHG emissions, even if allocated to n-caproate, is not representing the actual reduction potential.

However, this analysis does show that the carbon footprint of the current design of the indirect route is positive and significantly higher than conventional produced n-caproate. This highlights a major bottleneck that has to be overcome if the indirect route is ever to be implemented as effective CCU technology. Especially improvements in the utility usage and CO_2 off-gas recycling are required.

4.6.4 Competitive Advantage and Bottlenecks

The analysis of the quantitative performance indicators (Table 4.6) can be combined to find the competitive advantage and bottlenecks of the indirect route. Numerous definitions of 'competitive advantage' exist, but here it refers to factors leading to a better performance, return and/or value compared to other processes (Foss and Knudsen 2003). The competitive advantage can lie in a variety of aspects, such as the firm's resources, capabilities and/or market position (Sigalas and Economou 2013). Bottlenecks refer to the main factors hampering the overall performance.

Competitive Advantage

The competitive advantage of the indirect route should be discussed in comparison with the direct route. As can be seen in Table 4.6, the product selectivity towards n-caproate is considerable higher then in the direct route. However, in terms of economic and environmental performance, the indirect route performs worse.

Nonetheless, when considering implementation at the Port of Rotterdam, the following should be considered. Even though the overall route is complex, the route shows an excellent opportunity to be 'split'. For example, one can start with n-caproate production out of syngas. It is also possible to start with syngas formation and add the fermentation steps afterwards. It is advised to start with one part and focus on the second part later on. Splitting up the indirect route into these two blocks would considerably decrease the risk, as expressed by interviewee *GOV.INV #1*. Furthermore, it provides flexibility and the possibility for alternations based on the operating plant's characteristics.

Identified Bottlenecks

The analyses made in this report, show which parameters mostly influence the economic and environmental performance of the indirect route. These factors are;

1. The high energy demand of the electrolyzers.
2. The high capital cost of the electrolyzers, especially the AEL.
3. The n-caproate concentration retrieved during fermentation. (Leading to a high energy demand of the down-stream processing.)
4. The CO_2 off-gas emitted during pre-treatment.
5. The CO_2 off-gas emitted during fermentation.

It should be noted that some of the identified bottlenecks are expected to be overcome. Firstly, the energy efficiency and capital cost of the electrolyzers are expected to drastically improve in the coming 30 years (Taibi et al. 2020) (De Luna et al. 2019). For AEL, an energy efficiency increase of $\approx 30\%$ per kg H_2 and a price reduction of 25% is expected (Taibi et al. 2020). The capital cost of a SOEC are expected to decrease with 70% (Mathiesen et al. 2013). Another option is to implement a co-electrolyzer which combines H_2O and CO_2 electrolysis (H. Zhang and Desideri 2020). Implementing one electrolyzer instead of two could potentially limit capital cost. In this report, co-electrolysis is not considered since it has a TRL of 2 (Roh et al. 2020). Nonetheless, it can be interesting to follow its development and assess a scenario in which co-electrolysis replaces the AEL and SOEC.

Secondly, future research could look into the CO_2 off-gas produced during the pre-treatment and fermentation. A trade-off between the CO_2 emission and the impurity concentration need to be made. Higher levels of impurities lead to a shorter lifetime of the SOEC electrolyzer. Scenario's with different electrolyzers might result in different pre-treatment requirements. Since the (sulfur) impurity level in the Porthos stream is relatively low (20 ppm), it might be feasible to skip the pre-treatment. Furthermore, a scenario in which the fermentation off-gas is recycled to the SOEC could be researched. Another option to limit CO_2 emissions is by optimizing the syngas composition. As described in Jack et al. 2019, the product spectrum is influenced by the CO and H_2 content.

Chapter 5

Conclusion

In this chapter, the two research questions are answered. Based on these answers, the main research question is answered and elaborated upon.

5.1 Research Question #1

The first research question is: *"With which performance indicators do scientists and early-stage investors assess the overall performance of a CO_2 utilizing technology?"*. To answer this question, several steps are taken.

Firstly, the technological innovation system of the indirect route is drafted. This system enables the analysis of factors impacting the progression of the innovation. By using the TIS, systemic problems hampering CCU innovation at the Port of Rotterdam are found. These bottlenecks could not be retrieved solely from the interviews conducted. Bottlenecks hampering CCU development at the Port of Rotterdam are: missing capabilities at the actors, weak connections between the networks, insufficient funding and a lack of intellectual property protection.

Secondly, the stakeholders with a high influence and interest in low TRL CCU technologies at the Port are characterized. Interviewees are chosen based on the technological innovation system and the influence-interest grid. In total, 8 scientists working on CCU, 3 private early-stage investors, 2 governmental-funded early-stage investors, 1 governmental party and 1 NGO are interviewed. Based on these interviews and a literature review, the viewpoint of the stakeholders on the assessment of the indirect route is obtained. It is found that both scientists, as well as the investors assess such a technology differently. Scientists tend to analyze and weigh technical parameters significantly more than early-stage investors. On the contrary, early-stage investors use multiple strategical/organisational parameters. This is a category hardly used by scientists.

Another finding is that both stakeholder groups emphasize the importance of the quantitative economic and environmental performance. The quantitative view on sustainability by the investors is often not expected by the interviewed scientists. On the other hand, early-stage investors emphasize the importance of a trustworthy risk assessment. However, they tend to limit the amount of technical parameters assessed and view it merely as 'black-box'. It can be argued that encompassing more technical parameters could lead to a better risk assessment.

The interviews led to the addition of three parameters to the overall performance assessment. In total, the following performance indicators are assessed: 1) CO_2 Conversion Efficiency, 2) Specific Primary Energy Consumption, 3) Product Selectivity, 4) Technology Readiness Level, 5) Capital Expenditures, 6) Operational Expenditures, 7) Minimum n-Caproate Selling Price, 8) Carbon Footprint, 9) Greenhouse Gas Reduction

Potential, 10) Competitive Advantage.

Combining the findings of the TIS and the interviews showed the following. ESIs face a difficulty for the technology's risk assessment. This difficulty is caused by a lack of resources. A method to overcome this is by enhancing the connection between researchers and ESIs. Scientists can help ESIs with this risk assessment. On the other hand, scientists are advised to broaden their performance assessment with strategical parameters. This is an aspect at which ESIs can help scientists. The connection between scientists and ESIs can start by conducting interviews, as done in this research.

5.2 Research Question #2

The second research question is: *How does the technical, economic and environmental performance of the indirect route compare to the direct route and which improvements can be made to enhance its performance?*.

The parameters used to assess the environmental, technical and economic performance are those retrieved from the first research question. The quantification of these parameters is based on simulating the indirect route in Aspen plus. The obtained simulation is validated by checking the mass and energy balances. Furthermore, the yields and conversions of the simulation match experimental results, retrieved from various scientific papers.

An overview of the performance of the indirect route is shown in Table 5.1. The performance is split between the pre-treatment, the process and the down-stream processing. By doing so, insight is gained into which part of the process performs better/worse. Moreover, the performance of the direct route is shown to enable a comparison.

Table 5.1: Overview of the technical, economic and environmental assessment of both the direct and indirect route. An explanation of each parameter is described in chapter 4. Note that the direct route is excluding pre-treatment. *Based on; 1) Luo et al. 2022, 2) Jourdin et al. 2020, 3) Roy et al. 2022.*

		Indirect Route				Direct Route
		Pre-treatment	Production	DSP	Total	Total
TECHNICAL	*CO_2 Conversion efficiency*	72%	75%	-	54%	94%[1]
	Specific Primary Energy Cons.	0.005 GJ/kg_{Cap}	0.180 GJ/kg_{Cap}	0.166 GJ/kg_{Cap}	0.351 GJ/kg_{Cap}	0.1 GJ/kg_{Cap}[1]
	Product Selectivity	-	Caproate (1 kg/kg) Acetate (0 kg/kg) Butyrate (1.23 kg/kg) Biomass (0.69 kg/kg)	-	Caproate (1 kg/kg) Acetate (0 kg/kg) Butyrate (1.23 kg/kg) Biomass (0.69 kg/kg)	Caproate (1 kg/kg[2]) Acetate (7.40 kg/kg) Butyrate (2.71 kg/kg) Biomass (- kg/kg)
	TRL	9	3	4	3	3-4[3]
ECONOMIC	*CAPEX*	-	-	-	e 166,298,000	e 93,100,000[1]
	OPEX	-	-	-	e 58,725,000	e 34,000,000[1]
	Min. Caproate. Selling Price	-	-	-	€3924 per tonne	€3584 per tonne
ENVIRONMENTAL	*Carbon Footprint*	-	-	-	7.3 kg_{CO_2} /$kg_{Caproate}$	N/A

Looking at Table 4.6, the following conclusions can be drawn. First, the indirect route has a CO_2 conversion of 54%. This is lower than that of the direct route. Part of this is caused by the pre-treatment method, which is absent in the direct route's simulation. Another contributing factor to the lower CO_2 conversion is the emitting of the fermentor off-gas.

Secondly, the indirect route utilizes 0.35 GJ for the production of 1 kg of n-caproate. This is significantly larger than the energy requirement of the direct route. This energy usage is mainly dominated by the electrolyzers and high-energy demand of the downstream processing.

In terms of product selectivity, the indirect route performs better. For the production of 1 kg of n-caproate, less side-products are being made. This eases downstream processing and ensures that the highest price per carbon atom is reached. A downside of the indirect route is the biomass production, which adds complexity to the downstream processing. Nonetheless, formed biomass is an excellent opportunity to be used as energy source. This could lead to lower external energy source requirements.

The technology readiness levels of both routes are comparable. Even thought the indirect route contains technologies with a higher TRL, the technology with the lowest TRL dictates the overall classification. Therefore, the indirect route has a TRL of 3-4. The direct route is also in between 3-4.

In terms of economic performance, the indirect route has a higher CAPEX and OPEX compared to the direct route. The higher CAPEX is mainly caused by the costs of the alkaline electrolyzer. The higher OPEX follows from the high energy usage.

The CAPEX and OPEX also influence the minimum *n*-caproate selling price. This price is set at €3924 per tonne. For the direct route, the minimum price is €3584 per tonne. Factors mostly influencing this price are the revenue generated by the industrial oxygen sold, the costs on utility usage and the capital costs of the alkaline electrolyzer.

Lastly, the environmental performance of the indirect route is computed. No environmental assessment is available for the direct route. For the environmental performance, the carbon footprint and the GHG reduction potential are retrieved. The indirect route emits 7.3 kg CO_2 per kg of *n*-caproate. The current *n*-caproate production process emits 0.07 kg CO_2 per kg of *n*-caproate. One of the main important focus points of the indirect route is thus to reduce its carbon footprint.

It is desirable to decrease the emission of the indirect route, as the purpose is to reduce the amount of global CO_2 emissions. The size of the carbon footprint is mostly caused by the high utility usage. This might be overcome by looking into more sustainable energy sources and by limiting energy usage of the process. It is expected that a lot of potential for less utility usage is possible. Namely, the developed design had minimal heat integration and had conservative estimates on energy efficiency.

Nonetheless, the comparisons made in this report should be made with caution. The design and simulation of both the direct and indirect route is made on a range of assumptions. As both technologies are in an early-stage of development a high level of uncertainty is present. A sensitivity analysis is conducted to account for a part of this uncertainty. This analysis showed that the economic performance is significantly impacted by the alkaline electrolyzer cost, the electricity cost and the oxygen price. The carbon footprint is significantly dependent on the CO_2 emissions of the utilities.

5.3 Overall Conclusion

To conclude, the overall research question is answered. This question is: ***How is the ex-ante performance of the indirect route and direct route compared, taking both scientists' as well as early-stage investors' perspectives into account?***

Scientists and early-stage investors show different methods to compare the performance of low TRL CCU technologies. Nevertheless, their methods do show overlap. The early-stage investors focus on strategical, economical and environmental parameters. The scientists value technical, environmental and economical parameters more. Both groups lay an importance on economic and environmental profitability. Their differences lie within the focus on its technological performance or its strategical performance.

Based on the performance indicators assessed, the indirect route is at this moment, less favorable than the direct route. This is mainly caused by the following factors. Firstly, it has a relatively high utility usage caused by the electrolyzers and the low *n*-caproate concentration in the broth. Secondly, the capital expenditure is dominated by the alkaline electrolyzer. Thirdly, the revenue of the direct route is larger, since more industrial oxygen is produced. This factor contributes to the lower minimum *n*-caproate selling price of the direct route. Lastly, the relatively high utility usage, combined with the CO_2 conversion of 54% result in a net positive carbon footprint. It is desirable to reach net zero CO_2 emission. Part of these factors could potentially be improved by optimizing the pre-treatment method, implementing heat integration and reaching higher CO_2 conversion rates during fermentation.

Chapter 6

Limitations and Future Research

In this chapter some limitations of this study are discussed. Based on these limitations and the results found areas for future research are recommended.

Increase Robustness of the Pugh Matrix

The electrolyzers' characteristics have a significant impact on the indirect route's performance. The SOEC and AEL are chosen based on the Pugh matrices drafted. Pugh matrices are used due to their ability to handle a large number of decision criteria in a relatively easy manner (Pugh 2009). Furthermore, it makes decision making more objective and enables the comparison of qualitative and quantitative metrics (Pugh 2009). However, the Pugh matrix as applied in this research also has some weaknesses. Firstly, its criteria and the weight allocation to these are not validated by the group of stakeholders involved. The criteria are retrieved from literature reviews and weight allocation can in general be done by the researcher (e.g. (Mia et al. 2018)). Nonetheless, the outcome of the matrix would be more robust if assessed by the relevant stakeholders (Pugh 2009). Secondly, the outcomes of the Pugh matrix can be validated by adding a robustness analysis. This includes varying several scores to research its impact on the outcome (Pugh 2009). Thirdly, some aspects have a low granularity. This is an inherent characteristic of the Pugh matrix (Pugh 2009). The low granularity is expected to be especially relevant when looking at the CO_2 electrolyzers' impurity tolerance. In this research, a look into the impurity tolerance in general is given. For future research, it is advised to look specifically into the impurities present in the feedstream and its implications on the pre-treatment.

Increase Robustness of the Influence-Interest Grid

Similar to the Pugh-matrix, the robustness of the II-grid can be increased by involving the stakeholders. The stakeholders can be asked to rank themselves and other parties on the II-grid. This method does require a clearly communicated definition of 'influence' and 'interest'. Once the II-grid is drafted, it should also be checked by all stakeholders involved. This would enlarge the robustness of the II-grid (Bryson 2004).

Elaborate the comparison of the Indirect and Direct Route

Currently, the direct route is performing better at economical parameters. It also has a higher CO_2 conversion rate, but a carbon footprint is absent. It would be interesting to compare the carbon footprint of both technologies to be able to compare their environmental sustainability. Especially since the goal of CCU is to limit CO_2 emissions. The carbon footprint of the direct route can be calculated with the approach used in this study.

Enhance the Indirect Route's Performance

As stated previously, one of the factors hampering the indirect route's performance is the relatively high utility usage, CO_2 emission and electrolyzer cost. Several methods could potentially enhance the indirect route's performance.

Firstly, heat integration should be applied. This can be done via the Pinch Analysis or mathematical programming (Morar and Agachi 2010). By applying heat integration, the utility usage will decrease. Secondly, a scenario in which the formed biomass is used as energy source can be developed. Since the biomass leaving the reactor is wet, it has to be dried before it can be used as energy source. Future research could develop such a scenario and research if it results in an improved performance. Thirdly, scenario's with different type of electrolyzers can be researched. For example, a SOEC can be replaced by a molten carbonate electrolyzer, which has less strict pre-treatment requirements (Küngas 2020). Another option is to implement a co-electrolyzer. This single electrolyzer can produce syngas out of CO_2 and H_2O as well (Menon et al. 2015). Having an electrolyzer which can handle higher impurities is expected to result in less pre-treatment costs and less CO_2 emissions. A fourth option is to analyze the impact of various syngas compositions on the CO_2 emissions and production yields. As stated by Jack et al. 2019, changing the syngas composition also changes the product spectrum. This could lead to higher n-caproate yields and lower CO_2 emissions.

Include Policy Makers' Perspective in the Assessment

In this research early-stage investors and scientists are interviewed. Their perspective is taken into consideration as they are analyzed to have a high influence and interest. Other parties that have a high influence and interest are policy makers. These include the National Government and the European Union. The inclusion of these parties was out of scope for this research. Nonetheless, this stakeholder group can be included to enlarge the analysis on the different stakeholders' perspective.

Review the Role of Social Parameters in Cleantech Development

This research does not consider social parameters. Moreover, these parameters are minimally mentioned by the stakeholders interviewed. The participants that do mention the social parameters are mostly related to the national government. The social parameters might be underrepresented in this research as policy makers are out of scope. Future research might include policy makers and also focus more on the social aspects of sustainability. It can be interesting to see which role the social parameters play in e.g. the (governmental) funding and investment in cleantech.

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Contents

Appendix A

Personal Background and Interview Guide

A.1 Personal Background

As stated by Kincheloe 2011, a researcher's personal background and social position cannot be seen separately from the qualitative research (s)he conducts. Therefore, it is important to mention my background in the field of carbon capture and utilization technologies. I have worked for the past 6 years looking into novel bio-technologies with the objective to improve human health and/or decrease carbon emissions. I see climate change as the most pressing issue of the moment. During my studies, I have conducted research in the field of microbial electrosynthesis, sustainable aviation fuel production and (microbial) plastic recycling.

Next to my research interests, I have been donating to one of the NGOs mentioned in this report for over 3 years (not interviewed). I also have close contacts to some private equity firm employees. Their stories made me wonder how they guide their decision making and what their role in the energy transition can be.

It should be noted that I do not have a background in social sciences, nor am I experienced with conducting interviews. Biases are reduced to a minimum by applying the methodology as described in chapter 2.

A.2 Interview Guide

Previous to conducting the interviews, interview guides were drafted, both for the researchers working on CCU technologies and for investing parties. These guides were tested and revised. The revised versions are shown below. Keep in mind, that the interview format used is semi-structured. This means that deviations from this guide were anticipated on and encouraged.

Interview Guide used for Interviewing Scientists

When interviewing scientists the following questions were asked.

1. Could you tell me something about yourself?
2. What was/is your motivation to work in this research field?
3. What would you say is the overall goal of your research?

After these questions a brief summary of the *n*-caproate production technology as discussed in this report was given. When the technology was understood by the participant, the following questions were asked.

4. Do you think that commercial application of the designed process or of one of the technologies that it uses can be reached? Why?
5. Do you think certain parameters have to be reached before successful commercialization is possible?
6. Which parameters would you use to assess and compare these type of CCU technologies? Are they the same parameters as those important for commercialization?
7. How do you assess and determine these parameters?
8. In your opinion, how do you think that early-stage investors would assess the discussed route?
9. How do you think they assess an investment opportunity and which parameters are important to them?
10. Is there anything else that you would like to share about this topic or that you want to point out?

Interview Guide used for Interviewing Investors and Governmental Parties

When interviewing investors (both governmental funded and private funded) the following questions were asked. These questions are also similar to the questions addressed to the governmental party.

1. Could you tell me something about yourself?
2. What has been and is your motivation to work in this sector?
3. What type of cleantech investments does your party has in its portfolio? What is your budget for these type of technologies?
4. Which role do you play in stimulating innovation and up-scaling of sustainable technologies?

After these questions a brief summary of the *n*-caproate production technology as discussed in this report was given. When the technology was understood by the participant, the following questions were asked.

5. How would you assess this investment opportunity? Which method do you use?
6. Which target indicators do you use for its assessment and are these different than for other cleantech investments?
7. Which parameters are more important for a lower TRL cleantech investment? Is it different than for a higher TRL?
8. From your perspective, how do you think that scientists compare different cleantech options? Which parameters do they find important?
9. Is there in your opinion a gap between the focus of investors and of scientists? If so, where is this gap?
10. Is there anything else that you would like to share about this topic or that you want to point out?

Appendix B

Literature Review on Parameters to assess the Technology's Performance

The parameters identified via literature research are shown. When parameters show large dependency on each other, they are grouped as one. The parameters are identified for both a scientific and an early-stage investor's perspective.

The parameters from a scientists' perspective are retrieved by looking into specific technologies. These technologies are; microbial electrosynthesis, syngas fermentation and carbon capture & utilization technologies.

The parameters describing the perspective of early-stage investors are retrieved by looking into papers discussing cleantech investments.

B.1 Parameters from a Scientist's Perspective

The parameters from a scientist's perspective are shown in Table B.1 and Table B.2.

B.2 Parameters from an Early-stage Investor's Perspective

The parameters from an early-stage investor's perspective are shown in Table B.3.

Table B.1: Overview of the parameters to assess relevant technologies performance [1/2]. The parameters are retrieved from literature research. The parameters that have a large dependency on each other are grouped.

Category	Parameter	Sources	Grouped Parameters
Economic	Levelised costs of chemicals	Wood et al. 2021	Minimum product selling price
Economic	CAPEX	Wood et al. 2021	CAPEX
Economic	OPEX	Wood et al. 2021	OPEX
Economic	Expected profit	Wood et al. 2021	Profit
Economic	Cash flows	Wood et al. 2021	Annual cash flow
Technical	Plant life	Wood et al. 2021	Plant operational life time
Technical	Plant capacity	Wood et al. 2021	Plant production capacity
Economic	Hurdle rate	Wood et al. 2021	Hurdle rate
Technical	Construction period	Wood et al. 2021	Construction period
Technical	Faradaic Efficiency	Jourdin et al. 2020	Energy efficiency
Technical	e- distribution into products	Jourdin et al. 2020	Energy efficiency
Technical	CO2 conversion efficiency	Jourdin et al. 2020	Substrate conversion efficiency
Technical	Product(s) concentration	Jourdin et al. 2020	Product concentration
Technical	Substrate conversion efficiency	Jourdin et al. 2020	Substrate conversion efficiency
Economic	Electricity cost	Jourdin et al. 2020	Energy usage
Economic	Water cost	Jourdin et al. 2020	Water usage
Economic	CO2 cost or revenue	Jourdin et al. 2020	Minimum product selling price
Economic	Organic waste stream cost	Jourdin et al. 2020	OPEX
Environmental	Wastewater treatment	Jourdin et al. 2020	Waste generation and treatment
Economic	Plant production capacity	Jourdin et al. 2020	Plant production capacity
Economic	Gross Margin	Verma, B. Kim, et al. 2016	Gross profit margin
Technical	Operating cell potential	Verma, B. Kim, et al. 2016	Energy usage
Technical	Faradaic Efficiency	Verma, B. Kim, et al. 2016	Energy efficiency
Technical	TRL	Jarvis and Samsatli 2018	TRL
Technical	Plant operational life time	Jarvis and Samsatli 2018	Plant operational life time
Economic	CAPEX	Jarvis and Samsatli 2018	CAPEX
Economic	OPEX	Jarvis and Samsatli 2018	OPEX
Economic	Product price	Jarvis and Samsatli 2018	Minimum product selling price
Environmental	Electricity usage	Jarvis and Samsatli 2018	Energy usage
Environmental	Net CO2 utilization	Jarvis and Samsatli 2018	CO2 utilization
Environmental	Carbon utilization efficiency	Roh et al. 2020	Substrate conversion efficiency
Environmental	Primary energy efficiency	Roh et al. 2020	Energy efficiency
Environmental	Specific primary energy consumption	Roh et al. 2020	Energy usage
Environmental	Carbon footprint of the CU product	Roh et al. 2020	Carbon footprint
Environmental	Specific GHG reduction	Roh et al. 2020	GHG reduction
Environmental	GHG reduction potential	Roh et al. 2020	GHG reduction potential
Economic	Direct operating cost	Roh et al. 2020	Minimum product selling price
Economic	Gross operating margin	Roh et al. 2020	Gross operating margin
Environmental	GHG Avoidance cost	Roh et al. 2020	GHG Avoidance cost
Economic	CO2 cost	Somoza-Tornos et al. 2021	Minimum product selling price
Economic	Electrolyzer electricity	Somoza-Tornos et al. 2021	Energy usage
Economic	OPEX	Somoza-Tornos et al. 2021	OPEX
Economic	CAPEX	Somoza-Tornos et al. 2021	CAPEX
Environmental	Global Warming Impact	Somoza-Tornos et al. 2021	GHG Reduction potential

Table B.2: Overview of the parameters to assess relevant technologies performance [2/2]. The parameters are retrieved from literature research. The parameters that have a large dependency on each other are grouped.

Category	Parameter	Sources	Grouped Parameters
Economic	Production cost of product	Munasinghe and Khanal 2010	Minimum product selling price
Technical	Fermentation yield	Munasinghe and Khanal 2010	Substrate conversion efficiency
Economic	Total production costs	X. Sun et al. 2019	Total production costs
Economic	Minimum product selling price	X. Sun et al. 2019	Minimum product selling price
Economic	Total capital investment	de Medeiros, Noorman, et al. 2020	CAPEX
Economic	Minimum product selling price	de Medeiros, Noorman, et al. 2020	Minimum product selling price
Technical	Heat efficiency	de Medeiros, Noorman, et al. 2020	Energy efficiency
Economic	CAPEX	de Medeiros, Noorman, et al. 2020	CAPEX
Economic	OPEX	de Medeiros, Noorman, et al. 2020	OPEX

Table B.3: Overview of the parameters used by early-stage investors to assess cleantech investment opportunities. The parameters are retrieved from literature research. The parameters that have a large dependency on each other are grouped.

Category	Parameter	Sources	Grouped Parameters
Technical	Scalable process	Hargadon and Kenney 2011	Scalability
Economic	Return on investment	Gaddy et al. 2017	Return on investment
Economic	Risk	Gaddy et al. 2017	Risk of investment
Economic	Market size and growth	Hargadon and Kenney 2011	Market growth rate
Economic	Potential for large and rapid payoff	Hargadon and Kenney 2011	Potential for easy liquidation
Environmental	Preparing for the energy transition	Hegeman and Sørheim 2021	Preparing for energy transition
Environmental	Exploring the possibility for a more sustainable portfolio	Hegeman and Sørheim 2021	Preparing for energy transition
Social	Contribute to local knowledge creation	Hegeman and Sørheim 2021	Local knowledge creation
Social	Contribute to local entrepreneurship	Hegeman and Sørheim 2021	Local entrepreneurship
Strategic	Obtaining strategic returns	Hegeman and Sørheim 2021	Strategic returns
Strategic	Widening client base	Hegeman and Sørheim 2021	Widening client base

Appendix C

Participant List

Some characteristics of the participants of the semi-structured interviews are shown in Table C.1.

For each participant his/her function or career moment is mentioned. In order to ensure the anonymity of the scientists, it is chosen to rank their position as 'junior', 'medior' or 'senior'. This ranking is based on Faniko et al. 2022. 'Junior' refers to PhD candidates. 'Medior' is used to describe postdocs, senior researchers and assistant professors. Lastly, 'senior' entails associate professors and full professorship positions.

The investing parties were asked to give an indication of their budget available and the average ticket size of an investment. Note that their given budget range shows the budget specifically for cleantech or 'high-risk' investments. Different budgets were available for conventional investments. In terms of ticket size, these values should be seen as an rough indication of the size of projects that they are interested in, not as a clear minimum or maximum. As stated by participant *ESI #2*, when deciding upon an investment, the terms at which is invested play a large role on the investment size as well.

Table C.1: Overview of the list and characteristics of participants. 'FO' refers to family offices, 'VC' to venture capitalist and 'PE' to private equity. 'Junior' refers to PhD candidates, 'medior' to postdocs, senior researchers and assistant professors. 'Senior' refers to associate professors and full professors. The budget of investors is given as: 'k'; thousand, 'mln'; million, 'bln'; billion, 'n.a.'; not applicable.

ID	Party	Function / Career Moment	Budget Range (EUR)	Av. Ticket size (EUR)
GOV.INV. #1	Governmental Investor	Investment Manager	1-5 bln	5-25 mln
GOV.INV. #2	Governmental Investor	Investment Analyst	100-150 mln	200k - 10 mln
GOV. #1	Governmental Party	Subsidy coordinator	10-15 bln	n.a.
ESI #1	FO/VC	Managing Dir. of Investments	200-250 mln	100k - 5 mln
ESI #2	FO/VC	Board Member / Dir. of Investments	350-400 mln	1-5 million
ESI #3	VC/PE	Board Member	400-450 mln	50-200 million
SCI #1	e-refinery/University	Junior	n.a.	n.a.
SCI #2	e-refinery/University	Senior	n.a.	n.a.
SCI #3	University	Junior	n.a.	n.a.
SCI #4	University	Junior	n.a.	n.a.
SCI #5	University	Medior	n.a.	n.a.
SCI #6	University	Medior	n.a.	n.a.
SCI #7	University	Medior	n.a.	n.a.
SCI #8	University	Senior	n.a.	n.a.
NGO #1	Non-governmental institution	Advisor Sustainable Ports & Industry	n.a.	n.a.

Appendix D

Interview Summaries

In this Appendix the summaries of the conducted interviews are given. The participants are categorized into scientists, early-stage investors, governmental funded investors, governmental parties and NGOs.

D.1 Governmental Funded Investors

Governmental Funded Investor #1

Background Information

Personally, I see climate change as the biggest threat that we are facing today. I really value that we are a party that plays an active role in mitigating this issue. We stimulate start-ups which enable CO_2 reduction, as this is not being done enough by the market. By doing so, we make the world a bit better.

Assessment of Investment Opportunity

On a high level, we look at the impact, risk and return of an investment. First of all, a process has to be commercially viable to be financed. The time horizon in which this viability is reached can be 10- 15 years, which is a longer timeframe than generally taken by other investment parties. Since we are a governmental party, we can only fund up to 50% of an investment. The other part should come from the private sector. The private investment parties are also the sector that determine the value of a business case. Next to this, we have our own model to determine our internal return requirements, to check if the investment fits the minimum return goal that we have.

Next to the commercial viability, we use a model that looks at the TRL, (level of) IP protection/infringement and the quality of the management team. The lower the TRL, the more complex it is to determine these indicators. These parameters are used to reflect the amount of risk that is present. We are able to bear quite a large risk and are also willing to take high risks compared to other investing parties.

As a third factor, we look at impact. Impact refers to which product or process you will replace, which part of its market and what is your efficiency gain?

Before an investment is made, we always do an ESG and KYC check. These checks are always performed, but the focus can be different per project. When looking at an investment at the Port of Rotterdam, we would focus on risks. Are hazardous chemicals used and how is waste handled? What is the risk of explosion or other type of accidents? What is the impact on the region and its inhabitants?

In terms of KPI, the following three indicators are important; CO_2 reduction potential, FTE and 'RD'. However, both FTE and RD are points of discussion. For 'RD', the question is how to define and measure it. With FTE this is more clear, but it is difficult to set the trade-off between CO_2 emission reduction and FTE creation. If a investment opportunity, compared to another option, has less FTE creation, but enables more CO_2 reduction, are you then going to reject it?

Factors important at a lower TRL

When looking at a lower TRL, the factors described above might not yet be very clear. The following parameters become then more important; product market size, scalability of the process, CO_2 reduction enabled, availability of other [not CO_2] feedstock, harmfulness of the chemicals released and the LCA. An LCA can be difficult at a low TRL, so you have to see to which extend it can be performed. A large part of the assessment of these parameters are making assumptions.

In general, we have a broad range of investments in our portfolio, so the KPI's differ per case.

Case specific parameters

In your case *[producing caproate via syngas formation and fermentation]*, you can split the required investments in two parts. Firstly you need funding to further develop the technology and secondly you need funding to build the plant in the Port of Rotterdam and actually produce your caproate. I would focus mostly on the risks of this investment. The risk consists if several aspects.

First Risk Aspect

Investors generally view this process as something goes into your plant and something gets out. The margin between the in and outgoing is very important. In your case, there is no price relation between CO_2 and caproate. It can then be very important to make sure that you can buy the CO_2 at a fixed price from your producers. Furthermore, it is a big advantage if you set-up a long-term sales deal with customers of caproate.

Note, it is important to define your benchmark. Are you aiming to replace the current mode of caproate production, or are you aiming to substitute another product? This impacts which market you are looking at and thus the effect that you have on the market. Maybe one pilot plant does not impact the market, but also consider building multiple plants.

Second Risk Aspect

Secondly, I would want to know if it is difficult to build the plant. This difficulty is determined by looking at aspects like; is it the first-time plant and does it consist of novel and risky equipment. In your case it is a first-time plant, but the equipment and processing steps seem not very complex to me.

Third Risk Aspect

Another risk factor is the risk of competitors. You want to know how easy another party can do the same. An important metric for this is its IP protection.

A way to limit the risk is to let another party produce the syngas. You can then focus on the fermentation. Otherwise you have to optimize both the electrolysis and the fermentation. This is quite ambitious so to say, so maybe you can start a partnership with companies that build electrolysers.

View on Scientists' Perspective

The difference between us and scientists, is that scientists' main focus is on discovering novelties. This makes sense, since their metric is 'publications' and you cannot publish something if it is not novel. As investor, you prefer to use and scale-up something once it is proven. You do not focus on further researching it.

In a way, you could say that by conducting their research, scientists do focus on the component ‘impact’. Furthermore, they are also well aware that a process should be financially viable, so I think the aspect ‘return’ is also covered. However, in my opinion, the ‘risk’ aspect is a bit lacking. The focus is a lot on reaching the highest efficiencies and conversions and the price complementing this. However, the risk from translating something from lab scale to a large scale is often not really accounted for.

Governmental Funded Investor #2

Background Information

I have a background in Engineering. I want to use this background to build a bridge between investments and the energy transition. This is one of the reasons why I work at this company.

Personally, I feel that financing is often the bottleneck in realizing and commercializing disruptive engineering innovations. I think that the importance of suitable and directed investments will be key in facilitating the Energy transition, which we desperately need.

Assessment of Investment Opportunity

When looking at the technology you propose, I would say that there are multiple methods to reach commercialization. You could license the IP and have someone else build it, partner a corporate who can develop the plant with all its utilities and put your focus on the fermentation part, do everything together in a consortium, or start a company and do everything yourself. Depending on the business-plan a different method to assess the opportunity would be suitable.

If you would start your own company focusing on the syngas formation and fermentation, we would first check if the start-up fits our mandate. This mandate includes the location of the company and where it has its impact (both social as environmental), TRL, CO_2 reduction potential, size of investment required and the presence of co-investors. We can only finance up to 50% of a start-up, the remaining part should be financed by investors from the private sector. Furthermore, the benchmark for CO_2 emission reduction is 100 kton in 5 years.

If an investment fits our mandate, I would look at the following aspects: the team, the technology/IP roadmap, the market potential of the product, the competition in the branche, the financials, potential partners, the funding need and the company's use of funds, the capitable potential, minimal usage of scarce or harmful materials, risk of failure and the social governance and diversity clauses. It is difficult to make a ranking of importance for these indicators, since they can balance each other out. For example, less CO_2 reduction can be balanced out by more job creation.

When looking at a technology with a lower TRL, the following indicators become more important: IP ownership, the team and the (expected) market size and growth of the product of interest. The potential of a technology should be bigger at an earlier TRL in order to get the same valuation as other investments.

With IP ownership, we try to assess the novelty of the technology. Can you patent the technology? Is there a chance that other firms had patented a part of your process? The characteristics of the team working in the start-up are also very important. Characteristics that we are looking for in a team are; diversity, critical thinking, relevant skills and background knowledge and (financial) planning. The team can give trust to the assumptions made about the business case.

It is also very important to address if the technology is really offering a solution to the problem. Often a solution is thought of without connecting to the party that has the problem and seeing which solution they want.

View on Scientists' and Investors' Perspective

Keep in mind that all aspects of an investment opportunity can be assessed, but these outcomes cannot be measured on the same scale. The investment decision is often made based on gut feeling and experience. I think that having an Engineering background can help investors making better cleantech investment decisions. It helps them to grasp the concepts and technological risk that the innovation entails.

In my experience, investors are only looking at the technology as a risk. It is viewed as a 'black-box' model with a certain likelihood of reaching a promised yield. Without understanding of the technology, this risk estimate can be completely off. Here, scientists can play a role, since they often have knowledge about competing technologies on technical aspects. For example, they might be aware of the differences in energy usage or catalyst need of different technologies. However, they are less skilled in comparing the investment opportunity to other non-competing technologies. Based on these findings, I would highly support the following;

- Collaboration between researchers at universities and investors should be enhanced. They can complement each other's knowledge for the assessment of an investment opportunity.
- Venture capitalists, private equity companies and incumbent firms should integrate more people with an Engineering Background in their investment teams. Often these companies hire an external party to perform an assessment of a certain technology. However, then there will always be a step in which information is lost.

D.2 Governmental Parties

Governmental Party #1

Different views on Parameters important for CCU Assessment

In general, there are two different views on CCU at governmental institutions.

View 1: Climate Perspective
The first view, which is also my personal view, is looking at it from a climate's perspective. This means that CO_2 reduction is the starting point. When you try to address the CO_2 reduction of a technology, life cycle assessments (LCAs) are the most important. An LCA mainly looks at the origin of the CO_2 and the origin of the energy you use. Other factors do also count, dependent on your process. However, these two origins are the most important. Based on the LCA you can see if and within which boundaries the CCU technology can work.

For CCU it would be better if the CO_2 source is biogenic instead of fossil-based. Of course, when you use fossil-based CO_2 , you procrastinate CO_2 emission and prevent some of the usage of virgin oil. However, in a world in which we want to achieve zero emissions, this method does not fit. Its CO_2 reduction is too small.

When a CO_2 source comes from a biogenic source or via direct air capture, the timescale is much shorter. The CO_2 is still emitted, but its impact on the atmosphere is neglectable.

Setting the boundaries of the LCA is very difficult and we, *[the Dutch Government]*, do not have specific rules for it. When assessing a project, we want to have the LCA as broad as possible. However, we are not yet very familiar with LCA assessments and are looking to incorporate it more. This also has to do with the absence of scientific consensus on the LCA. The research conducted by Andrea Ramirez is something that we look into for the LCA assessments of potential projects.

We, as stakeholder, are also working on integrating the Sustainable Development Goals (SDGs) into our assessment of new innovations. However, we are still looking for a suitable method to do so. At the moment, the main focus is on the CO_2 emission reduction.

View 2: Industry's Perspective
The other perspective is from a industry point of view. At the moment the industry uses a lot of carbon and this need will remain in the future. Therefore, a carbon source will be required, indicating the need to create a carbon circle neutral to the CO_2 present in the atmosphere. When looking from this perspective, it is important to look at two points. 1) What does it replace and 2) which time period will it stay out of the atmosphere? Even when energy sources are changing to hydrogen and electricity instead of hydrocarbons, there are still processes requiring a carbon input. In the future, it should be assessed where this carbon comes from, but the reduction of CO_2 emission has a priority at the moment.

Currently, most regulations are drafted from the first perspective, but a discussion is present to incorporate the second perspective more.

Assessment of CCU Technologies

When looking at which routes have the potential to make an impact, we look at the (technical) LCA, as explained previously. Next to this the following factors play a role: the fit and potential of the technology for the Netherlands, the (national) knowledge already present about this technology and the TRL/maturity of a technology. CCU is a very broad group of technologies, so when assessing which type of CCU route would fit, these factors are important.

Fit of the Technology
When looking at the fit of the technology to the Netherlands, we look at the Dutch characteristics. For example, we *[the Netherlands]* do not necessarily have a large and cheap renewable energy source. If your process requires hydrogen, you have to assess if it is feasible to produce it in the Netherlands, or to import it from a country who is more fit for its production. This discussion can be followed-up by, why should we import the hydrogen and not the chemical product of the CCU process?

Of course, opinions about the ability for renewable energy production in the Netherlands vary. It is also very much focused on hydrogen as the future energy carrier. Keep in mind that it is very difficult to quantify the 'fit with the Netherlands' and to reject projects based on this.

Next to this, the Dutch infrastructure should be fit for the technology. In the case of CCU, the Porthos infrastructure and the Delta Corridor are very valuable. Both projects are building a backbone for CO_2 and/or hydrogen transport that different parties can use. So, when a project uses this infrastructure, it can be seen as an advantage.

Present (national) knowledge of the Technology
Here, we assess the knowledge of the Netherlands on a technology. In general, we have a strong knowledge position in the field of CCU. Dutch universities and also institutions such as TNO, Avantium and the Institute for Sustainable Process Technology conduct research focused on CCU. This has its origin in the strong chemical sector of the Netherlands and the oil-refineries that we have. Due to this origin in chemicals and refineries, it does make sense to have the next generation of energy production in the Netherlands.

Different assessments based on TRL level

Up to TRL 6, we are not critically looking at its geographical location. Once, the scale-up phase starts, we do consider that the technology should be able to commercially operate within the Netherlands.

However, our policy is based on the climate guidelines set for 2030. This means that you should have at least a first demo-plant and a pathway to reach commercialization in 2030. Furthermore, different requirements are present for different TRLs. For a pilot, the technology should be (scientifically) novel worldwide. Here, our role is also to interfere with market failure, as private investors do not want to bear the risk. Contrary to pilots, demonstration plants can use a technology that has already been shown before.

Political view on CCU

A problem with CCU is that no clear CO_2 reduction 'amount' has been set for it. When you look at the climate policy that the Dutch government has set for the industry, several measures that they can take to reach emission reduction are mentioned. However, these measures never include CCU. The reason behind this is that it has never been proven that CCU has a significant contribution to CO_2 reduction. We are not sure if it eventually will be needed. So a discussion about when, and in which situations CCU can contribute has to be held.

On top of that, the European Union has added a restriction for national governments to support CCU investment projects. Phases earlier than the demonstration plant (R&D and pilot) can be subsidized by the national government. After these phases the project becomes an investment project. Governmental support for CCU investment projects is blocked by European legislation. This restriction is set as it has not been proven that the party executing the CCU process has a protective effect on the environment. The building of a demonstration plant is followed by market introduction and scale-up. For this phase governmental support is possible, as the subsidy specific for this phase is an explicit exception on European legislation.

Context in which CCU has added value

In my opinion, the advantage of CCU over other sustainable technologies is the possibility to make 'tailor-made' chemicals. This gives you a flexibility. For example, CCU could focus on producing sustainable aviation fuel. The production of sustainable aviation fuel is very difficult, but will be required in the future. Alternatives such as electric airplanes are not possible according to experts and other modes of transport substituting airplanes are also not likely. However, for CCU to produce bio-kerosine a lot of energy has to be put into the process. On top of this, the CO_2 is quickly emitted when being used. So this is still quite a challenge.

To conclude, you should look for niche applications where sustainable alternatives are absent and the value of your 'tailor-made' chemicals is larger.

D.3 Early-Stage Investors

Early-Stage Investor #1

Background Information

The origin of our company is in agriculture. Nowadays, our company is moving more and more into investments in technology start-ups. We like everything that is disruptive in a way, so it can be biotech, but also artificial intelligence related. For me personally, I wanted to work in private equity or venture capital. I picked this firm because it is relatively small and I was already acquainted with the CEO. At our firm you get a lot of responsibilities and freedom starting at your first day. This helps you to learn very fast and develop yourself. I would say that challenging myself and developing my skills are two of my main personal goals.

Assessment of Investment Opportunity

I always immediately think about the following questions: 1) Is there a market for this company? 2) Can it bring a product to the market at low production costs? 3) Does this company has a future? 4) Which value does this company have and do want to 'hop on' at this value?

Furthermore a lot of subjective factors play a role, especially about the people in the start-up. It may sound a bit weird, but we want to like the people within the start-up and know if they have the qualities that we are looking for. We look at their education, their achievements at previous companies/entrepreneurial activities and if they are capable of leading a company. I also highly value the feeling that I get when I sit around a table with them.

Economic Factors

Next to the above mentioned factors, we mostly look at financials. We want to know the product costs per unit and its potential price. For a chemical process, this includes the price of the substrates, the energy price/usage (price can fluctuate heavily) and the product price. If the margin between the costs and selling price is large enough, it becomes okay to, for example, build an expensive factory. These 'unit economics' are the most important. If these are positive, we also want to know the CAPEX and the payback time. You can use that to calculate all the other stuff, such as IRR *[internal rate of return]*, NPV *[net present value]* etc.

In my opinion the entrepreneur has to present these economic metrics to me. But that does not mean that I use his/her values. I use the unit economics to calculate the economic metrics myself. However, I want to know if the entrepreneur has the skills to make these type of calculations and know what they mean. Then, I compare our values and we start negotiating.

If a company already has had some sales, I want to know how they get these sales. How much marketing and sales costs did they have to achieve their sales? However, if a company is in the phase previous to sales, this all becomes very speculative. They always show you sales going from zero to a few million in a couple of years. This just tells me very little. Without sales, it becomes harder to evaluate a company's worth and the risk gets higher.

Specifically, we did invest in a company when there were no sales at the point of investment. This company now generates revenue, but I still think we invested too much in them compared to the revenue that they currently generate. This altered my attitude towards these type of investments. We are much more aware of the risks of these type of companies. But of course, each case is different. It all depends on the value that a company has compared to its revenue. We would still invest in companies with zero sales if it is a good business case.

The main important parameters to look at for a company that did not have any sales are: 1) unit economics 2) large market size 3) the team.

What is a good business case?

In my opinion the follow factors make a good business case. The most important are the people that lead the company. If these leaders have a very good track record, it helps a lot. This gives you more belief in the numbers that they present you. I have less faith in two newbies who have not achieved anything in corporate business, but did follow an excellent education. I always look at the numbers, but in a very early phase, the people behind it give the numbers credibility. If Elon Musk would come to me and gives some projections about why humankind want to purchase his product X in 10 years, I would be more likely to believe it then when someone fresh from the university would.

Furthermore, we always keep the exit strategy in mind. An exit can be through multiple ways, it can be an IPO *[initial public offering]*, selling our shares to another (investment) company. This exit strategy is dependent on the phase in which this company is. We invest in several stages, from seed funding up until series F. For seed funding up until series B, we invest on our 'own'. For larger series, we invest via a fund.

A third factor that plays a role is if a party in our network invests in it. A significant part of our investment opportunities reach us via our network. It can be because we already know the entrepreneurs and they approach us, or because another investment party informs us and asks if we want to join.

Environmental Factors

We want a company to run on a timeframe of ¿10 years, so we look at the sustainability of a company. We only invest if it suits our sustainability demands. For example, I would never invest in an oil field. However, since we are a small firm, our assessment of sustainability is a bit blunt and not very quantitative. The reason of this is two-fold. Firstly, we do not have expertise in assessments such as a carbon footprint analysis or similar analyses. Secondly, we do not have to report to an external party, as we are a family company. The shareholders have their own intrinsic motivation to be sustainable, so all investment decisions that we make, are based on innovations improving something that we care about.

Our sustainability assessment consists of grouping investment opportunities into three categories. These categories are: 'sustainable' , 'neutral' and 'not sustainable'. For the assessment of sustainability we value a lot if the novelty of the company improves the current situation. With 'improvement' I mean that it has a positive CO_2 impact. So, if this company would not be present and the status quo would stay, would the CO_2 emission be worse? The CO_2 impact includes CO_2 emitted by the process energy consumption. This assessment is based on 'common sense' and logic. It is not very quantitative.

If they company was larger, we would focus more on quantitative life cycle analyses. However, we do not have the FTE and expertise for it at the moment. In the future, we would want to improve our method of environmental analysis. Since we do not have this expertise, we value it highly if the people presenting their business case have conducted these environmental analyses. We always want to see what their CO_2 reduction is compared to the status quo. Parties often present this to me as 'tree equivalents' or 'cars equivalent' or something like that. I do not care which equivalent you use, I want the quantitative number of reduction in CO_2 .

For chemical processes, some additional sustainability factors play a role. You have to be aware of handling hazardous chemicals safely and having proper waste disposal. Next to this, I am also interested in the nitrogen emission because of the political debate that is currently happening. However, the CO_2 emission is the most important environmental factor.

Parameters more important when looking at a low TRL

Well, if a technology is really novel and innovative, we work with a longer payback time. An average payback time would be 5 to 10 years. For a novel sustainable technology this can be 15-20 years. In my opinion, there also is a role of the government to play in the cleantech segment. At a lower TRL, the risk is higher. The government or governmental investors should be involved to bear a part of this risk. This will stimulate private investors to invest as well.

I think that the first up-scaled CCU plant would probably be making economic losses. Nevertheless, it could have other advantages in terms of knowledge creation and emission reduction. With the current business case, I, as a private company, cannot invest in it. We are not a charity. If it was up to me, I would say that the government should step in with subsidies to cover for these economic losses. In a way this is happening with the carbon credit system. I think this system is not really functioning yet in Europe, but it is a start. I think that you should directly tax CO_2 . As a results, using CO_2 as a substrate would provide you with money. The price of CO_2 should be steered by the European Union and grow over time. This gives the incentive to limit CO_2 emissions.

Another reason to invest at a low TRL could be to help it develop further and then sell the technology to a large polluting incumbent firm. But for me, it is very difficult to assess how much resources are still needed to bring a technology at such a low TRL to the next phase. As a result, I cannot give a specific value to the investment. This makes it more difficult and more risky to invest compared to other type of business cases.

View on Scientists' Perspective

In my opinion, I think that scientists working on these type of technologies are very much focused on the percentage of CO_2 that is converted into their product. I think that they are less focused on the costs that accompany this high conversion. They stir their research into reaching higher conversion efficiencies, not on limiting costs. For example, if you have option A which is 90% efficient and option B which is 60% efficient. If A is twice the price of B, I prefer having two times B.

I do not think it is 'wrong' or anything that they focus on the technological aspects. It is why they chose to be a researcher and, you know, maybe the economics will follow if the technology improves. I am not really sure, but I do think that if you want a technology to be deployed in society, you have to 'optimize the business case' instead of optimize the technology.

Early-Stage Investor #2

Background Information

Our core business has been in retail property for over 50 years. However, approximately 10 years ago we started to diversify our investment portfolio, also looking into more international businesses. Investing in these type of projects *[cleantech projects]* is quite new to our company. We do not really have a separate budget for cleantech, but do want to have approximately 20% of our portfolio in Private Equity.

Assessment of Investment Opportunity

The most important for us is to target an investment on a return basis. At the moment cleantech can be interesting due to government support and changes in gas prices. I think that these two factors will cause renewable energy projects to become economically viable. It is also a type of investment that limits the downside risk, as sustainable energy projects are here to stay. However, we do not really account for the environmental benefits on itself when assessing an investment.

The metrics that I use are mainly the discounted cash flow. I use this to estimate what the business is worth. The other option is to use the internal rate of return. The ROIC (Return on Invested Capital) within the business is for me quite an important thing as well. I think this is important, because if they generate new money within the business, they can use it for a variety of options. This minimizes the risk that they come back to you asking for more funding. For these type of parameters, you can always look at the pears and which value they have. The listed pears have public information available, such as the PE-ratio *[market capitalization / net profit]*. We compare the PE-ratio of a business to its pears, but also on a absolute basis.

Obviously, I also look at the management team. I want to know what their expertise and experience is. I want to know if I can trust them. Next to this, having a competitive advantage is also always very important.

Looking at Cleantech Investments

We are negotiating to form a deal on investing in a (biochemical) sustainable energy producing plant. This deal came through us via a party in our network. This party is also trying to diversify its portfolio and is a bit ahead of us in this area in a sense. They are involved with the founders of the plant for some years now. The main founder of the plant has a background in biochemical engineering and studied at a prestigious university. He has been working on this technology for over 10 years now and I think he has build up a lot of IP *[intellectual property]* in these years. I think that their IP is also their competitive advantage.

Obviously, it is quite capital intensive to invest in a plant, so the budget for this project is more than what we would generally invest. Overall, I think that this business has several advantages. Firstly, I think that the cleantech business has some strong tailwind behind it. Furthermore, the product that this project produces will be directly sold to company *[X,Y,Z]*. Next to this, they can generate the green certificates, as they are reducing carbon.

However, when a project is not really our expertise, we might mitigate the technology risk by giving a loan first. The loan can then be converted into shares, once we are comfortable with how the business is performing. This gives us some flexibility to first understand the business. For us, it is quite difficult to really understand the technicalities. We want to see if they deliver their forecasts, since we can only assess the numbers. For us, the timeframe of an investment is not really an issue. We do not have any outside shareholders, so if our portfolio underperforms in the short-term, it does not bother us. For example, we could give a loan for 2 years first, then if the forecasts were correct, we can convert it into equity and become long-term shareholders.

View on Scientists' Perspective

I do not really have contact with researchers. However, I would advise scientists to always keep the investor in mind. Whatever they are working on, it has to be economically viable. For any investor, to build out the idea of that scientist, it has to be something that: 1) you can apply to the economy and 2) you can get a return on. What is the point of developing something mind-blowing if you cannot roll it out to the general public?

As a final note, I want to state that the mindset of our company is different than that of investment parties such as a pension fund. These parties require specific annual returns and they are not taking risks as we do. I would advise scientists to take these parties also into account, because an innovation has to be funded somehow.

Early-Stage Investor #3

Background Information

I have always had an affinity with finance. I have had a long time experience in investment banking and was interested in PE *[private equity]* as well. So, when a colleague of mine asked me to join his company in PE, I did. This happened about 20 years ago. The company was very small and PE was a very new sector in the Netherlands. Other financial sectors such as M&A *[Mergers & Acquisitions]* already had a 'cool' image, but this was not the case for PE. Now, our company has grown a lot and PE is looked at very differently.

Our company is structured with two teams. One of those teams has an investment horizon of 5-7 years, the other team has a horizon of over 10 years. We investment in the regions of the BENELUX, DACH and North America.

[The rest of the interview will focus on the team with a 10+ years investment horizon]

Assessment of Investment Opportunity

We have two main criteria that have to be passed. The first one is the ESG scan and the second is having a positive cashflow. The positive cashflow gives a good predictability of metrics such as the company's development, up-scaling, market value etc. If it passes these criteria, we look at the track record of a company and the people who own/lead it. In general, the companies that we look into have a market value of 50 to 200 million.

We also look at sustainability, but how this is measured is different per company. We want our companies to work on sustainability in a way that fits their business. Eventually all our companies have to meet 4 or 5 UN Sustainability Goals. If they are not working on it when we invest in them, we introduce it. Since we only invest in companies in which we get a majority of the ownership, we can ensure its introduction.

The assessment of sustainability is different per company, it can be measured via its carbon footprint or via waste production.

If I have to rank these metrics based on importance it would be the following. The positive cashflow is the most important. This is followed by the track record of the company and of its owners. Sustainability ranks third. Not because we do not find it important, but because we can change it once we have invested in the company. Therefore it is not a deal breaker.

Since your process does not have a positive cashflow yet, we would not invest in it. The phase in which it is, is too 'pre-mature' for the companies that we target. We only invest after all the investment series are finished.

We do not have expertise in the niche of sustainable chemical processes, which makes us hesitant to invest in a process like this. A scenario in which we would invest in a such a process is the following. We would consider to join if a company in which we have already invested, will propose and invest in your process. Even if it does not fit our requirements.

D.4 Scientists

Scientist #1

Background Information

At first I really thought that I would not pursue a career in research. However, this view changed during my master thesis. I really enjoyed working on Microbial Electrosynthesis and continued to work with my supervisor from that moment. My motivation is actually two-fold. Firstly, I enjoy performing research. Secondly, I want to work on a topic that contributes to the bio-based circular economy. If it would not fit this view, I do not want to work on it.

Assessment of Technology's Performance

I think that the TRL of MES is around 3-4 at the moment. This means that we are moving towards pilot-scale. In general for CO_2 utilizing technologies two points should be focused on before up-scaling can be reached. The process should have the potential of profitability and have a proven impact on sustainability. I think that the sustainability is more important than the profitability, but the potential should be there.

For MES there are still a few bottlenecks present, as discussed below.

Technical Parameters
Firstly, you want to reach the highest percentage of energy possible to be fixed in your product. A lot of steps are present between the energy source and the product caproate. Furthermore, you want to reach a high concentration of caproate in your fermentation. The largest issue at the moment is the downstream processing. Due to the low product concentrations, it requires a lot of energy. Unfortunately not a lot of innovation is present on other DSP methods. As we produce a mixture of compounds, you could also see if there are certain fermentations that can work with this mixture. This simplifies the DSP.

Environmental Parameters
When you look at the DSP, the issue can be summarized to looking at the energy efficiency of the process. At the long term, the energy source will be renewable. Nevertheless, you still need to limit your energy requirement. In the future, there will be competition between (electrochemical) processes for energy. Then choices have to be made at which process is better.

The same holds for CO_2 . I think the CO_2 footprint of the process has to be limited of course. However, we use CO_2 as a substrate. In the future, more processes using this feedstock will be present. I think that there will still be enough CO_2 , but it might not be in the pure form and continuous stream that you can retrieve now. This will impact the price of CO_2 and thus the profitability of your process. Note, this is my personal opinion, I did not research these topics.

I find the water impact also a very important environmental parameter. In the future, I think it is very advantageous if you utilize less water than your competing processes.

Next to this, I think that the safety of a process should be taken into account as well. For MES, this is not really an issue when compared to e.g. the reactions occurring at water electrolysis.

Economic Parameters
I think that the production price of the product is important to look at. This is coupled to the energy usage of course. Also other compound usage effects this price, such as the substrate and water usage.

Next to this, the scale at which you produce your caproate is important as well. This is also connected to your product selectivity and CO_2 conversion rate. The process should be performed at a scale that is relevant.

The usage of scarce materials should be limited as well. Currently, MES uses iridium as anode, which we should eventually change in my opinion. I see the use of scarce materials as an economic issue, since there will be a large demand for these type of materials in the future. Of course it is also important from a sustainability point of view.

View on Early-stage Investors' Perspective

I think that investors mainly want to invest in processes that have a future. They are interested in the concept / story that a process shows. I think that the concept of using CO_2 as a feedstock can be very appealing. There is already a shift that shows the importance of the social impact that a company has. Nevertheless, there are some processes present that are close to industrial application, but do not make sense when quantitatively looking at their sustainability aspect. So maybe their story was very nice, but the eventually reached sustainability and also profitability is doubtful.

Well, if I was an investor I would also want to see some quantitative data. For example, the improvement of the technology over time. I would want to know if there are fundamental bottlenecks, such as those present at the conversion of CO_2 to methane. Nevertheless, there is still invested in this process, because the story is appealing. Some fundamental bottlenecks are being dependent on fossil-fuels or the characteristics of the microorganisms used.

Next to this, I think that they find it important if the reaction rates and efficiencies that we reach at lab-scale can also be reached at larger scales.

Scientist #2

Background Information

I am a researcher in the field of biotechnology. My main interest in this field is its quick development. I think that it can be used to achieve a circular economy. My research focuses on finding options for industrial-scaled production with biotechnology.

Assessment of the Technology's Performance

Some parameters are important to be reached before either MES or syngas fermentation can be reached on a commercial level. The most important is to have a certain minimum current density in scalable reactors with an acceptable CAPEX. When you look at the whole value chain from CO_2 to product, you should also look at the land use that is required to generate the required renewable electric power. I think that you should assess it as a fully cyclic system. With a fully cyclic system I mean that no mass input or output is present. This cyclic end goal should be leading.

However, when you look at the initial commercialization of your process, it will probably not be the full process. The companies that will start with your process cannot take responsibility for the whole value chain, so they will use different indicators. I think that the CAPEX, OPEX and TRL are then more important. I also think that an outlook on the product market and the accompanying risks are taken into account.

View on Early-stage Investors' Perspective

In my opinion, I think that investment parties would be mostly interested in the potential to commercialize the process in a few years. However, I also think that they would want to see if the product range can be extended. I agree with the view of widening the product range. I think that producing caproate is low hanging fruit. The feasibility of widening the product range will be critical for each of the technologies *[Both MES and syngas formation & fermentation]*.

Personal Note

At the moment MES might not be competitive with the petrochemistry. However, at some point it will not compete with this industry, but with other renewable methods that can produce the same compounds. When this situation occurs, MES is competitive because it is a very direct route.

When looking at syngas fermentation, it is already commercial. Steel syngas and gasified domestic waste is fermented into ethanol. I think that CO_2 electroreduction to syngas (and subsequent fermentation) is a better comparison to MES, but I do not know if it can become competitive.

You could also look into another technology for sustainable caproate production. This is via VFA *[volatile fatty acid]* production. This technology is being employed by Chaincraft Technology. However, it is unclear to me if the DSP can achieve pure caproate in this way.

Scientist #3

Background Information

When I was studying I thought that I would not pursue a career in research. However during my Master thesis I really enjoyed what I was doing. Eventually I got persuaded to stay in research. I enjoy modeling and looking into reactor designs. I am also interested in the production of biofuels, because I feel like I am working on something that is worth working on. I think that my core motivation is to help the world to move away from using fossil fuels. In my opinion, one of the promising methods to reach this is syngas fermentation.

Assessment of Technology's Performance

In my opinion, the most important is the circularity of the feedstock. This is a difficult point to determine, but you want to have it worked out conceptually speaking. What does the carbon cycle that you're working with look like? How much energy does it require? As the process is quite energy intensive, you want to obtain your syngas cheaply and from a renewable source. When you look at Lanzatech, they are using steel-mill off-gas. This is not a renewable source, as it originates from natural gas. Eventually, they are delaying the carbon cycle, which is not really sustainable in a way. If you have an energy source that is circular, it has a huge advantage.

The distillation steps of syngas fermentation require a lot of energy. Next to this, it will also require a significant amount of energy if you have to gasify your feedstock. So you should ensure that you have a renewable source for this heating.

Secondly, I think that you need to have a high production target (so gram per liter per hour). You should also consider the opportunity costs of your substrate and the price of the product that you are producing. This is important, as syngas can also be burnt to produce heat. Thus your product should be worth more than the heat produced with syngas.

Taking this into account, it makes more sense to produce ethanol from syngas fermentation than caproate. Ethanol has several advantages as it is; 1) an easy chemical, 2) known by everybody, 3) you can convert it into other products such as bio-plastics and bio-fuels. 4) Vehicles that we are using currently only need minor adjustments to be converted to be fueled by bio-ethanol. That would be ideal. You don't have to change from a combustion engine if you use bio-ethanol as fuel. So the adaptation from our way of living towards a sustainable society, is much more reachable if we change to bio-ethanol instead of another sustainable source. I feel like the caproate market is much smaller and more specific than ethanol.

Thirdly, I think that the substrate conversion efficiency is also very important. This advances the economic business case of the process. In my opinion, I think that the price of your sustainable product should be competitive with the current price. If it is not competitive, there is always a 'secret backdoor' to the non-sustainable method and people will have an incentive to use it.

View on Early-stage Investors' Perspective

I think that investors mainly focus on the financial picture. Metric as NPV and IRR are used. For them the most important in terms of sustainability is having a nice storyline. I think that analyses such as LCA's are too technical for investors. It is a very difficult and complicated issue about where to put the boundaries for environmental analyses. I also would not know where these boundaries exactly are. An investor often hears a 10-minute pitch and then talks with a COO. Well, then you are quickly convinced if you hear about the amount of tons CO_2 that is captured. Even though these CO_2 tons are emitted afterwards. I think that the carbon dioxide emissions or the amount which is utilized as feedstock is important to investors, but not decisive. To summarize, investors would mainly look at the IRR and NPV. The amount of CO_2 reduction is also considered, but not really decisive or analyzed by them.

Scientist #4

Background Information

I have a background in chemical engineering. After my studies I have been teaching for some years and then I picked up research again. The focus of my research is not per se on looking at caproate production, but broader. I look at all the potential chemical products that can be made via sustainable production pathways. I research which type of products and which combination makes sense to commercialize in the future. The goal is to look at the production pathway from the feedstock to the (range of) products. The production pathway consists of several steps. For each step I try to see where the challenges lie and propose approaches to overcome these challenges.

Parameters for the Assessment of a Production Pathway

We have three pillars that we look at. One of them is economics. Here, we look at the profitability of the process. I think that developing a profitable business case is a basic thing that all engineers try to achieve. If you do not make a profit, who is going to invest? Secondly, we look at the sustainability. Thirdly you have the social part. We look at its impact on the society.

Economic Parameters

Assessment of the profitability of a process depends on the data that you have. You have to take into account what makes sense to compare. For example, if you want to compare multiple potential products, I would suggest to use annual production costs over NPV *[net present value]*. For the calculation of the NPV market prices are used. These are very volatile, so then you should do a sensitivity analysis. When you look at annual production costs this is not required. The annual production cost show you have much you need to invest to produce that unit of product. When you are comparing products, you can select for a product with a low annual production cost.

However, once you develop your process further, it makes a lot of sense for the investors to see the NPV and the ROI *[return on investment]*. These two metrics are easy for people on the 'outside' to understand and to get an idea of your process. So in that case it makes sense to look at these metric. It really depends on the purpose of your project which metric you use.

Environmental Parameters

I have not focused much on the environmental analysis. I have done some preliminary analysis based on the stoichiometry of the process. For this analysis, I look at how much carbon is fixed in the product. For syngas fermentation, I think that fixing carbon in the product is more sustainable than generating electricity from the syngas. In this way, syngas fermentation has a lower carbon footprint than generating energy.

For the environmental analysis, I am planning to incorporate a detailed LCA *[life cycle assessment]* in my research. This is to indicate areas of improvement within the process. For the LCA multiple options are possible. You can set the boundaries at gate-to-gate, so from the feedstock to the product. Here, you can see if the unit operations has a higher impact on the environment. If you also want to take the impact of your feedstock into account, you have to reset your limits to cradle-to-gate. Thirdly, if you want to compare different products, you should use cradle-to-grave. You then look at questions such as; where does this particle end up? What is the use of the product? Personally, I am going to use cradle-to-gate, since I compare different feed-stocks and focus on the process section.

Parameters for the Assessment of the Indirect Route

When looking specifically at your process, I think that some of the factors that are mentioned previously should be taken into account.

Economic Parameters

In terms of economics, your process should be profitable. You can split this analysis in the CAPEX *[capital expenditures]* and OPEX *[operational expenditures]*. By looking at these values, you can see where you can save some money.

Technical Parameters

Important metrics are the overall volumetric productivity and the product concentration. The overall volumetric productivity is the amount that you produce over the bioreactor volume. When you have a high volumetric productivity, you can save some capital expenditure, as your reactor is smaller. In terms of product concentration it is better to reach a higher concentration. The problem with many biotechnology processes is the low titer. It costs a lot of energy to recover your product. So a high concentration saves you a lot of energy.

I think that the collaboration between the microbiologists and the process technologists is very important. The technologists can perform the economic calculations, but the microbiologists can give you the limits to what is possible for the process conditions. The collaboration between these two groups is required to compute the target values of the technical parameters. It is important to find out which key player in the process design has a high impact on the technical parameters. This approach is also used by Lanzatech.

Environmental Parameters

Overall, I think that you should take into account the carbon footprint, the water usage and the energy usage. Of course your environmental and economic parameters are related in a way. For example, you want to limit your fossil-fuel based energy usage due to its impact on the environment, but it will also enhance your profitability. Overall, approaches to improve your process are to use process integration and intensification. These areas can lead to both economic as well as environmental improvements.

Impact of Influential People

Next to the discussed parameters there is another force that is important if you want to develop your process further. I think it is not in the scope of your project, but the impact of the policy can also be significant. If you want to take a technology to an industrial scale, you need a lot of support from the outside, of people with influence. With people that have influence I mean the people that make decisions about funding and investing. It makes a huge difference if they support this type of technology. It impacts the pace at which you can reach commercialization.

View on the Assessment Parameters important for Early-stage Investors

I think that this stakeholder want to know how quickly they can get their returns. So they look at NPV, ROI and payback time. To be honest, I do not know if they have any sustainability policies. Even if they do, I think that the most important will be the economic metrics mentioned. All other advantages are a nice extra.

Although I have to add that I feel like sustainability is becoming more and more a necessity now. So, I think that they would not invest in a very profitable, but very polluting technology. Policy making can make an impact here as well, since the economics of a sustainable process can be improved by giving subsidies. Overall, we as scientists might have a vision, but there is a reality too. It will take some time to put sustainability on the first place for different actors.

Personal Note

I think that your process has two advantages. Firstly, you use a fermentation, which has not the 'extreme' conditions that chemical syngas conversions have. Therefore, your process probably uses less energy and is thus cheaper/more sustainable. I would say it is inherently sustainable. Secondly, you can produce a wide variety of products with syngas fermentation. Overall, I think you could make the process more sustainable in various ways, but this is not where the current focus should be on.

Taking into account the current status of the process, I think the focus should be on reaching profitability. Compared to the fossil-based products, it is more expensive to use a bio-based route. Overall, I think that there is definitely a future for syngas fermentation. When you look at the success of Lanzatech, it is an inspiring technology to work with.

Scientist #5

Background Information

I have an engineering background, so I do have the all the fundamentals to understand technical designs. However, my research focus is about implementing technologies in the most sustainable way. I try to understand the potential trade-offs between economic, technical and environmental aspects of a new technology. I use these aspects to guide decision making in the design of processes and the supply chain. In my opinion, it is important to focus on the integral sustainability, so not only the process design, but also including the supply chain, bio-hubs and the society as a whole.

I want to understand how the chemical sector in general can be improved from the sustainability perspective. My research provides the data for this discussion, and is less focused on the narrative aspect of it. Based on the data I try to understand the potential of a technology.

Parameters Important for the Assessment of a Novel Technology

The parameters that I look at depend very much per case. However, I think that parameters that describe environmental benefit are very important to take into account. For almost every case, the carbon footprint is important to consider. However, there are more, case-specific, factors. For example, when producing sustainable aviation fuel from biomass, the biomass availability should be considered as well.

The largest part of the decision making will be based on environmental and economic parameters. On top of that some analysis on the macro-economic aspects can be considered, such as GDP generation and job generation. Something that is becoming more and more important is also the effect on resource materials and energy dependence.

Once a technology becomes at the level that process simulation is possible, the following factors become important to check: process efficiency, total production cost and minimum product selling price. The minimum product selling price also takes into consideration the production scale and certain taxes. These parameters give a main idea of the differences between the new and traditional technologies. Based on these indicators, you can derive other indicators, such as net present value, payback time etc.

Something that you should always consider is the production scale. This impacts many parameters. I personally also look into the market size of the product. You could have two options; 1) a process that results in a large increase in sustainability for a product with a small market, and 2) a process with a smaller sustainability increase for a product with a large market. The latter might then have a larger overall impact and a more significant contribution.

Environmental Parameters
From an environmental perspective the greenhouse gas emissions and primary energy use become important. It is important to account for all the activities and impacts that are generated by the destruction of the raw materials to the conversion into the final product. This is quite a difficult process as you have to decide where to set the boundaries and which database and method you are going to apply. And then geographical conditions can also change the analysis due to different energy grid mixes and efficiencies.

As an environmental database you could use SimaPro, but you probably also have to perform your own estimations and calculations specific for your process.

Using Parameters to Guide Decision Making

When you want to use the parameters to guide decision-making, you have to keep the following in mind. For decision making, you will have to involve multiple stakeholders. These stakeholders all have their own parameters that they find important, so you have to balance this as well. It can be quite tricky to balance out the different interests.

When looking from my personal perspective, I would say that reaching some significant environmental benefits is the most important requirement of a process. This includes looking at the difference of the novel and conventional process at; the primary energy use, carbon footprint, carbon efficiency of the process. Only after taking these environmental factors into account, the economics play a role. But that is my personal view on the topic.

Process Specific Parameters

When looking at the current design and stage of your process, I think that the technical challenges are still pretty large. I think that significant improvements need to be done to reach a decent level of product concentration, reaction rate and tolerance.

When I look at the product that you are focusing on, it might be too specific and the market size might be too small. Maybe it is interesting to focus more on the platform and the specific technology and less on the specific product.

View on Investors' Perspective

Since the TRL is still really low, I think that investors would first look at some technical parameters, so looking at the titer, rate and yield of your fermentation process. Furthermore, they probably take into account the total production cost and the maximum capacity of the fermentor. In general, I think that investors would see this as a high risk investment. Before doing any scaling-up, some decent performance at the bench-level should be reached.

From my own perspective and from an investors' perspective, I think that checking the production cost of the new technology with respect to the traditional technology is always important.

Overall, I think that the decision making of investors is probably 80% based on economics and 20% on environmental factors. Economics do not have to be as good as the traditional process, as in the short or long term, environmental benefits will play a role as well. Something as carbon taxes will be implemented, so the reduction in greenhouse gas emissions will positively influence the economics in a later timescale. In a way, the environmental benefits will become 'monetizable' due to policy making.

Scientist #6

Background Information

I became a researcher out of a mixture of curiosity and wanting to have an impact. My area of expertise is in bio-technology, so I feel like this is the area in which I can contribute to reach a circular (bio)-economy.

Assessment of the Technology's Performance

Technical Parameters
I think that the factors to look at are in a way similar for each bio-process. You always want to look at the yield of your product and the productivity. When looking at chain-elongation, a third parameter can be added to this, namely product specificity. Multiple products can be made and there is a competition between which one is produced. You want to steer the process into making your desired product. In a way this is related to the yield of your process, but it also shows the fraction of your product in relation to the by-product. If you desired product has a higher fraction in the overall product stream, it is easier to separate it. The separation step is most of the time the most costly and energy requiring step. Selectivity can be defined in two ways; 1) how much carbon is going to your final product, 2) how much energy is going to your final product.

Furthermore, you want to know the characteristics of the separation step of the process. If you are performing liquid-liquid extraction, you want to know how selective the solvent is to what you want to extract and how much the solvent can extract. You should also look at the nature of the solvent, if it is toxic or from a renewable source, et cetera.

Economic Parameters
On lab-scale it is difficult to assess the economics. I always try to keep my process as simple and efficient as possible. In the end this will help the economics I believe. This is my approach of taking economic factors into account. However, overall I think that if you want to make the technology viable, you should look at: target market, the purity of the product that you need to achieve and its safety. For example, if you want to sell caproate as a feed additive, it might have to fulfill certain regulations. I think these three factors will impact the price and market at which you can sell.

Once these parameters are pointing in the right direction, you could explore the possible applications in (other) markets and the market size. Which size of the market can you cover with your product? This is a concern for caproate production, since that market is not that big. The potential is there to produce more than what is needed. Something that you could look into is to extend the application of caproic acid, which would enlarge the market.

Environmental Parameters
I think that you have to make sure that you are using a low-value renewable carbon source and that you use a renewable energy source.

Perspective on Early-stage Investors' view

I am not really familiar with terms such as venture capitalists and private equity. However, I do have some experience with start-ups that are looking for funding via contests. So, from this perspective, I think that venture capitalists look at different, competing start-ups and then let these start-ups be evaluated by a panel of experts. This will give them an idea of how the profits of a business case are going to be. I also think that they are more likely to invest in a disruptive technology, because that has much more potential to result in a lot of money.

In my opinion, for investors in general, their main concern is the large capital investment required to start the project. Next to this they worry about the value that they can obtain. Ideally, you want a very cheap process that creates a lot of value. The investors want to maximize their money.

Personal Note

For reaching a circular economy, I think that the parties with a long time frame can play a huge role. These are parties such as the government and incumbent firms. Policy makers can promote the investments in sustainable technologies by subsidizing a part of the investment. Especially when a company has just started, but some research still needs to be conducted. Maybe the government can subsidize this research, while the part focusing on the commercialization is funded by investors. Something like that.

I also think that the incumbent oil-companies, which have a lot of money, should be stimulated to spend their budget on (sustainable) R&D projects on the long-term. They can do this, since they do not have the risk of going bankrupt on the short-term. Overall, I feel like the parties with a longer time-frame for their returns have a large role to play in investing in sustainable technologies with a low technology readiness level. They are the parties that can invest in it without going bankrupt in the short-term.

Scientist #7

Background Information

My research is focusing on bioprocess engineering. I am mainly interested in how the processes on a lab scale can be up-scaled, but also how plant processes can be down-scaled. I focus on the bioreactor characteristics. My research is mostly based on modeling and making simulations.

I have worked in the industry as well, but I returned to research. While working in the industry, I performed research as well. However, the goal was always to make a profit. Personally, I felt that the moment that the research really came to a scientifically interesting point, we already stopped. When you feel to limited by doing corporate research, you switch to academia. Next to this, I also really wanted to contribute to education.

Assessment of Technology's Performance

Technical Parameters
So my research is about the upscaling and downscaling of processes. The parameters that I find important to assess if a technology can be upscaled are the following. Firstly, the mass transfer from the gas to liquid phase should be high enough. This is a very typical parameter that is taken into account. A second metric could be the mixing time or shear stress in a reactor. This could damage your cell culture.

However, you could also turn the question around. One of the highest risks for a large scale process is that your cells are continuously in a different environment. A solution to this issue is having a robust microorganism. A fragile microorganism will need a significant part of their energy to get accustomed to the changing environment. As a result, you loose a part of your production capacity. One approach to tackle this is to make your microorganism more fit to the circumstances by genetic modification or by targeted evolution.

But altering the microorganism is not per se required. We try to take the larger scale as a starting point. What are the issues that we expect for the microorganisms? Then we test our lab experiments and simulations already with those issues in mind. We use it to adapt our reactor and process design or to see its limits.

I think that you should be aware of the effect on your microorganism that issues such as the change in pressure and the composition of your medium have. As an example, when a reactor becomes higher, the pressure on your gases increases. Your microorganisms might not be able to handle that. Also, ethanol is a compound known to influence the size of your bubbles. This influences your mass transfer. This is quite important, since the process is mass transfer restricted.

People are very interested in the product diversification of, for example, syngas fermentation. However, you should be aware of the impact of the altering on the robustness of your microorganism. For the production of ethanol this seems fine, but for other products I am not so sure.

Environmental Parameters
Well, I have to say that this is less my expertise. However, I think that it is the most important to make sure that your process makes sense in terms of increased sustainability.

When you look at fermentation you always have to keep the substrate source in mind. The advantage of syngas fermentation is that it uses a waste stream as substrate. This is a waste stream that is abundant for the coming years. Obviously, I think that you should assess its carbon footprint and the other metrics that you use when making an LCA.

For the usage and availability of hydrogen this is a different discussion. You also have to consider the alternative use of your substrate and energy. You could use hydrogen to produce bio-fuels, but if that requires more energy input than to run the car on hydrogen it makes no sense. You could summarize this as the return on energy.

Thirdly you should consider the use of scarce materials. I think this will be fine for your process, but for sustainable processes in general I would take this into account.

Economic Parameters

From an economic perspective I think that the CAPEX is an important metric. It is an advantage to your process if you can run continuously. This is dependent on the stability of your microorganisms, but I think the outlook on this part for syngas fermentation is good. If you had to run a fed-batch, it would influence your economics as you have a significant downtime et cetera. This is especially important when you produce bulk products with a low price.

View on Early-stage Investors' Perspective

Looking at the current view on climate in society, I think that sustainability is quite important to investors. However, I think that their assessment of sustainability is much more qualitative than quantitative. I mean, there is a reason why there is a lot of 'green-washing'. That is all based on qualitative arguments instead of quantitative analyses.

Next to this I think that Lanzatech has really helped to improve the attitude of investors. Ten years ago, investors might have been hesitant. Now, Lanzatech has shown what is possible. This probably eases funding for other sustainable biochemical processes.

Of course, the economic parameters remain the most important for investors. I think that they will use parameters such as internal rate on investment. They most important for them is to get their money back (with profit). I also think that the expected production price of your product compared to its market price is assessed as well. Maybe the outlook and characteristics for the market in general plays a role too.

Personal Note

Unfortunately not many literature sources are present about issues that were present for the up-scaling of syngas fermentation. The found successes and failures open up after several years. This is unfortunate as it makes it more difficult for your process to identify bottlenecks.

I also think that the downside of syngas formation and fermentation is that you have to produce CO out of CO_2 . It would be more beneficial if you could use a microorganism that could immediately use CO_2 as substrate.

Scientist #8

Background Information

I have been working and am working on several topics, including biotechnology, chain-elongation and electrification. Furthermore I collaborate with industrial partners to map processes, especially processes occurring at the harbor*. I also collaborate with partners that utilize syngas for their product manufacturing. Next to this, I am a co-founder from a technological spin-off company.

I would say that I am focused on not only research, but also on the implementation of the discovered novelties. There is an urgency to come up with new methods to use carbon, such as CCS and CCU. Especially CCU is something that the industry is interested in, so this is an incentive to perform research in this area. Furthermore with CCU and CCS, you can really make an impact in CO_2 emission reduction.

In contrast to CCU, implementing CCS will require little novel technology development. Therefore, I think that CCS will be implemented sooner than CCU. Nevertheless, eventually the industry will be more interested in CCU, as CCU gives you a product in return for the investment that you made.

Parameters important for the Assessment of a Technology

Product Market
In my opinion, the market of your product is everything. Caproic acid does have an application as feed additive. However, I think that the larger and more profitable markets can be found in producing higher-value chemicals. Especially the iso-forms, iso-caproic acid and iso-caprylic acid, are interesting and required for aviation fuel. You can focus on product diversification and form a product portfolio of your process. I would first make a business case for the caproate production. Once the plant is built, you can focus your R&D on reaching product diversification.

When talking about innovation, I think that you should keep the following in mind. The most difficult thing to do, is to introduce a new product in a new market. Then you have a challenge on each aspect. Since the market of caproate is not very large, you have to be careful with the amount that you are going to produce. Once you produce more than the demand on the existing market, you have to search for new applications of caproate. Most of the time, the successful entry at a new market is dependent on having a lower price than the current chemical used. This is not the case for your produced caproate. Therefore, you have to focus and be competitive within the present market. The advantage of this market is that the conventional produced caproate will decline as it is an unsustainable process. So maybe there is place for a 10 kt plant in the current market, but in the meantime you have to develop higher worth applications. I think that you should definitely focus on product diversification.

Looking at your production process, your caproic acid will be more expensive than that produced via palm oil refineries. You have to transform the most oxidized form of carbon to a reduced form, which will require quite some energy. On a large scale, this will become a challenge. Therefore, it might be valuable to look at its niche application. A common way of thought is that everything has to be on a large scale. The economic value of the product is often taken from the bulk market. However, there might by niche applications at which it is very convenient to produce caproic acid. If you convert your caproic acid into fuels and produce it locally, you might beat the alternative based on less transportation costs, storage costs etc.

Partnerships within the Industrial Cluster
For each business case that you develop, you also have to consider the partnerships that you will form within your industrial cluster. In my experience, it can take years before two or more companies from different sectors collaborate. So if you want to bring a refinery together with a feed producer it requires time and effort. Therefore, you definitely have to look into the organizational structure. Who will use your caproic

acid and with which application? Which companies are involved?

Technical Parameters

Personally, I think that syngas fermentation is much more applicable for large scale operations than microbial electrosynthesis. This is because the up-scaling of microbial electrosynthesis causes large issues. It has a low-conductivity solution, requires membranes and other difficult technicalities. Contrary to this, the production of syngas is already possible in large systems.

It is always tricky to compare technologies. You should compare technologies in the context to where they are made for. Otherwise you risk getting conclusions about the technology that are not very 'clear'. In my opinion, MES is applicable for small-scale, local production. A lot of companies that do not produce tones of CO_2 , but still want to reduce their emissions could potentially use it. If you look for a process at the Port of Rotterdam, it is not going to work. For the Port, (a large scaled production), the crucial factors are: economy, intensity and efficiency. In Rotterdam, the energy is retrieved from windmills. As a result, a very intense and large scale energy stream is coming in. This requires a large-scale stable process that converts this energy, which brings you to the syngas route. So, before comparing the technologies, you should set the different routes of the technologies. Then you have to ask yourself, what are the constraints and what are the goals of these routes?

When looking more specifically at your process, you should consider the downstream processing. This is often very energy intensive. You could assess if there is also an application that does not require such a high purity. The chemical industry is moving towards looking at a product's characterization instead of its composition. Maybe you can find an caproate application that avoids you to reach such a high purity. For example, when looking at animal nutrition, it is not a problem if you have a mixture of butyrate and caproate.

Environmental Parameters

I think that you want to have lower CO_2 emissions than your reference process. I think this is the most important.

In terms of energy usage, I would assume that we eventually have sustainable energy sources. So the usage of energy is important from an economic point of view, not per se environmentally. Nevertheless, the source of your CO_2 is important as well. If this source is from a fossil-based, is your produced caproate then sustainable? This is an interesting debate.

A third factor that is important, and that in my opinion is not highlighted enough currently, is the usage of scarce materials. Especially catalytic materials often use these type of metals. It is difficult to quantify this, but it is a point to take into account. At the moment the usage of these materials might not be an issue, since the focus is on reducing CO_2 emissions. However, once these reductions are achieved, this will be (one of) the next issue(s).

When quantifying the CO_2 emissions and energy usage, you should work with the expected future values. So when quantifying metrics, you should use the energy source(s) that are expected to be used at the time that your plant is operating. I would suggest you use the expected energy mix of 2030.

Working with a low TRL Technology

In your case, the syngas fermentation has a low TRL, while the syngas formation is already (close to) commercialization. I would maybe advise you to look as if you can ensure that the process of syngas formation is not dependent on the syngas fermentation. You do not have to convert all your syngas immediately to caproate. Firstly, you try to make a deal with a customer that is willing to pay a premium price for your sustainable caproate. Then you use a part of the syngas stream to produce caproate. The main syngas stream is used for more conventional processes or sold as product. Later on, you can keep increasing the amount of syngas used for your process. This is how you mitigate a part of the uncertainty.

Parameters important by Early-Stage Investors

I do not really work with investors or have much experience working with them. I know that there is an increased interest among venture capitalists to look at sustainability. Within Europe sustainability demands are set for each investment/subsidy. This impacts the choices made by venture capital funds. In the end these funds' goal is to make a profit. If a start-up is not qualified for subsidies, the business is less attractive. The venture capital funds are very sensitive to this. I think that the policy makers can stimulate sustainable investments via these type of restricted subsidies.

Energy Usage & Fluctuation Management

When focusing more on the syngas fermentation route, it eventually comes down to the energy usage. I think that catalyzing CO_2 to CO is a positive aspect. A catalytic process can handle fluctuations very well, in contrast to a biological process. So, it is beneficial that you start with a catalysis step, which can handle the fluctuating energy and CO_2 input. But then… In real life, it is not that easy to convert CO to all these other compounds such as ethanol and caproate. This is where biological processes can help. So, I think that your process is a very good mixture between catalytic and biological processes. The catalytic aspect handles the fluctuation and the biological aspect the chain-elongation. Especially once you have ethanol and acetate, a biological fermentation is beneficial. Some scientists are developing catalytic chain-elongation, but why would you want to develop this if the biological route works fine?

Policy Framework

Finally, I would say that you also have to keep the policy specific for your final process in mind. For example, if you want to use caproic acid in the agricultural sector, you have a different policy framework compared to other sectors. Currently, the agriculture is not part of the carbon credit system. So if you produce animal feed additives, who will get the carbon credits? You will not get any credits if you produce caproic acid for the agricultural sector. Obviously, this influences your business case.

**Not the Port of Rotterdam*

D.5 Non-Governmental Organizations

Non-Governmental Party #1

Background Information

My educational background is in Chemistry. During my career I have focused on energy policies and on topics such as energy, waste and pollution. At the moment I advise [the NGO] about topics related to the energy transition at the Port of Rotterdam.

Our NGO is actively looking into CCS *[Carbon capture and storage]* and CCU *[Carbon capture and utilization]* projects. We are also involved with the Porthos, Aramis and CO_2 smart-grid projects. On these topics we collaborate with other regional and national NGOs who share our aim to protect the environment. Our mindset to topics such as CCS and CCU is really to look at these innovations in a 'positive' way. We are open to see what these innovations bring and how they can enhance sustainability, within the framework of concrete improvement on decarbonisation, by a variety of measures in industrial processes.

For the energy transition at the Port of Rotterdam in general, we collaborate not only with regional and national parties, but also with European and International parties. In my opinion this is also necessary as the Port is an international harbor and the novel technologies are also internationally being developed.

We do not only collaborate with other NGOs and the Port of Rotterdam. We have a good connection with the municipality of Rotterdam, the PoR, DeltaLinqs, a variety of industrial companies (in transition), and multiple research funds. With these parties we have extensive conversations about the national Climate Agreement and of industrial processes, transport, storage and transfer, its implications for the Port concerning renewable energy sources and decarbonisation. Furthermore we advise the research funds towards which research area funding should go. We are also focusing on stimulating discussion among scientists about the usage of CCU and other technologies. However, we would like to enhance our connection with research groups like Andrea Ramirez' group. I think that we could collaborate more and mutually benefit from this. Next to our collaborations and advising function towards projects, we are also developing our own strategy for the decarbonization of the Industry in North-West Europe.

Parameters important for the Assessment of CCU Technologies

Environmental Parameters
When looking at novel technologies that might be implemented at the Port of Rotterdam, we mostly focus on sustainability. The following metrics are important; CO_2 emission, energy usage, NOx 'footprint', micro pollution and macro pollution. The analyses should be performed from 'cradle-to-grave'. Especially at CCU it is important to measure the time-frame at which the CO_2 remains out of the atmosphere. The energy usage is important to limit as well, even if it is retrieved from a sustainable source. The NOx 'footprint' is quite a new metric, but is of importance taking into account the nitrogen-discussion that is present in the Netherlands. So you have to limit the NOx emissions of your process. Micro pollution refers to all additional chemicals that are required for your process. This micro pollution is really an important point that should not be neglected. For example, the production of PFAS *[per- and polyfluoroalkyl substances]* should be limited and the waste properly handled. With macro pollution issues such as air and water pollution are meant.

Product Application and Profitability
Next to these environmental factors, I would also advice you to look into the specific application of caproate. It is a chemical with a variety of usages, but it might help if you set for which specification you want to use it. This impacts the LCA *[Life Cycle Assessment]* of your process. If you use caproate as a fuel, the CO_2 will be emitted quite soon. It might be better to produce a substance with an application holding the CO_2 from

the atmosphere for a longer time period.

You could research the aspects of process optimization and intensification. Your CCU process might fit better at a smaller scale with a higher flexibility.

In terms of economics, I think it is really difficult to express the value created by a CCU process in money. The additional value of your process is the increased quality of the (local) environment. But, who is going to pay for it? I think that you should aim to make it economically profitable, but this can via multiple ways. Firstly, your process on its own does not have to profitable per se, as long as the industrial cluster in which it is embedded is profitable. I also think that profitability can be reached by the carbon trading system set by the European Union. When it is implemented on a larger scale it has more impact. However, the current trading system has already led towards more sustainable innovations. The government could also use different stimulation methods to enhance sustainable innovations.

Local Geographical Parameters
We highly value the quality of the direct environment as well. This consists of three pillars; nature recreation, air quality and noise levels. Periodically we have meetings with inhabitants of the region to discuss the new developments at the Port. The interest for these meetings has been improved over the years, but we would like to involve them more.

Next to these social parameters, the risk that your process brings is also important to valuate. I think that using a biochemical process instead of a process with high pressures and temperatures is an advantage in limiting the risks of hazardous accidents.

View on CCU Technologies

Within the European Union, a discussion about CCU in general is present. What can be its role within the energy transition? You have to be aware of what its 'true' sustainability is. It should not become a 'easy way out' for polluting incumbents, such as the steel and oil industry, if it is not inherently sustainable. The focus should be on keeping CO_2 out of the atmosphere for a long time period.

This is also my advise to scientists. There is pressure from the industry to implement sustainable technologies in the short term. Researchers and the industries often have close contacts. I think that it is important for (among others) scientists to keep the goal in the picture and not feel pressured by industrial parties. The overall CO_2 reduction should be the focus point. For CCU, it should become clear what the final consequences are in terms of CO_2 emissions and the environment.

Regardless of the view on CCU, the current refineries do have to change their processes. Personally, I feel that they should focus more on sustainable processes. Neste and other refineries are looking into electrification. However, the advantage of biochemical processes over electrification is that it operates at not such high temperature or pressures.

Role that Early-stage Investors could play

To be honest, I do not know much about these parties. I am aware of the presence of quite some investors in sustainable innovations. They also focus on topics such as biochemical innovations. However, I have no idea what their size and impact is. I am not sure if you really want to make the energy transition dependent on venture capitalists and these type of parties.

Nevertheless, we did have contact with the Erasmus University. When discussing the value assessment of a company, they stated that the discussion about including the value of the environment is growing. Of course, it is difficult to give a certain price to the environment. This is a point of debate. For example, Shell's shareholders started a discussion about the value of the environment and how to include it.

I think that investment parties are looking more and more into sustainability. It might be because of outside pressure. But I also think that another factor plays a role. In the end, companies and investment funds are run by people. If people have a certain mindset, the company's attitude changes.

Appendix E

Property Methods utilized in the Process Simulation

Below, the property methods used in Aspen Plus are elaborated upon. These methods include; non-random two-liquid and UNIFAC combined with Hayden O'Connell, Peng-Robinson and the Electrolyte non-random two liquid.

Non-Random Two-Liquid and Hayden-O'Connell Equation-of-State

The main physical property system set is the Non-Random Two-Liquid phase combined with Hayden-O'Connell equation-of-state (*NRTL-HOC*). This method is chosen as NRTL is highly recommended for highly non-ideal chemical systems. The Hayden-O'Connell equation-of-state is used for the vapor phase. HOC accounts for strong association and solvation effects. This includes the calculation of these effects on organic acids, which are the main compounds in the route modeled in this report (AspenTech 2019).

Universal Quasi-Chemical Models and Hayden-O'Connell Equation-of-State

This physical property system is set for the extraction. *UNIFAC* is a strong predictive model for the activity coefficients of liquid interactions (AspenTech 2019). Its approach is to fragment each molecule into different sections. The equations used by this method to calculate liquid-liquid interactions can be found in AspenTech 2019. All the parameters that it uses are retrieved from the Aspen Physical Property System. The HOC equation-of-state is added to account for the vapor phase.

Peng-Robinson Equation-of-State

For the processing of the CO_2 feedstream the method *PENG-ROB* is used, which is based on the Peng-Robinson equation-of-state. Peng-Robinson can be used to accurately model polar, non-ideal chemical systems. Multiple property methods based on the Peng-Robinson equation-of-state are present in Aspen. PENG-ROB is the standard Peng-Robinson equation-of-state, which uses its original formulation. This method is chosen as it is the recommended method for applications such as gas processing (AspenTech 2019).

Electrolyte Non-Random Two-Liquid

The fourth property method used in this report is Electrolyte NRTL (*ELECNRTL*). This method is designed for modeling aqueous and mixed solvent electrolyte systems, using the Redlich-Kwong equation-of-state. ELECNRTL is based on two main assumptions; 1) the like-ion repulsion assumption and 2) the local electroneutrality assumption. The like-ion repulsion assumption is based on the repulsion between two anions and two cations. Therefore it states that the local composition of cations around cations is zero (AspenTech 2019).

The second assumption is the local electro-neutrality assumption. Here it is stated that the distribution of cations and anions around a central molecular species is in such a way, that the net local ionic charge is zero (AspenTech 2019).

Appendix F

Oxygen Streams Produced during CO_2 and H_2O Electrolysis

Next to H_2 and CO, oxygen is being produced during the electrolyses. Industrial oxygen is sold with a purity of $\geq$ 99.9% O_2, 50 °Cand a pressure of 150 bar. Its average price is € 376 per m^3 ($= \frac{0.376\ euro/L}{1.429\ kg/L}$ = € 0.263 per kg) (Made-in-China 2022). A rough estimation of the CAPEX and OPEX to upgrade the produced oxygen to industrial standards is made. As the oxygen produced by the AEL does not consist of a purity $\geq$ 99.9%, this stream is discarded. The oxygen stream of the SOEC has a purity of $\geq$ 99.9%, thussolely a pressure increase is necessary. This is performed by a multi-stage compressor.

The OPEX is assumed to be dominated by the power that the compressor utilizes. It is assumed that the compressor operates with an isentropic efficiency of 85% and that the system behaves as an ideal gas.

Firstly, the ideal compression ratio is calculated following Equation F.1. The compression ratio is used to calculate the work performed. This calculation is shown in Equation F.2 (López-Paniagua et al. 2020).

$$r = r_t^{\frac{1}{n}} \tag{F.1}$$

r	Compression ratio
r_t	Total pressure ratio ($\frac{P_{out}}{P_{in}}$)
n	Compressor stages

$$w = -\frac{1}{\eta} \times R \times T_1 \times \frac{k}{k-1} \times n \times (r^{\frac{k-1}{k}} - 1) \tag{F.2}$$

w	work performed
η	Isentropic Efficiency (85%)
R	Universal Gas Constant ($8.314 \frac{J}{mol \times K}$)
T_1	Temperature at end of each compression phase (323.15 K)
k	Polytropic constant (1.41 for isentropic processes (López-Paniagua et al. 2020))
n	Total number of compression stages
r	Compression ratio (see Equation F.1)

The CAPEX of the compressor is calculated based on the correlation to the power requirement. This correlation is described by Peters et al. 2003 Figure 12-28 to 12-30. Note that several CAPEX calculation methods for multi-stage compressors can be used. The results from these different methods show large variability (Luyben 2018). Therefore, this CAPEX calculation should be merely seen as a back-of-the-envelope estimation.

Oxygen produced during CO_2 Electrolysis

The oxygen stream leaves the SOEC at a pressure of 10 bar and a temperature of 750 ℃. Following Equation F.1, the optimal compression ratio is:

$$r = (\frac{150}{10})^{\frac{1}{7}} = 1.47$$

The work performed by the compressor is:

$$w = -\frac{1}{0.85} \times 8.314 \times 323.15 \times \frac{1.41}{1.41-1} \times 7 \times (1.47^{\frac{1.41-1}{1.41}} - 1) = -9020\frac{J}{mol}$$

The oxygen stream has a molar density of 0.0426×10^{-3} mol $\times$ m^{-3} and a volumetric flow of 1860 $m^3 \times h^{-1}$. The amount of work in kW required is thus:

$$w = \frac{9020\frac{J}{mol} \times 0.0426 \times 10^3 \frac{mol}{m^3} \times 1860\frac{m^3}{h}}{3600\ \frac{sec}{h}} \approx 198.53\ kW$$

Considering a price of €0.106 per kWh and a production of 2536.2 kg $\times$ h^{-1} oxygen, the OPEX per kg oxygen is calculated to be:

$$OPEX = \frac{0.106 \times 198.53}{2536.2} = €\ 0.0083\ kg^{-1}$$

The obtained power requirement is used to estimate the CAPEX based on Peters et al. 2003. For a centrifugal compressor, a CAPEX of ≈ 100,000 USD (= € 94,000) is expected. Taking a one-year payback period, this result in a cost of:

$$Capital\ Cost\ Compressor \approx \frac{94,000}{20288\ tonne} = €\ 0.0046\ kg^{-1}$$

This result in an estimated € 0.013 per kg oxygen. With a selling price of € 0.263 per kg, it is judged feasible to upgrade this oxygen stream to industrial oxygen.

Oxygen produced during Water Electrolysis

During H_2O electrolysis, 3.195 ton oxygen is produced per hour. The stream leaves the AEL at a pressure of 6.7 bar. However, the purity of the outgoing stream is not in line with industrial applications. The oxygen stream is considerably large and upgrading could be considered. Nevertheless, this is judged to be outside of the scope of this research.

Appendix G

Pugh Matrices for CO_2 and H_2O Electrolyzers

The data used to guide the decision making for selecting electrolyzers is shown in this Appendix. Firstly, two knock-out critera have to be passed. Secondly, the electrolyzers that pass the knock-out criteria are compared.

Knock-out Criteria

The knock-out criteria are: a TRL below 3 and a current density below 200 mA/cm^2. The criteria of a TRL of 3 or above is set, as starting from this TRL valid *ex-ante* analyses can be made (Van der Spek, Ramirez, et al. 2017). The second criterium is set as an electrolyzer with a lower current density is in several sources described as not industrially relevant (Burdyny and W. A. Smith 2019) (Liu et al. 2019) (Yu Yang and Li 2021).

G.1 CO_2 Electrolyzers

The following CO_2 electrolysis options are compared; Low-temperature electrolysis, molten carbonate electrolysis and solid oxide electrolysis. For each of the three options several design characteristics are researched. These characteristics are compared to the other electrolysis options. This comparison can be seen in the Pugh matrix as described in Figure 3.2.1. The data on which this Pugh matrix is based is shown in this Appendix.

Characteristics of low-temperature electrolysis are shown in Table G.1, of molten carbonate electrolysis in Table G.2 and of SOEC in Table G.6.

G.2 H_2O Electrolyzers

The following H_2O electrolysis options are compared; alkaline (AEL), polymer exchange membrane (PEMEL), solid-oxide cells (SOEC) and anion exchange membrane (AEM). For each of the options several design characteristics are researched. These characteristics are the same ones as used for the assessment of the CO_2 electrolyzers. The comparison of the H_2O electrolyzers can be seen in the Pugh matrix as described in Figure 3.2.3. The values are shown in this Appendix. Characteristics of alkaline electrolysis are shown in Table G.4, of PEMEL in Table G.5 and of SOEC electrolysis in Table G.6.

Table G.1: Characteristics of low-temperature electrolysis

Category	Criterium	1. Low-Temperature	*Sources*
Risks	TRL	4	(Küngas 2020)
	Proven Durability (h)	4380	(Küngas 2020), (Kutz et al. 2017)
Process Properties	Operating Temperature (℃)	30-60	(Küngas 2020), (Endrodi et al. 2019), (Dufek et al. 2012), (Wakerley et al. 2022)
	Faradaic Efficiency (%)	70%-75%	(Endrodi et al. 2019)
	Partial Current Density (mA/cm^2)	~250	(Endrodi et al. 2019)
	Operating Cell Voltage (V vs SHE)	4.5 V - 5.5 V	(Küngas 2020), (Endrodi et al. 2019), (Dufek et al. 2012)
	Conversion Efficiency (%)	30%-45%	(Küngas 2020), (Endrodi et al. 2019), (Dufek et al. 2012)
	Tolerance to (sulphur) Impurities	Low	(Küngas 2020), (Endrodi et al. 2019), (Dufek et al. 2012)
Economics	CAPEX	Medium	(Küngas 2020), (Endrodi et al. 2019), (Dufek et al. 2012)
Environmental Sustainability	Catalyst/Electrolyte Material	Ag, Au, IrO2 solid ion-selective membranes, aqueous solutions	(Küngas 2020), (Verma, Hamasaki, et al. 2017), (Wu et al. 2016), (Y. Chen et al. 2012), (Shen et al. 2019) (Hauch et al. 2020) (Delacourt et al. 2007)
	Electric Power Consumption (kWh/nm3)	~9-10	(Küngas 2020), (Endrodi et al. 2019), (Dufek et al. 2012)

Table G.2: Characteristics of molten carbonate electrolysis

Category	Criterium	2. Molten Carbonate	*Sources*
Risks	TRL	5	(Küngas 2020)
	Proven Durability (h)	100-120	(Küngas 2020) (Kaplan et al. 2010)
Process Properties	Operating Temperature (℃)	500-800	(Küngas 2020)
	Faradaic Efficiency (%)	100%	(Küngas 2020)
	Partial Current Density (mA/cm^2)	~550	(Kaplan et al. 2010)
	Operating Cell Voltage (V vs SHE)	1.8 V - 2.5 V	(Küngas 2020), (Kaplan et al. 2010)
	Conversion Efficiency (%)	100%	(Küngas 2020), (Kaplan et al. 2010)
	Tolerance to (sulphur) Impurities	High	(Küngas 2020), (Kaplan et al. 2010)
Economics	CAPEX	Low	(Küngas 2020), (Kaplan et al. 2010)
Environmental Sustainability	Catalyst/Electrolyte Material	Molten Li_2O / Li_2CO_3, Carbon melt	(Hauch et al. 2020), (Küngas 2020)
	Electric Power Consumption (kWh/nm3)	~2.5-3.0	(Küngas 2020), (Kaplan et al. 2010)

Table G.3: Characteristics of solid oxide electrolysis

Category	Criterium	3. Solid Oxide Electrolysis Cells	*Sources*
Risks	TRL	8	(Küngas 2020)
	Proven Durability (h)	8500-10,000	(Küngas 2020), (Song et al. 2019)
Process Properties	Operating Temperature (℃)	700-900	(Küngas 2020), (Sánchez et al. 2019), (C. Zhang et al. 2017), (Bevilacqua et al. 2015)
	Faradaic Efficiency (%)	100%	(Küngas 2020), (Huang et al. 2019)
	Partial Current Density (mA/cm^2)	~800	(Küngas 2020)
	Operating Cell Voltage (V vs SHE)	1 V - 1.5 V	(Küngas 2020), (Huang et al. 2019), (Ebbesen and Mogensen 2009)
	Conversion Efficiency (%)	80%-90%	(Küngas 2020), (Ebbesen and Mogensen 2009)
	Tolerance to (sulphur) Impurities	Medium	(Küngas 2020), (Kaplan et al. 2010)
Economics	CAPEX	Low	(Küngas 2020), (Kaplan et al. 2010)
Environmental Sustainability	Catalyst/Electrolyte Material	Nickel, stabilized zirconias (YSZ), doped cerias, lanthanums	(Küngas 2020), (Hauch et al. 2020), (Shen et al. 2019), (Kharton et al. 2004), (Zhan and Zhao 2010)
	Electric Power Consumption (kWh/nm3)	~2.0-2.5	(Küngas 2020), (Ebbesen and Mogensen 2009)

Table G.4: Characteristics of H_2O alkaline electrolysis.

Category	Criterium	1. Alkaline	*Sources*
Risks	TRL	8	(Hauch et al. 2020), (Babic et al. 2017), (Xiang et al. 2016)
	Proven Durability (h)	60,000	(Taibi et al. 2020), (Babic et al. 2017)
Process Properties	Operating Temperature (°C)	60-90	(Xiang et al. 2016), (Taibi et al. 2020)
	Operating Pressure (bar)	1-30	(Taibi et al. 2020)
	Faradaic Efficiency (%)	100	(Sanchez et al. 2020)
	Partial Current Density (mA/cm^2)	200-1000	(Babic et al. 2017), (Taibi et al. 2020) (O. Schmidt et al. 2017)
	Operating Cell Voltage (V vs SHE)	1.5 V - 2.4 V	(Hauch et al. 2020)
	Conversion Efficiency (%)	90	(Breeze 2019)
	Tolerance to Impurities	Impacted by iron, chromium, copper, silicon, aluminium & boron	(Taibi et al. 2020)
Economics	CAPEX (USD/kW)	500-1000	(Taibi et al. 2020), (Babic et al. 2017), (Brauns and Turek 2020)
Environmental Sustainability	Catalyst/Electrolyte Material	Nickel, 25-35 wt% KOH	(Taibi et al. 2020), (Babic et al. 2017), (Xiang et al. 2016)
	Electric Power Consumption (kWh/m^3)	4.5-6.6	(O. Schmidt et al. 2017)

Table G.5: Characteristics of H_2O PEM electrolysis. An 'X' indicated that no thrustworthy value under these circumstances could be found.

Category	Criterium	2. Polymer Exchange Membrane	*Sources*
Risks	TRL	8	(Hauch et al. 2020)
	Proven Durability (h)	50,000-60,000	(Taibi et al. 2020), (Babic et al. 2017), (Koponen et al. 2017)
Process Properties	Operating Temperature (°C)	70-90	(Babic et al. 2017), (Taibi et al. 2020)
	Operating Pressure (bar)	30-70	(Babic et al. 2017), (Taibi et al. 2020)
	Faradaic Efficiency (%)	100	(Koponen et al. 2017), (Persson et al. 2020), (Garcıa-Valverde et al. 2012)
	Partial Current Density (mA/cm^2)	600-2000	(O. Schmidt et al. 2017)
	Operating Cell Voltage (V vs SHE)	1.5 V - 2.0 V	(Hauch et al. 2020) (Xiang et al. 2016)
	Conversion Efficiency (%)	X	
	Tolerance to Impurities	Ion-poisoning by Cu, Fe, & Ca	(Babic et al. 2017)
Economics	CAPEX (USD/kW)	700-1400	(Taibi et al. 2020), (Babic et al. 2017)
Environmental Sustainability	Catalyst/Electrolyte Material	Platinum, IrO_3 PFSA membranes	(Babic et al. 2017), (Taibi et al. 2020), (Xiang et al. 2016)
	Electric Power Consumption (kWh/m^3)	4.2-6.6	(O. Schmidt et al. 2017)

Table G.6: Characteristics of H_2O solid oxide electrolysis. An 'X' indicated that the values, under circumstances comparable to the other characteristics, could not be found. *Indicates that value is retrieved from expert elicitation, as reported by O. Schmidt et al. 2017.

Category	Criterium	3. Solid Oxide Cells	*Sources*
Risks	TRL	3	(Hauch et al. 2020)
	Proven Durability (h)	<20,000	(Taibi et al. 2020)
Process Properties	Operating Temperature (°C)	600-900	(Babic et al. 2017), (Taibi et al. 2020)
	Operating Pressure (bar)	~1	(Taibi et al. 2020)
	Faradaic Efficiency (%)	100	(Hu et al. 2022)
	Partial Current Density (mA/cm^2)	300-2000	(O. Schmidt et al. 2017)
	Operating Cell Voltage (V vs SHE)	0.9 V -1.5 V	(Hauch et al. 2020) (Xiang et al. 2016)
	Conversion Efficiency (%)	X	
	Tolerance to Impurities	Poor	(Y. Wang et al. 2017)
Economics	CAPEX (USD/kW)	>2000	(Taibi et al. 2020)
Environmental Sustainability	Catalyst/Electrolyte Material	Nickel, YSZ	(Xiang et al. 2016), (Taibi et al. 2020)
	Electric Power Consumption (kWh/m^3)	>3.7*	(O. Schmidt et al. 2017)

Appendix H

Composition of Feedstock Streams

A detailed overview of the stream compositions of Porthos and both nutrient streams can be found in this Appendix.

H.1 Porthos Stream

Table H.1: Composition of the Porthos CO_2 stream. The maximum levels of the impurities shown are used for the simulation in Aspen. *Retrieved from (Porthos 2019).*

Component	Mole Base
CO2	$\geq$ 95%
H_2O	$\leq$ 70 ppm
H_2	$\leq$ 0.75%
N_2	$\leq$ 2.4%
Ar	$\leq$ 0.4%
CH_4	$\leq$ 1%
CO	$\leq$ 750 ppm
O_2	$\leq$ 40 ppm
Total Sulfur-contained compounds (COS, DMS, H_2S, SO_x, mercaptan)	$\leq$ 20 ppm ($H_2S \leq$ 5 ppm)
Total NO_x	$\leq$ 5 ppm
EtOH	$\leq$ 20 ppm

Table H.2: Overview of the composition of the nutrient stream added to the syngas fermentation. The mass flow of this stream is set to 100.3% of the nitrogen to be consumed by the biomass. This composition is retrieved from Phillips et al. 1993. Trace materials in the medium with a concentration below 1 mg/L are not included.

Nutrient	Concentration (gr/L)
$MgCl_2 \cdot 6\ H_2O$	0.5
$NaCl$	0.2
$CaCl_2 \cdot 2\ H_2O$	0.2
$ZnSO_4 \cdot 7\ H_2O$	0.001
H_3BO_3	0.003
$CoCl_2 \cdot 6\ H_2O$	0.002
$FeCl_2 \cdot 4\ H_2O$	0.015
$(NH_4)_2HPO_4$	2
H_3PO_4	0.0015
KCl	0.15

H.2 Nutrient Composition Fermentation #1

H.3 Nutrient Composition Fermentation #2

Table H.3: Overview of the composition of the nutrient stream added to the chain-elongation. The mass flow of this stream is set to 100.3% of the nitrogen to be consumed by the biomass. This composition is retrieved from P. Yang et al. 2018. Trace materials in the medium with a concentration below 1 mg/L are not included.

Nutrient	Concentration (gr/L)
$MgCl_2 \cdot 6\ H_2O$	0.4
$NaCl$	1
$CaCl_2 \cdot 2\ H_2O$	0.15
KCl	0.5
KH_2PO_4	0.2
NH_4Cl	50
$NaHCO_3$	252

Appendix I

H_2S Removal of the Porthos Stream

The level of SO_2 and H_2S impurities in the Porthos feedstream are $\leq$ 15 ppm and $\leq$ 5 ppm respectively (Porthos 2019). These concentrations are higher than the accepted range for solid oxide electrolyzers (SOECs). The maximum allowable concentrations are 1 ppm of H_2S and 0.5 ppm of SO_2 (Wasajja et al. 2020) (Jeanmonod et al. 2020). Thus, removal of both SO_2 and H_2S is required.
Decreasing the H_2S concentration in the Porthos stream can be achieved via several technologies. These can be categorized into either physical-chemical technologies or biotechnological (Allegue et al. 2012) (Georgiadis et al. 2021). For the removal of H_2S, physical-chemical technologies include adsorption, scrubbing and membrane purification. Examples of biotechnological cleaning processes are using a biofilter (commercially available as BiogasCleaner® and Biopuric®) or bioscrubber (commercialized as Thiopaq™) (Allegue et al. 2012). In general, the biotechnological cleaning processes are less expensive and more easily maintainable compared to physical-chemical technologies (Allegue et al. 2012). However, it also shows two main disadvantages when being placed in the context of the design in this report. Firstly, for H_2S concentrations lower than 50 ppm, an additional cleaning step is required (Allegue et al. 2012). Secondly, the microorganisms in the biological system are aerobic (Allegue et al. 2012). As the syngas fermentation is performed by anaerobic microorganisms, this would imply that first saturation with and then removal of oxygen would be required (Morvan et al. 2021). Due to these disadvantages, physical-chemical cleaning is preferred.

For physical-chemical cleaning both adsorption, absorption and membrane purification are compared. According to Allegue et al. 2012, the most common H_2S removal technologies in these categories are:

- Adsorption on impregnated activated carbon (commercialized as a.o. Sulfusorb®).
- Adsorption on molecular sieve.
- Adsorption using iron oxides (commercialized as a.o. SulfaTreat® and Sulphur-Rite®).
- Absorption with chelated-iron salt solutions (commercialized as a.o. LO-CAT® and SulFerox®).
- Absorption with frozen methanol (commercialized as Rectisol®).
- Absorption with a mixture of dimethyl ether and polyethylene glycol (commercialized as Selexol®).
- Gas-gas separation by solid membranes.
- Catalytic oxidation to form SO_2 (commercialized as hybrid CrystaSulf®)

In order to decide which pre-treatment method will be utilized, some knock-out criteria are set. Factors that would lead to a 'knock-out' of a technology are:

- **Sulphur purification levels of $\leq$ 1 ppm are not reachable with solely this technology.** The goal is to decrease the sulphur concentration to $\leq$ 1 ppm in order to prevent decreasing the performance of the SOEC and fermentation. If the technology requires an additional sulphur removal technology to reach this level, it is disregarded.
- **The technology also removes carbon dioxide.** Some sulphur removal technologies also remove CO_2 . These technologies are used to purify e.g. biogas. However, as CO_2 is the feedstock for the SOEC, CO_2 removal is undesired.
- **The technology is known to be not cost-competitive with alternatives.** Some technologies have higher operational cost than their direct alternatives.
- **The purification method creates notorious hazardous waste streams.** By utilizing some technologies, the stream containing the removed sulphur needs to be regenerated or discarded (landfilling). The regeneration of the waste stream could be notoriously hazardous due to causing bed fires and using dangerous chemicals. The sulphur removal technology is judged not suitable if the waste stream is polluting and the regeneration is notoriously hazardous.

An overview of the technologies and the identified knock-out criteria are shown in Table I.1. Here, it can be seen that either using absorption with chelated iron-salt solutions or the catalytic oxidation to SO_2 is preferred.

Absorption with chelated iron-salt solutions is commercialized as LO-CAT® and MINI-CAT® by Gas Technology Products - Merichem and as SulFerox® by Shell and Dow (Allegue et al. 2012). The process consists of three steps namely 1) absorption with iron-chelate to form S^0, 2) regeneration of the iron-chelate and 3) processing of the produced sulfur. Due to the capital expenditures, LO-CAT and MINI-CAT are advised to use for sulphur loads of 200 to 10,000 kg/day (Chemicals 2015). Sulferox™is shown to be economically beneficial starting from a sulfur capacity of 50 kg per day (Bowman 1991). The sulfur load retrieved from the Porthos stream will be approximately 1 kg per day.

The catalytic conversion of H_2S to SO_2 can be seen as a one-step process. Here, the CO_2 stream and air are mixed within a reactor. This reactor contains a sulfur-resistant, platinum-based catalyst (Dalrymple 2004). This catalyst favours the formation of SO_2 over other potential products. The disadvantage of this process is its relatively high operating temperature (200 ℃) and the usage of a platinum-based catalyst (Dalrymple 2004).

Eventually, catalytic conversion to SO_2 is chosen over absorption with LO-CAT® / Sulferox®. This is caused by the notion of the relatively low amount of H_2S present in the Porthos stream. Due to this low amount and the inevitable requirement for SO_2 clean-up, LO-CAT® / Sulferox® is expected to result in higher process costs.

Table I.1: Overview of the knock-out criteria for the commonly used H_2S removal technologies. *Based on: Allegue et al. 2012, Zappa 2001 and Mondal et al. 2011.*

	Technology	Purification levels of >1 ppm not possible	Removes also CO_2	OPEX Significantly higher compared to alternatives	Creates notorious hazardous waste streams	*Sources*
Adsorption	Impregnated Activated Carbon				X	Zappa 2001
	Molecular Sieve			X		Allegue et al. 2012
	Iron Oxide	X			X	Allegue, Zappa
Absorption	Frozen methanol		X			Mondal et al. 2011, Allegue et al. 2012
	Dimethyl Ether & Polyethylene Glycol		X	X		Mondal et al. 2011, Allegue et al. 2012
	Chelated iron-salt solutions					
Membranes	Gas-gas separation by solid membranes			X		Allegue et al. 2012
Conversion to SO_2	Catalytic oxidation					

Appendix J

Aspen Flowsheets

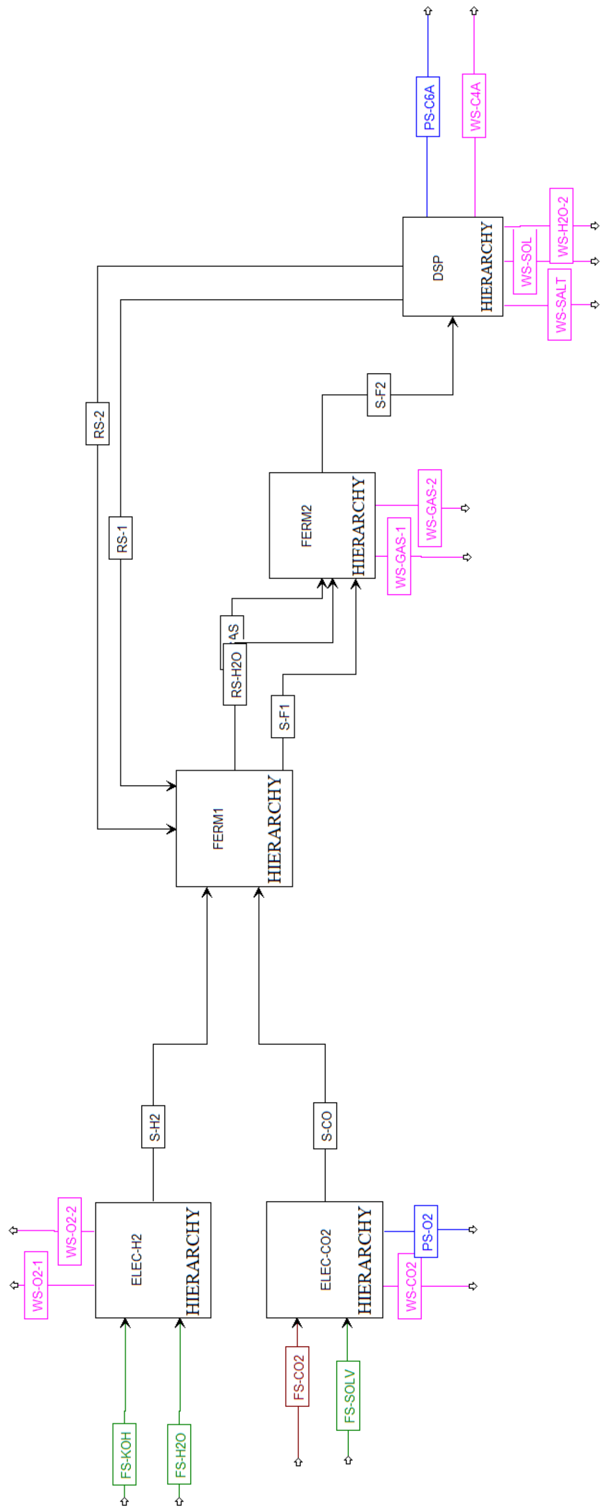

Figure J.1: Overall Overview of the Aspen Flowsheet. The hierarchy blocks represent H_2O electrolysis (*'ELEC-H2'*), CO_2 electrolysis (*'ELEC-CO2'*), ethanol production (*'FERM1'*), *n*-caproate production (*'FERM2'*) and downstream processing (*'DSP'*).

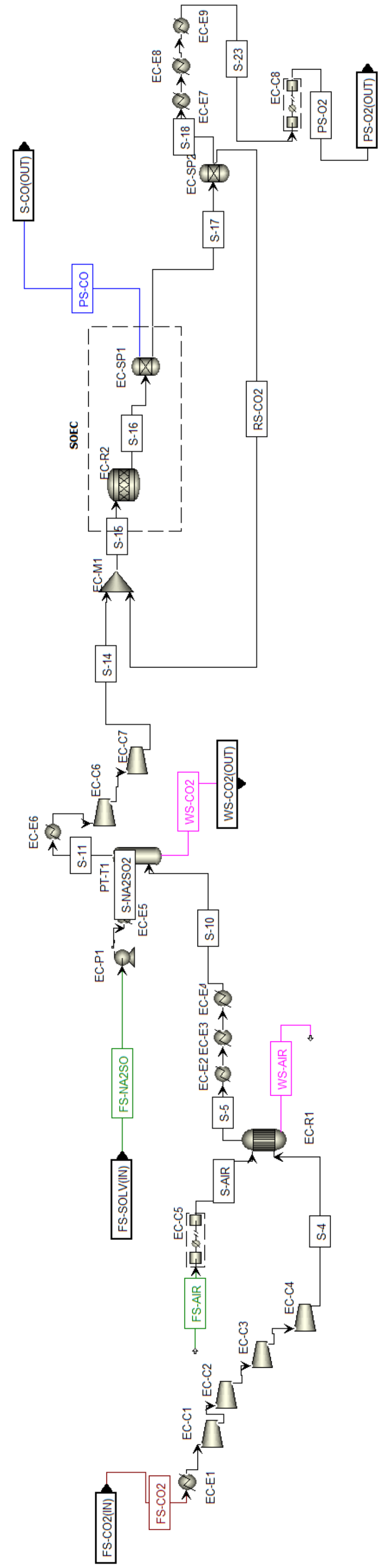

Figure J.2: Aspen Flowsheet of CO_2 pre-treatment and Solid Oxide Electrolyzer

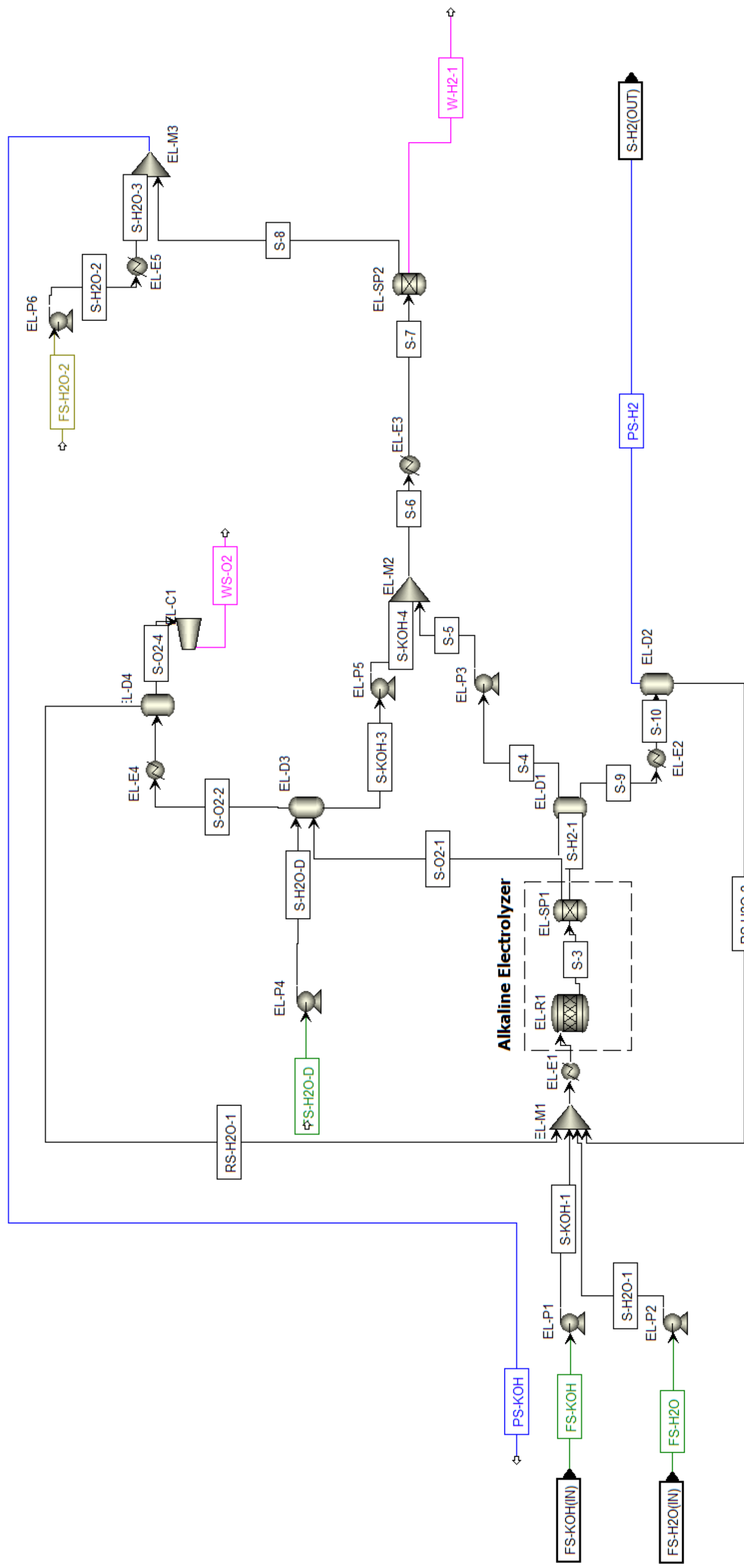

Figure J.3: Aspen Flowsheet of Alkaline Electrolysis

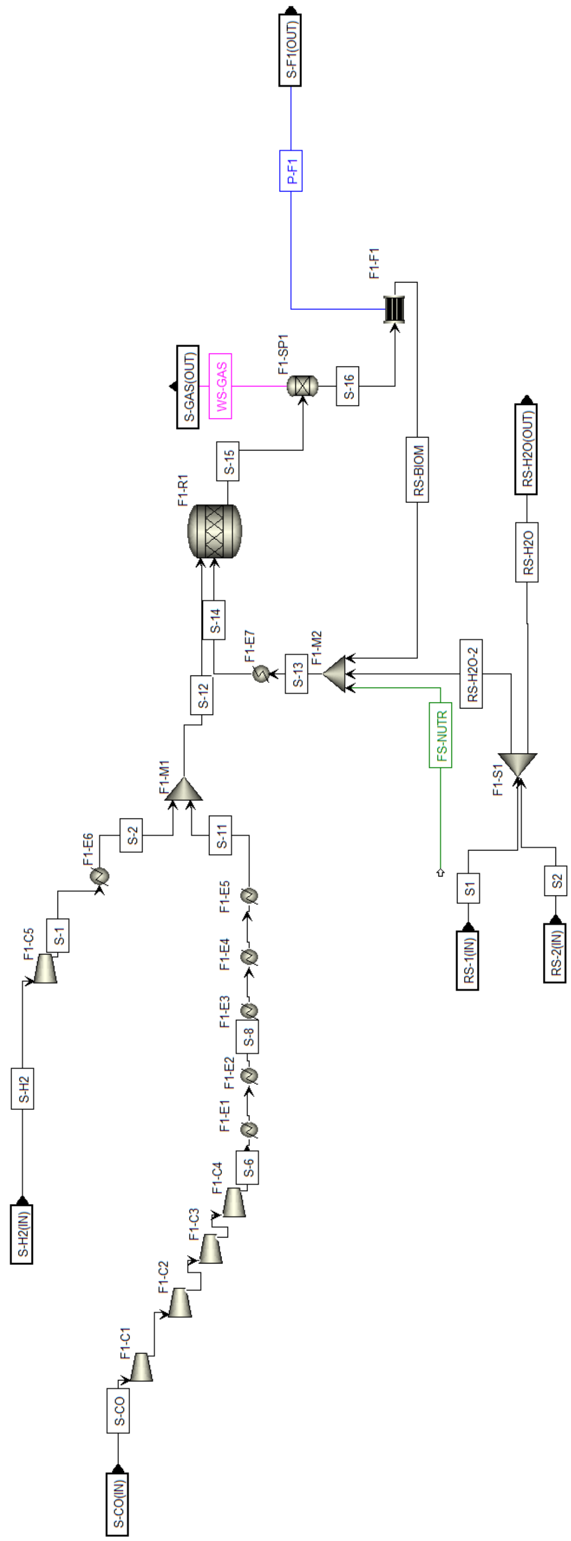

Figure J.4: Aspen Flowsheet of syngas fermentation

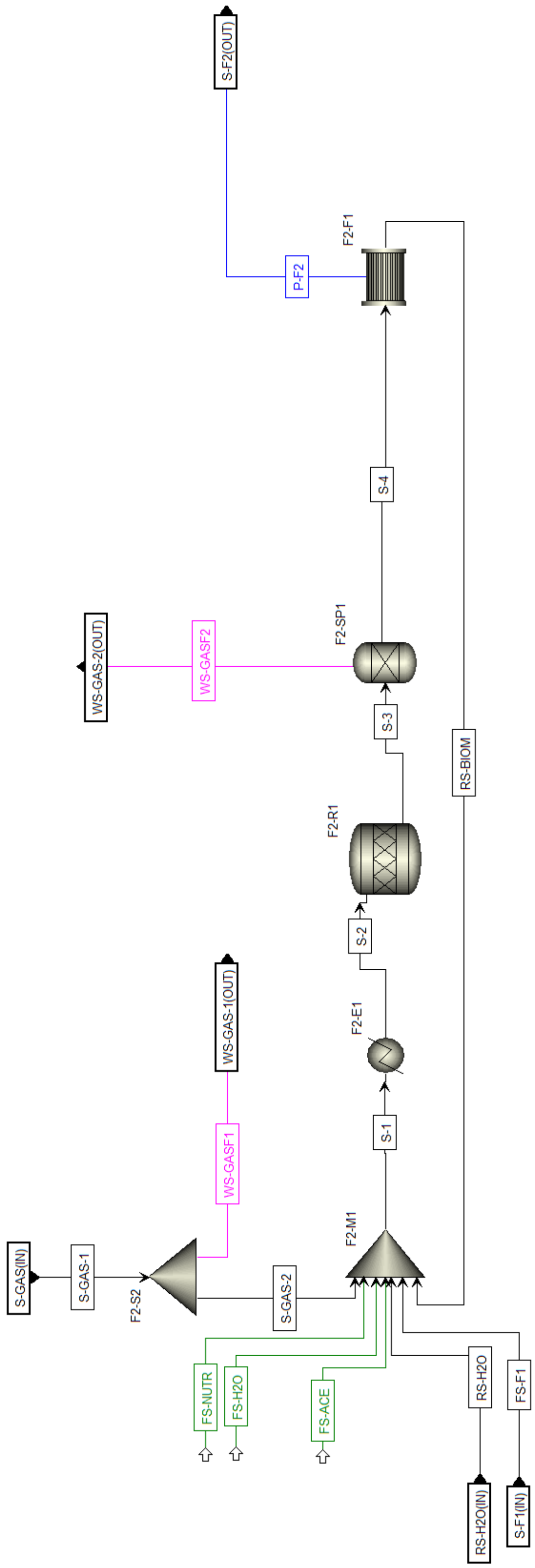

Figure J.5: Aspen Flowsheet of chain elongation

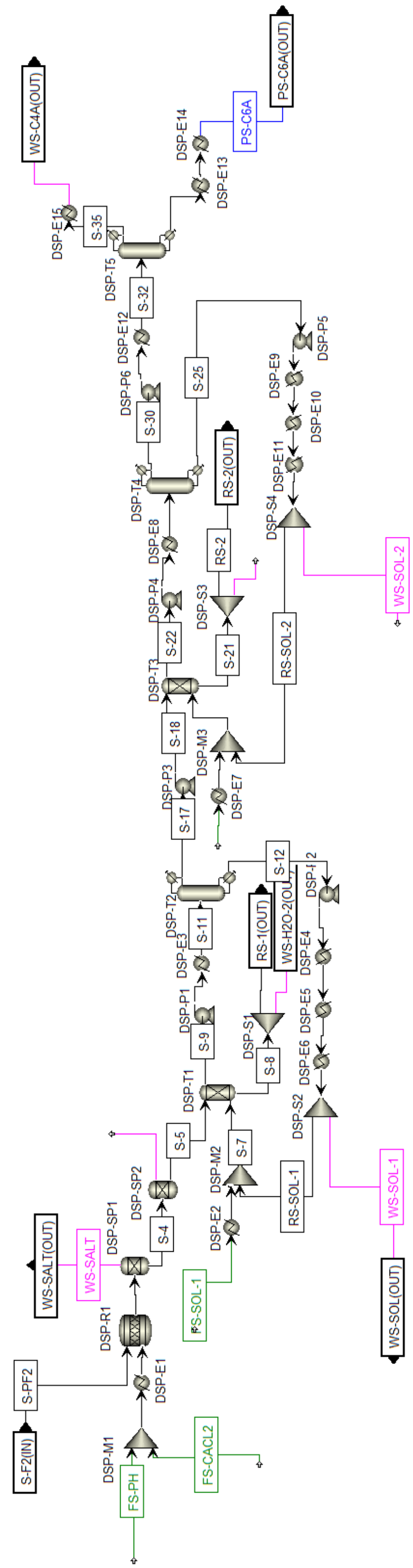

Figure J.6: Aspen Flowsheet of downstream processing

Appendix K

Mass Balances of the Indirect Route

Table K.1: Detailed mass balances and stream compositions of the Alkaline Electrolyzer. Waste streams are shown in pink.

Block ELEC-H2							
Mass in				**Mass out**			
Components		*kg/h*	*kmol/h*	*Components*		*kg/h*	*kmol/h*
Feedstock Water	H_2O	2623.6	145.6	Hydrogen	H_2	296.5	147.1
					H_2O	25.6	1.4
Electrolyte	KOH	1577.2	28.1	Electrolyte	KOH	1577.2	28.1
	H_2O	1927.7	107.0		H_2O	1927.7	107.0
Process Water	H_2O	58.1	3.2	Oxygen	O_2	2353.2	73.5
					H_2O	6.4	0.4
TOTAL		6187	284			6187	358

Table K.2: Detailed mass balances and stream compositions of the Solid Oxide Electrolyzer. Waste streams are shown in pink.

Block ELEC-CO2							
Mass in				**Mass out**			
Components		*kg/h*	*kmol/h*	*Components*		*kg/h*	*kmol/h*
Feedstock CO_2	CO_2	9694.2	220.3	Product stream CO	CO	4444.9	158.7
	CO	4.9	0.2		H_2	3.5	1.7
	H_2	3.5	1.7		H_2O	4.7	0.3
	O_2	0.3	0.0		N_2	152.7	5.5
	H_2O	0.3	0.0		CH_4	29.7	1.9
	N_2	155.3	5.5		Ar	35.1	0.9
	CH_4	37.1	2.3		SO_2	0.0	0.0
	Ar	36.9	0.9				
	SO_2	0.2	0.0	Product-Oxygen	O_2	2536.2	79.3
	H_2S	0.0	0.0				
	NO_2	0.1	0.0	Waste streams	CO	0.1	0.0
					O2	0.0	0.0
Air inflow	O_2	0.1	0.0		H_2O	1429.3	79.3
	N_2	0.2	0.0		CO_2	2717.8	61.8
					N_2	2.7	0.1
Na_2SO_3 Solvent	H_2O	1433.8	79.6		CH_4	7.3	0.5
	Na_2SO_3	116.3	0.9		Ar	1.8	0.0
					SO_2	0.3	0.0
					Na_2SO_3	116.3	0.9
					NO_2	0.1	0.0
TOTAL		11483	312			11483	391

Table K.3: Detailed mass balances and stream compositions of syngas fermentation.

Syngas Fermentation							
Mass in				**Mass out**			
Components		*kg/h*	*kmol/h*	*Components*		*kg/h*	*kmol/h*
Hydrogen	H_2	296.5	147.1	PRODUCT-1	Acetate	149.5	2.5
	H_2O	25.6	1.4		Acetic Acid	71.7	1.2
					Butyric acid	142.3	1.6
Carbon Monooxide	CO	4444.9	158.7		Caproic acid	0.0	0.0
	H_2	3.5	1.7		H_2O	38514.3	2137.9
	H_2O	4.7	0.3		H^+	9.4	9.3
	N_2	152.7	5.5		$HPO_4{}^{(2-)}$	326.3	3.4
	CH_4	29.7	1.9		EtOH	1454.3	31.6
	Ar	35.1	0.9		$MgCl_2 \cdot 6\ H_2O$	7.0	0.0
	SO_2	0.0	0.0		NaCl	2.8	0.0
					$CaCl_2 \cdot 2\ H_2O$	2.8	0.0
RS-WATER-IN	Acetatic acid	71.7	1.2		$(NH_4)_2HPO_4$	2.0	0.0
	Butyric acid	142.3	1.6		KCl	2.1	0.0
	Caproic acid	0.0	0.0		Biomass	837.2	34.0
	H_2O	38248.1	2123.1				
Nutrients	H_2O	92.9	5.2	RS-GAS	CO	444.5	15.9
	$MgCl_2 \cdot 6\ H_2O$	7.0	0.0		H_2	41.7	20.7
	NaCl	2.8	0.0		CO_2	1787.8	40.6
	$CaCl_2 \cdot 2\ H_2O$	2.8	0.0		N_2	152.7	5.5
	$(NH_4)_2HPO_4$	451.0	3.4		CH_4	29.7	1.9
	KCl	2.1	0.0		Ar	35.1	0.9
TOTAL		44013	2452			44013	2307

Table K.4: Detailed mass balances and stream compositions of chain-elongation. Waste streams are shown in pink.

FERM-2							
Mass in				**Mass out**			
Components		*kg/h*	*kmol/h*	*Components*		*kg/h*	*kmol/h*
PRODUCT-1	Acetate	149.5	2.5	PRODUCT-2	Acetate	549.3	9.3
	Acetic Acid	71.7	1.2		Butyrate	435.3	5.0
	Butyric acid	142.3	1.6		Butyric acid	1082.8	12.3
	Caproic acid	0.0	0.0		Caproate	1226.8	10.7
	H_2O	38514.3	2137.9		Caproic Acid	0.3	0.0
	H^+	9.4	9.3		H_2O	292085.6	16213.2
	$HPO_4^{(2-)}$	326.3	3.4		Cl^-	7	0.2
	EtOH	1454.3	31.6		H^+	32.0	31.8
	$MgCl_2 \cdot 6\ H_2O$	7.0	0.0		HPO_4^{2-}	326.3	3
	NaCl	2.8	0.0		$MgCl_2 \cdot 6\ H_2O$	7.1	0.0
	$CaCl_2 \cdot 2\ H_2O$	2.8	0.0		NaCl	3.0	0.1
	$(NH_4)_2HPO_4$	2.0	0.0		$CaCl_2 \cdot 2\ H_2O$	2.8	0.0
	KCl	2.1	0.0		$(NH_4)_2HPO_4$	2.0	0.0
	Biomass	837.2	34.0		KCl	2.2	0.0
					Biomass	861	34.9
					Na^+	14.1	0.6
					HCO_3^-	25.7	0.4
Feedstream-A	Acetate	476.8	8.1				
	H_2O	422.3	23.4				
	H^+	8.1	8.1				
	$MgCl_2 \cdot 6\ H_2O$	0.1	0.0				
	NaCl	0.2	0				
	$CaCl_2 \cdot 2\ H_2O$	0.0	0				
	KCl	0.1	0				
	KH_2PO_4	0.0	0				
	NH_4Cl	10.2	0.2				
	Na^+	14.1	0.6				
	$HCO3^-$	37.3	0.6				
RS-GAS	CO	444.5	15.9	WS-GAS	CO	444.5	15.9
	H_2	41.7	20.7		H_2	58.9	29.2
	CO_2	1787.8	40.6		CCO_2	1754.4	39.9
	N_2	152.7	5.5		N_2	152.7	5.5
	CH_4	29.7	1.9		CH_4	29.7	1.9
	Ar	35.1	0.9		Ar	35.1	0.9
RS-WATER-IN	Acetic acid	473.9	7.9				
	Butyric acid	940.5	10.7				
	Caproic acid	0.3	0.0				
	H_2O	252741	14029				
TOTAL		299138	16396			299138	16415

Table K.5: Detailed mass balances and stream compositions of downstream processing. Waste streams are shown in pink.

DSP							
Mass in				**Mass out**			
Components		*kg/h*	*kmol/h*	*Components*		*kg/h*	*kmol/h*
PRODUCT-2	Acetate	549.3	9.3	PS-C6A	Acetic acid	0.1	0.0
	Butyrate	435.3	5.0		Butyric acid	10.9	0.1
	Butyric acid	1082.8	12.3		Caproic acid	1237.5	10.7
	Caproate	1226.8	10.7		H_2O	1.5	0.1
	Caproic Acid	0.3	0.0				
	H_2O	292085.6	16213.2	WS-C4A	Acetate	10.7	0.2
	Cl^-	7	0.2		Butyrate	424.0	4.8
	H^+	32.0	31.8		Caproate	0.1	0.0
	HPO_4^{2-}	326.3	3		H_2O	168.1	9.3
	$MgCl_2 \cdot 6\ H_2O$	7.1	0.0				
	NaCl	3.0	0.1	WS-SALT	$CaHPO_4$	2160.2	15.9
	$CaCl_2 \cdot 2\ H_2O$	2.8	0.0		Biomass	860.5	34.9
	$(NH_4)_2HPO_4$	2.0	0.0				
	KCL	2.2	0.0	WS-HCl	Cl(-)	1132.5	31.9
	Biomass	861	34.9		H^+	32.0	31.8
	Na^+	14.1	0.6		$MgCl_2 \cdot 6\ H_2O$	7.1	0.0
	HCO_3^-	25.7	0.4		NACL	3.0	0.1
					$CaCl_2 \cdot 2\ H_2O$	2.8	0.0
					$(NH_4)_2HPO_4$	2.0	0.0
					KCl	2.2	0.0
					Na^+	14.1	0.6
					HCO_3^-	25.7	0.4
FS-A	H_2O	535.6	29.7	RS-WATER-OUT	Acetic acid	545.1	9.1
	H^+	25.1	25.0		Butyric acid	1082.8	12.3
	HPO_3^{2-}	1197.6	12.5		Caproic acid	0.3	0.0
	Cl^-	1125.8	31.8		H_2O	290989.3	16152.3
	Ca^{2+}	636.3	15.9				
				WS-H_2O	Acetate	2.7	0.0
					Butyrate	5.4	0.1
					Caproate	0.0	0.0
					H_2O	1462.3	81.2
FS-SOL	TOA	466.3	1.3	WS-SOL	TOA	466.1	1.3
TOTAL		300649	16438			300649	16397

Appendix L

Background Calculations Alkaline Electrolyzer

The alkaline electrolyzer used for the indirect route is based on the model proposed by Sanchez et al. 2020. The Faradaic efficiency and operating cell voltage are calculated in this appendix, using the parameters determined by Sanchez et al. 2020.

L.1 Faradaic Efficiency

Equation L.1 shows the calculation for the Faradaic efficiency.

$$\eta_F = \left(\frac{i^2}{f_{11} + f_{12} \times T + i^2}\right) \times (f_{21} + f_{22} \times T) \tag{L.1}$$

η_F	Faradaic Efficiency
i	Current Density (4500 $\frac{A}{m^2}$)
f_{11}	Faradaic Efficiency constant 1 (478645.74 $\frac{A}{m^4}$)
f_{12}	Faradaic Efficiency constant 2 (-2953.15 $\frac{A}{(m^4 \times ℃)}$)
T	Temperature (75 ℃)
f_{21}	Faradaic Efficiency constant 3 (1.03960)
f_{22}	Faradaic Efficiency constant 4 (-0.00104 ℃$^{-1}$)

$$\eta_F = \left(\frac{4500^2}{478645.74 + -2953.15 \times 75 + 4500^2}\right) \times (1.03960 - 0.00104 \times 75) = 0.95$$

L.2 Operating Cell Voltage

The operating cell voltage is calculated following Equation L.2 (Ulleberg 2003).

$$V_{cell} = V(rev) + (r_1 + r_2 \times T) \times i + s \times \log\left[\left(t_1 + \frac{t_2}{T} + \frac{t_3}{T^2}\right) \times i + 1\right] \tag{L.2}$$

V_{cell}	Operating cell voltage (V)
$V(rev)$	Reversible cell voltage (1.23 V)
r_1	Polarization Curve constant r1 (4.45×10^{-5} $\Omega \times m^2$)
r_2	Polarization Curve constant r2 (6.88874×10^{-9} $\frac{\Omega \times m^2}{°C}$)
T	Temperature (75 °C)
i	Current Density (4500 $\frac{A}{m^2}$)
s	Polarization Curve voltage (0.338 V)
t_1	Polarization Curve constant t1 (-0.01539 $\frac{m^2}{A}$)
t_2	Polarization Curve constant t2 (2.00181 $\frac{m^2 \times °C}{A}$)
t_3	Polarization Curve constant t3 (15.242 $\frac{m^2 \times °C^2}{A}$)

$$V_{cell} = 1.23+(4.45\times10^{-5}+6.889\times10^{-9}\times75)\times4500+0.338\times\log\left[\left(-0.01539+\frac{2.00181}{75}+\frac{15.242}{75^2}\right)\times4500+1\right] = 2.04\ V$$

The calculated 2.04 V is in line with the cell potential estimated from the graphs shown in Sanchez et al. 2020. Here a cell potential of 1.8-2.2 V matches with a current density of 4500 A/m^2.

Appendix M

Background Information on the Economic Evaluation

In this Appendix some background information on the capital and operational expenditure (CAPEX and OPEX) calculations is given. It shows the derivation of the equipment cost for items not (correctly) included in the Aspen Process Economics Analyzer (APEA). These items are 1) the direct oxidation at the pre-treatment of the Porthos stream (ELEC-CO2.PT-R1 in the Aspen Flowsheet), 2) the SOEC for CO_2 electrolysis (ELEC-CO2.EC-R2), 3) the AEL for H_2O electrolysis (ELEC-H2.EL-R1) and 4) both liquid-liquid extraction columns at the DSP (DSP.T1 and DSP.T3). Next to the equipment costs, this Appendix also shows the price list used to derive the raw material costs, utility costs and revenue of the indirect route.

M.1 Equipment Cost

Direct Oxidation Column

The equipment cost of the direct oxidation column is retrieved by using the so-called *"Six-Tenths Rule"* (Towler and Sinnott 2013). This method relates the capital cost of a piece of equipment to its capacity via Equation M.1.

$$C_2 = C_1 \times \frac{S_2}{S_1}^{0.6} \tag{M.1}$$

C_2 Capital cost of the plant with capacity S_2
C_1 Capital cost of the plant with capacity S_1

In order to apply the *"Six-Tenths Rule"*, the capital cost and capacity of the same unit in a different process needs to be known. For direct oxidation, a unit operated with a flow of 13,093 m^3/hr with a corresponding price of 6,700,000 USD is reported by Meyer 2010. Note, this price includes the compression of the required in going air.

The flow of the direct oxidation in the indirect route is 245 m^3/hr. Following Equation M.1, this leads to a capital cost of:

$$C_2 = 6,700,000 \times \frac{245}{13093}^{0.6} = 615710\, USD$$

$$C_2\ (EUR) = 615710 \times 0.94 = 578,767 EUR$$

Thus, a price of €578,767 is assumed for the direct oxidation, including the compressor used for air compression (ELEC-CO2.EC-C5).

Solid Oxide Electrolysis Cell

The equipment costs of the SOEC is assumed to be mainly dominated by its area costs. The total area of the SOEC is calculated by Equation M.2

$$Area = \frac{Q}{j} \tag{M.2}$$

Q	Total charge
j	Current density (0.850 A/cm^2, (Küngas 2020))

Of which the total charge is determined by:

$$Q = \frac{n \times F \times N_{prod}}{\eta_F}$$

n	Amount of electrons (2)
F	Faraday Constant (96485)
N_{prod}	Amount produced (168.9 kmol/hr, see Appendix K)
η_F	Faradaic Efficiency (100%, (Küngas 2020))

$$Q = \frac{2 \times 96485 \times 168.9}{1} = 32.59 \times 10^6 \; kA$$

$$Area = \frac{32.59 \times 10^6}{0.85 \times 10^4} = 3834 \; m^2$$

SOECs have a price of 570-590 USD per m^2 (Küngas 2020). Taking an average of 580 USD, the capital cost for the SOEC is estimated at:

$$Equipment\ Cost\ SOEC = 3834 \times 580 \times 0.94 = 2,090,530 \; EUR$$

Alkaline Electrolyzer

The equipment cost of the AEL is based on the known equipment cost for AELs with a similar performance to the one described in this research. In general, AELs cost 500-1000 USD per kW (Taibi et al. 2020). An average price of 750 USD per kW is assumed. The AEL utilizes 16943.5 kW, as described in subsection 4.5.2. This results in an estimated equipment cost of

$$Equipment\ Cost\ AEL = 16943.5 \times 750 \times 0.94 = 11,945,168 \; EUR$$

Liquid-Liquid Extraction

For the determination of the LLE column costs, a similar approach as for the SOEC is followed. The capital costs are estimated based on the area required. The area is retrieved following the methodology described by Saboe et al. 2018. Here, the area of the extractor is calculated based on:

$$Productivity \times V_F = A_m \times Product\ Flux \tag{M.3}$$

$Productivity$	Rate of product formed per fermentation volume
V_F	Volume of bioreactor broth (L)
A_m	Membrane area (m^2)
$Product\ Flux$	Rate of product extraction per membrane area, 10 gr/(hr m^2))

Rewriting gives:

$$A_m = \frac{Productivity \times V_F}{Product\ Flux}$$

For the first LLE, this results in:

$$A_m = \frac{4.12 \times 10^{-3} \times 300,780}{10 \times 10^{-3}} = 123,819\ m^2$$

For the second LLE:

$$A_m = \frac{0.346 \times 3573}{10 \times 10^{-3}} = 123,759\ m^2$$

One unit of the LLE membrane contains 560 m^2 and has a price of 7200 EUR (SGProjects 2022) (3M 2022). Thus the amount of units are;

$$Units\ LLE\ \#1 = \frac{123,819}{560} = 221$$

$$Units\ LLE\ \#2 = \frac{123,759}{560} = 221$$

This result in a total equipment cost of:

$$Equipment\ Costs = (221 + 221) \times 7200 = 3,182,400\ EUR$$

M.2 Operational Expenditures

Price List

An overview of the price of each compound stream is shown in Table M.1. The expenses made are divided into the raw materials, utilities and waste treatment. The product prices are used to calculate the revenue.

Raw Materials and Waste Disposal

An overview of the in- and outgoing streams and their cost associated is shown in Table M.2. The cost are derived from Table M.1. The raw material cost (total of $\approx$ 7.4 million) and the total waste disposal cost (total of $\approx$ 3.86 million) are used to calculate the operational expenditure of the plant. The revenue streams are used for the calculation of the minimal caproate selling price.

Table M.1: Price list of the compounds and utilities.

Price list				
	Component	Price	Unit	Source
FEEDSTOCK	H_2O	1.02	EUR/m^3	Waternet 2019
	CO_2	-60.00	EUR/t	Porthos 2019
	Nutrients Fermentation #1	270.00	EUR/m^3	Estimation based on composition
	Nutrients Fermentation #2	590.00	EUR/m^3	Estimation based on composition
	Acetate	0.65	EUR/kg	Jourdin et al. 2020
	$CaCl_2$ solution	1.10	EUR/m^3	Alibaba 2022a
	H_3PO_4 85 wt% stream	0.03	EUR/kg	Alibaba 2022b
	TOA solution	1.03	EUR/kg	Alibaba 2022c
UTILITIES	Very low pressure steam	1.79	EUR/GJ	Aspen default
	Low pressure steam	1.79	EUR/GJ	Aspen default
	Medium pressure steam	2.07	EUR/GJ	Aspen default
	High pressure steam	2.35	EUR/GJ	Aspen default
	Very high pressure steam	2.35	EUR/GJ	Aspen default
	Hot Oil /Very high T	3.29	EUR/GJ	Aspen default
	Fired Heat	4.00	EUR/GJ	Aspen default
	Chilling water	0.20	EUR/GJ	Aspen default
	Cooling water	0.20	EUR/GJ	Aspen default
	Electricity	0.11	EUR/kWh	Statline 2022a
WASTE STREAMS	Oxygen	0	EUR/t	
	CO_2 offgas	43.37	EUR/t	Worldbank 2022
	Waste water	0.05	EUR/m^3	Turton et al. 2008
	Solid waste	-33800	EUR/t	Turton et al. 2008
	HCl	13.70	EUR/t	Government 2022
	TOA	13.70	EUR/t	Government 2022
PRODUCTS	Caproate	4400	EUR/t	See section 1.1.1
	Butyrate 70 wt%	0	EUR/kg	
	Industrial Oxygen	376	EUR/m^3	Made-in-China 2022

Table M.2: Overview of the in- and outgoing streams of the process and the corresponding material cost, waste disposal cost or revenue generated. Stream flows are retrieved from the Aspen simulation. Prices are retrieved from the price list shown above.

	Process Section	Stream	Flow (t/yr)	Flow (m3/yr)	Price	Price Unit	Stream Cost (EUR/yr)
Raw Materials	ELEC-H2	Feedstock Water	21454	21454	1.02	EUR/m^3	€ 21,926
	ELEC-CO_2	Feedstock CO_2	79462		-60.0	EUR/t	-€ 4,767,716
		Air inflow	2.4		0.0	EUR/m^3	€ 0
		Na_2SO_3 Solvent	12400	208	15547.60	EUR/m^3	€ 3,233,901
	FERM1-F1	Nutrients-Ferm 1	4472	4276	270.00	EUR/m^3	€ 1,154,640
	FERM2-F2	Nutrients-Ferm 2	546	1631	590.00	EUR/m^3	€ 962,578
		Acetate-Ferm 2	3880		650	EUR/t	€ 2,522,000
		Additional Water	3320		1.02	EUR/m^3	€ 2,656
	DSP	$CaCl_2$	16408	50613	1.10	EUR/m^3	€ 55,573
		H_3PO_4 Stream	11800		31.63	EUR/t	€ 373,206
		TOA-stream	3728		1030	EUR/t	€ 3,839,840
	TOTAL		**157472**				**€ 7,398,603**
Waste streams	ELEC-H2	Oxygen stream	18872		0	EUR/t	€ 0
	ELEC-CO_2	Waste pre-treatment	34214		27.76	EUR/t	€ 949,695
	FERM-F2	Offgas	19803		31.23	EUR/t	€ 618,392
	DSP	Waste water DSP	11768	94144	0.05	EUR/m^3	€ 4,952
		Solid waste	24188		33.80	EUR/t	€ 817,538
		TOA Waste	3729	5412	0.05	EUR/m^3	€ 285
		HCl	9786		150.40	EUR/t	€ 1,471,887
		Butyrate stream	4824		0	EUR/t	€ 0
	TOTAL		**127184**				**€ 3,862,748**
Product Streams	ELEC-CO2	Oxygen stream	20290	108000	376	EUR/m3	€ 40,608,000
	DSP	Caproate stream	10000		4400	EUR/t	€ 44,000,000
	TOTAL		**30290**				**€ 84,608,000**

Appendix N

Background Information on the Environmental Evaluation

This Appendix shows an overview of the used CO_2 emission factors of the raw materials and utilities. This data is used to calculate the CO_2 emission and the carbon footprint of the indirect route. The carbon footprint of the raw materials, waste streams and utilities is calculated by multiplying the stream flow with the CO_2 equivalent. All utilities are assumed to have a CO_2 energy source efficiency of 1.

For the hot and cold utilities natural gas is set as the so-called ultimate fuel source. The CO_2 emission factor of natural gas is 56.6 kg_{CO_2} /GJ (Zijlema 2020). The CO_2 emissions associated with electricity usage are based on the composition of the Dutch electricity grid (Statline 2022b). The composition of this grid is shown in Table N.1. The weighted average of the CO_2 emission factors are used to compute the electricity emission factor (53.7 kg_{CO_2} /GJ).

Table N.1: Composition of the Dutch electricity mix and the corresponding CO_2 emission factors in 2019. Based on Statline 2022b and Zijlema 2020. The CO_2 emission factor of electricity is calculated to 53.7 kg_{CO_2} /GJ. *This emission factor is calculated based on the average factor of coal and natural gas.

	Electricity Source	Percentage of total (%)	CO2 Emission factor (kg/GJ)
Fossil-fuel based	Natural gas	58	56.6
	Coal	15	94.0
	Other sources	3	75.3*
Renewable	Solar/wind/water	14	0
	Biomass	5	90.8
	Other sources	5	0
Weighted Average			**53.7**

An overview of the carbon footprint of the raw materials, waste streams and utilities is shown in Table N.2. The total annual carbon emissions caused by the indirect route is 266 kt.

Table N.2: Overview of the carbon footprint of the raw materials, waste streams and utilities used in the indirect route. **The carbon footprint of the nutrients is based on the footprint of the main compounds. For the first fermentation this is $(NH_4)_2PO_4$. For the second fermentation this is $NaHCO_3$. **The carbon footprint of the solvent triethylamine is taken due to a lack of data for trioctylamine.*

	Process Section	Stream	Flow (t/yr)	CO_2 Eq (t CO_2 /t)	Carbon Footprint (t/yr)	*Source*
Raw Materials	ELEC-H2	FS Water	21454	0.0008	17	*EcoInvent v3.7.1*
	ELEC-CO_2	FS CO_2	79462	-1.0	-79462	-
		Air inflow	2.4	0.0	0	-
		Na2SO3	12400	0.47	5828	*Winnipeg 2022*
	FERM1-F1	Nutrients - Ferm 1*	4472	0.70	3130	*Ledgard et al. 2011*
	FERM2-F2	Nutrients - Ferm 2*	546	1.17	638	*Winnipeg 2022*
		Acetate	3880	0.0371	144	*EcoInvent v3.7.1*
		Additional Water	3320	0.0008	3	*EcoInvent v3.7.1*
	DSP	$CaCl_2$	16408	0.89	14603	*Winnipeg 2022*
		H_3PO_4	11800	1.45	17110	*Winnipeg 2022*
		TOA**	3728	0.705	2628	*Ethos 2013, TEA taken*
	TOTAL Materials		**157472**		**-35361**	
Waste streams	ELEC-H2	Oxygen stream	18872	0	0	
	ELEC-CO_2	Emissions pre-treatment	34214	1.00	34214	-
	FERM-F2	Offgas	19803	1.00	19803	-
	DSP	Waste water	11768	0.00039	5	*EcoInvent v3.7.1*
		Solid waste	24188	0.0025	60	*Benalcázar et al. 2017*
		TOA**	3729	0.705	2629	*Azapagic et al. 2013*
		HCl	9786	0.39	3787	*Benalcázar et al. 2017*
		Butyrate stream	4824	0	0	Feedstock other process
	TOTAL Waste		**127184**		**60498**	
			Energy (GJ/yr)			
Utilities		Hot Utilities	1,416,214	0.057	94303	*Zijlema 2020*
		Cold Utilities	1534797	0.057	86869	*Aspen default*
		Electricity		0.054	43093	*Based on Table N.1*
	TOTAL Utilities				**224266**	
TOTAL					**249,400**	

Appendix O

Sensitivity Analysis

This appendix shows the sensitivity of the minimum caproate selling price and the carbon footprint to some of the economic/environmental parameters.

O.1 Economic Sensitivity Analysis

The minimum caproate selling price (MCSP) is computed based on several cost components. These components are the CAPEX, OPEX and the revenue. For all components a cost estimate is used. Since estimations are made, it is insightful to see the impact of price alternations on the MCSP. This analysis can be found in this Appendix.

For the sensitivity analysis, the parameters influencing the CAPEX, OPEX and revenue generation the most are varied. These are; 1) the equipment cost of the alkaline electrolyzer (CAPEX), 2) the electricity price (OPEX) and 3) the industrial oxygen price (revenue). Since the prices of each component are linearly related to the MCSP, solely two price levels are necessary for the determination of the sensitivity. The price levels of the parameters are varied between -33% of the base case price and +33%. The results are plotted in Figure O.1.

From the parameters depicted in Figure O.1, the oxygen price has the largest impact on the MCSP. If the oxygen price decreases with 33%, the MCSP increases with 35%. This level of correspondence is expected. Namely, the oxygen price has a direct impact on the revenue generated and thus a direct impact on the MCSP. The parameter with the second largest impact is the electricity cost. If the electricity cost are 33% lower, the MCSP decreases with 21%. The third parameter researched is the equipment cost of the AEL. Here, the price of -33% and +33% correspond to the lowest and highest price for AEL as reported by Taibi et al. 2020. The cheapest AEL would decrease the MCSP with 11%.

O.2 Environmental Sensitivity Analysis

This sensitivity analyses shows the impact of several parameters on the carbon footprint of the indirect route. The parameters assessed are; 1) direct CO_2 emission during the pre-treatment, 2) electricity usage, 3) cold utility usage and 4) hot utility usage. These parameters are varied due to two reasons. Firstly, these have the largest impact on the carbon footprint. Secondly, these parameters are expected to have a different CO_2 emission over time due to the transition of the Dutch energy grid.

As shown in Figure O.2, the annual CO_2 emissions are the most sensitive to the hot and cold utility emissions. This is in line with the expectations, as these utilities are the largest contributor to the overall carbon

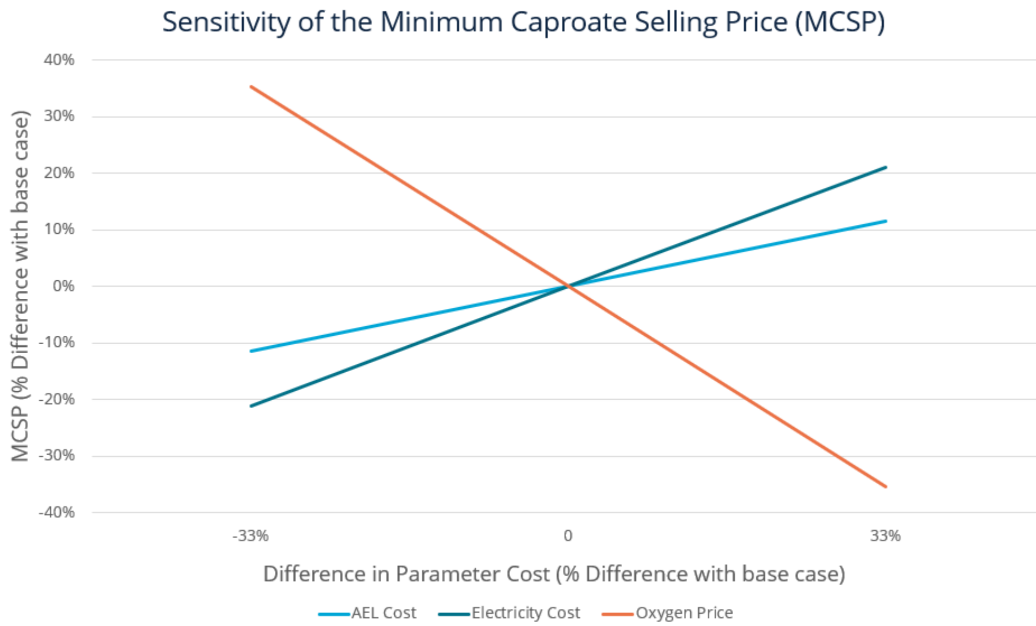

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Figure O.1: Sensitivity analysis of the minimum caproate selling price. The sensitivity on the following parameters is determined: 1) equipment cost of the alkaline electrolyzer, 2) electricity price, 3) the industrial oxygen price. Each parameter price is adjusted by -33% and +33%.

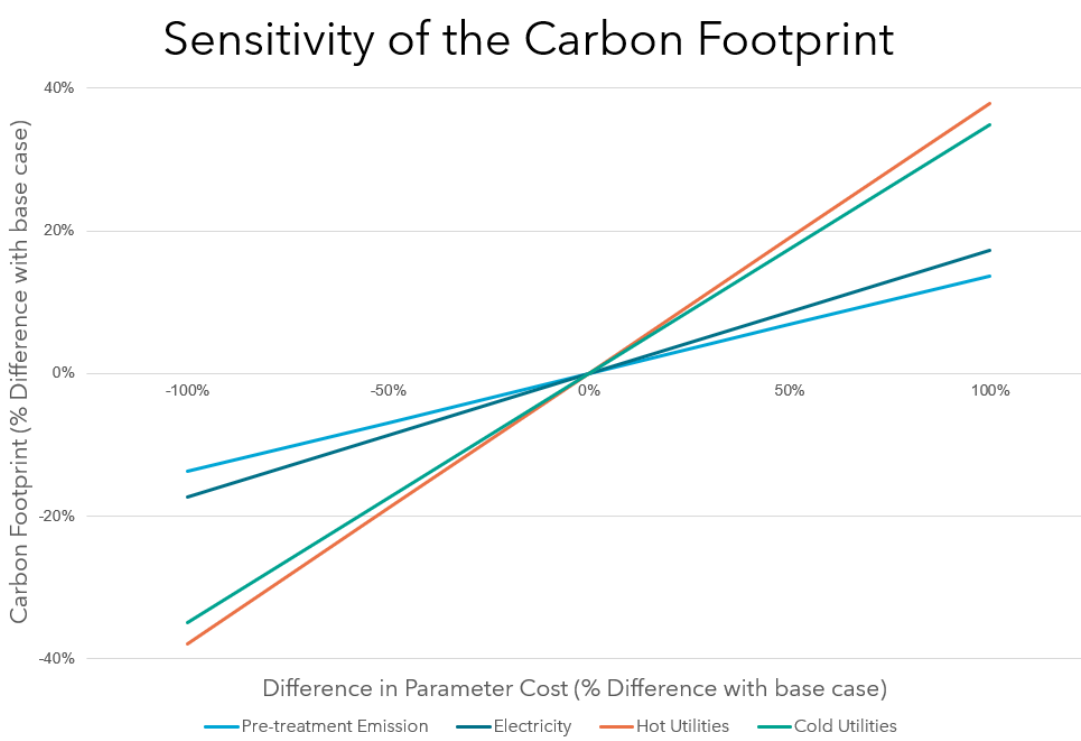

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Figure O.2: Sensitivity analysis of the annual carbon footprint. The sensitivity on the following parameters is determined: 1) direct CO_2 emission during pre-treatment, 2) electricity usage, 3) cold utility usage and 4) hot utility usage. The parameters are assessed for the scenario's in which there is no CO_2 emission, 50% of the emission, 150% or 200%.

footprint of the indirect route. Furthermore, the CO_2 pre-treatment emission has the lowest impact on the total emissions. But, removal of the pre-treatment would still result in 16% less carbon emissions. Note, if less CO_2 is emitted during pre-treatment, it is plausible to assume that also less CO_2 will be required as feedstock. Therefore, the CO_2 emission decrease accomplished is probably less then 16%.