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A conceptual case study of microbial electrosynthesis

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CO_2

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A conceptual case study of microbial electrosynthesis

Jisiwei LUO

Feasibility of Flexible CO_2 Conversion Technologies Powered by Renewable Electricity

A conceptual case study of microbial electrosynthesis

Dissertation

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for my parents and wife
献给我的父母及太太

Contents

Summary **5**

Samenvatting **11**

Nomenclature **17**

1 Introduction **19**

1 Research background 20

2 Knowledge gaps 26

3 Research questions 26

4 Research approach 27

5 Dissertation outline 29

2 Development of a conceptual framework for evaluating the flexibility of future chemical processes **37**

1 Introduction 40

2 Methodology 44

3 State-of-the-art 45

4 Framework for comparing and assessing flexibility 52

5 Conclusion 61

3 Impact of intermittent electricity supply on a conceptual process design for microbial conversion of CO_2 into hexanoic acid **71**

1 Introduction 74

2 Methodology 76

3 Results and discussion 86

4 Conclusions 91

4 Battery use or chemical storage for intermittent renewable electricity? A comparison for a microbial CO_2 electrolysis plant **97**

1 Introduction 100
2 Methodology 101
3 Results and discussion 115
4 Conclusion 124

5 Life cycle assessment of hexanoic acid production via microbial electrosynthesis and renewable electricity: Future opportunities 131

1 Introduction 133
2 Methodology 134
3 Results and discussion 140
4 Conclusion 147

6 Conclusion 153

1 Overview 154
2 Research outcomes 154
3 Limitations 163
4 Recommendations 166

A Appendix A: Literature search and mapping 169

A.1 Searching criteria for the literature search performed on Scopus 170
A.2 Details on mapping parameters of the bibliometric graphs in VOSviewer . 171

B Appendix B: Supporting information for process design and techno-economic assessment 173

B.1 Technical specifications of microbial electrosynthesis 174
B.2 Details of the process route 176
B.3 Decomposed models for distillation columns 177
B.4 Validation of the process model 181
B.5 Inputs for techno-economic assessment 183
B.6 Operating schemes 190
B.7 Energy consumption at the equipment level 194
B.8 Hypothesis check 195

C Appendix C: Supporting information in other types of files 199

D Appendix D: Supporting information for environmental assessment 201

D.1 Energy and mass balances 202
D.2 Life cycle inventory 204
D.3 Sensitivity analyses 207
D.4 Information on alternative SAFs 208
D.5 Information on alternative biofuels 208
D.6 Relevant hypothesis 209
D.7 Data support for figures 211

Curriculum Vitæ **215**

List of Publications **217**

Acknowledgements **219**

Summary

In 2021, the EU announced its aim to reach climate neutrality by 2050. In 2024, the EU recommended a 90% reduction in net greenhouse gas (GHG) emissions by 2040 compared to 1990 levels. According to the IPCC Sixth Assessment Report issued in 2022, the gate to reach the 1.5°C goals is closing but still possible. This, however, requires immediate and profound changes across all sectors of our economy.

In 2022, among all industries, the chemical industry was responsible for 10% of the total CO_2 emitted by the industrial sector. Hence, the chemical industry needs to accelerate its defossilisation. To achieve this, fossil-based fuels and feedstock should be replaced by alternatives featuring lower environmental impacts. For instance, fossil-based carbon sources currently used as feedstock can be replaced by CO_2 captured from the air or industrial emissions, while fossil-based fuels used in utilities can be substituted with renewable energy such as solar, wind, and geothermal. The combination of renewable energy and CO_2 as carbon feedstock has resulted in the development of carbon capture and utilisation powered by intermittent renewable electricity (IRE).

Nonetheless, it is challenging for electrochemical processes to deal with irregular fluctuations in the electricity supply. Insufficient electricity supply can result in a lower production rate, while excessive electricity supply can damage electrolysers. Furthermore, these variances can be much higher than the disruptions studied in conventional process system engineering. It is difficult to manage the variances to maintain a long-term and steady production rate and quality of products simply by control systems without taking care of the flexibility of chemical facilities. Therefore, it is important to understand how electrochemical plants can be operated flexibly under a fluctuating electricity supply. Moreover, even if electrolysers could be fully flexibly operated, current downstream processing (DSP) technologies, as well as their corresponding equipment, are all designed for continuous operation. Hence, designing an electrochemical plant with flexibility in mind is essential.

Furthermore, a feasibility study is necessary to understand the market competitiveness of a new technology. It provides not only a holistic view of novel technologies at an industrial scale but also valuable insights for their further development. Otherwise, the potential bottlenecks in the technical performance, investment risk, and/or environmental hotspots might be overlooked.

Electrochemical processes powered by renewable electricity to produce chemicals are gaining momentum in the chemical industry. A vast number of researchers have explored water electrolysis at an industrial scale. However, fewer studies have investigated the electrosynthesis of the target product under intermittent electricity supply. Hence, given the EU's ambition regarding carbon neutrality by 2050 and the

chemical sector being a major CO_2 emitter, novel CO_2 electrochemical conversion technologies coupled with IRE should be further investigated. This dissertation aimed to understand:

what process designs and conditions could facilitate the upscaling of a novel CO_2 electrochemical plant under intermittent renewable electricity supply?

This main research question was divided into three research sub-questions as below, which were studied and understood accordingly in order to answer the main research question.

1. **What does flexibility mean when designing flexible novel chemical processes?**
2. **How does intermittency affect the techno-economic and environmental performances of a novel CO_2 electrochemical plant?**
3. **What factors can potentially influence the competitiveness of a novel CO_2 electrochemical technology against its market competitor?**

For sub-question 1, a systematic literature review on flexibility spanning from 1990 to 2020 was conducted. The background of flexibility was revisited, and a conceptual framework for defining, designing, and evaluating flexibility for novel flexible chemical processes was proposed. This framework encloses definitions, elements, types, and indicators of flexibility.

For sub-question 2, an electrochemical plant centred on microbial electrosynthesis (MES) producing hexanoic acid was designed and modelled in Aspen Plus, where liquid-liquid extraction (LLE) and vacuum distillation were selected as DSP technologies. This MES plant produces 99wt% hexanoic acid from CO_2 captured from flue gas at an industrial scale (10 kt/y). The volume flexibility of the MES plant was explored at the equipment level by fixing the size of distillation-based columns and varying the throughput rates. Then, the plant, in the form of its mass and energy balances, was coupled with IRE (i.e., solar and wind) profiles and buffering units (batteries and a storage tank) using Python scripts. Later, an optimisation of the plant scheduling and the size of the storage tank was also performed to reach the optimal economic potential for this plant. Finally, how the intermittency impacted the plant's techno-economic performance, and carbon footprint was assessed.

For sub-question 3, the techno-economic and environmental performances of hexanoic acid produced from MES were compared to those of its competitors. Two future value chains for hexanoic acid were considered. The first value chain expanded to incorporate CO_2 capture activity and produced hexanoic acid as the final product with the same functions as today's. Its competitors were plant-based and fermentative hexanoic acid. The second value chain expanded to incorporate CO_2 capture activity and the activity of upgrading hexanoic acid to n-alkanes, which can be marketed as neat sustainable aviation fuel (SAF). Its competitors are currently certified (neat) SAFs.

In the end, we obtained the relevant insights to answer the main research question from the technical, economic, and environmental aspects as below:

Technical aspect

First of all, regardless of whether continuous or intermittent electricity supply is used, the productivity and product concentration of the electrolysers should be improved. Otherwise, complex DSP technologies and purification trains could be required, which can indirectly restrict the flexibility of the plant. For example, in the MES plant, two cycles of liquid-liquid extraction and solvent regeneration with stringent operating conditions heightened the chance of decreasing the volume flexibility of the plant. Additionally, more utilities and chemicals can be consumed in the DSP to recover and purify the products. On the other hand, this suggests that electrolysis technologies with low productivity and a dilute product stream can better aim for potential applications where less concentrated products are required.

When IRE is coupled, though electrolysers might be flexible in terms of throughput rate, the DSP technologies might still be subject to stringent operating conditions. Their inflexibility would significantly affect production time and quantity, thus affecting economic outcomes. Therefore, designers should stress the choice of flexible technologies for the entire plant, including DSP. In addition, consciously sizing equipment to accommodate expected fluctuations is essential; the volume flexibility of all the equipment in the entire plant should match. Furthermore, buffering units can smoothen the intermittency by decoupling the less flexible units from the more flexible units. Their sizing and scheduling as how much and when to store or drain, can also impact the plant's volume flexibility. Lastly, installing smaller parallel units instead of one larger unit can keep the production ongoing when the electricity supply is relatively low by shutting down part of the parallel units.

The pattern of electricity profiles also matters. When the available electricity is more often below the minimum required load for production or above the maximum tolerable load of the plant, the available electricity is more likely not used, leading to less production. The peaks and valleys in IRE profiles are never perfectly alternating, so the extra electricity available in the previous hour cannot always be stored and used to compensate for the electricity shortage in the next hour. Sometimes, the electricity shortages are too long, and it will be cost-prohibitive to install buffering units such as storage tanks to fill the gap. Therefore, choosing less intermittent electricity profiles in the first place and implementing design strategies to counteract the fluctuations can be helpful.

Economic aspect

When the novel electrochemical plant is driven by constant grid electricity, its product might be competitive but not advantageous in today's market due to the high CAPEX of the specific equipment and the operating costs of electricity consumption. With intermittency, the sunk cost appears to worsen further. Therefore, the technology has to be enhanced and is indeed under continuous improvement so that equipment costs become much lower. Moreover, a cheaper electricity deal should be made between the plant and renewable electricity suppliers. Cheap buffering units, such as storage tanks, can enhance the plant's volume flexibility by smoothening the intermittency and promoting production quantity while improving economic outcomes. Optimising the scheduling of the plant, in addition to implementing buffering units, can further promote volume flexibility, production, and hence economic performance. The aim is to minimally invest in their capital costs while using them to promote production maximally. On the other hand, the product can also have a chance in the market if its market price increases in the future, implying 1) a soaring demand for the product in general, 2) competing but less sustainable production routes being charged significantly for waste generation, 3) a collapse in its production via other cheaper pathways, or 4) a striking change in consumer's behaviour.

Environmental aspect

Combining electrolysis with renewable electricity exhibits lower environmental impacts than current grid electricity. However, it is not necessarily cleaner than its market competitors. The possible fossil-based utilities, solvents, and/or other chemicals used in the DSP can be a bottleneck, which is essentially linked to the DSP technologies selected. Moreover, the carbon intensity of the CO_2 feedstock stream also matters, as the CO_2 might not be biogenic or atmospheric and the capture process consumes energy, solvent, and/or chemicals.

This dissertation performed an ex-ante assessment of a novel technology, which required several assumptions and rendered limitations. An important limitation of this work is that ramping rates were not considered. This work was conducted as a first exploration of flexibility in a novel plant (technology readiness level 3). Introducing ramping rates would require experimental data. Therefore, the results obtained in this dissertation are optimistic, and it can be expected that additional penalties will occur for both production quantity and utility consumption. Also, the advantages of batteries might become more apparent in preventing the shutdown of production. Furthermore, the two main DSP technologies used in this dissertation were membrane-based LLE and vacuum distillation. The possibility that they would impact the environmental performances was already known before the modelling. However, they were still selected owing to the lack of data and models of potentially cleaner DSP technologies.

This thesis only looked at one design strategy to cope with intermittency (use of buffers). Other design strategies for volume flexibility can be investigated, such as deploying more flexible DSP technologies or modularising the units. If other flexibility types are also desired for the plant, the interaction between different flexibility types should also be studied. Furthermore, today's hexanoic acid has a niche market owing to its current commercial production method. Just replacing the current market of plant-based hexanoic acid with MES-based hexanoic acid can be challenging. First, plant-based hexanoic acid is much cheaper as it is a by-product. Additionally, hexanoic acid from the bio-fermentation route is also highly competitive, given its higher technology readiness level and similar levelised production cost. Therefore, creating more demand to expand the hexanoic acid market and/or its derivatives is necessary. This thesis indicates that upgrading hexanoic aid to n-alkanes is not attractive from an environmental perspective unless significant changes in the process occur. Other options, such as adipic acid, could be explored.

Finally, the industrial sector, together with the power supplier, should make a joint effort so that the deployment of electricity-based chemical processes can make a significant contribution to the defossilisation of the industrial sector.

Samenvatting

In 2021 kondigde de EU haar doelstelling aan om in 2050 klimaatneutraal te zijn. In 2024 deed de EU de aanbeveling om de netto broeikasgasemissies tegen 2040 met 90% te verminderen ten opzichte van 1990. Volgens het zesde evaluatierapport van het IPCC, dat in 2022 werd gepubliceerd, is het nog mogelijk om de vereiste doelstellingen te behalen om de gemiddelde temperatuurstijging te limiteren tot 1,5°C. Echter vereist dit snelle en ingrijpende veranderingen in alle sectoren van onze economie.

Van alle industrieën was de chemische industrie in 2022 verantwoordelijk voor 10% van de totale CO_2-uitstoot van de industriële sector. De chemische industrie zal daarom dus ook haar defossilisatie moeten verrsnellen. Om dit te bereiken moeten fossiele brandstoffen en grondstoffen worden vervangen door alternatieven met een lagere impact op het milieu. Zo kunnen de huidige fossiele grondstoffen die als koolstofbron worden gebruikt,worden vervangen door CO_2 dat uit de lucht of industriële emissies wordt opgevangen, terwijl fossiele brandstoffen die in nutsbedrijven worden gebruikt, kunnen worden vervangen door hernieuwbare energie zoals zonne-, wind- en geothermische energie. De combinatie van hernieuwbare energie en CO_2 als koolstofbron heeft geresulteerd in de ontwikkeling van de afvang en gebruik van koolstof in combinatie met intermittent renewable electricity (IRE).

Het is echter een uitdaging voor elektrochemische processen om om te gaan met onregelmatige fluctuaties in de elektriciteitsvoorziening. Een gebrekkige elektriciteitsvoorziening kan leiden tot een lagere productiesnelheid, terwijl een te hoge elektriciteitsvoorziening de elektrolysers kan beschadigen. Bovendien kunnen deze variaties veel groter zijn dan de verstoringen die in conventionele Process Systems Engineering worden onderzocht. Het is moeilijk om deze variaties te beheren om een stabiele productiesnelheid en -kwaliteit op lange termijn te behouden door enkelregelsystemen te gebruiken zonder rekening te houden met de flexibiliteit van chemische installaties. Daarom is het belangrijk om te begrijpen hoe elektrochemische processen flexibel kunnen worden bediend bij een fluctuerende elektriciteitsvoorziening. Bovendien, zelfs als elektrolysers volledig flexibel zouden kunnen worden bediend, zijn de huidige downstream processing (DSP) technologieën en de bijbehorende apparatuur allemaal ontworpen voor continue werking. Daarom is het essentieel om bij het ontwerp van een elektrochemische installatie rekening te houden met flexibiliteit.

Bovendien is een haalbaarheidsstudie noodzakelijk om inzicht te krijgen in de concurrentiekracht van een nieuwe technologie op de markt. Het biedt niet alleen een holistische kijk op nieuwe technologieën op industriële schaal, maar ook waardevolle inzichten voor hun verdere ontwikkeling. Zonder deze haalbaarheidsstudie zouden de potentiële knelpunten in de technische prestaties, het investeringsrisico en de milieuproblemen wel eens over het hoofd gezien kunnen worden.

Elektrochemische processen op basis van hernieuwbare elektriciteit voor de productie van chemicaliën worden steeds belangrijker voor de chemische industrie. Een groot aantal onderzoekers heeft waterelektrolyse op industriële schaal onderzocht, maar een stuk minder studies hebben de elektrosynthese van het doelproduct met variabele elektriciteitsvoorziening onderzocht.Gezien de ambitie van de EU met betrekking tot koolstofneutraliteit in 2050 en gezien het feit dat de chemische sector een belangrijke CO_2-uitstoter is, moeten nieuwe CO_2 elektrochemische conversietechnologieën in combinatie met IRE verder worden onderzocht. Dit proefschrift was gericht op het begrijpen van:

welke procesontwerpen en -condities kunnen de opschaling van een nieuwe CO_2 elektrochemische installatie onder intermitterende hernieuwbare elektriciteitslevering vergemakkelijken?

Deze hoofdonderzoeksvraag werd onderverdeeld in drie deel onderzoeksvragen, zoals hieronder beschreven, die dienovereenkomstig werden bestudeerd en begrepen om de hoofdonderzoeksvraag te beantwoorden.

1. **Wat betekent flexibiliteit bij het ontwerpen van flexibele nieuwe chemische processen?**
2. **Hoe beïnvloedt intermittentie de technisch-economische en milieuprestaties van een nieuwe CO_2 elektrochemische fabriek?**
3. **Welke factoren kunnen mogelijk het concurrentievermogen van een nieuwe CO_2 elektrochemische technologie ten opzichte van zijn concurrent op de markt beïnvloeden?**

Voor deelvraag 1 werd een systematisch literatuuronderzoek naar flexibiliteit van 1990 tot 2020 uitgevoerd. De achtergrond van flexibiliteit werd opnieuw bekeken en er werd een conceptueel kader voorgesteld voor het definiëren, ontwerpen en evalueren van flexibiliteit voor nieuwe flexibele chemische processen. Dit raamwerk omvat definities, elementen, soorten en indicatoren van flexibiliteit.

Voor deelvraag 2 werd een elektrochemische installatie met microbiologische elektrosynthese (MES) voor de productie van hexaanzuur ontworpen en gemodelleerd in Aspen Plus, waarbij vloeistofo-vloefstofextractie (LLE) en vacuümdestillatie werden geselecteerd als DSP-technologieën. Deze MES-installatie produceert 99wt% hexaanzuur uit CO_2 dat is opgevangen uit industriële schaal rookgas (10 kt/y). De volumeflexibiliteit van de MES-installatie werd op het niveau van de apparatuur onderzocht door de grootte van de distillatiekolommen vast te zetten en de doorvoersnelheid te variëren. Vervolgens werd de installatie, in de vorm van massa- en energiebalansen, gekoppeld aan IRE-profielen (d.w.z. zonne- en windenergie) en buffereenheden (batterijen en een opslagtank) met behulp van Python-scripts. Later werd ook de planning van de installatie en de grootte van de opslagtank geoptimaliseerd om het optimale economische potentieel voor deze installatie te bereiken. Ten slotte werd beoordeeld hoe de intermitterende werking de technisch-economische prestaties van de installatie en de koolstofvoetafdruk beïnvloedde.

Voor deelvraag 3 werden de technisch-economische en milieuprestaties van hexaanzuur uit MES vergeleken met die van zijn concurrenten. Twee toekomstige waardeketens voor hexaanzuur werden overwogen. De eerste waardeketen werd uitgebreid met CO_2-afvangactiviteiten en produceerde hexaanzuur als eindproduct met dezelfde functies als nu. De concurrenten waren plantaardig en fermentatief hexaanzuur. De tweede waardeketen breidde zich uit met CO_2-afvang en de opwaardering van hexaanzuur tot n-alkanen, die op de markt kunnen worden gebracht als onverdunde duurzame vliegtuigbrandstof (SAF). De concurrenten zijn de huidigegecertificeerde (zuivere) SAF's.

Uiteindelijk hebben we de relevante inzichten verkregen om de belangrijkste onderzoeksvraag te beantwoorden vanuit de technische, economische en milieuaspecten, zoals hieronder beschreven:

Technisch aspect

Ten eerste, moeten de productiviteit en productconcentratie van de elektrolysers worden verbeterd, ongeacht of er een continue of intermitterende elektriciteitsvoorziening wordt gebruikt. Zonder deze verbeteringenzouden complexe DSP-technologieën en zuiveringstreinen nodig kunnen zijn, wat indirect de flexibiliteit van de installatie kan beperken. In de MES-fabriek bijvoorbeeld, werd de kans op vermindering van de volumeflexibiliteit van de fabriek verhoogd, doordat er twee cycli van vloeistof-vloeistof extractie en solvent regeneratie met strikte operatie condities nodig waren, om de vereiste product concentratie te behalen. Bovendien kunnen de lage productconcentraties uit de reactor het verbruik van nutsvoorzieningen en chemicaliën verhogen om de producten terug te winnen en te zuiveren in de DSP.om in verhogen . Aan de andere kant suggereert dit dat elektrolysetechnologieën met een lage productiviteit en een verdunde productstroom zich beter kunnen richten op potentiële toepassingen waar minder geconcentreerde producten nodig zijn. Tot slot, kan het installeren van kleinere parallelle eenheden in plaats van één grotere eenheid de productie op gang houden wanneer de elektriciteitsvoorziening relatief laag is door een deel van de parallelle eenheden uit te schakelen.

Wanneer het proces gekoppeld is aan IRE, kunnen elektrolysers weliswaar flexibel opereren in termen van doorvoersnelheid, maar de DSP-technologieën kunnen nog steeds onderworpen zijn aan strikte operatie condities. Het gebrek aan flexibiliteit bij de DSP-technologieën zou een aanzienlijke invloed hebben op de productietijd en -hoeveelheid en dus ook op de economische resultaten. Ontwerpers moeten daarom de nadruk leggen op de keuze van flexibele technologieën voor de hele fabriek, inclusief de DSP. Daarnaast is een bewuste dimensionering van apparatuur om verwachte fluctuaties op te vangen essentieel; de volumeflexibiliteit van alle apparatuur in de hele fabriek moet overeenkomen. Bovendien kunnen buffereenheden de intermittentie afvlakken door de minder flexibele eenheden los te koppelen van de meer flexibele eenheden. De dimensionering en planning van deze buffereenheden, zoals hoeveel en wanneer moet worden opgeslagen of afgetapt, kan ook van invloed zijn op de volumeflexibiliteit van de installatie.

Het patroon van elektriciteitsprofielen is ook van belang. Wanneer de beschikbare elektriciteit vaker lager is dan de minimaal vereiste belasting voor productie of hoger dan de maximaal aanvaardbare belasting van de fabriek, is de kans groter dat de beschikbare elektriciteit niet wordt gebruikt, wat leidt tot minder productie. De pieken en dalen in IRE-profielen zijn nooit perfect afwisselend, de extra elektriciteit die in het vorige uur beschikbaar was, kan dus niet altijd worden opgeslagen en gebruikt om het elektriciteitstekort in het volgende uur te compenseren. Soms zijn de elektriciteitstekorten te lang en is het te duur om buffereenheden zoals opslagtanks te installeren om het gat op te vullen. Daarom kan het nuttig zijn om in eerste instantie te kiezen voor minder intermitterende elektriciteitsprofielen en ontwerpstrategieën te implementeren om de fluctuaties tegen te gaan.

Economisch aspect

Wanneer de nieuwe elektrochemische installatie wordt aangedreven door constante netstroom, is haar product misschien wel concurrerend maar niet voordelig op de huidige markt vanwege de hoge CAPEX van de specifieke apparatuur en de bedrijfskosten van het elektriciteitsverbruik. Met intermittentie lijken de verzonken kosten nog hoger te worden. Daarom moet de technologie worden verbeterd en wordt ze inderdaad voortdurend verbeterd, zodat de kosten van de apparatuur veel lager worden. Bovendien moet er een goedkopere elektriciteitsdeal worden gesloten tussen de fabriek en de leveranciers van hernieuwbare elektriciteit. Goedkope buffereenheden, zoals opslagtanks, kunnen de volumeflexibiliteit van de centrale vergroten door de intermittentie af te vlakken en de productiehoeveelheid te bevorderen, en kunnen daarmee de economische resultaten verbeteren. Het optimaliseren van de planning van de fabriek, naast het implementeren van buffereenheden, kan de volumeflexibiliteit en de productie, en dus ook de economische prestaties verder verhogen. Het doel is om zo min mogelijk te investeren in de kapitaalkosten van deze maatregelen, terwijl ze gebruikt worden om de productie maximaal te bevorderen. Anderzijds zou het product ook een kans kunnen maken op de markt als zijn marktprijs in de toekomst stijgt, wat impliceert dat 1) de vraag naar het product in het algemeen stijgt, 2) concurrerende maar minder duurzame productieroutes aanzienlijk worden aangerekend voor afvalproductie, 3) de productie ervan via andere, goedkopere routes instort, of 4) het gedrag van de consument opvallend verandert.

Milieuaspect

De combinatie van elektrolyse met hernieuwbare elektriciteit heeft een lagere impact op het milieu dan elektrolyse met de huidige netstroom. Het is echter niet noodzakelijkerwijs schoner dan de concurrenten op de markt. De mogelijke fossiele grondstoffen, oplosmiddelen en/of andere chemicaliën die in de DSP worden gebruikt, kunnen een knelpunt vormen dat voornamelijk samenhangt met de gekozen DSP-technologieën. Bovendien is de koolstofintensiteit van de CO_2 -grondstofstroom ook van belang, aangezien de CO_2 mogelijk niet biogeen of atmosferisch is en het afvangproces energie, oplosmiddelen en/of chemicaliën verbruikt.

Dit proefschrift voerde een ex-ante beoordeling uit van een nieuwe technologie, waarvoor verschillende aannames en beperkingen nodig waren. Een belangrijke beperking van dit werk is dat er geen rekening is gehouden met ramping rates. Dit werk werd uitgevoerd als een eerste verkenning van flexibiliteit in een nieuwe installatie (technology readiness level 3). Het introduceren van ramping rates zou experimentele gegevens vereisen. De resultaten die in dit proefschrift zijn verkregen zijn daarom optimistisch, en het is te verwachten dat de daadwerkelijke productiehoeveelheid en elektriciteitsverbruik nadeliger zullen uitpakken. Daarentegen kunnen de voordelen van batterijen duidelijker worden doordat ze het stilleggen van de productie kunnen voorkomen. Verder waren de twee belangrijkste DSP-technologieën die in dit proefschrift werden gebruikt membraan gebaseerde vloeistof-vloeistof extractie en vacuümdestillatie. De mogelijkheid dat deze procestechnologieën de milieuprestaties zouden beïnvloeden was al bekend voor de modellering. Toch werden ze geselecteerd vanwege het gebrek aan gegevens en modellen van potentieel schonere DSP-technologieën.

In dit proefschrift hebben we slechts naar *éé*n ontwerpstrategie gekeken om met intermittentie om te gaan (het gebruik van buffers). Andere ontwerpstrategieën voor volumeflexibiliteit kunnen worden onderzocht, zoals het inzetten van flexibelere DSP-technologieën of het modulariseren van de eenheden. Als er ook andere soorten flexibiliteit gewenst zijn voor de installatie, moet ook de interactie tussen de verschillende soorten flexibiliteit worden bestudeerd. Bovendien heeft hexaanzuur op het moment een nichemarkt vanwege de huidige commerciële productiemethode. Alleen al het vervangen van de huidige markt van plantaardig hexaanzuur door hexaanzuur op basis van MES, kan een uitdaging zijn. Ten eerste is plantaardig hexaanzuur veel goedkoper omdat het een bijproduct is. Daarnaast is hexaanzuur uit de biovergistingsroute ook zeer concurrerend, gezien de hogere technology readiness level en vergelijkbare genivelleerde productiekosten. Daarom is het nodig om de markt van hexaanzuur en/of zijn derivaten uit te breiden door meer vraag naar deze producten te creëren. Deze dissertatie geeft aan dat het opwaarderen van hexaanzuur tot n-alkanen niet aantrekkelijk is vanuit milieuoogpunt, tenzij er significante veranderingen in het proces plaatsvinden. Andere opties, zoals adipinezuur, zouden kunnen worden onderzocht.

Tot slot, zou de industriële sector samen met de energieleverancier een gezamenlijke inspanning moeten leveren, zodat de inzet van op elektriciteit gebaseerde chemische processen een belangrijke bijdrage kan leveren aan de defossilisering van de industriële sector.

Nomenclature

AF Allocation factor
AIS Available input space
ANP Annualised net profit
AP Aspen Plus
ASTM American Society for Testing and Materials
ASU Air separation unit
ATJ Alcohol-to-jet

BE Belgium
BESS Battery energy storage system

C6A Caproic/Hexanoic acid
CAPEX Capital expenditures
CCO Crude coconut oil
CCS Carbon capture and storage
CCU Carbon capture and utilisation
CEPCI Chemical Engineering Plant Cost Index
CSAM Cropland Spatial Allocation Model

DAC Direct air capture
DIS Desired input space
DLO Direct land occupation
dLUC Direct land use change
DR Demand response
DSM Demand-side management
DSP Downstream processing

EAC Equivalent annualised cost
EC Electricity consumption
EIS Expected input space
EU European Union

FE Faradaic efficiency
FT Fischer

GHG Greenhouse gas
GLO Global
GLOBIOM Global Biosphere Management Model
GWP Global warming potential

HEFA Hydroproccessed esters and fatty acids
HFS-SIP Hydroprocessing of Fermented sugars - synthetic iso-paraffins
HOC Hayden-O'Connel
HT High temperature

IGCC Integrated gasification & combined cycle
iLUC Indirect land use change
IMAGE Integrated Model to Assess the Global Environment
IPCC Intergovernmental Panel on Climate Change
IRE Intermittent renewable electricity
ISO International Organization for Standardization

LCA Life cycle assessment
LCI Life cycle inventory
LCIA life cycle impact assessment
LLE Liquid-liquid extraction
LLPS Low-low-pressure steam
LMTD Log-mean temperature difference
LPC Levelised production cost
LPS Low-pressure steam
LRR Load ratio range
LT Low temperature
LUC Land use change

MEA Monoethanolamine
MES Microbial electrosynthesis
MILP Mixed-integer linear programming
MINLP Mixed-integer non-linear programming
MIQCP Mixed-integer quadratically constrained programming
MPS Medium-pressure steam

NGCC Natural gas combined cycle
NL Netherlands
NRTL Non-random two-liquid

OPEX Operating expenses

PhD Doctor of Philosophy
PSE Process system engineering
PV Photovoltaics

REC Range of effective capacities
RED Renewable Energy Directive
RER Europe
RES Renewable energy sources

SAF Sustainable aviation fuel
SCCA Short-chain carboxylic acid
SOEC Solid oxide electrolysis cell
SPK Synthetic paraffinic kerosene
SR Solvent regeneration
ST Storage tank

TD Dehydration column
TEA Techno-economic assessment
TOA Trioctylamine
TRL Technology readiness level

UN United Nations
UNIFAC Universal quasichemical functional-group activity coefficients
US United States

VCA Volatile fatty acid

1

Introduction

1 Research background

Global surface temperature between 2011 and 2020 was 1.1°C higher than the pre-industrial time and is likely to reach 1.5°C between 2021 and 2040 if the warming rate remains unchanged [1]. In the past few decades, the sea level in different regions has been rising steadily owing to the acceleration of ice melting, and the number of wildfires as well as hurricanes around the world has soared [2, 3]. These consequences, resulting from and exacerbated by global warming, undeniably affect life on Earth. Therefore, global warming must be mitigated to prevent possible future catastrophic impacts on our planet. In 2015, the Paris Agreement was signed at the UN Climate Change Conference to limit the global temperature to 2°C above the pre-industrial level, preferably 1.5°C [4]. Since the root cause of global warming is the excessive concentration of greenhouse gases (GHGs) in the atmosphere, in 2021, the EU announced its aim to reach climate neutrality by 2050 [5]. In 2024, the EU recommended a 90% net GHG emissions reduction by 2040 compared to 1990 levels [6]. According to the IPCC Sixth Assessment Report issued in 2022, the gate to reach the 1.5°C goals is closing but still possible [7]. This, however, requires immediate and profound changes across all sectors of our economy.

The industrial sector contributed 9 Gt of CO_2 emissions in 2022, falling behind the pace suggested in the "Net Zero Emissions by 2050 Scenario", which expects less than 7 Gt of CO_2 from the industrial sector by 2030 [8]. Among all industries, the chemical industry was responsible for 935 Mt of direct CO_2 emissions due to the production of primary chemicals, accounting for 10% of total CO_2 emitted by the industrial sector [9]. Hence, it is important for the chemical industry to accelerate its energy transition and defossilisation. To achieve this, fossil-based fuels and feedstocks need to be replaced by alternatives featuring lower environmental impacts. For instance, fossil-based carbon sources currently used as feedstock can be replaced by CO_2 captured from the air or industrial emissions, while fossil-based fuels used in utilities can be substituted with renewable energy such as solar, wind, and geothermal. The combination of renewable energy and CO_2 as carbon feedstock has resulted in the development of electricity-based carbon capture and utilisation (CCU) powered by intermittent renewable electricity (IRE). Moreover, the potential of consuming fluctuating electricity could enable CCU processes powered by IRE to be a promising solution towards demand response (DR), which is a decarbonising strategy adopted by the power sector.

1.1 Carbon capture and utilisation via electrochemistry

CCU via electrochemistry is composed of two steps. In the first step, CO_2 is separated from other compounds present in the industrial emissions or atmosphere. Then, CO_2 is electrochemically reduced to chemicals or fuels. This conversion is commonly called CO_2 electroreduction or CO_2 electrolysis (I will use both terms interchangeably in this chapter), where the C atoms gain electrons, and their oxidation state is reduced. Here, electricity is no longer simply a type of utility but also the key source that activates the reactions. Hence, electricity is considered a feedstock in electrochemistry.

1.1.1. CO_2 capture

CO_2 is usually fed into an electrolyser at high purity for stable and efficient conversion. Otherwise, impurities or toxic compounds can lead to, for instance, electrode passivation [10, 11]. Therefore, as the first stage of the entire CCU process, CO_2 capture and purification is crucial. Note that purification is seen as part of CO_2 capture in this dissertation.

Capture from industrial emissions

Carbon dioxide emitted from industrial or combustion processes can be captured on-site for use as a feedstock for the synthesis of other carbon-containing products (i.e., CCU) or stored in a geologic formation (i.e., carbon capture and storage; CCS). Industrial emission streams contain not only CO_2 but also other gaseous components such as H_2O, O_2, NO_x, SO_x, HCl or volatile organic compounds. Once captured and purified to the required levels for transportation, cleaned CO_2 is transported to the electrochemical plant for conversion and downstream processing.

CO_2 concentration in flue gas from natural gas power plants is 3-4%, 10-15% in pulverised coal plants, and 15-30% in steel and cement plants [12]. Various technologies for CO_2 capture from flue gas in different sectors have been studied, as briefly summarised in Table 1.1. Note that some technologies have reached a technology readiness level (TRL) of 9 and have been widely implemented in the industry [12, 13].

Table. 1.1. Examples of CO_2 capture technologies in different types of plants, also including direct air capture. Data retrieved from [12], unless otherwise stated. The costs were originally in US dollars and were converted to Euros using 2019's average exchange rate, 1:1.12 [14]. TRL: technology readiness level. NGCC: natural gas combined cycle. IGCC: integrated gasification & combined cycle.

CO_2 source	Technology	TRL	Levelised cost (€/t CO_2 captured)
Cement plant	Calcium looping	6	18-67
	Partial Oxyfuel calciner	6	54
	Amine scrubbing	6	43-67
Steel plant	Amine scrubbing	9	58-106
Oil refinery	Amine scrubbing	9	31-89
Steam reforming plant	Amine scrubbing	9	52-90
Ethanol plant	Dehydration	9	13 [15]
Power plant (pulverised coal)	Post-combustion amine scrubbing	9	66-74
Power plant (NGCC)	Post-combustion amine scrubbing	9	79-92
Power plant (IGCC)	Pre-combustion	7	87-146
Air	Solid direct air capture	8-9	714-893 [16]
	Liquid direct air capture	8-9	357-563 [16]

Capture from air

There are two main types of direct air capture (DAC) technologies, namely solid and liquid. Solid DAC first binds CO_2 using solid amine-functionalised sorbents, then releases CO_2 using ambient-pressure steam (~100°C), and finally separates the steam and CO_2. Climeworks is a pioneer in solid DAC and has been commercially operating solid DAC plants since 2009 (`https://climeworks.com/`). Liquid DAC first absorbs CO_2 by an aqueous basic solution (e.g., KOH), then converts the CO_2-rich solution to $CaCO_3$ using the $Ca(OH)_2$, and finally calcinates the $CaCO_3$ (~900°C) to release CO_2. Carbon Engineering is a representative of liquid DAC companies and expects to operate its first commercial plant in 2025 (`https://carbonengineering.com/`). No matter whether liquid or solid, the average cost of DAC is notably higher than capturing from industrial emissions [12], as can be seen in Table 1.1. The possible causes are: 1) lack of supply chain, 2) first-of-a-kind plants, and 3) a vast energy consumption due to the low concentration of CO_2 present in the atmosphere (i.e., 0.04 vol%) [17].

1.1.2. CO_2 electroreduction

CO_2 electroreduction belongs to and is often labelled as a Power-to-Chemical, Power-to-Gas, or Power-to-Fuel technology, depending on the product. CO_2 electroreduction can be direct or indirect. A direct conversion reduces CO_2 to the final product by an electrolyser in a single step. In an indirect conversion, CO_2 is first reduced to CO. Then, CO is upgraded into the final product via electrochemical, thermochemical, or fermentative conversion. Additionally, there is also CO_2 co-electrolysis with the presence of H_2O. According to the operating temperature, CO_2 electrolysers are classified into low-temperature (LT) and high-temperature (HT) electrolysers.

LT CO_2 electrolysers can be operated below 100°C, with the electrolytes being aqueous solutions [18]. LT CO_2 electrolysers can be equipped with a cation, an anion, or a bipolar exchange membrane. In general, O_2 is produced in the anode chamber while CO_2 is fed into the cathode chamber and reduced to a target product such as formic acid [11]. The electrolysis catalysts are primarily metals. However, in recent years, microorganisms have gained attention because of their ability to form longer carbon chains and higher resistance to impurities [19–21].

A solid oxide electrolyser cell (SOEC) is a HT electrolyser, where the electrolytes are solid oxides with high melting temperatures and good ionic conductivity [22]. SOECs are equipped with metal catalysts and operated between 500 and 850°C [23]. In a typical SOEC, CO_2 alone or with steam are brought into contact with the cathode catalyst. Then, CO or syngas is generated as a product and leaves the electrolyser via the cathode. O_2^- is also formed in the cathode layer, though it penetrates through the solid electrolyte to the anode layer and it is eventually converted into O_2 [23].

Table 1.2 summarises a state-of-the-art of products generated from direct CO_2 electrolysis and co-electrolysis. To date, only limited technologies have reached a demonstration scale. For example, Voltachem (`https://www.voltachem.com/`) operates a LT CO_2 electrolysis plant producing formate at a demonstration scale (TRL 7-8). Sunfire, for instance, runs a HT water-CO_2 co-electrolysis pilot plant producing syngas (TRL 6-7) (`https://www.sunfire.de/en/`). Topsoe has licensed the pilot production of CO via HT CO_2 electrolysis (TRL 6-7) (`https://www.topsoe.com/`).

Table. 1.2. Overview of direct CO_2 electroreduction products. Note that the prices were estimated using renewable electricity but without considering their intermittency. The costs were originally in US dollars and were converted to Euros using 2019's average exchange rate, 1:1.12 [14]. Temp.: temperature. HT: high temperature. LT: low temperature. e^-: electrons required. TRL: technology readiness level. Ref.: references.

Product	Temp.	e^-	Cathode catalyst	TRL	Levelised cost (€/kg)	Market price (€/kg)	Ref.
CO	HT	2	Metal	7-8	0.16-0.57	0.13	[24]
Syngas	HT	4	Metal	6-7	1.90	0.17-0.43	[23]
Formic acid	LT	2	Metal	6-7	0.09-2.35	0.45	[24]
Methanol	LT	6	Metal	3	0.48-2.36	0.23	[24]
Methane	LT	8	Metal	3	0.96-5.11	0.11	[24]
Acetic acid	LT	8	Microorganism	3	5.80	0.58	[25]
Ethanol	LT	12	Metal	3	0.33-10.06	0.43	[24]
Ethylene	LT	12	Metal	3	0.58-4.39	0.52	[24]
Butyric acid	LT	20	Microorganism	3	7.77	1.61	[25]
Hexanoic acid	LT	32	Microorganism	3	8.84	3.30	[25]

1.1.3. Downstream processing

Downstream the electrolyser, the products synthesised through electrolysis are prepared to fulfil the product market requirements (e.g., purity) o. CO_2 electroreduction does not often generate highly concentrated product streams, except for CO and syngas. Table 1.3 provides an overview of current leading DSP technologies accompanying CO_2 electroreduction [26]. Note that these DSP technologies are all mature. However, the required purification train can be energy-intensive and/or expensive. Therefore, DSP can impact the techno-economic and environmental performances of CCU processes.

1.2 Intermittent renewable electricity

In 2022, the EU achieved a renewable energy share of 23% in its gross final energy consumption [30]. Specifically, renewable electricity represented 41% of the EU's gross electricity consumption in 2022. Among the total electricity generated from all renewable sources, wind accounted for 37.5%, while solar made up 18.1% [30], and the European Commission aims to increase the renewable energy share to 45% by 2030 [31].

Table. 1.3. Overview of current recovery and separation methods for dilute streams of CO_2 electroreduction.

Technology	Advantages	Disadvantages	Ref.
Solvent extraction	• Low capital costs	• Acidification required	[27]
	• High yield of product	• Further process to regenerate solvent	
	• High selectivity	• High energy demand	
Precipitation	• Low capital costs	• Undesired solid waste generation	[27]
	• High yield of product	• High membrane fouling	
	• High purity of product	• High capital costs	
Reverse osmosis	• High purity of product	• High costs	[27, 28]
	• Low energy demand	• High energy demand	
	• High selectivity	• High energy demand	
Adsorption	• High selectivity	• High membrane fouling	[27]
Electrodialysis	• High purity of product	• Further process to purify	[27]
	• No acidification	• High capital costs	
Distillation	• High purity of product	• High energy demand	[27]
Membrane separation	• Low energy demand	• High membrane fouling	[27]
	• High yield of product	• High membrane fouling	
Nanofiltration	• Reduced chemical usage	• Further process to purify	[28, 29]
	• Low energy demand		

However, increasing shares of wind and solar electricity will pose challenges to the grid due to their intermittent nature. Hence, the power sector has indicated that DR, which relies on the load shift from the customer's side (e.g., the industrial sector), will be needed [32]. Electrochemical processes could potentially support intermittent electricity generation through 1) DR modulation and 2) by lowering the demand on the minimum threshold power that the grid or even standalone renewable electricity providers have to guarantee. The reason is that electrochemical conversion technologies 1) are more flexible in terms of starting up and shutting down than traditional thermal-based technologies and 2) consume electricity as feedstock.

Nonetheless, it is challenging for electrochemical processes to deal with irregular fluctuations in the electricity supply, especially when coupled with standalone renewable electricity providers. Insufficient electricity supply can result in a lower production rate, while excessive electricity supply can lead to damage to electrolysers [32, 33]. Furthermore, these variances can be much higher than the disruptions studied in conventional process system engineering (PSE). It can be difficult to manage the variances to maintain a long-term and steady production rate and quality of products simply by control systems without taking care of the flexibility of chemical facilities [34]. Therefore, it is important to understand how electrochemical plants can be operated flexibly under a fluctuating electricity supply. Moreover, even if electrolysers can be fully flexibly operated, current DSP technologies, are generally designed for continuous operation. Hence, it is important to gain knowledge about the trade-offs of designing an electrochemical plant with flexibility in mind.

1.3 Flexibility

Flexibility is often referred to as operational flexibility [35] or process flexibility [36]. In PSE, flexibility is seen as a component of operability, accompanied by controllability, reliability, and resiliency [37]. Operability is the ability of a chemical plant to perform satisfactorily when the operating conditions deviate from the nominal design conditions [38]. Controllability exhibits the quality and stability of a process when responding to short-term disturbances and transitions from one operating point to another [35, 39]. Controllability thus relies on the design and implementation of a control system that directs and regulates equipment behaviour [39–41]. Reliability corresponds to the probability of mechanical or electrical failure during normal operation [35]. Resiliency indicates the ability of the plant to move quickly and smoothly from one operating condition to another [42], including the ability to recover from process perturbations [38]. Resiliency essentially reflects a system's inherent dynamic characteristic without deploying a control system [43]. Flexibility, therefore, represents the ready and static capability of a plant to operate over a range of conditions feasibly [43], which is enabled by the process configuration and equipment design without involving a control system.

As a result, flexibility has been a key option to cope with various types of uncertainties [44]. For example, flexible processes have been purposed for processing feedstock of varying compositions [45], operating under fluctuating electricity prices [46], or meeting volatile customer demand [47]. While a set of methods and indicators have been developed for designing and quantifying flexibility [35, 48, 49], these were intended for conventional chemical processes whose dynamics are well-understood and are already equipped with a comprehensive control system. Consequently, it is difficult to compare the flexibility of candidate designs whose process configuration is still under development and dynamics are unknown.

1.4 Feasibility and competitiveness

The pathway to enable broad adoption of novel technologies is usually underpinned by the information obtained from feasibility studies [50, 51]. A feasibility study dives into detail and investigates critical aspects of the technologies (e.g., technical, economic, and environmental), evaluating the likelihood of their success. This is crucial because it not only provides a holistic view of novel technologies at an industrial scale but also valuable insights for their further development. Otherwise, the potential bottlenecks in the technical performance, investment risk, and/or the environmental hotspots might be overlooked.

Apart from the technical capabilities of the focused technologies (e.g., energy efficiency, product yield), some studies on upscaling of low-TRL technologies from lab to industrial applications also encompass system conditions. In this dissertation, "system conditions" is seen as an umbrella term for external conditions outside the plant enclosing the technology, which cannot be manipulated by designers or engineers. These conditions can be, but are not confined to, the quality and availability of feedstock [52], market demand [53], market competition [25], external infrastructure requirements [25], utility price [54, 55], equipment cost [23], and even policies [56]. For example, for emerging technologies making use of renewable feedstock and or energy, the quality and availability of the renewables can directly affect the production quantity or quality, indirectly impacting the profitability [45, 52]. Moreover, cutting-edge electrolysers that are currently expensive can dominate the capital expenditure on equipment acquisition, which is a key determinant of profitability [10]. Additionally, the use of scarce noble metals (e.g., palladium) as catalysts creates sustainability concerns both for their mining impacts and future resource availability [57]. And while many novel technologies proposed to replace conventional technologies are expected to have lower environmental footprints (or at least, lower global warming potential), their environmental performance does not decide their market competitiveness. For the further development and upscaling of these technologies, their competitiveness should be examined from all aspects (e.g., technical, economic, environmental, and societal) in advance.

2 Knowledge gaps

Electrochemical processes powered by renewable electricity to produce chemicals are gaining momentum in the chemical industry. A vast number of researchers have explored water electrolysis at an industrial scale, for e.g., [34, 58–60]. However, fewer studies have investigated the electrosynthesis of the target product under intermittent electricity supply, for e.g., [33, 46, 61]. Given the ambition of the EU regarding carbon neutrality by 2050 and the chemical sector being a major CO_2 emitter, CO_2 electrochemical conversion technologies coupled with IRE should be further investigated. Based on section 1, the following knowledge gaps have been identified:

- Lack of understanding, evaluation and application of the concept of "flexibility" in the design of future electrochemical plants.
- Lack of knowledge on how intermittency would affect the techno-economic and environmental performances of a novel CO_2 electrochemical plant.
- Limited knowledge about the competitiveness of novel CO_2 electrochemical conversion technologies driven by renewable electricity in the market, especially in the market of products with a longer carbon chain.

3 Research questions

Based on the knowledge gaps identified, the overarching aim of this dissertation is:

to understand which process designs and conditions could facilitate the upscaling of a novel CO_2 electrochemical plant under intermittent renewable electricity supply

This aim was divided into three research questions:

1. What does flexibility mean when designing flexible novel chemical processes?
2. How does intermittency affect the techno-economic and environmental performances of a novel CO_2 electrochemical plant?
3. What factors can potentially influence the competitiveness of a novel electrochemical technology powered by renewable electricity against its market competitors?

4 Research approach

This PhD work started with a systematic literature review on the topic of flexibility in the chemical engineering field. Then, a sequence of ex-ante assessments centred on a preselected novel technology was conducted, which included process design, techno-economic assessment (TEA), optimisation of the scheduling, and life-cycle assessment (LCA).

4.1 Case study - microbial electrosynthesis

In this dissertation, microbial electrosynthesis (MES) was chosen as an illustrative case study to represent cutting-edge CO_2 electroreduction technologies. MES has several advantages compared to other electroreduction technologies, including:

1. Microorganisms are more tolerant against impurities in the CO_2 feed stream than metal-based catalysts [62, 63].
2. Microorganisms can directly produce carbon chains longer than C_2 via chain elongation, while metal catalysts cannot [21].

The MES technology selected can convert CO_2 to medium-chain carboxylic acids. The technology is currently at a lab scale (TRL 3) [64]. Among the possible product acids, hexanoic acid, also known as caproic acid, has the highest market value. Historically, it has been a by-product of the fractional distillation of coconut or palm kernel oil and currently has a niche global market [65]. Moreover, it has a promising future because of its potential to be upgraded to, for instance, n-alkanes, which are suitable as a blender for traditional aviation fuel [66, 67]. Another potential market, if hexanoic acid ω-oxidation is successfully developed, is the replacement of fossil adipic acid (also known as hexanedioic acid) in nylon production by renewable adipic acid.

Fig. 1.1 provides a schematic diagram of a MES electrolyser. It consists of an anode and a cathode compartment that are divided by a cation exchange membrane. The metal catalysts on the anode splits water into H^+, electrons, and O_2. O_2 leaves the chamber from the head space, and H^+ cations penetrate to the cathode chamber through the membrane. The microbial cells on the cathode take up CO_2, electrons and H^+, and produce longer carbon products possibly via the Wood-Ljungdahl pathway [25]. Note that this specific MES electrolyser is an in-house technology unique at the Delft University of Technology, being developed by Dr. Ludovic Jourdin [63, 68–70]. Dr. Ludovic Jourdin uses a mixed microbial consortium consisting of Burkholderiales, Clostridiales, Natranaerobiales, and Methanobacteriales for this MES electrolyser [64].

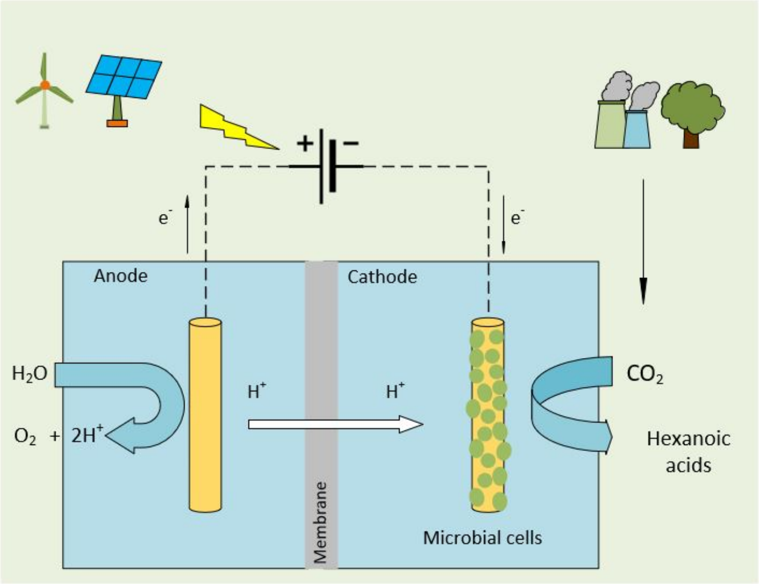

Fig. 1.1. Schematic configuration of a MES electrolyser

4.2 Ex-ante assessment

To evaluate the lab-scale technology as if it was already available at an industrial scale, a process was first designed based on various inputs and simulated in Aspen Plus v12 [71]. The process started with the supply of captured, cleaned (i.e., assumed 100%) CO_2 to the MES electrolyser. The product from the electrolyser is highly diluted, and thus, a DSP train was designed to reach the purity required for selling at market conditions. Importantly, Dr. Ludovic Jourdin and colleagues provided the technical specifications such as mass and energy balances of the MES electrolyser [69] and made near-future projections on some of its performance parameters, which were at the basis of the work done in this PhD thesis. In addition, the selection of DSP technologies separating and purifying hexanoic acid was based on the experimental work and the Aspen Plus simulation performed in [72].

Since the kinetics of this specific MES electrolyser are unknown, the unit was modelled as a black box in Aspen Plus. It was represented by a calculator block, where its mass and energy balances were coded using Fortran. Mass and energy balances obtained from the process simulation served as the basis for the techno-economic assessment. Technical performance was characterised by annual product quantity, energy consumption, and a flexibility range. The flexibility range was estimated at both equipment and plant levels. At the equipment level, the range was estimated by fixing the equipment size and varying the flow rates in Aspen Plus. At the plant level, a Python script was written to connect the Aspen process model with the selected intermittent electricity profile to identify the electricity power range between which the plant could operate satisfyingly. Capital expenditure (CAPEX), operating expenses (OPEX), levelised production cost (LPC), and annualised net profit (ANP) were used to assess the economic performance of the plant. The CAPEX was calculated based on the equipment cost information available in Aspen Process Economic Analyzer v12, which uses data from the process simulated in Aspen Plus.

The use of batteries and a tank was considered as buffering units to boost production and enhance flexibility at the plant level. A mixed-integer nonlinear programming (MINLP), particularly mixed-integer quadratically constrained programming (MIQCP) problem was developed to optimise the size of the buffering units and the scheduling of the plant, i.e. when and how much product can be produced to reach optimal economic performance. It was programmed in Python-Pyomo [73, 74] and solved by Gurobi [75]. The calculation was performed in DelftBlue supercomputer [76].

A life cycle assessment was performed on a cradle-to-gate basis to compare the MES technology with its competitive technologies [50]. The Life Cycle Inventory (LCI) covers the range from when resources are extracted from the environment until after they are emitted into the environment or sent to the next gate. The LCI was constructed using SimaPro 9.6 with data from the commercial databases Ecoinvent 3.8 [77] and Agri-footprint 5.0 [78]. Process data required for the LCI were derived from the Aspen Plus simulations and complemented with data from relevant literature. The impact assessment followed the ReCiPe Midpoint Hierarchist method with a 100-year time horizon of environmental impacts [79]. The indicators selected were global warming potential (GWP; CO_2eq), land use change (LUC; m^2a crop eq), indirect land use change emissions (iLUC emissions; CO_2eq) and water consumption (m^3).

5 Dissertation outline

This dissertation is arranged as follows:

Chapter 2:

This chapter answers the first research question. It reviews how flexibility has been historically approached in the field of chemical engineering, especially in PSE. A conceptual framework for designing and evaluating the flexibility of future chemical processes is proposed, which encloses definitions, elements, types, and indicators of flexibility. This framework identifies not only flexibility types in the chemical industry and common strategies adopted to enable them but also elements of flexibility that could help process designers define their design needs related to designing flexible chemical processes. Additionally, it proposes a set of indicators that could help process designers evaluate the flexibility of process design of low-TRL technologies so that it would be possible to compare the level of flexibility among different design options.

Chapter 3:

This chapter addresses the second research question. A chemical plant producing hexanoic acid from CO_2 captured from flue gas is designed. The plant uses MES as its core conversion unit and is powered by IRE (i.e., solar and wind). In this chapter, the volume flexibility of the MES plant is explored. The chapter studies how the intermittency of different renewable electricity profiles impacts the plant's techno-economic performance and identifies the trade-offs of deploying batteries for increasing the plant's volume flexibility. The design and assessment of the flexible MES plant follow the framework proposed in chapter 2.

Chapter 4:

This chapter extends the work carried out in chapter 3 and finishes answering the second research question of this thesis. The chapter explores the techno-economic implications of using batteries versus storage tanks in the MES plant for buffering the intermittency due to the use of IRE. Moreover, a MIQCP is applied to optimise the storage tank size and the scheduling of the plant, thereby allowing the assessment of how optimisation can improve the plant's volume flexibility and economic performance. Additionally, in this chapter, a carbon footprint assessment is conducted on a cradle-to-gate basis to compare the difference in emissions between using the IRE and constant grid electricity supply.

Chapter 5:

This chapter answers the final research question. It examines the environmental implications of deploying MES to produce hexanoic acid. With this aim, two future value chains for hexanoic acid are proposed and modelled. The first value chain incorporates CO_2 capture and considers the production of hexanoic acid as the final product with the same functions as today's. The second value chain incorporates CO_2 capture and considers the production and upgrading of hexanoic acid to n-alkanes and sells n-alkanes as the final product, as a blending component of conventional aviation fuel to form sustainable aviation fuel (SAF).

Chapter 6:

The final chapter concludes this dissertation by summarising the findings and providing an answer to each research question. It also points out the limitations of this dissertation and provides recommendations for future work.

References

[1] IPCC. Climate Change 2021: The Physical Science Basis. IPCC, 2021. DOI: `10.1017/9781009157896`.

[2] S. Dangendorf et al. “Persistent acceleration in global sea-level rise since the 1960s”. Nature Climate Change. 99. 2019. Pp. 705–710. DOI: `10.1038/s41558-019-0531-8`.

[3] A. Kumar, S. Nagar, and S. Anand. “Climate change and existential threats”. Global Climate Change. 2021. Elsevier. Pp. 1–31. DOI: `10.1016/b978-0-12-822928-6.00005-8`.

[4] IPCC. Global warming of 1.5°C. World Meteorological Organization, 2018. DOI: `10.1017/9781009157940`.

[5] European Commission. 2021. Fit for 55. URL: `https://www.consilium.europa.eu/en/policies/green-deal/fit-for-55-the-eu-plan-for-a-green-transition/`. (Access date: 10 Oct 2023).

[6] European Commission. 2024. Commission presents recommendation for 2040 emissions reduction target to set the path to climate neutrality in 2050. URL: `https://ec.europa.eu/commission/presscorner/detail/en/ip_24_588`. (Access date: 19 Feb 2024).

[7] IPCC. Climate change 2022: Impacts, adaptation and vulnerability. IPCC, 2022. DOI: `10.1017/9781009325844`.

[8] IEA. CO_2 Emissions in 2022. IEA, 2023. URL: `https://www.iea.org/reports/co2-emissions-in-2022`.

[9] IEA. 2023. Chemicals. URL: `https://www.iea.org/energy-system/industry/chemicals`. (Access date: 19 Feb 2024).

[10] M. Jouny, W. Luc, and F. Jiao. “General Techno-Economic Analysis of CO Electrolysis Systems”. Industrial & Engineering Chemistry Research. 576. 2018. Pp. 2165–2177. DOI: `10.1021/acs.iecr.7b03514`.

[11] O. G. Sanchez, Y. Y. Birdja, M. Bulut, J. Vaes, T. Breugelmans, and D. Pant. “Recent advances in industrial CO_2 electroreduction”. Current Opinion in Green and Sustainable Chemistry. 16. 2019. Pp. 47–56. DOI: `10.1016/j.cogsc.2019.01.005`.

[12] F. Kazemifar. “A review of technologies for carbon capture, sequestration, and utilization: Cost, capacity, and technology readiness”. Greenhouse Gases-Science and Technology. 121. 2022. Pp. 200–230. DOI: `10.1002/ghg.2131`.

[13] M. Bui et al. “Carbon capture and storage (CCS): the way forward”. Energy & Environmental Science. 115. 2018. Pp. 1062–1176. DOI: `10.1039/c7ee02342a`.

[14] European Central Bank. 2022. Euro foreign exchange reference rates. URL: `https://www.ecb.europa.eu/stats/policy_and_exchange_rates/euro_reference_exchange_rates/html/eurofxref-graph-usd.en.html`. (Access date: 17 Oct 2022).

[15] P. Bains, P. Psarras, and J. Wilcox. “CO_2 capture from the industry sector”. Progress in Energy and Combustion Science. 63. 2017. Pp. 146–172. DOI: `10.1016/j.pecs.2017.07.001`.

[16] Oxford Institute for Energy Studies. Scaling Direct Air Capture (DAC): A moonshot or the sky's the limit? 2023. URL: `https://www.oxfordenergy.org/publications/scaling-direct-air-capture-dac-a-moonshot-or-the-skys-the-limit/`.

[17] K. S. Lackner and H. Azarabadi. "Buying down the Cost of Direct Air Capture". Industrial & Engineering Chemistry Research. 6022. 2021. Pp. 8196–8208. DOI: `10.1021/acs.iecr.0c04839`.

[18] W. Chung, W. Jeong, J. Lee, J. Kim, K. Roh, and J. H. Lee. "Electrification of CO_2 conversion into chemicals and fuels: Gaps and opportunities in process systems engineering". Computers & Chemical Engineering. 170. 2023. P. 108106. DOI: `10.1016/j.compchemeng.2022.108106`.

[19] X. Christodoulou, T. Okoroafor, S. Parry, and S. B. Velasquez-Orta. "The use of carbon dioxide in microbial electrosynthesis: Advancements, sustainability and economic feasibility". Journal of CO_2 Utilization. 18. 2017. Pp. 390–399. DOI: `10.1016/j.jcou.2017.01.027`.

[20] F. Enzmann, F. Mayer, M. Rother, and D. Holtmann. "Methanogens: biochemical background and biotechnological applications". AMB Express. 81. 2018. P. 1. DOI: `10.1186/s13568-017-0531-x`.

[21] A. P. Borole et al. "Efficient Conversion of Aqueous-Waste-Carbon Compounds Into Electrons, Hydrogen, and Chemicals via Separations and Microbial Electrocatalysis". Frontiers in Energy Research. 6. 2018. P. 94. DOI: `10.3389/fenrg.2018.00094`.

[22] F. Salomone, E. Giglio, D. Ferrero, M. Santarelli, R. Pirone, and S. Bensaid. "Techno-economic modelling of a Power-to-Gas system based on SOEC electrolysis and CO methanation in a RES-based electric grid". Chemical Engineering Journal. 377. 2019. P. 120233. DOI: `10.1016/j.cej.2018.10.170`.

[23] R. J. Detz et al. "Electrochemical CO_2 conversion technologies: state-of-the-art and future perspectives". Sustainable Energy & Fuels. 723. 2023. Pp. 5445–5472. DOI: `10.1039/d3se00775h`.

[24] A. Somoza-Tornos, O. J. Guerra, A. M. Crow, W. A. Smith, and B. M. Hodge. "Process modeling, techno-economic assessment, and life cycle assessment of the electrochemical reduction of CO_2: a review". iScience. 247. 2021. P. 102813. DOI: `10.1016/j.isci.2021.102813`.

[25] J. C. Wood et al. "Strategies to improve viability of a circular carbon bioeconomy-A techno-economic review of microbial electrosynthesis and gas fermentation". Water Research. 201. 2021. P. 117306. DOI: `10.1016/j.watres.2021.117306`.

[26] M. Atasoy, I. Owusu-Agyeman, E. Plaza, and Z. Cetecioglu. "Bio-based volatile fatty acid production and recovery from waste streams: Current status and future challenges". Bioresource Technology. 268. 2018. Pp. 773–786. DOI: `10.1016/j.biortech.2018.07.042`.

[27] S. Aghapour Aktij, A. Zirehpour, A. Mollahosseini, M. J. Taherzadeh, A. Tiraferri, and A. Rahimpour. "Feasibility of membrane processes for the recovery and purification of bio-based volatile fatty acids: A comprehensive review". Journal of Industrial and Engineering Chemistry. 81. 2020. Pp. 24–40. DOI: `10.1016/j.jiec.2019.09.009`.

[28] Y. H. Cho, H. D. Lee, and H. B. Park. "Integrated Membrane Processes for Separation and Purification of Organic Acid from a Biomass Fermentation Process". Industrial & Engineering Chemistry Research. 5130. 2012. Pp. 10207–10219. DOI: `10.1021/ie301023r`.

[29] B. Van der Bruggen, M. Manttari, and M. Nystrom. “Drawbacks of applying nanofiltration and how to avoid them: A review”. Separation and Purification Technology. 632. 2008. Pp. 251–263. DOI: `10.1016/j.seppur.2008.05.010`.

[30] Eurostat. 2023. Renewable energy statistics. URL: `https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Renewable_energy_statistics#Wind_and_water_provide_most_renewable_electricity.3B_solar_is_the_fastest-growing_energy_source`. (Access date: 04 Sept 2023).

[31] European Commission. Renewable energy targets. 2023. URL: `https://energy.ec.europa.eu/topics/renewable-energy/renewable-energy-directive-targets-and-rules/renewable-energy-targets_en#:~:text=The%5C%202030%5C%20targets,-Building%5C%20on%5C%20the&text=The%5C%20Commission%5C%20presented%5C%20Europe’s%5C%20new,overall%5C%20energy%5C%20mix%5C%20by%5C%202030.`.

[32] C. Hoffmann et al. “Assessing the Realizable Flexibility Potential of Electrochemical Processes”. Industrial & Engineering Chemistry Research. 6037. 2021. Pp. 13637–13660. DOI: `10.1021/acs.iecr.1c01360`.

[33] M. Del Pilar Anzola Rojas, M. Zaiat, E. R. Gonzalez, H. De Wever, and D. Pant. “Effect of the electric supply interruption on a microbial electrosynthesis system converting inorganic carbon into acetate”. Bioresource Technology. 266. 2018. Pp. 203–210. DOI: `10.1016/j.biortech.2018.06.074`.

[34] A. Huesman. “Integration of operation and design of solar fuel plants: A carbon dioxide to methanol case study”. Computers & Chemical Engineering. 140. 2020. P. 106836. DOI: `10.1016/j.compchemeng.2020.106836`.

[35] R. E. Swaney and I. E. Grossmann. “An index for operational flexibility in chemical process design. Part I: Formulation and theory”. AIChE Journal. 314. 2004. Pp. 621–630. DOI: `10.1002/aic.690310412`.

[36] E. N. Pistikopoulos and T. A. Mazzuchi. “A Novel Flexibility Analysis Approach for Processes with Stochastic Parameters”. Computers & Chemical Engineering. 149. 1990. Pp. 991–1000. DOI: `10.1016/0098-1354(90)87055-T`.

[37] I. E. Grossmann, K. P. Halemane, and R. E. Swaney. “Optimization Strategies for Flexible Chemical Processes”. Computers & Chemical Engineering. 74. 1983. Pp. 439–462. DOI: `10.1016/0098-1354(83)80022-2`.

[38] I. E. Grossmann and M. Morari. “Operability, Resiliency, and Flexibility: process design objectives for a changing world”. Carnegie Mellon University. Journal contribution. 2018. DOI: `10.1184/R1/6467234.v1`.

[39] E. Svensson, K. Eriksson, and T. Wik. “Reasons to apply operability analysis in the design of integrated biorefineries”. Biofuels, Bioproducts and Biorefining. 92. 2015. Pp. 147–157. DOI: `10.1002/bbb.1530`.

[40] P. A. Bahri, J. A. Bandoni, and J. A. Romagnoli. “Integrated flexibility and controllability analysis in design of chemical processes”. AIChE Journal. 434. 1997. Pp. 997–1015. DOI: `10.1002/aic.690430415`.

[41] A. Malcolm, J. Polan, L. Zhang, B. A. Ogunnaike, and A. A. Linninger. “Integrating systems design and control using dynamic flexibility analysis”. AIChE Journal. 538. 2007. Pp. 2048–2061. DOI: `10.1002/aic.11218`.

[42] M. Morari. "Flexibility and Resiliency of Process Systems". Computers & Chemical Engineering. 74. 1983. Pp. 423–437. DOI: `10.1016/0098-1354(83)80021-0`.

[43] I. E. Grossmann, B. A. Calfa, and P. Garcia-Herreros. "Evolution of concepts and models for quantifying resiliency and flexibility of chemical processes". Computers & Chemical Engineering. 70. 2014. Pp. 22–34. DOI: `10.1016/j.compchemeng.2013.12.013`.

[44] A. N. Ajah and P. M. Herder. "Addressing flexibility during process and infrastructure systems conceptual design: Real options perspective." International Conference on Systems, Man and Cybernetics, Vol 1-4, Proceedings. 2005. Pp. 3711–3716. DOI: `10.1109/ICSMC.2005.1571723`.

[45] N. Kou and F. Zhao. "Techno-economical analysis of a thermo-chemical biofuel plant with feedstock and product flexibility under external disturbances". Energy. 3612. 2011. Pp. 6745–6752. DOI: `10.1016/j.energy.2011.10.031`.

[46] L. C. Bree et al. "Techno-Economic Comparison of Flexibility Options in Chlorine Production". Industrial & Engineering Chemistry Research. 5926. 2020. Pp. 12186–12196. DOI: `10.1021/acs.iecr.0c01775`.

[47] E. Kondili, C. C. Pantelides, and R. W. H. Sargent. "A general algorithm for short-term scheduling of batch operations-I. MILP formulation". Computers & Chemical Engineering. 172. 1993. Pp. 211–227. DOI: `10.1016/0098-1354(93)80015-f`.

[48] D. A. Straub and I. E. Grossmann. "Evaluation and Optimization of Stochastic Flexibility in Multiproduct Batch Plants". Computers & Chemical Engineering. 162. 1992. Pp. 69–87. DOI: `10.1016/0098-1354(92)80007-V`.

[49] V. D. Dimitriadis and E. N. Pistikopoulos. "Flexibility Analysis of Dynamic-Systems". Industrial & Engineering Chemistry Research. 3412. 1995. Pp. 4451–4462. DOI: `10.1021/ie00039a036`.

[50] T. Langhorst et al. Techno-economic assessment & life cycle assessment guidelines for CO_2 Utilization (Version 2.0). Global CO_2 Initiative, 2022. DOI: `10.7302/4190`.

[51] D. W. Green and R. H. Perry. Perry's Chemical Engineers' Handbook/edition Don W. Green y Robert H. Perry. McGraw-Hill Inc., 2019.

[52] J. C. Meerman, A. Ramirez, W. C. Turkenburg, and A. P. C. Faaij. "Performance of simulated flexible integrated gasification polygeneration facilities. Part A: A technical-energetic assessment". Renewable & Sustainable Energy Reviews. 156. 2011. Pp. 2563–2587. DOI: `10.1016/j.rser.2011.03.018`.

[53] Z. Verwater-Lukszo and K. J. Keesman. "Computer-aided development of flexible batch production recipes". Production Planning & Control. 64. 2007. Pp. 320–330. DOI: `10.1080/09537289508930286`.

[54] S. Avraamidou, S. G. Baratsas, Y. H. Tian, and E. N. Pistikopoulos. "Circular Economy - A challenge and an opportunity for Process Systems Engineering". Computers & Chemical Engineering. 133. 2020. P. 106629. DOI: `10.1016/j.compchemeng.2019.106629`.

[55] H. Teichgraeber and A. R. Brandt. "Optimal design of an electricity-intensive industrial facility subject to electricity price uncertainty: Stochastic optimization and scenario reduction". Chemical Engineering Research & Design. 163. 2020. Pp. 204–216. DOI: `10.1016/j.cherd.2020.08.022`.

[56] C. Bataille et al. "A review of technology and policy deep decarbonization pathway options for making energy-intensive industry production consistent with the Paris Agreement". Journal of Cleaner Production. 187. 2018. Pp. 960–973. DOI: `10.1016/j.jclepro.2018.03.107`.

[57] T. Okoroafor, S. Haile, and S. Velasquez-Orta. “Life Cycle Assessment of Microbial Electrosynthesis for Commercial Product Generation”. Journal of Hazardous Toxic and Radioactive Waste. 251. 2021. P. 04020062. DOI: `10.1061/(Asce)Hz.2153-5515.0000537`.

[58] G. Wang, A. Mitsos, and W. Marquardt. “Renewable production of ammonia and nitric acid”. AIChE Journal. 666. 2020. e16947. DOI: `10.1002/aic.16947`.

[59] C. Chen and A. D. Yang. “Power-to-methanol: The role of process flexibility in the integration of variable renewable energy into chemical production”. Energy Conversion and Management. 228. 2021. P. 113673. DOI: `10.1016/j.enconman.2020.113673`.

[60] E. Moioli, A. Wotzel, and T. Schildhauer. “Feasibility assessment of small-scale methanol production via power-to-X”. Journal of Cleaner Production. 359. 2022. P. 132071. DOI: `10.1016/j.jclepro.2022.132071`.

[61] K. Thummar, R. Abang, K. Menzel, and M. T. de Groot. “Coupling a Chlor-Alkali Membrane Electrolyzer Cell to a Wind Energy Source: Dynamic Modeling and Simulations”. Energies. 152. 2022. P. 606. DOI: `10.3390/en15020606`.

[62] L. Rovira-Alsina, M. Dolors Balaguer, and S. Puig. “Transition roadmap for thermophilic carbon dioxide microbial electrosynthesis: Testing with real exhaust gases and operational control for a scalable design”. Bioresource Technology. 365. 2022. P. 128161. DOI: `10.1016/j.biortech.2022.128161`.

[63] N. J. Harmon and H. Wang. “Electrochemical CO_2 Reduction in the Presence of Impurities: Influences and Mitigation Strategies”. Angewandte Chemie International Edition. 6152. 2022. e202213782. DOI: `10.1002/anie.202213782`.

[64] L. Jourdin et al. “High Acetic Acid Production Rate Obtained by Microbial Electrosynthesis from Carbon Dioxide”. Environmental Science & Technology. 4922. 2015. Pp. 13566–74. DOI: `10.1021/acs.est.5b03821`.

[65] E. C. Canapi, Y. T. V. Agustin, E. A. Moro, E. Pedrosa, and M. L. J. Bendano. “Coconut Oil”. Bailey’s Industrial Oil and Fat Products. F. Shahidi. Vol. 1-6. 2005. John Wiley & Sons. Chap. Coconut Oil. Pp. 123–147. DOI: `10.1002/047167849X`.

[66] J. H. Miller, G. R. Hafenstine, H. H. Nguyen, and D. R. Vardon. “Kinetics and Reactor Design Principles of Volatile Fatty Acid Ketonization for Sustainable Aviation Fuel Production”. Industrial & Engineering Chemistry Research. 618. 2022. Pp. 2997–3010. DOI: `10.1021/acs.iecr.1c04548`.

[67] U.S. Department of Energy. Sustainable Aviation Fuel: Review of Technical Pathways. U.S. Department of Energy, 2020. DOI: `10.2172/1660415`.

[68] L. Jourdin, M. Winkelhorst, B. Rawls, C. J. N. Buisman, and D. P. B. T. B. Strik. “Enhanced selectivity to butyrate and caproate above acetate in continuous bioelectrochemical chain elongation from CO_2: Steering with CO_2 loading rate and hydraulic retention time”. Bioresource Technology Reports. 7. 2019. P. 100284. DOI: `10.1016/j.biteb.2019.100284`.

[69] L. Jourdin, J. Sousa, N. van Stralen, and D. P. B. T. B. Strik. “Techno-economic assessment of microbial electrosynthesis from CO_2 and/or organics: An interdisciplinary roadmap towards future research and application”. Applied Energy. 279. 2020. P. 115775. DOI: `10.1016/j.apenergy.2020.115775`.

[70] O. Cabau-Peinado, A. J. J. Straathof, and L. Jourdin. “A General Model for Biofilm-Driven Microbial Electrosynthesis of Carboxylates From CO_2”. Frontiers in Microbiology. 12. 2021. P. 669218. DOI: `10.3389/fmicb.2021.669218`.

[71] AspenTech. Aspen Plus v12. URL: `https://www.aspentech.com/en/products/engineering/aspen-plus`.

[72] P. O. Saboe et al. "In situ recovery of bio-based carboxylic acids". Green Chemistry. 208. 2018. Pp. 1791–1804. DOI: `10.1039/c7gc03747c`.

[73] M. L. Bynum et al. Pyomo-Optimization Modeling in Python. Third. Vol. 67. Springer Optimization and Its Applications. Springer, 2021. DOI: `10.1007/978-3-030-68928-5`.

[74] W. E. Hart, J. P. Watson, and D. L. Woodruff. "Pyomo: modeling and solving mathematical programs in Python". Mathematical Programming Computation. 33. 2011. Pp. 219–260. DOI: `10.1007/s12532-011-0026-8`.

[75] Gurobi Optimization. Gurobi Optimizer Reference Manual. 2023. URL: `https://www.gurobi.com`.

[76] DHPC. DelftBlue Supercomputer (Phase 1). 2022. URL: `https://www.tudelft.nl/dhpc/ark:/44463/DelftBluePhase1`.

[77] G. Wernet, C. Bauer, B. Steubing, J. Reinhard, E. Moreno-Ruiz, and B. Weidema. "The ecoinvent database version 3 (part I): overview and methodology". International Journal of Life Cycle Assessment. 219. 2016. Pp. 1218–1230. DOI: `10.1007/s11367-016-1087-8`.

[78] B. Durlinger, M. Tyszler, J. Scholten, R. Broekema, and H. Blonk. "Agri-footprint; A life cycle inventory database covering food and feed production and processing". The 9th International Conference on Life Cycle Assessment in the Agri-Food Sector. American Center for Life Cycle Assessment. 2014.

[79] M. Goedkoop, R. Heijungs, M. Huijbregts, A. De Schryver, J. Struijs, and R. van Zelm. ReCiPe 2008. Ministry of Housing, Spatial Planning and Environment, 2013. URL: `https://www.rivm.nl/sites/default/files/2018-11/ReCiPe%202008_A%20lcia%20method%20which%20comprises%20harmonised%20category%20indicators%20at%20the%20midpoint%20and%20the%20endpoint%20level_First%20edition%20Characterisation.pdf`.

2

Development of a conceptual framework for evaluating the flexibility of future chemical processes

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Chapter-specific nomenclature

μ	A measure function calculating the size of the corresponding space
N_{fp}	Number of feedstock types that produce a given product type p
m_p	Quantity of a given product type p produced
m_p^{design}	m_p under the designed scenario
m_U	Quantity of utility usage
m_U^{design}	m_U under the designed scenario
N_{pf}	Number of product types that are produced from a given feedstock type f
m_f	Quantity of a given feedstock type f
m_f^{design}	m_f under the designed scenario
$\dot{m}_{in/out}^{max}$	Maximally throughput rate leading to meet product specifications, either inlet or outlet flowrate
$\dot{m}_{in/out}^{min}$	Minimally throughput rate leading to meet product specifications, either inlet or outlet flowrate
$\dot{m}_{in/out}^{design}$	Designed throughput rate
$\dot{m}_{(in/out)}$	A given throughput rate
$t_{preparation}$	The time between the moment the production order is received and when the production actually starts
$t_{productioncycle}$	Time spent on a complete production cycle
N_{sl}	Number of production schemes that can be exercised on a given process line l

Abstract

Incorporating (operational) flexibility into process design has been a key approach to cope with uncertainties. The increasing penetration of renewables and the need to develop new low-carbon technologies will increase the demand for flexibility in chemical processes. This chapter presents a state-of-the-art review focusing on the origin, definition, and elements of flexibility in the chemical engineering context. This chapter points out a significant overlap in terminology and concepts, making it difficult to understand and compare flexibility potential and constraints among studies. Further, this chapter identifies a lack of available metrics for assessing specific types of flexibility and the need for developing indicators for exploring the potential flexibility of novel chemical processes. This chapter proposes a classification of flexibility types and provides an overview of design strategies that have been adopted so far to enable different types of flexibility. Finally, it offers a conceptual framework that can support designers to evaluate specific types of flexibility in early-stage assessments of novel chemical processes.

1 Introduction

Chemical companies adopt emerging technologies or adapt existing technologies to maintain or improve their competitiveness. However, external factors such as volatile market conditions or changing environmental policies introduce uncertainties affecting process or company performance. Trade-offs can arise in terms of effort, time, cost, or technical performance when a company fails to adopt novel technologies or adapt existing technologies to respond to emergent uncertainties. Introducing flexibility into a plant or a process design is one of the most opted responses to cushion the potential effects of uncertainties [1].

Flexibility in chemical processes is not a new or unfamiliar topic. Back in 1962, Thomas [2] suggested increasing attention to batch processing plants. They had the flexibility for easy expansion to respond to local steadily increasing market demand and the flexibility for multipurpose applications to accommodate variations in process conditions and change product types. More importantly, they were more economically feasible [2]. During the 1980s and 1990s, researchers investigated the optimal design of flexible chemical processes or plants under uncertainties, focusing on applying mathematical approaches [3–9]. The research was based on the premise that a flexible plant is expected to guarantee a feasible region of process operating parameters that are manageable via manipulating control variables [6, 10]. With the advent of the 21st century, the potential for producing multiple products, namely polygeneration, gained attention in the literature. For instance, Yamashita and Barreto [11] studied integrated energy systems that could be designed with output flexibility. The system was amenable to diverse feedstocks and capable of flexibly producing various products, including electricity. Meerman et al. [12] explored the flexible operation of an integrated gasification poly-generation plant that had both feedstock (i.e., coal and different types of biomass) and output flexibility (electricity at peak hours and biofuels during off-peak hours) as a way to respond to changes in market conditions.

The results of a bibliometric analysis focusing on flexibility in the chemical industry over the past three decades are shown in Fig. 2.1-2.3. The figure illustrates the changes in research scope of flexibility in the chemical industry (the size of the circles reflects the frequency with which the keyword appears in the literature inventory. The distance between the two circles reflects the closeness of their connection. See section 2 for more information.). In the 1990s, as can be seen in Fig. 2.1, the most common keywords were mathematical models, optimisation, process control, computer simulation, scheduling, algorithms, and flexible manufacturing systems. Approaches were developed mostly related to numerical analysis, often used to identify trade-offs between capital cost and flexible process design in terms of, among others, operating conditions and equipment selection [8, 13, 14]. Studies made use of mathematical models such as mixed integer linear programming (MILP) or mixed integer nonlinear programming (MINLP) to determine, for instance, optimal scheduling patterns of flexible batch operation processes to minimise the changeover time between different operations, maximising the production time and manufacturing flexibility to meet volatile market demands [15–17]. Computer simulation has been a valuable tool since then, and it is not surprising that it appeared prominently in the research at the time.

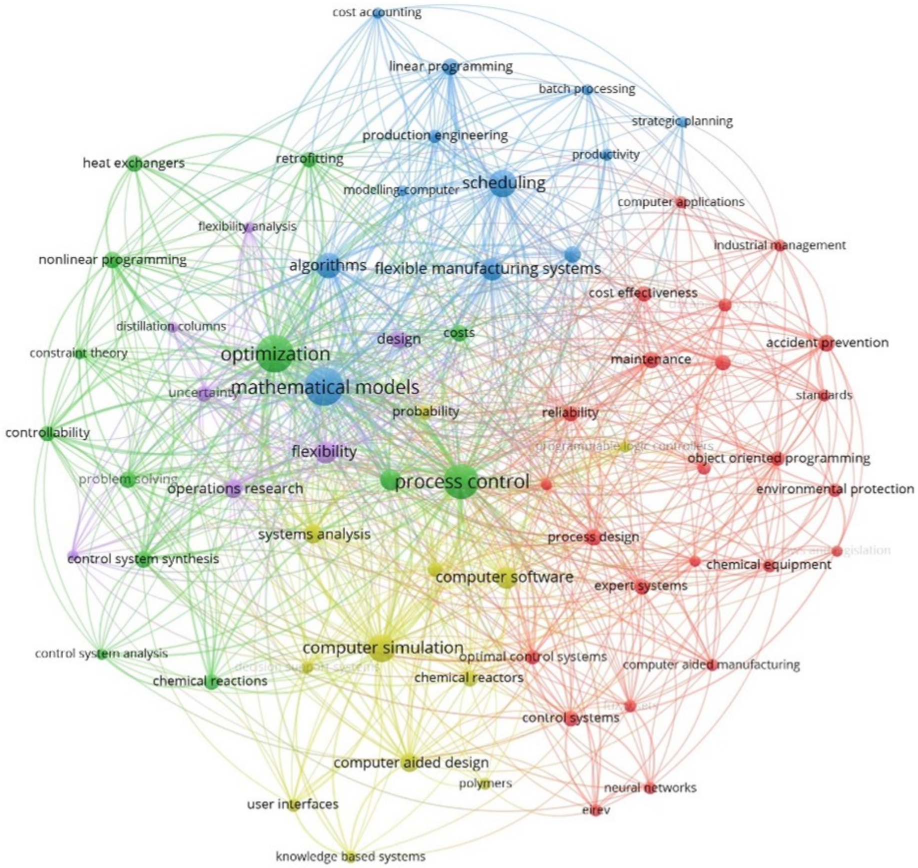

Fig. 2.1. Bibliometric analysis network maps of flexibility-related keywords in the chemical industry in 1990-1999.

During the first decade of the 21st century (see Fig. 2.2), flexibility included more frequently business, safety, and environmental aspects. However, some of these elements had already emerged in the previous decade. As the oil crisis that occurred in the 1990s ended and a further take-off in the chemical industry happened, an increasing number of studies were published on how to manage a chemical company flexibly in terms of, for instance, investment and marketing [18–21]. Meanwhile, costs and environmental impacts started to be used not only to monitor performance but often also as indicators of the feasibility of investing in (flexible) chemical plants [22–25]. Regarding the technical design of a chemical plant, driven by safety concerns, equipment was required to be designed with flexibility in mind so that variations in operating conditions could be accommodated to avoid severe equipment failure and, hence, entire process failure [22, 26].

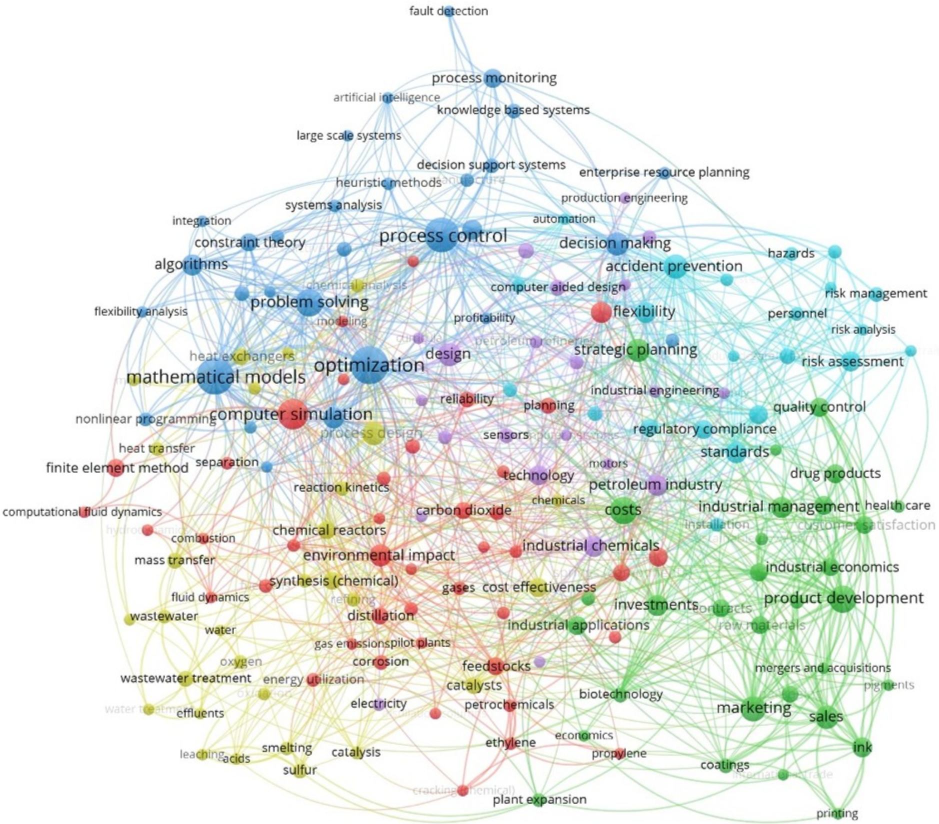

Fig. 2.2. Bibliometric analysis network maps of flexibility-related keywords in the chemical industry in 2000-2009.

With the growth of environmental awareness in the last decade, a more comprehensive range of environment-related topics appeared in flexibility studies (see upper left quadrant in Fig. 2.3), exemplified by issues such as energy efficiency, energy utilisation, carbon dioxide, renewable energy sources (RES), and biomass. Of particular interest for the design of flexible chemical processes is the variable supply of energy from renewable sources. For instance, the seasonality of biomass and its variability in origin and type [27] have resulted in studies focusing on the design of chemical plants with feedstock flexibility at their core [28, 29]. Similarly, "smart power grids", a topic that at first sight seems irrelevant to the chemical industry, has emerged in flexibility studies. It is often used in conjunction with terms referring to significant deployment of RES such as solar and wind energy [30, 31], illustrating a current trend of further coupling the chemical and the power sectors. The increasing penetration of intermittent RES in the power grid has brought up technical challenges for the chemical industry, as it is now expected that the chemical industry will conduct flexible operations within a range of loads to help balance fluctuations in electricity supply [32].

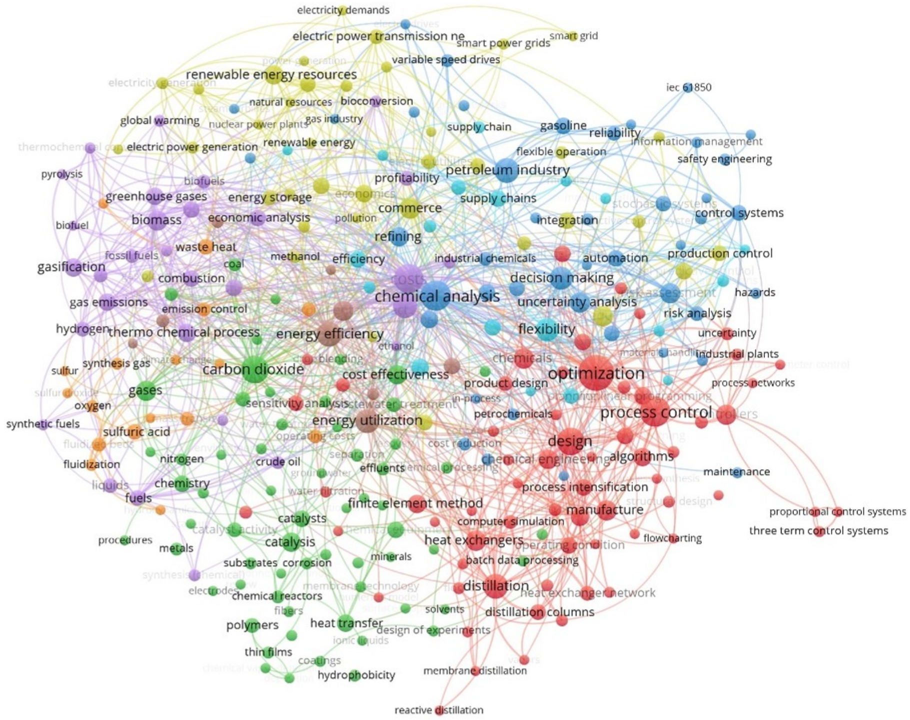

Fig. 2.3. Bibliometric analysis network maps of flexibility-related keywords in the chemical industry in 2010-July 2020.

The overview above points out a change in the attributes and goals through which flexibility has been defined over time. This is not always obvious as the same terminology is often used, but its meaning changes. For example, while flexible operation is described in some studies as the ability to operate over a range of operating conditions [7, 13], others define it as the ability to easily switch between operations [16, 33]. The term is the same, but the implications are different. Other terms that are used to mean the same or overlapping concepts are, for instance, feedstock flexibility [28, 29, 34], fuel flexibility [12], volume flexibility [35, 36], operational flexibility [7, 37]. Using similar terminology to refer to different concepts, some of them overlapping, creates confusion in the field, making it difficult to compare studies and assess the types of flexibility and their potential. The conflating terminology also makes it difficult to select indicators to evaluate and monitor flexibility. In literature, several metrics for quantifying flexibility, such as flexibility index [7], stochastic flexibility index [8, 9, 38, 39], and dynamic flexibility index [40] are available, which involve three kinds of variables (i.e., control, design, and state) and uncertain parameters. These metrics originate in the field of process systems engineering. They aim to analyse the overall flexibility of chemical processes and help designers identify optimal designs that balance the degree of flexibility and cost. It is, however, unclear how to apply these metrics to assess designs of future concepts, that is, theoretical designs of technologies that are not yet at a commercial scale. In these cases, uncertain parameters, especially the three kinds of variables described previously and their relation to each other, are not well understood. Therefore, for such designs, there should be simplified and explorative metrics that allow evaluating and comparing the flexibility of different plant designs or plant configurations.

Given the importance of flexibility in the coming decades, there is a need to harmonise flexibility-related terminology, concepts, and indicators to decrease confusion for researchers new to the topic. Moreover, it is essential to propose a framework that can suffice the assessments of the comparisons among novel designs. Such a framework can support designers and decision-makers in the chemical industry to better understand the types of flexibility they are designing towards, how different types of flexibility interact with each other, and how to assess the level of specific flexibility types a design has. However, such a systematic framework is currently lacking, though some studies have already worked on harmonising the definitions of several flexibility types and reviewing known strategies to enhance feedstock flexibility [34, 41]. This chapter aims to fill this gap by examining how flexibility has been studied and proposing a conceptual framework for evaluating specific flexibility types of novel chemical processes. The framework encloses definitions, elements, types, and indicators of different flexibility types in the chemical (including biochemical) engineering context. In light of the future coupling between the chemical industry and the energy system, we are particularly interested in the demand for flexibility of chemical processes.

2 Methodology

This chapter departed from definitions, taxonomies, and other relevant concepts of flexibility presented in the literature of chemical engineering. First, a systematic literature search was performed to retrieve information needed for constructing the framework. Then, a framework was developed that combines definitions, elements, types, and indicators of flexibility.

The literature review focused on journal papers studying flexibility from 1990 - July 2020 via Scopus. The goal was to make an inventory of (i) the definitions used, (ii) existing taxonomies, and (iii) indicators used to assess flexibility. Furthermore, to make certain that biochemical technologies were also included, as they are expected to play a role in flexibility in the future chemical industry, searching criteria relating to biochemical technologies were added. The search criteria are given in Appendix A.

In total, 1521 studies were identified on Scopus. Studies that look into the flexibility of materials and do not focus on the chemical industry or study flexibility at molecular or laboratory scales were excluded. This resulted in 1249 that were further analysed. Both author and indexed keywords of the 1249 studies were mapped by decade using VOSviewer. VOSviewer is a software tool for creating bibliometric maps based on the correlation amongst a set of data. It allows to generate network maps and identify correlations. For further information on this tool, we refer to `https://www.vosviewer.com/`. The results of this analysis have been discussed in section 1. To prepare the literature inventory, a sample of 106 papers was further analysed to develop a conceptual framework for evaluating the flexibility of novel chemical processes.

For each study, the goal of each study was first summarised, and the terms used for different kinds of flexibility were documented along with their implicit or explicit definition. However, if a term was mentioned without a definition and the definition could not be derived from the study, the term was not further considered in the review. In addition, the design strategies used to enable each kind of flexibility were also documented, if any. Flexibility types (i.e., some of the flexibility terminologies) without design strategies were excluded from the framework. Second, when possible, the relation amongst different flexibility types was captured. Finally, indicators used to measure or evaluate flexibility were noted, if any.

3 State-of-the-art

3.1 Definition of flexibility

In chemical engineering, one of the most common uses of flexibility is as a component of operability, which is often called operational flexibility [7, 28, 36, 42–51] or process flexibility [38, 52–56]. Flexibility is usually defined as the ready capability of a plant to operate over a range of conditions feasibly [57]. Walsh and Perkins [58] considered operability as the ability of a system to tackle uncertainty, accommodate disturbances, and resolve concerns for reliability and maintenance. Bahri, Bandoni, and Romagnoli [59] indicated that operability is easy to operate and control a process. Grossmann and Morari [60] defined operability as the ability of a chemical plant to perform satisfactorily under conditions different from the nominal design conditions. Operating condition is an umbrella term that can refer to process operating parameters (e.g., temperature, flow rates, and pressure), product specifications, feed quality, and so on [60, 61]. "Ready" implies the ability to accommodate expected (e.g., stochastic process operating parameters [38]) or wanted uncertainties in some conditions (e.g., intermittent renewable energy supply). Flexibility is incorporated in the design of the physical process line(s), where related unit operations and equipment are specified, denoted as process [44, 53, 62] or processing route [52]. This chapter addresses it as a process line.

Other components of operability refer to controllability, reliability, and resiliency [4, 7, 60, 63, 64]. Controllability addresses the quality and stability a process presents when responding to short-term perturbations and transitions from one operating point to another [7, 64]. Controllability thus relies on designing and implementing a control system that directs and regulates equipment behaviour [22, 64, 65]. Reliability is associated with the probability of mechanical or electrical failure during normal operation [7]. Resiliency is sometimes defined as the ability of the plant to move fast and smoothly from one operating condition to another [61], or as the dynamic capability to quickly recover from process disturbances in a fast and smooth manner [60]. Resiliency has the ultimate goal of determining a system's inherent dynamic characteristic (e.g., deadtime [66]) without selecting a particular controller [57]. In recent years, resilience engineering [67, 68] has become a popular topic in system engineering. The perception of resilience in this context is different from the one used in the chemical engineering context. The discussion on resilience engineering is outside the scope of this chapter.

Finally, it is important to note that while most studies examine flexibility as a characteristic of steady systems [15, 58], some studies have studied flexibility in the context of dynamic systems [38, 57, 64, 65]. Steady-state flexibility is the flexibility discussed in the two previous paragraphs. Among the papers studied in this review, only Grossmann, Calfa, and Garcia-Herreros [57] explicitly explained that realising dynamic flexibility in a plant involves identifying manipulated variables that guarantee feasible operation in the worst case of time-varying uncertain parameters. The authors suggest that "dynamic flexibility" is not designed for a particular transient disturbance but for the overall dynamic performance of a plant. This chapter focuses on steady-state flexibility, which is shortly referred to as flexibility.

3.2 Types of flexibility

Different terms of flexibility can be identified (see Table 2.1). A problem, however, is that the definitions used for the different terminologies overlap in literature (see Table 2.2). In this section, the definitions used in each case are further discussed. It should be noted that flexibility terminologies "operational flexibility" and "process flexibility" are also found in the literature, and they have already been identified as synonyms of "flexibility" in section 3.1. Therefore, though they are listed below, they are not discussed in detail in this section.

3.2.1. Same concepts- different terminologies

3.2.1.1 The ability to handle changes in quantities and/or qualities of inflow materials

Feedstock flexibility, fuel flexibility, raw material flexibility, electrical flexibility, and load flexibility are terms used in the literature to indicate the ability of a piece of equipment, a process or a plant to handle changes in quantities and/or qualities of inflow materials. Quality refers to the chemical compositions or physical properties (e.g., boiling point, density, state of matter, and size). Raw material flexibility or feedstock flexibility is often studied as an option to maximise the flexibility of a complex processing network and minimise the net present value of its operations [55, 100]. For instance, in the petrochemical industry, pipelines were designed early on to handle crudes with different qualities to avoid the high capital cost of installing dedicated pipelines as well

Table. 2.1. Flexibility terminologies identified in the literature.

Terms	References
Operational	[7, 28, 34, 36, 37, 42–51, 60, 69–71]
Process	[22, 29, 38, 52–56, 72, 73]
Feedstock	[12, 28, 34, 41, 46, 53–55, 74–77]
Raw material	[55, 78]
Fuel	[11, 12]
Plant	[12, 27, 32, 47, 50, 72, 79–82]
Volume	[21, 35, 36, 52, 53, 83, 84]
Product	[28, 34, 46, 52, 53, 55, 77, 78, 81, 84, 85]
Production	[12, 86–89]
Expansion	[1, 36]
Scheduling	[87, 90]
Recipe	[53, 91]
Capacity	[34, 36, 46, 85, 92]
Location	[46, 92]
Innovation	[46]
Load	[93, 94]
Electrical	[95, 96]
Others (without any term)	[2–6, 8–10, 13, 15–20, 23, 24, 30, 31, 33, 40, 57–59, 61–66, 97–106]

as to accommodate fluctuations in crude flow rate [5]. Another design strategy to enable raw material flexibility is to produce the main product from different raw materials by using different production schemes [52]. A production scheme, also called production pathway [29, 51, 52], specifies the requirements for the raw material, the product qualities and the synthetic pathway (including unit operations, and hence their corresponding process operating parameters as well as utilities) to complete the conversion. In this case, process line design (e.g., equipment selection and sizing) plays a major role in enabling raw material flexibility.

With the development of biotechnology and the need to reduce CO_2 emissions, the use of non-fossil feedstocks has gained relevance in the chemical industry. Due to the uncertainties in the long-term availability of, e.g., lignocellulosic feedstocks and the need to minimise the dependence on a given type of feedstock, designing processes that can deal with the use of multiple types of feedstocks has gained relevance. Common strategies are to (i) select and/or design equipment that can deal with variations in types of feedstocks [12, 28], (ii) blend different types of feedstocks [101], and (iii) install buffer unit(s) to regulate fluctuations in, e.g., chemical composition. Kou and Zhao [28], for instance, proposed a plant design based on a gasifier that was capable of converting multiple types of feedstocks into syngas. Their design contains an extra process unit to regulate the fluctuating ratio of components in the syngas stream before the syngas is sent to the following conversion unit. Similar examples are published in other works [27, 29, 53, 74].

RES are, however, not only renewable carbon feedstocks. In recent years, the introduction of RES with intermittent nature has resulted in challenges in balancing the power grid. With the potential of using electrified chemical processes in the industrial sector as a Demand-Side Management (DSM) strategy or as an energy storage, requirements for electrical flexibility or load flexibility are emerging. This kind of flexibility is then defined as the ability of a machine, process or plant to cope with uncertainties in power supply. There are three general design strategies explored in literature [44, 70, 71, 93–95, 102], (i) selecting and/or designing equipment (function-wise) so that it can be dynamically operated; (ii) selecting and/or oversizing equipment (capacity-wise) that meet wide load requirements, and (iii) installing buffer units (e.g., batteries for buffering electricity supply fluctuations or storage tanks for decoupling units with flowrate fluctuations from steadily operated units and hence buffering changing flowrates) to cope with the uncertainties in qualities and quantities of flows caused by fluctuating electricity supply. To lower operating costs, the ability to adjust electricity consumption subject to changing electricity prices is also studied in, for instance, the flexible operations of air separation plants [104].

3.2.1.2 The ability to change the qualities of outflow materials

The ability to produce outflow products with different qualities is referred to in the literature as product flexibility or recipe flexibility. This type of flexibility may be required when reactions inherently result in multiple products [55]; or when a company aims to maximise the flexibility of a process network containing multiple process lines and to minimise its operating costs or diversify revenues [27, 53]; Mansoornejad, Chambost, and Stuart [52] pointed out that recipe flexibility is basically a strategy to enable product flexibility, where different production schemes are exercised on either the same process line or different process lines, but certainly with different operating conditions. Note that though some facilities can produce a set of products with different qualities, they are not considered flexible with regard to the outflow materials if the products can only be produced in fixed proportions at all times [55]. Two strategies are frequently employed to realise this type of flexibility [27, 28, 52]: (i) select synthetic pathways that inherently result in multiple products, and (ii) implement different production schemes. Uria-Martinez, Leiby, and Brown [76] and Norton and Grossmann [55] pointed out that different production schemes can be completed in the same process line by sharing part of the same process line or in a dedicated process line.

3.2.1.3 The ability to vary throughput

The need to vary throughput over time is driven by uncertainties in product demand or feedstock availability. Several terms, such as volume flexibility, production flexibility, capacity flexibility, and expansion flexibility, are used in the literature to describe this type of flexibility. Despite the different terms, three common design strategies can be identified to enable this type of flexibility [53, 73, 78, 88], namely, (i) designing equipment to handle peaks in flowrates; (ii) installing parallel same units or even entire process lines so that some equipment can be switched on/off to adjust the overall production level, and (iii) robust scheduling. Note that the ability to adjust production level via expanding or contracting is denoted as capacity flexibility by Worsdorfer, Lier, and Crasselt [92] as well as expansion flexibility by others [1, 36] who are particularly interested in designing modular plants.

3.2.1.4 The ability to switch to another production scheme

Another type of flexibility is the ability of a plant to switch to another production scheme. This is usually required for plants where part (or all) of production resources are shared among different production schemes. Mansoornejad, Chambost, and Stuart [52] described product flexibility (denoted as production flexibility by Meerman et al. [12]) as the ability to economically changeover to produce a new (set of) product(s), which is different from the definition of product flexibility in section 3.2.1.2. Polygeneration facilities are a typical example of plants that are designed around the idea of production flexibility, for instance, [12]. The design strategies in literature [12, 52] to address this type of flexibility are (i) select and/or design equipment that is able to handle inflow materials with different qualities and/or produce outflow materials with different qualities and (ii) select or design production schemes and equipment that can be switched on/off at request.

3.2.2. Concepts with agreement on terminologies

Scheduling flexibility is the ability to adjust the allocation of production resources for different production cycles over time. It is a type of flexibility that is historically present in batch or semi-continuous processes, where part of or the entire production resources could be shared among more than one production scheme over time. A set of production resources refers here to a process line and all relevant materials that could be processed (e.g., raw materials) or consumed (e.g., utilities and labour) on a line for a production cycle. A production cycle includes all the time spent making a product, from the preparation of production resources until the product is packed up and ready for delivery. The realisation of scheduling flexibility considers the process design and the effort of supply chain planning. However, in this chapter, only design strategies related to process design are addressed. In literature [5, 15, 103], flexibility has also been studied regarding scheduling multipurpose plants, though they did not explicitly use the term. Nowadays, some electrochemical plants, where electricity acts mainly as a feedstock type, are expected to be designed with scheduling flexibility so production cycles can be scheduled easily at request, responding to DSM [95]. Scheduling flexibility is often embedded into the plant design via (i) equipment sizing or (ii) installing multiple same units or process lines [5].

A summary of the different terminologies and concepts and the overlap between them is provided in Table 2.2. Note that location flexibility and innovation flexibility were rarely the focus of studies dealing with flexibility, and the respective design strategies were hardly found in the literature. Therefore, they are not discussed further in this chapter. The term operational flexibility and process flexibility are identical to flexibility, as explained in section 3.1. Hence, they are also not further elaborated in this section. Moreover, plant flexibility is an umbrella term for all types of flexibility that a plant has. Thus, it is not a specific type of flexibility that can be enabled via specific design strategies.

Table. 2.2. Overview of overlap between flexibility terminologies

	Flexibility terminology	Concept/definition
Same or similar concepts, different terminologies	Feedstock, Fuel, Raw material, Electrical, Load	Ability to handle changes in quantities and/or qualities of inflow materials
	Product, Recipe	Ability to change the quality of outflow materials
	Production, product	Ability to switch to a different production scheme
	Volume, Capacity, Production, Expansion	Ability to vary throughput
Concepts matched with a unique terminology	Scheduling	Ability to adjust resource allocation to different production cycles
	Location	Ability to move a plant from one place to another
	Innovation	Ability to adapt to try out innovative products and processes
Same terminology applied to different concepts	Operational	Ability to operate over a range of conditions feasibly
	Plant	Ability of a plant to operate over a range of conditions

3.3 Hierarchical levels of flexibility

In the literature, there are three hierarchical levels often considered during plant design: plant, process line and equipment. The plant level involves all process lines and their corresponding production schemes in a plant. A process line was previously defined in section 3.1. The process line level further incorporates the production schemes that can be exercised on it. The equipment level indicates a single piece of equipment and everything related to it (e.g., dimensions, functions or utilities usage). In some multipurpose plants, changes in, e.g., feedstock type, product type, and throughput, are tackled by installing dedicated process lines or by modifying the process line that will be used by multiple production schemes [52, 55, 76]. Modifying a process line requires installing or removing extra equipment or modifying single pieces of equipment. For instance, if a gasifier does not have the ability to handle inflow syngas with fluctuating CO/H_2 ratio, extra equipment can be installed to adjust the ratio ahead of the gasifier [12]. Examples of design details at the equipment level can also be seen in electrochemical plants, where electrolysers must be selected or designed with the ability to cope with fluctuations in electricity supply [44, 93, 95] and in multi-feedstock and multiproduct bio-based plants where different biomass feedstock types are handled through the same set of pre-treatment and conversion units while following upgrading and purification units are dedicated to each product [12, 27, 28, 76]. It should be noted that often more than one level has to be considered simultaneously to enable flexibility.

3.4 Indicators for evaluating flexibility

To understand flexibility, it is important to not only define the concept but also to develop indicators that allow us to assess and monitor it. Most indicators in the literature originate from the field of process control. The most known is the flexibility index developed by Swaney and Grossmann [7] followed by other metrics developed upon it (e.g., stochastic flexibility index [8, 9, 38, 39], dynamic flexibility index [40]). They are used for characterising and quantifying the overall operational flexibility of high-TRL technologies with all the involved variables (i.e., design, state, and control) and uncertain parameters known. The flexibility index calculates the size of the space of uncertain parameters (e.g., throughput, temperature, pressure) over which steady-state operation of chemical processes could be feasibly managed by adjusting the control variables (e.g., flow rates, valve coefficient) [7, 60, 72, 84]. It is, however, difficult to apply it when the values of the variables (i.e., design, state, and control) and the relations among them are not fully understood, which is the case in ex-ante technology assessments of low-TRL technologies. Such designs are not technologically ready to be assessed using the flexibility index. A similar metric to the flexibility index is the operability index (also known as output controllability index), proposed by Vinson and Georgakis [105]. A comprehensive study on the similarities and differences between the flexibility index and the operability index was done by Lima et al. [72]. Different to the flexibility index, which measures the space of parameters that can be manipulated by control variables, the operability index calculates the extent to which the desired output variables (e.g., purity of products, product quantity) can be achieved using available input variables (e.g., purity of feedstock, inflow rates) with the presence of known disturbances [72]. A variant of operability index is the servo operability index (also noted as servo output controllability index), also developed by Vinson and Georgakis [105]. In contrast to the operability index, the desired output variables are translated into corresponding desired input variables. Therefore, these two metrics focus on the input and output variables, and hence can be incorporated to designs at the process synthesis phase, where the process control structure is unknown while the control objectives are known [72, 105, 106]. These metrics reflect the overall operability of designs on different hierarchical levels to achieve desired results. It should be noted that the metrics are not intended for quantifying specific flexibility types, and therefore require (minor) adaptions.

It is, however, surprising that there is a lack of a standardised set of indicators that allows evaluating specific flexibility types in literature. Also, in many studies, explicit indicators are lacking altogether. Flexibility is often used rather as part of the scoping of the studies than a goal that needs to be evaluated. In the studies that attempted to evaluate specific flexibility types, two categories of indicators were used to compare the degree of flexibility between design options. One category measures the range of available options. The other focuses on impacts (also noted as trade-offs by some researchers). For the first category, for instance, the number or type of feedstocks that can be processed is used as an indicator of flexibility in selecting equipment [12, 28]. In the articles studying the ability to deal with fluctuating electricity, normalised maximum ramping rates, maximum turndown ratios, response time, the range of operable current density, peak-to-base load ratio, or load range are often used as indicators of flexibility [44, 70, 93–95, 102].

For the second category, in order to compare alternative flexible designs, researchers have also considered impacts on economic, technical or environmental performances as indicators of flexibility. Impacts are case-specific, and hence, the acceptability of impacts is subjective, which in many studies is simply described as "without violating the design specifications or constraints" [22, 60, 69]. However, there are studies where specific indicators are used to evaluate impacts. The overall economic performance of a plant has widely been applied as an indicator because economics is one of the most important drivers for enabling all kinds of flexibility. Huesman [44] quantified the impact of flexibility on economic performance by comparing the profits of two electrochemical plants powered by electricity with different levels of intermittency. Energy efficiency is seen as an indicator where flexibility in handling uncertainties in production rate [93], and feedstock and product qualities are studied [12, 95]. Downtime has also been used as an indicator where the changeover between production schemes is frequently required [87, 95], because it affects the production time and, hence, the overall production level.

4 Framework for comparing and assessing flexibility

In this section, we present a framework developed to support the identification, comparison and evaluation of flexibility in the early-stage design and the ex-ante assessments of novel chemical processes.

4.1 Step 1 - Define uncertainties

As discussed in section 3.1, flexibility is implemented to respond to uncertainties, either stochastic process operating parameters or expected uncertainties. Therefore, the first step is to identify the uncertainties that the design needs to respond to. Answering the following questions can help designers in this task:

- What are the potential sources of uncertainties? (e.g., feedstock qualities/quantities, product qualities/quantities)
- What are the boundaries of uncertainties? (e.g., highest or lowest possible flowrates)
- What is the expected frequency of changes in operating parameters, over a given time horizon? (e.g., flowrate fluctuates at all times or only once between two production cycles)

4.2 Step 2 - Define flexibility

After the uncertainties are identified, the needs for flexibility have to be defined. Table 2.3 depicts five types of flexibility identified from the literature review: feedstock flexibility, product flexibility, volume flexibility, scheduling flexibility, and production flexibility. As discussed in section 3.2, they are directly derived from the sources of uncertainties introduced to processes. The identification of the needs is case-specific. Therefore, the flexibility types should be adapted when needed (this will be explained in section 4.2.1). Moreover, it should be stressed that when dealing with changes in quantities of the inflow materials (i.e., part of feedstock flexibility), this type of flexibility is essentially analogous to volume flexibility. Therefore, accordingly, the design strategies and indicators of volume flexibility can be applied.

Table. 2.3. Classification of flexibility types and their respective concept and design strategies.

Type	Concept	Design strategies
Feedstock	The ability to handle changes in quantities and/or qualities of inflow materials	(i) Implement different production schemes to produce different product types (ii) Blend different types of feedstocks (iii) Select and/or design the equipment that can deal with variations in feedstock quality (iv) Install buffer unit(s) to regulate fluctuations in feedstock quality.
Product	The ability to change the qualities of outflow materials	(i) Select synthetic pathways that inherently produce multiple products (ii) Implement different production schemes
Volume	The ability to vary throughput	(i) Select and/or design (function-wise) equipment that can deal with variations in throughput (ii) Select and/or design equipment (capacity-wise) that meet wide load requirements (iii) Install buffer units to decouple units with variations in throughput from steadily operated units (iv) Install parallel units or process lines (v) Robust scheduling
Scheduling	The ability to adjust resources allocation for different production cycles	(i) Oversize equipment (ii) Install parallel same units or process lines
Production	The ability to switch to exercise another production scheme	(i) Select and/or design equipment that can handle inflow materials with different qualities and/or produce outflow materials with different qualities (ii) Select and/or design production schemes and equipment that can be switched on/off at request

4.2.1. Define flexibility by specifying the elements of flexibility

Based on the literature review, we identify five elements that need to be considered when defining flexibility: (i) target, (ii) range, (iii) hierarchical level, (iv) timescale, and (v) impact. Such a definition can therefore be: the ability of [a plant/process line/equipment] to operate over [a range of operating conditions] on [a certain timescale basis] to cope with [a target] with acceptable [impact]. The contents of the brackets need to be specified in each case.

- **Target.** A target is derived from the sources of uncertainties and elaborates the content of a flexibility type, which narrows down the design scope. For instance, if the general concept of feedstock flexibility is defined as "the ability to handle changes in quantities and/or qualities of inflow materials", then it is necessary to explicitly describe the flexibility type, for example, "the ability to cope with fluctuating electricity supply". The target here is a fluctuating electricity supply.
- **Range.** Flexibility is designed to handle deviations from nominal operating conditions. A range indicates how many options are available once the operating conditions deviate from the nominal ones. A range is derived from the boundaries of uncertainties. They can be a series of continuous values (e.g., 30-50 kg/hr) or a set of discrete criteria (e.g., product types such as biofuel or hydrogen). Continuing with the example above, the range can be expressed, for instance, as "the ability to operate over 20-110% of the nominal electricity load to cope with fluctuating electricity supply".
- **Hierarchical level.** The hierarchical level reflects the degree of detail a design needs to reach in order to meet the design requirements derived from the flexibility needs. The hierarchical levels also reflect at which level the flexibility needs to be assessed for a given purpose. The amount of data and requirements decreases with the level of aggregation. For instance, Wang, Mitsos, and Marquardt [93] used peak-to-base load ratio to evaluate a plant's flexibility with regard to operations powered by intermittent renewable electricity, while Buttler and Spliethoff [94] used the range of load ratio to compare the flexibility among different electrolysers in relation to operation under fluctuating electricity supply. Continuing with the example above, if only the electrolyser requires flexibility, then the definition becomes "the ability of the electrolyser to operate over 20-110% of the nominal electricity load to cope with fluctuating electricity supply".
- **Timescale.** Uncertainties are time-dependent. A unit time period can be a second, an hour, a day, a season, or a production cycle, etc. Selecting the unit of time will depend on the goal of the assessment. For example, some biorefineries have to change feedstock type every season, while some multiproduct batch plants may need to change over to another production scheme after every production cycle. Adding the timescale to the above example, the definition can be elaborated as "the ability of an electrolyser to operate over 20-110% of its nominal electricity load to cope with fluctuating electricity supply at all times".

- **Impact.** Designing for flexibility often results in impacts when compared to a reference design. Such impacts concern, for example, technical performance (e.g., conversion efficiency, product purity), economic performance (e.g., net present value, payback time), human resources (e.g., time, effort) and/or environmental performance (e.g., global warming potential, acidification). Impacts can be either positive or negative (i.e., penalties). Impacts are often quantified by comparing the performance of the (relatively more) flexible design to the performance of a reference design. Specifying impacts or limits to impacts in advance can help narrow down the number of design options. For instance, adding the requirements related to impacts to the above example, the flexibility can be then finally specified as "the ability of an electrolyser to operate over 20-110% of its nominal load to cope with fluctuating electricity supply at all times while keeping the overall conversion efficiency above 80% at minimum cost, effort or downtime".

4.2.2. Pay attention to possible relations among different types of flexibility

When designing novel chemical processes, it should be noted that a need for a given type of flexibility might trigger the need for other types of flexibility. For example, production flexibility will be needed when feedstock and or product flexibility is enabled at the equipment and or process line level. Production flexibility might, in turn, trigger the need for scheduling flexibility. Another example at a different level is the expectation from power companies for (electro)chemical plants to have enough scheduling flexibility to operate at request, which would trigger the need for the plants to have feedstock flexibility [95]. However, interactions among different flexibility types are case-specific and often only detectable during the design procedure, leading to iterative work.

4.3 Step 3 - Apply design strategies for flexibility

Once the needs for flexibility are defined, the following step is to identify and select strategies to address flexibility. Table 2.3 summarises design strategies identified in the literature for the five general flexibility types. Note that the strategies can be considered in any order depending on the purpose of the study. Furthermore, note that if changes in the quantities of inflow materials are expected (i.e., part of feedstock flexibility), the design strategies are similar to those of volume flexibility.

4.4 Step 4 - Evaluate flexibility

As discussed in section 3.4, indicators for evaluating specific flexibility types are scarce in the literature, and if available, they often focus on one type of flexibility. This section provides illustrative examples of standardised indicators per type and hierarchical level (see Table 2.4). The list is not exhaustive and can be further expanded or adapted over time. Some of the indicators were based on literature (i.e., No. 1 and 8). Others are proposed to make the assessment of different types of flexibility more comprehensive. Note that flexibility is, in fact, a relative value (flexible compared to), and hence, the value of an indicator should be compared between a (relatively more or less) flexible design and a reference design.

Flexibility can impact a plant at different hierarchical levels, as discussed in section 3.3. Whether such impact is considered acceptable is case-specific, and it is up to the evaluator to decide whether a given impact is acceptable. For instance, increasing flexibility at the cost of environmental or economic performance. Therefore, the table does not specify a desired direction for the impacts. Furthermore, note that when there is only one process line in a plant, the indicators at the process line level can also be applied to the plant level. In addition, when the assessment concerns theoretical designs, for instance, designs of novel plants that are not commercial. In this case, some of the indicators in the table are not applicable. Examples of implementing some of the indicators in Table 2.4 are briefly illustrated below.

Feedstock flexibility

One indicator (No. 2 in Table 2.4) that can be used to characterise this type of flexibility is "the ability to use varying feedstock types while producing the same product type in a given period of time". Its math expression quantifies the maximum number of feedstock types that can be used to produce a given product and is reported as an absolute value. For instance, a process line uses a feedstock type to produce a product. Due to the unavailability of the feedstock in winter, the designers introduce another feedstock type to keep the operation ongoing. As a result, feedstock flexibility is increased at the process line level. However, using the second feedstock type would result in twice as much energy being used at the same production rate. Not using the second type of feedstock would increase the risk of having to close up the plant for periods of time (and thus, result in economic losses). Hence, the indicators can provide insights into the trade-offs. Nevertheless, they do not suggest any acceptability. Stakeholders have to determine the trade-offs between the feedstock flexibility that increases the revenue and utility usage that leads to cost penalties.

There is also a more complex indicator (No. 1) that characterises "the ability to handle expected changes in feedstock qualities while satisfying the product specifications in a given period of time". It is an indicator adapted from the operability index introduced by other works [72, 105, 106], where more detailed explanations and illustrations are available. It sheds light on the extent to which the potential changes in input variables (e.g., concentration, moisture content, and temperature) are within the design range. The design range is based on the equipment design and output specifications. Equipment design determines the range in the input variables that a given equipment can handle, which is referred to in the operability index as available input space (AIS) [105]. In the case of concentration, for instance, this would mean the range between the lowest and highest concentrations specified in the equipment design. The output specifications determine the range of values of input variables that lead to desired output variables, which is referred to in the operability index as desired input space (DIS) [105]. The range in potential changes in the input variables is referred to in this chapter as expected input space (EIS). All the input variables here only characterise feedstock qualities. In this context, the indicator reflects how much a design can accommodate the uncertainties in the feedstock qualities. The maximum possible value of its math expression is 1. If it is below 1, it implies that the design still has room for improvement from a technical perspective.

Product flexibility

Similar to the feedstock flexibility indicator, an indicator (No. 5) that gives an absolute value is proposed. This indicator is defined as "the ability to produce a variety of product types while using the same feedstock type in a given period of time". It provides information about the maximum number of product types that can be produced by a given feedstock type, for instance, at the plant level. Note that the value of the indicator can differ between hierarchical levels. The total number of products may be higher at the plant level than at the process line or even at the equipment level, indicating that the measure of flexibility is highly dependent on the level at which it is evaluated. As it was discussed before, the evaluation of flexibility to explore potential impacts, for instance in terms of additional costs or even additional profit.

Volume flexibility

An indicator (No. 8) that can be used to assess volume flexibility is "the ability to cope with changes in throughput rates without violating the equipment design in a given period". The throughput rate can be characterised by either the mass or volumetric flow rate. Its math expression elucidates a range of throughput rates, allowing it to meet product specifications, which are normalised to the designed throughput rate. For instance, the nominal load of a given commercial electrolysis stack that uses renewable electricity is 20 kW. However, it also produces the product as long as the load of the stack is between 5 kW and 22 kW. According to the indicator, the volume flexibility is 25% 110% at the equipment level. However, when the load is between 25% and 50%, though the product specifications are satisfied, the product yield (impact in this example) drops by 15%, calculated using the math expression of the No. 10 indicator.

Scheduling flexibility

Scheduling flexibility is only applicable when the design is physically available. The indicator (No. 12) characterises "the ability to start a production cycle without wasting much time in preparation in a given period of time". Its math expression can be used to calculate the ratio between time spent on preparation and time of the whole production cycle. The lower it is, the higher the scheduling flexibility the design has. The indicator (No. 15) provides insight into the reduction in production quantity due to time spent in preparation, compared to the scenario when fewer production cycles (can be 1 by design) are required to be executed in a given period of time. Stakeholders then need to decide the extent to which the scheduling flexibility of the design should be so that it responds faster to the supply chain planning. However, they also have to balance it with certain impacts in terms of, for instance economic performance.

Production flexibility

If production flexibility is defined as "the ability to alternate production schemes on the same process line in a given period of time", the indicator (No. 14) can cast light on it. Its math expression quickly counts the maximum production schemes that can be exercised on a given process line, which is an absolute value. The higher the value is, the more flexible the process line is. However, switching between different production schemes on the same process line usually does not sacrifice nothing at all times. The math expression of the No. 15 indicator quantifies, for example, how much utility water is used to clean the process line for the switch. Stakeholders should weigh the importance between production flexibility that might, for instance, lower the capital cost and the extra utility usage that could, for instance, increase the operating cost.

Table. 2.4. Examples of indicators for evaluating flexibility.

Type	No.		Definition	Long math expression	Description	More flexible when[a]	Object[b]	Levels[c]
Feedstock	1	Range	The ability to handle expected changes in feedstock qualities while satisfying the product specifications in a given period of time	$\frac{\mu(DIS \cap AIS \cap EIS)}{\mu(EIS)}$ (adapted from [105])	To what extent the potential changes in input variables are within the design range based on the equipment design and output specifications	↑	E,N	1,2
	2	Range	The ability to use varying feedstock types while producing the same product type in a given period of time	$\max(N_{fp})$	Maximum number of feedstock types that can be used to produce a given product type	↑	E,N	1,2,3
	3	Impact (technical)	Changes in the amount of product as a consequence of changes in feedstock types in a given period of time	$\mathrm{m}_p - m_p^{design}$[d]	The deviation in the quantity of a given product type compared to the designed value		N	2, 3
	4	Impact (technical)	Changes in the use of utilities as a consequence of changes in feedstock types in a given period of time	$\mathrm{m}_U - m_U^{design}$[e]	The deviation in utility usage compared to the designed value		N	1, 2, 3
Product	5	Range	The ability to produce a variety of product types while using the same feedstock type in a given period of time	$\max(N_{pf})$	Maximum number of product types that can be produced from a given feedstock type	↑	E,N	1, 2, 3
	6	Impact (technical)	Changes in the amount of feedstocks used as a result of changes in the product types in a given period of time	$\mathrm{m}_f - m_f^{design}$	The deviation in the total quantity of a given feedstock type compared to the designed value		N	2, 3
	7	Impact (technical)	Changes in the use of utilities as a consequence of changes in product types in a given period of time	$\mathrm{m}_U - m_U^{design}$	The deviation in utility usage compared to the designed value		E,N	1, 2, 3
Volume	8	Range	The ability to cope with changes in throughput rates without violating the equipment design in a given period of time	$\frac{\dot{m}_{in/out}^{max}}{\dot{m}_{in/out}^{design}} \sim \frac{\dot{m}_{in/out}^{min}}{\dot{m}_{in/out}^{design}}$[f] (adapted from [94])	Throughput rate range that allows to meet product specifications, normalised to the designed throughput rate	↑	E,N	1, 2, 3

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[a] The arrows indicate the desired direction of flexibility compared to an alternative (e.g., the higher the value, the more flexible the design).

[b] Object indicates whether the indicators are applicable to an existing (E) or a new (N) design.

[c] Level 1, 2, and 3 corresponds to equipment, process line, and plant level, respectively.

[d] Whenever there is a m_p in the expression, m_p should be adjusted when needed to fit in each hierarchical level.

[e] Whenever there is a m_U in the expression, m_U should be adjusted when needed to fit in each hierarchical level.

[f] Whenever there is a $\dot{m}$ in the expression, $\dot{m}$ should be adjusted when needed to fit in each hierarchical level.

Type	No.		Definition	Long math expression	Description	More flexible when	Object	Levels
Volume	9	Range	The ability to cope with expected changes in throughput rates without unwanted results in a given period of time	$\frac{\mu(DIS \cap AIS \cap EIS)}{\mu(EIS)}$ (adapted from [105])	To what extent the potential changes in input variables are within the design range based on the equipment design and output specifications	↑	E,N	1, 2, 3
	10	Impact (technical)	Changes in the product quantity as a consequence of changes in the throughput rates in a given period of time	$\frac{m_p}{m_f} - \frac{m_p^{design}}{m_f^{design}}$	The deviation in product yield compared to the designed value		N	2, 3
	11	Impact (technical)	Changes in the use of utilities as a consequence of changes in throughput rates in a given period of time	$\mathrm{m}_U - \frac{m_U^{design} \dot{m}_{in/out}}{\dot{m}_{in/out}^{design}}$	The deviation in utility usage compared to the designed value multiplied by the load ratio		N	1, 2, 3
Scheduling	12	Range	The ability to start a production cycle without wasting much time in preparation for a given period of time	$\frac{t_{preparation}}{t_{productioncycle}}$	The ratio of the time spent on preparation to the time duration of a complete production cycle	↓	E	1, 2, 3
	13	Impact (technical)	Changes in the amount of product as a consequence of changes in production cycles in a given period of time	$\mathrm{m}_p - m_p^{design}$	The deviation in the quantity of a given product type compared to the designed value		E	1, 2, 3
Prodcution	14	Range	The ability to alternate production schemes on the same process line in a given period of time	$\max_l N_{sl}$	Maximum number of production schemes on a given process line	↑	E,N	2
	15	Impact (technical)	The quantity of utilities spent for switching between production schemes in a given period of time	$\mathrm{m}_U^{switching}$	Utility usage for switching between production schemes		E	1, 2, 3

5 Conclusion

This chapter aimed to develop a conceptual framework of flexibility that can serve as a conceptual guideline for the design and assessment of novel flexible chemical processes. The chapter identified how flexibility-related topics have evolved in the past three decades, shifting from focusing on the optimisation of, mostly, well-understood high-TRL processes to the designing of novel chemical processes that employ renewable energies such as biomass, intermittent renewable electricity and others, which inherently carry additional uncertainties. We identified significant overlaps in terminology and concepts, resulting in confusion when comparing different studies dealing with flexibility. Based on the literature, we proposed a definition and identified 5 types of flexibility: feedstock flexibility, product flexibility, volume flexibility, scheduling flexibility and production flexibility. Furthermore, the chapter identified design strategies that are adopted to enable these types of flexibility, from which process designers could draw lessons when designing for similar flexibility needs.

To support the design and assessment of different flexibility types, we identified 5 elements of flexibility: target, range, hierarchical level (i.e., equipment, process line or plant), timescale and impact. Further, as standardised indicators to evaluate the specific flexibility types of processes are largely lacking, the chapter proposed a first set of indicators for evaluating specific flexibility types independent of a control structure. In further work, the indicators should be tested and further refined, and economic as well as environmental perspectives should be further incorporated. In this chapter utilities are considered part of the production scheme, however, since utilities and their related equipment also gained attention in the context of flexibility (e.g., heat exchange network), utilities should be incorporated as a separate factor into the framework.

Finally, it is important to stress that coupling the energy sector with increasing penetration of renewable energy and the chemical industry will remain a key challenge in the coming decades. The need and requirement for flexibility will gain increasing importance for both sectors and will play a key role in the way novel chemical processes are designed and implemented. The development of methodologies that support the assessment of flexibility options early on requires further work and attention from the academic and industrial communities.

References

[1] A. N. Ajah and P. M. Herder. "Addressing flexibility during process and infrastructure systems conceptual design: Real options perspective." International Conference on Systems, Man and Cybernetics, Vol 1-4, Proceedings. 2005. Pp. 3711–3716. DOI: `10.1109/ICSMC.2005.1571723`.

[2] L. R. Thomas. "Batch processing plants". The Canadian Journal of Chemical Engineering. 404. 2011. Pp. 179–182. DOI: `10.1002/cjce.5450400413`.

[3] I. E. Grossmann and K. P. Halemane. "Decomposition Strategy for Designing Flexible Chemical-Plants". AIChE Journal. 284. 1982. Pp. 686–694. DOI: `10.1002/aic.690280422`.

[4] I. E. Grossmann, K. P. Halemane, and R. E. Swaney. "Optimization Strategies for Flexible Chemical Processes". Computers & Chemical Engineering. 74. 1983. Pp. 439–462. DOI: `10.1016/0098-1354(83)80022-2`.

[5] I. E. Grossmann and R. W. H. Sargent. "Optimum Design of Multipurpose Chemical Plants". Industrial & Engineering Chemistry Process Design and Development. 182. 2002. Pp. 343–348. DOI: `10.1021/i260070a031`.

[6] I. E. Grossmann and R. W. H. Sargent. "Optimum Design of Chemical-Plants with Uncertain Parameters". AIChE Journal. 246. 1978. Pp. 1021–1028. DOI: `10.1002/aic.690240612`.

[7] R. E. Swaney and I. E. Grossmann. "An index for operational flexibility in chemical process design. Part I: Formulation and theory". AIChE Journal. 314. 2004. Pp. 621–630. DOI: `10.1002/aic.690310412`.

[8] D. A. Straub and I. E. Grossmann. "Evaluation and Optimization of Stochastic Flexibility in Multiproduct Batch Plants". Computers & Chemical Engineering. 162. 1992. Pp. 69–87. DOI: `10.1016/0098-1354(92)80007-V`.

[9] D. A. Straub and I. E. Grossmann. "Integrated Stochastic Metric of Flexibility for Systems with Discrete State and Continuous Parameter Uncertainties". Computers & Chemical Engineering. 149. 1990. Pp. 967–985. DOI: `10.1016/0098-1354(90)87053-R`.

[10] K. P. Halemane and I. E. Grossmann. "Optimal Process Design under Uncertainty". AIChE Journal. 293. 1983. Pp. 425–433. DOI: `10.1002/aic.690290312`.

[11] K. Yamashita and L. Barreto. "Energyplexes for the 21st century: Coal gasification for co-producing hydrogen, electricity and liquid fuels". Energy. 3013. 2005. Pp. 2453–2473. DOI: `10.1016/j.energy.2004.12.002`.

[12] J. C. Meerman, A. Ramirez, W. C. Turkenburg, and A. P. C. Faaij. "Performance of simulated flexible integrated gasification polygeneration facilities. Part A: A technical-energetic assessment". Renewable & Sustainable Energy Reviews. 156. 2011. Pp. 2563–2587. DOI: `10.1016/j.rser.2011.03.018`.

[13] G. Fichtner, H. J. Reinhart, and D. W. T. Rippin. "The Design of Flexible Chemical-Plants by the Application of Interval Mathematics". Computers & Chemical Engineering. 1411. 1990. Pp. 1311–1316. DOI: `10.1016/0098-1354(90)80013-2`.

[14] D. K. Varvarezos, I. E. Grossmann, and L. T. Biegler. "A Sensitivity Based Approach for Flexibility Analysis and Design of Linear Process Systems". Computers & Chemical Engineering. 1912. 1995. Pp. 1301–1316. DOI: `10.1016/0098-1354(94)00118-8`.

[15] E. Kondili, C. C. Pantelides, and R. W. H. Sargent. “A general algorithm for short-term scheduling of batch operations-I. MILP formulation”. Computers & Chemical Engineering. 172. 1993. Pp. 211–227. DOI: `10.1016/0098-1354(93)80015-f`.

[16] L. Mockus and G. V. Reklaitis. “Mathematical programming formulation for scheduling of batch operations based on nonuniform time discretization”. Computers & Chemical Engineering. 2110. 1997. Pp. 1147–1156. DOI: `10.1016/S0098-1354(96)00325-0`.

[17] Z. Verwater-Lukszo and K. J. Keesman. “Computer-aided development of flexible batch production recipes”. Production Planning & Control. 64. 2007. Pp. 320–330. DOI: `10.1080/09537289508930286`.

[18] F. G. A. de Bakker, O. A. M. Fisscher, and A. J. P. Brack. “Organizing product-oriented environmental management from a firm’s perspective”. Journal of Cleaner Production. 105. 2002. Pp. 455–464. DOI: `10.1016/s0959-6526(02)00012-4`.

[19] R. Karuppiah and I. E. Grossmann. “Global optimization for the synthesis of integrated water systems in chemical processes”. Computers & Chemical Engineering. 304. 2006. Pp. 650–673. DOI: `10.1016/j.compchemeng.2005.11.005`.

[20] J. Ayers. “Demand-Driven Supply Chain Implementation”. Chemical Engineering Progress. 10212. 2006. Pp. 21–23.

[21] K. Ferdows and C. Carabetta. “The effect of inter-factory linkage flexibility on inventories and backlogs in integrated process industries”. International Journal of Production Research. 442. 2006. Pp. 237–255. DOI: `10.1080/00207540500268947`.

[22] A. Malcolm, J. Polan, L. Zhang, B. A. Ogunnaike, and A. A. Linninger. “Integrating systems design and control using dynamic flexibility analysis”. AIChE Journal. 538. 2007. Pp. 2048–2061. DOI: `10.1002/aic.11218`.

[23] C. Capello, S. Hellweg, B. Badertscher, H. Betschart, and K. Hungerbuhler. “Part 1:: The ecosolvent tool -: Environmental assessment of waste-solvent treatment options”. Journal of Industrial Ecology. 114. 2007. Pp. 26–38. DOI: `10.1162/jiec.2007.1231`.

[24] J. D. Villegas and E. Gnansounou. “Techno-economic and environmental evaluation of lignocellulosic biochemical refineries: need for a modular platform for integrated assessment (MPIA)”. Journal of Scientific & Industrial Research. 6711. 2008. Pp. 927–940.

[25] J. Petrie and B. Alexander. “Considerations of process flexibility in design of chemical processes for satisfaction of economic and environmental objectives”. Second International Symposium on Environmentally Conscious Design and Inverse Manufacturing, Proceedings. 2001. Pp. 1012–1017. DOI: `10.1109/.2001.992511`.

[26] D. S. Dvoretskii, S. I. Dvoretskii, and G. M. Ostrovskii. “Integrated design of power- and resource-saving chemical processes and process control systems: Strategy, methods, and application”. Theoretical Foundations of Chemical Engineering. 421. 2008. Pp. 26–36. DOI: `10.1134/S0040579508010041`.

[27] A. Giuliano, M. Poletto, and D. Barletta. “Process optimization of a multi-product biorefinery: The effect of biomass seasonality”. Chemical Engineering Research & Design. 107. 2016. Pp. 236–252. DOI: `10.1016/j.cherd.2015.12.011`.

[28] N. Kou and F. Zhao. “Techno-economical analysis of a thermo-chemical biofuel plant with feedstock and product flexibility under external disturbances”. Energy. 3612. 2011. Pp. 6745–6752. DOI: `10.1016/j.energy.2011.10.031`.

[29] K. S. Ng and E. M. Hernandez. “A systematic framework for energetic, environmental and economic (3E) assessment and design of polygeneration systems”. Chemical Engineering Research & Design. 106. 2016. Pp. 1–25. DOI: `10.1016/j.cherd.2015.11.017`.

[30] S. Abate, P. Lanzafame, S. Perathoner, and G. Centi. “New Sustainable Model of Biorefineries: Biofactories and Challenges of Integrating Bio- and Solar Refineries”. ChemSusChem. 817. 2015. Pp. 2854–66. DOI: `10.1002/cssc.201500277`.

[31] S. Yang, Q. Chen, Z. Q. Liu, Y. Wang, Z. Tang, and Y. Sun. “Performance analysis of the wind energy integrated with a natural-gas-to-methanol process”. Energy Conversion and Management. 173. 2018. Pp. 735–742. DOI: `10.1016/j.enconman.2018.07.068`.

[32] M. Bui, N. E. Flo, T. de Cazenove, and N. Mac Dowell. “Demonstrating flexible operation of the Technology Centre Mongstad (TCM) CO capture plant”. International Journal of Greenhouse Gas Control. 93. 2020. P. 102879. DOI: `10.1016/j.ijggc.2019.102879`.

[33] R. L. Tousain and O. H. Bosgra. “Market-oriented scheduling and economic optimization of continuous multi-grade chemical processes”. Journal of Process Control. 163. 2006. Pp. 291–302. DOI: `10.1016/j.jprocont.2005.06.009`.

[34] B. Bruns, F. Herrmann, M. Polyakova, M. Grunewald, and J. Riese. “A systematic approach to define flexibility in chemical engineering”. Journal of Advanced Manufacturing and Processing. 24. 2020. e10063. DOI: `10.1002/amp2.10063`.

[35] M. Heitmann, G. Schembecker, and C. Bramsiepe. “Framework to decide for a volume flexible chemical plant during early phases of plant design”. Chemical Engineering Research & Design. 128. 2017. Pp. 85–94. DOI: `10.1016/j.cherd.2017.09.028`.

[36] T. Seifert, A. K. Lesniak, S. Sievers, G. Schembecker, and C. Bramsiepe. “Capacity Flexibility of Chemical Plants”. Chemical Engineering & Technology. 372. 2014. Pp. 332–342. DOI: `10.1002/ceat.201300635`.

[37] N. Kou and F. Zhao. “Operational flexibility: A key factor in the development of biofuel technologies”. Sustainable Energy Technologies and Assessments. 1. 2013. Pp. 28–33. DOI: `10.1016/j.seta.2012.12.002`.

[38] E. N. Pistikopoulos and T. A. Mazzuchi. “A Novel Flexibility Analysis Approach for Processes with Stochastic Parameters”. Computers & Chemical Engineering. 149. 1990. Pp. 991–1000. DOI: `10.1016/0098-1354(90)87055-T`.

[39] D. A. Straub and I. E. Grossmann. “Design Optimization of Stochastic Flexibility”. Computers & Chemical Engineering. 174. 1993. Pp. 339–354. DOI: `10.1016/0098-1354(93)80025-I`.

[40] V. D. Dimitriadis and E. N. Pistikopoulos. “Flexibility Analysis of Dynamic-Systems”. Industrial & Engineering Chemistry Research. 3412. 1995. Pp. 4451–4462. DOI: `10.1021/ie00039a036`.

[41] J. Riese and M. Gr‘ijnewald. “Challenges and Opportunities to Enhance Flexibility in Design and Operation of Chemical Processes”. Chemie Ingenieur Technik. 9212. 2020. Pp. 1887–1897. DOI: `10.1002/cite.202000057`.

[42] V. S. K. Adi and C. T. Chang. “A mathematical programming formulation for temporal flexibility analysis”. Computers & Chemical Engineering. 57. 2013. Pp. 151–158. DOI: `10.1016/j.compchemeng.2013.04.001`.

[43] Q. Zhang and I. E. Grossmann. “Planning and Scheduling for Industrial Demand Side Management: Advances and Challenges”. Alternative Energy Sources and Technologies. 2016. Springer. Chap. 14. Pp. 383–414. DOI: `10.1007/978-3-319-28752-2_14`.

[44] A. Huesman. “Integration of operation and design of solar fuel plants: A carbon dioxide to methanol case study”. Computers & Chemical Engineering. 140. 2020. P. 106836. DOI: `10.1016/j.compchemeng.2020.106836`.

[45] E. Svensson, T. Berntsson, and A. B. Stromberg. “The value of flexibility for pulp mills investing in energy efficiency and future biorefinery concepts”. International Journal of Energy Research. 3814. 2014. Pp. 1864–1878. DOI: `10.1002/er.3195`.

[46] K. van Kranenburg, S. Sofra, D. Verdoes, and M. de Graaff. Small-scale flexible plants - Towards a more agile and competitive EU chemical industry. TNO, 2015. URL: `http://resolver.tudelft.nl/uuid:639798ee-c8ca-4949-9acf-24ac4c5eef25`.

[47] S. Lai and C. Hui. “Measurement of plant flexibility”. Computer Aided Chemical Engineering. 24. 2007. Pp. 189–194. DOI: `10.1016/S1570-7946(07)80055-1`.

[48] K. W. Hossiso and D. Ripplinger. “The Value of Switching Production Options in a Flexible Biorefinery”. Agricultural and Resource Economics Review. 461. 2017. Pp. 146–173. DOI: `10.1017/age.2016.37`.

[49] Y. C. Kuo and C. T. Chang. “On Heuristic Computation and Application of Flexibility Indices for Unsteady Process Design”. Industrial & Engineering Chemistry Research. 553. 2016. Pp. 670–682. DOI: `10.1021/acs.iecr.5b03593`.

[50] H. Kasivisvanathan, D. K. S. Ng, G. Poplewski, and R. R. Tan. “Flexibility Optimization for a Palm Oil-Based Integrated Biorefinery with Demand Uncertainties”. Industrial & Engineering Chemistry Research. 5514. 2016. Pp. 4035–4044. DOI: `10.1021/acs.iecr.5b03702`.

[51] E. Martinez-Hernandez, J. Sadhukhan, and G. M. Campbell. “Integration of bioethanol as an in-process material in biorefineries using mass pinch analysis”. Applied Energy. 104. 2013. Pp. 517–526. DOI: `10.1016/j.apenergy.2012.11.054`.

[52] B. Mansoornejad, V. Chambost, and P. Stuart. “Integrating product portfolio design and supply chain design for the forest biorefinery”. Computers & Chemical Engineering. 349. 2010. Pp. 1497–1506. DOI: `10.1016/j.compchemeng.2010.02.004`.

[53] L. P. Dansereau, M. El-Halwagi, B. Mansoornejad, and P. Stuart. “Framework for margins-based planning: Forest biorefinery case study”. Computers & Chemical Engineering. 63. 2014. Pp. 34–50. DOI: `10.1016/j.compchemeng.2013.12.006`.

[54] T. Silva-Fernandes, S. Marques, R. C. L. B. Rodrigues, M. C. Loureiro-Dias, C. Fonseca, and F. Girio. “Enzymatic hydrolyses of pretreated eucalyptus residues, wheat straw or olive tree pruning, and their mixtures towards flexible sugar-based biorefineries”. Biomass Conversion and Biorefinery. 64. 2016. Pp. 385–396. DOI: `10.1007/s13399-016-0201-2`.

[55] L. C. Norton and I. E. Grossmann. “Strategic planning model for complete process flexibility”. Industrial & Engineering Chemistry Research. 331. 2002. Pp. 69–76. DOI: `10.1021/ie00025a010`.

[56] T. V. Thomaidis and E. N. Pistikopoulos. “Optimal-Design of Flexible and Reliable Process Systems”. Ieee Transactions on Reliability. 442. 1995. Pp. 243–250. DOI: `10.1109/24.387378`.

[57] I. E. Grossmann, B. A. Calfa, and P. Garcia-Herreros. “Evolution of concepts and models for quantifying resiliency and flexibility of chemical processes”. Computers & Chemical Engineering. 70. 2014. Pp. 22–34. DOI: `10.1016/j.compchemeng.2013.12.013`.

[58] S. Walsh and J. Perkins. “Operability and Control in Process Synthesis and Design”. Advances in Chemical Engineering. Vol. 23. Advances in Chemical Engineering. 1996. Academic Press. Pp. 301–402. DOI: `10.1016/s0065-2377(08)60205-7`.

[59] P. A. Bahri, A. Bandoni, and J. Romagnoli. “Operability assessment in chemical plants”. Computers & Chemical Engineering. 20. 1996. S787–S792. DOI: `10.1016/0098-1354(96)00139-1`.

[60] I. E. Grossmann and M. Morari. “Operability, Resiliency, and Flexibility: process design objectives for a changing world”. Carnegie Mellon University. Journal contribution. 2018. DOI: 10.1184/R1/6467234.v1.

[61] M. Morari. “Flexibility and Resiliency of Process Systems”. Computers & Chemical Engineering. 74. 1983. Pp. 423–437. DOI: 10.1016/0098-1354(83)80021-0.

[62] Q. Chen and I. E. Grossmann. “Effective Generalized Disjunctive Programming Models for Modular Process Synthesis”. Industrial & Engineering Chemistry Research. 5815. 2019. Pp. 5873–5886. DOI: 10.1021/acs.iecr.8b04600.

[63] E. N. Pistikopoulos. “Uncertainty in-Process Design and Operations”. Computers & Chemical Engineering. 19. 1995. S553–S563. DOI: 10.1016/0098-1354(95)00119-M.

[64] E. Svensson, K. Eriksson, and T. Wik. “Reasons to apply operability analysis in the design of integrated biorefineries”. Biofuels, Bioproducts and Biorefining. 92. 2015. Pp. 147–157. DOI: 10.1002/bbb.1530.

[65] P. A. Bahri, J. A. Bandoni, and J. A. Romagnoli. “Integrated flexibility and controllability analysis in design of chemical processes”. AIChE Journal. 434. 1997. Pp. 997–1015. DOI: 10.1002/aic.690430415.

[66] B. R. Holt and M. Morari. “Design of resilient processing plants-V”. Chemical Engineering Science. 407. 1985. Pp. 1229–1237. DOI: 10.1016/0009-2509(85)85081-8.

[67] E. Hollnagel, D. D. Woods, and N. Leveson. Resilience engineering: Concepts and precepts. UK: Ashgate, 2006. URL: https://books.google.nl/books?hl=en%5C&lr=%5C&id=rygf6axAH7UC%5C&oi=fnd%5C&pg=PP1%5C&dq=Resilience+engineering:+Concepts+and+precepts%5C&ots=iq4ESZ9Z8i%5C&sig=wUeU68Ikmlgp69dcT8TQaeuu4tY%5C&redir_esc=y#v=onepage%5C&q=Resilience%5C%20engineering%5C%3A%5C%20Concepts%5C%20and%5C%20precepts%5C&f=false.

[68] E. Hollnagel. Resilience engineering in practice: A guidebook. UK: Ashgate, 2013. URL: https://books.google.nl/books?hl=en%5C&lr=%5C&id=1YHXCQAAQBAJ%5C&oi=fnd%5C&pg=PR13%5C&dq=Resilience+engineering+in+practice:+A+guidebook%5C&ots=NCmVmteG7t%5C&sig=7DBfvxmqxZHO2VhfsIWrVYRItBA%5C&redir_esc=y#v=onepage%5C&q=Resilience%5C%20engineering%5C%20in%5C%20practice%5C%3A%5C%20A%5C%20guidebook%5C&f=false.

[69] C. L. Zheng, F. Zhao, L. Y. Zhu, and X. Chen. “Operational Flexibility Analysis of High-Dimensional Systems via Cylindrical Algebraic Decomposition”. Industrial & Engineering Chemistry Research. 5910. 2020. Pp. 4670–4687. DOI: 10.1021/acs.iecr.9b06061.

[70] H. Teichgraeber and A. R. Brandt. “Optimal design of an electricity-intensive industrial facility subject to electricity price uncertainty: Stochastic optimization and scenario reduction”. Chemical Engineering Research & Design. 163. 2020. Pp. 204–216. DOI: 10.1016/j.cherd.2020.08.022.

[71] C. Chen and A. D. Yang. “Power-to-methanol: The role of process flexibility in the integration of variable renewable energy into chemical production”. Energy Conversion and Management. 228. 2021. P. 113673. DOI: 10.1016/j.enconman.2020.113673.

[72] F. V. Lima, Z. Jia, M. Ierapetritou, and C. Georgakis. “Similarities and differences between the concepts of operability and flexibility: The steady-state case”. AIChE Journal. 563. 2009. Pp. 702–716. DOI: 10.1002/aic.12021.

[73] A. Arora, J. Li, M. S. Zantye, and M. M. F. Hasan. “Process Design Frameworks for Economic Utilization of Small-Scale and Unconventional Feedstocks”. Proceedings of the 9th International Conference on Foundations of Computer-Aided Process Design. Vol. 50. Computer Aided Chemical Engineering. 2019. Elsevier. Pp. 83–88. DOI: `10.1016/b978-0-12-818597-1.50014-x`.

[74] C. Dou, R. Bura, S. Ewanick, and R. Morales-Vera. “Blending short rotation coppice poplar with wheat straw as a biorefinery feedstock in the State of Washington”. Industrial Crops and Products. 132. 2019. Pp. 407–412. DOI: `10.1016/j.indcrop.2019.02.033`.

[75] J. Jiang, J. Xu, and Z. Song. “Review of the direct thermochemical conversion of lignocellulosic biomass for liquid fuels”. Frontiers of Agricultural Science and Engineering. 21. 2015. Pp. 13–27. DOI: `10.15302/J-Fase-2015050`.

[76] R. Uria-Martinez, P. N. Leiby, and M. L. Brown. “Cost of Oil and Biomass Supply Shocks under Different Biofuel Supply Chain Configurations”. Transportation Research Record: Journal of the Transportation Research Board. 267224. 2018. Pp. 31–40. DOI: `10.1177/0361198118756876`.

[77] N. Dahmen, E. Henrich, and T. Henrich. “Synthesis Gas Biorefinery”. Advances in Biochemical Engineering/Biotechnology. Vol. 166. 2019. Springer. Pp. 217–245. DOI: `10.1007/10_2016_63`.

[78] D. Yue and F. You. “Planning and Scheduling of Flexible Process Networks Under Uncertainty with Stochastic Inventory: MINLP Models and Algorithm”. AIChE Journal. 595. 2013. Pp. 1511–1532. DOI: `10.1002/aic.13924`.

[79] S. Bensaid, R. Conti, and D. Fino. “Direct liquefaction of ligno-cellulosic residues for liquid fuel production”. Fuel. 941. 2012. Pp. 324–332. DOI: `10.1016/j.fuel.2011.11.053`.

[80] D. P. Hanak, C. Biliyok, and V. Manovic. “Calcium looping with inherent energy storage for decarbonisation of coal-fired power plant”. Energy & Environmental Science. 93. 2016. Pp. 971–983. DOI: `10.1039/c5ee02950c`.

[81] E. H. Stitt. “Alternative multiphase reactors for fine chemicals - A world beyond stirred tanks?” Chemical Engineering Journal. 901-2. 2002. Pp. 47–60. DOI: `PiiS1385-8947(02)00067-0Doi10.1016/S1385-8947(02)00067-0`.

[82] M. O. S. Dias et al. “Biorefineries for the production of first and second generation ethanol and electricity from sugarcane”. Applied Energy. 109. 2013. Pp. 72–78. DOI: `10.1016/j.apenergy.2013.03.081`.

[83] T. Becker, S. Lier, and B. Werners. “Value of modular production concepts in future chemical industry production networks”. European Journal of Operational Research. 2763. 2019. Pp. 957–970. DOI: `10.1016/j.ejor.2019.01.066`.

[84] B. Mansoornejad, E. N. Pistikopoulos, and P. Stuart. “Metrics for evaluating the forest biorefinery supply chain performance”. Computers & Chemical Engineering. 54. 2013. Pp. 125–139. DOI: `10.1016/j.compchemeng.2013.03.031`.

[85] S. Furer, J. Rauch, and F. J. Sanden. “Definitions of Multiproduct Plants and Flexibility Demands”. Multiproduct Plants. 2003. Wiley-VCH. Pp. 1–6. DOI: `10.1002/3527602070.ch1`.

[86] B. Mansoornejad, E. N. Pistikopoulos, and P. Stuart. “Incorporating Flexibility Design into Supply Chain Design for Forest Biorefinery”. J-for-Journal of Science & Technology for Forest Products and Processes. 12. 2011. Pp. 54–66.

[87] E. Capon-Garcia, S. Ferrer-Nadal, M. Graells, and L. Puigjaner. “An Extended Formulation for the Flexible Short-Term Scheduling of Multiproduct Semicontinuous Plants”. Industrial & Engineering Chemistry Research. 484. 2009. Pp. 2009–2019. DOI: `10.1021/ie800539f`.

[88] S. Sievers, T. Seifert, G. Schembecker, and C. Bramsiepe. “Methodology for evaluating modular production concepts”. Chemical Engineering Science. 155. 2016. Pp. 153–166. DOI: `10.1016/j.ces.2016.08.006`.

[89] K. Al-Qahtani and A. Elkamel. “Multisite facility network integration design and coordination: An application to the refining industry”. Computers & Chemical Engineering. 3210. 2008. Pp. 2189–2202. DOI: `10.1016/j.compchemeng.2007.10.017`.

[90] B. Stefansdottir, M. Grunow, and R. Akkerman. “Classifying and modeling setups and cleanings in lot sizing and scheduling”. European Journal of Operational Research. 2613. 2017. Pp. 849–865. DOI: `10.1016/j.ejor.2017.03.023`.

[91] S. Ferrer-Nadal, L. Puigjaner, and G. Guillen-Gosalbez. “Managing risk through a flexible recipe framework”. AIChE Journal. 543. 2008. Pp. 728–740. DOI: `10.1002/aic.11404`.

[92] D. Worsdorfer, S. Lier, and N. Crasselt. “Real options-based evaluation model for transformable plant designs in the process industry”. Journal of Manufacturing Systems. 42. 2017. Pp. 29–43. DOI: `10.1016/j.jmsy.2016.11.001`.

[93] G. Wang, A. Mitsos, and W. Marquardt. “Renewable production of ammonia and nitric acid”. AIChE Journal. 666. 2020. e16947. DOI: `10.1002/aic.16947`.

[94] A. Buttler and H. Spliethoff. “Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review”. Renewable & Sustainable Energy Reviews. 82. 2018. Pp. 2440–2454. DOI: `10.1016/j.rser.2017.09.003`.

[95] L. C. Bree et al. “Techno-Economic Comparison of Flexibility Options in Chlorine Production”. Industrial & Engineering Chemistry Research. 5926. 2020. Pp. 12186–12196. DOI: `10.1021/acs.iecr.0c01775`.

[96] J. Baetens, B. Zwaenepoel, J. D. M. De Kooning, G. Van Eetvelde, and L. Vandevelde. “Thermal systems in process industry as a source for electrical flexibility”. 2017 52nd International Universities Power Engineering Conference (UPEC). IEEE. 2017. Pp. 1–6. DOI: `10.1109/upec.2017.8231869`.

[97] N. Sammons, M. Eden, W. Yuan, H. Cullinan, and B. Aksoy. “A flexible framework for optimal biorefinery product allocation”. Environmental Progress. 264. 2007. Pp. 349–354. DOI: `10.1002/ep.10227`.

[98] A. Di Pretoro, L. Montastruc, F. Manenti, and X. Joulia. “Flexibility analysis of a distillation column: Indexes comparison and economic assessment”. Computers & Chemical Engineering. 124. 2019. Pp. 93–108. DOI: `10.1016/j.compchemeng.2019.02.004`.

[99] A. Di Pretoro, L. Montastruc, F. Manenti, and X. Joulia. “Flexibility Assessment of a Distillation Train: Nominal vs Perturbated Conditions Optimal Design”. 29th European Symposium on Computer Aided Process Engineering. Computer Aided Chemical Engineering. 2019. Elsevier. Pp. 667–672. DOI: `10.1016/b978-0-12-818634-3.50112-0`.

[100] N. V. Sahinidis and I. E. Grossmann. “Multiperiod investment model for processing networks with dedicated and flexible plants”. Industrial & Engineering Chemistry Research. 306. 2002. Pp. 1165–1171. DOI: `10.1021/ie00054a015`.

[101] S. Bello, G. Feijoo, and M. T. Moreira. “Energy Footprint of Biorefinery Schemes”. Energy Footprints of the Bio-refinery, Hotel, and Building Sectors. Environmental Footprints and Eco-design of Products and Processes. 2019. Springer. Chap. 1. Pp. 1–45. DOI: `10.1007/978-981-13-2466-6_1`.

[102] O. Osman, S. Sgouridis, and A. Sleptchenko. “Scaling the production of renewable ammonia: A techno-economic optimization applied in regions with high insolation”. Journal of Cleaner Production. 271. 2020. P. 121627. DOI: `10.1016/j.jclepro.2020.121627`.

[103] E. D. Adamides, E. C. Yamalidou, and D. Bonvin. “A systemic framework for the recovery of flexible production systems”. International Journal of Production Research. 347. 1996. Pp. 1875–1893. DOI: `10.1080/00207549608905002`.

[104] R. C. Pattison and M. Baldea. “Optimal Design of Air Separation Plants with Variable Electricity Pricing”. Proceedings of the 8th International Conference on Foundations of Computer-Aided Process Design. Computer Aided Chemical Engineering. 2014. Elsevier. Pp. 393–398. DOI: `10.1016/b978-0-444-63433-7.50050-x`.

[105] D. R. Vinson and C. Georgakis. “A new measure of process output controllability”. Journal of Process Control. 102-3. 2000. Pp. 185–194. DOI: `10.1016/S0959-1524(99)00045-1`.

[106] V. Gazzaneo, J. C. Carrasco, D. R. Vinson, and F. V. Lima. “Process Operability Algorithms: Past, Present, and Future Developments”. Industrial & Engineering Chemistry Research. 596. 2019. Pp. 2457–2470. DOI: `10.1021/acs.iecr.9b05181`.

3

Impact of intermittent electricity supply on a conceptual process design for microbial conversion of CO_2 into hexanoic acid

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Chapter-specific nomenclature

Symbols	
Jin_t	Electricity stored in the BESS at time t, GJ/h
$Jout_t$	Electricity discharged from the BESS at time t, GJ/h
J_t	Electricity consumption immediately used for hexanoic acid production at time t, GJ/h
P_t	Available electricity from the wind and/or solar farm at time t, GJ/h
V	Vector of hourly available electricity over hourly nominal electricity consumption (for intermediate calculation), %
A	Heat exchange surface area, m^2
C_v	Yearly coverage percentage of shortage hours at an available electricity power v, %
E	Electricity cost, M€/y
F	Feedstock cost, M€/y
J	Electricity consumption, GJ/h
$\dot{M}$	Mass flow rate at plant level, kt/y
$\dot{m}$	Mass flow rate at equipment level, t/h
n	Plant lifetime, years
Q	Heat duty, kJ/s
r	Discount rate, %
$Temp$	Temperature of the hot stream, K
$temp$	Temperature of the cold stream, K
U	Overall transfer coefficient, kJ/(s m^2 K)
UT	Utility cost at plant level, M€/y
v	Available electricity power generated by the wind and/or solar farm (time-independent), GJ/h
v^*	Available electricity power generated by the wind and/or solar farm (time-independent; for intermediate calculation), GJ/h
WT	Waste treatment cost, M€/y
$\mathbb{Z}$	Integers
θ	Price, €/kg
Φ	Statement inside the Iverson bracket

Superscripts	
H	Hybrid renewable electricity
i	Type of equipment (for volume flexibility analysis)
k	Case number, from 0 to 6
W	Wind electricity

Subscripts	
$C6A$	Hexanoic acid
in	Inlet
LB	Lower boundary
max	Maximum value
min	Minimum value
o	Nominal condition of the reference process
O_2	Oxygen
out	Outlet
t	Time, h
T	Time, h (1-8760 h)
UB	Upper boundary
y	Year

Acronyms	
AF	Allocation factor, %
CAPEX	Capital expenditure, M€/y
LMTD	Log-mean temperature difference, K
LPC	Levelised production cost, €/kg
LRR	Load ratio range, %
O&M	Operation and maintenance cost, M€/y
OPEX	Operating expenditure, M€/y
REC	Range of effective capacity, %

Abstract

Combining intermittent renewable electricity (IRE) with carbon capture and utilisation is urgently needed in the chemical sector. In this context, microbial electrosynthesis (MES) has gained attention. It can electrochemically produce hexanoic acid, a value-added chemical, from CO_2. However, there is a lack of understanding regarding how the intermittency of renewable electricity could impact the design of a MES plant. We studied this using Aspen Plus models. A MES plant that was powered by constant grid electricity could operate from 100% down to 70% of its nominal capacity, at which point the heat exchangers and the internal geometrical design of the distillation towers became bottlenecks. The levelised production cost of hexanoic acid (LPC_{C6A}) was estimated at 4.0 €/kg. Switching to IRE supply increased LPC_{C6A} to 5.3 €/kg (for wind electricity) and 4.7 €/kg (for hybrid renewable electricity). A battery energy storage system (BESS) was deployed. The lowest LPC_{C6A} was found at a BESS installation of 29 GJ/h for wind electricity (5.1 €/kg) and at 12 GJ/h for hybrid renewable electricity (4.7 €/kg). In both situations, the volume flexibility of the MES plant was not improved. At the investigated market and operating conditions, coupling IRE to the MES plant was economically infeasible.

1 Introduction

According to the IPCC Sixth Assessment Report, it is still possible to reach the 1.5 °C climate goals [1]. This, however, requires immediate and profound changes across different sectors. As a major emitter of greenhouse gases, the chemical sector should take urgent measures to reduce its emissions. A potential option is to accelerate the transition from fossil to renewable energy and shift to technologies that use low-carbon feedstocks and energy streams [2].

By having the potential to combine intermittent renewable electricity (IRE) with carbon capture and utilisation (CCU), electrochemical CO_2 utilisation has drawn significant attention in the chemical sector. Lately, microbial electrosynthesis (MES) has come into sight for its ability to convert CO_2 into volatile carboxylic acids (VCAs), such as formic, acetic, butyric acids, and hexanoic acid [3, 4]. Formic acid requires two electrons (2 e^-) when the faradaic efficiency (FE) is 100% and an electric energy of 3.88 kWh/kg at a FE of 90%. Similarly, acetic acid needs 8 e^- and 11.89 kWh/kg. Butyric acid asks for 20 e^- and 20.28 kWh/kg. Hexanoic demands 32 e^- and 24.60 kWh/kg [4]. Among all, hexanoic acid, also known as n-caproic acid, has the highest market price (i.e., 2.5-4.2 €/kg [5, 6]. Unlike the others, hexanoic acid only has one industrial production method, which is the fractional distillation of coconut or palm kernel oil. Additionally, it is a by-product accounting for less than 1 wt% [7]. Hence, its availability is constrained by the production of these two plant oils. Subsequently, it is subjected to disruptions in both markets caused by, for example, weather [8] or export bans [9]. However, high-purity hexanoic acid (i.e., >98 wt%) has a wide range of important applications, such as animal feed additive, flavour additive, and chemical raw material [10]. The use of MES has the potential to decouple the production of hexanoic acid from biomass and vegetable oils and expand what until now has been a niche market due to limited natural resources. For instance, as a longer carboxylic acid, hexanoic acid can be upgraded to a blend in sustainable aviation fuels via ketonisation and hydrodeoxygenation [11, 12].

As with any other electrochemical technology, MES can run flexibly on a fluctuating electricity supply [13–15]. However, the MES unit is simply part of a process. To meet product requirements, downstream processing (DSP) also plays a vital role. Since MES produces hexanoic acid in a dilute environment, rigorous DSP is required to reach a high-purity product stream. Published recovery and purification technologies for separating VCAs, such as hexanoic acid, from water, are energy-intensive and or costly [16–18]. They include distillation, reactive distillation, adsorption, electrodialysis, solvent extraction, nanofiltration, reverse osmosis, membrane separation, and combinations thereof. Novel methods like capacitive deionization are also being explored in this area [19]. Woo and Kim [20] modelled the recovery and purification of VCAs, including hexanoic acid, from a dilute aqueous stream in Aspen HYSYS. Their selected recovery method was liquid-liquid extraction (LLE), using nonyl acetate and hexyl acetate as solvents, followed by distillation. Saboe et al. [21] experimentally performed the extraction of hexanoic acid from a dilute stream using solvents Cyanex 923 and trioctylamine (TOA) in membrane-based LLE and following solvent regeneration. They also simulated solvent regeneration and ambient distillation units in Aspen Plus. Benalcazar et al. [22] simulated LLE of hexanoic acid with n-decane and subsequent purification by distillation in Aspen Plus. The overall recovery yield of hexanoic acid in these three studies was above 90%, and its purity was above 99 wt%.

However, the abovementioned DSP technologies have been developed for steady and continuous operations. Integrating IRE into an electrochemical plant will introduce fluctuations in the throughput rates of the DSP. A common tool to handle fluctuations is "flexibility" [23–25]. For coping with fluctuations in electricity supply and, consequently, volume/mass flowrates, the flexibility type desired is volume flexibility [25]. It is defined as the ability, at a hierarchical level (i.e., equipment, process route, or plant), to operate over a range of throughput rates on a given timescale basis (e.g., per second, per month) to cope with a target (e.g., variations in feedstock quantity) without unacceptable impacts (e.g., profitability). The incorporation of volume flexibility in the process design should lead to the operating window that guarantees the proper function of an electrochemical plant powered by IRE.

Nonetheless, the literature provides limited insights into the implications of incorporating intermittency and subsequent volume flexibility in the design of chemical processes, especially for technologies that are currently at a low technology readiness level (TRL), such as the MES technologies that are at a TRL of 2-3. Depending on the types of microorganisms, MES technologies can take in different feedstock and synthesise various products. The technical and/or economic performances of some MES technologies at the plant level have been evaluated by ex-ante assessments, though under constant power supply [6, 26–30]. For instance, Christodoulou et al. [31] estimated the production cost of direct conversion of CO_2 into formic, acetic, and propionic acids, methanol, and ethanol, respectively. Only formic acid and ethanol were reported to have a lower production cost than their market value when simply the assumed cheaper price but not the real intermittency of renewable electricity was considered. Shemfe et al. [29] assessed the production cost of the formic acid converted from CO_2, between 5-15 €/kg, which is lower than the market price. Nonetheless, the DSP was not included in their process system. Wood et al. [30] evaluated a range of products synthesised straight from CO_2 directly captured from air. The production costs are significantly higher than their market value. Jourdin et al. [6] examined the hexanoic acid production directly from CO_2 and short-chain carboxylic acids (SCCAs), respectively. Both the capital and operating costs of generating hexanoic acid from CO_2 are much lower than from SCCAs. However, the net present value is negative even without considering the cost of DSP. Promoting the electron selectivity towards hexanoic acid to 100% would make the process that encompasses the DSP profitable.

Up to date, the impact of IRE on the MES operation that produces carboxylic acids has only been investigated at a lab scale, e.g., [3, 32, 33], whereas the impact of IRE in the design of a MES plant that produces carboxylic acids is unknown. Beyond MES, some Power-to-Chemicals studies have considered design strategies for enhancing volume flexibility at different stages of TRL, e.g., [34–39]. For instance, Bree et al. [34] considered five strategies to enhance the volume flexibility of a conventional chlor-alkali process against the variable electricity supply: (i) oversizing the equipment;

(ii) adopting a more flexible conversion technology; (iii) installing storage tanks; (iv) incorporating a water electrolyser or fuel cell; (v) implementing a battery energy storage system (BESS). They concluded that, in their case, a more flexible technology economically performed better than a less flexible technology assisted by a BESS. In another example, Huesman [36] adopted a BESS to improve the flexibility of a methanol plant using CO_2 from direct air capture and H_2 from water electrolysis coupled with solar power, but the resulting penalty in the manufacturing cost was high. The intuitive approach to improving flexibility with a BESS seemed again hardly helpful, particularly regarding economics. Nonetheless, it is uncertain if this ineffectiveness of installing a BESS also applies to other electrochemical production systems.

Given the importance of an alternative production route of hexanoic acid and the flexible operation of electrochemical processes coupled with IRE, this chapter aims to contribute to the methodological approach for designing and assessing flexible processes at a low TRL, using microbial electrosynthesis of hexanoic acid as the only conversion technology. This chapter conducts an ex-ante assessment to evaluate the potential techno-economic performances of this specific MES technology, assuming it is available today. A plant centred on this specific MES technology and powered by IRE supply is designed. The DSP of the MES plant will rely on membrane-based LLE with TOA, vacuum distillation, and ambient distillation. In addition, as a strategy for enhancing the volume flexibility of the MES plant, a BESS will be deployed in the plant.

2 Methodology

2.1 Process system

2.1.1. Design consideration

The nominal production capacity of hexanoic acid was fixed at ca. 10 kt/y. The MES plant was designed to obtain an overall recovery yield of 99.8% of hexanoic acid at 99 wt% purity in liquid form. The remaining 1 wt% of the composition consists of water, acetic acid, butyric acid, and the extraction solvent. Due to the reaction stoichiometry, pure oxygen was produced as a by-product at ca. 22 kt/y [6]. The plant was assumed to be located in the Port of Rotterdam, the Netherlands. With construction starting in 2018 and operation in 2019, the lifetime of the plant was assumed to be 30 years [6]. Equipment with a shorter lifetime was assumed to be replaced after 15 years of operation. Furthermore, it was assumed that feedstock, except for electricity, was supplied as needed and that the product was delivered to the market without further packing or conditioning.

2.1.2. Process description

The MES unit was designed on the basis of experimental data used in [6]. The DSP was designed based on experimental and exhaustive Aspen Plus simulation results of a similar system in [21]. Fig. 3.1 is a simplified block flow diagram of the plant. Purge streams, heat exchangers, and centrifuges have been omitted from the figure for simplicity.

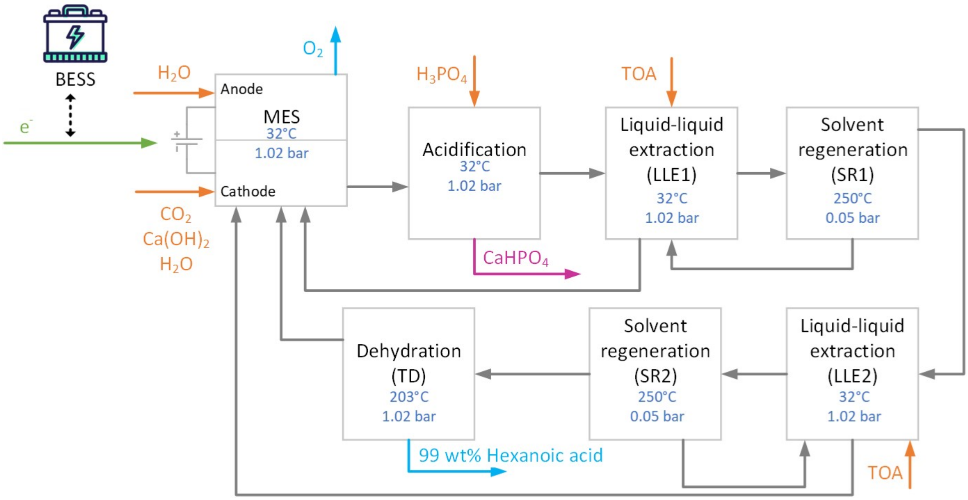

Fig. 3.1. Simplified block flow diagram of the MES plant. MES: microbial electrosynthesis; LLE: liquid-liquid extraction; SR: solvent regeneration; TD: dehydration column; TOA: trioctylamine.

MES is driven by electricity. A BESS is installed prior to it to buffer fluctuations in the electricity supply. Demineralised H_2O feeds the anode compartment of the MES, while demineralised H_2O, pure CO_2, and $Ca(OH)_2$ enter its cathode compartment. In the anode chamber, H_2O is split into O_2 and H^+. O_2 is vented from the headspace of the anode chamber. All H^+ passes through the membrane to the cathode compartment. The outlet stream of the cathode compartment contains aqueous acetate, butyrate, hexanoate, and their corresponding acids. The purity of the carboxylates and carboxylic acids is in total 1 wt% [6]. This outlet stream is acidified using aqueous H_3PO_4 to precipitate Ca^{2+} as $CaHPO_4$, which is removed using a centrifuge. The liquid stream from the acidification unit is sent to a membrane-based LLE (LLE1) that uses trioctylamine (TOA) as extracting solvent [21]. The extract stream is pre-heated before entering a vacuum solvent regeneration column (SR1). TOA from the bottom of SR1 is recycled to the LLE1. The overhead stream of SR1 contains carboxylic acids and water in a higher mass purity than in the outlet stream of the acidification unit. However, after a single extraction unit, this ratio is still below the azeotropic composition. Therefore, the overhead stream from SR1 is fed to a second membrane-based LLE with TOA as solvent (LLE2). The extract stream from LLE2 is pre-heated, centrifuged to remove salt precipitate, and sent to a second solvent regeneration column (SR2). The bottom stream from SR2 contains TOA and is recycled to LLE2. The overhead stream of SR2 is sent to a dehydration column (TD). Short-chain carboxylic acids (i.e., acetic and butyric acids) and water are separated from the hexanoic acid as distillate, and this distillate is recycled to the MES. The bottom stream of the dehydration column is the hexanoic acid stream, which is centrifuged to remove the remaining salt precipitate and cooled to room temperature. The final product stream is liquid hexanoic acid at 99 wt% purity. The two raffinate streams (from LLE1 and LLE2) and the distillate stream from the dehydration unit are cooled and recycled to the cathode compartment of MES, to enhance the overall yield of hexanoic acid on CO_2. A more detailed process description is presented in Appendix B, and the process flowsheet can be found in Appendix C.

2.1.3. Modelling approach and key assumptions

A non-random two-liquid thermodynamic model was chosen as the global property method with the Hayden-O'Connell equation of state for vapour phase properties, namely NRTL-HOC, in Aspen Plus v12 (referred to as Aspen hereafter). This thermodynamic property package can deal with dilute electrolyte streams and carboxylic acids.

MES has not been made a built-in model in Aspen. A dynamic computation model of MES could be incorporated into the simulation to enhance the accuracy [40]. However, the kinetic data of the MES-producing hexanoic acid is not available yet. Hence, it was modelled as a black box using an RYield model in Aspen, controlled by Fortran codes in a calculator block. It represents the MES by its mass balance, energy balance, and process parameters. All information, such as operating conditions, electron selectivity, productivity, and purity of the MES, is based on [6] and their previous experimental work cited therein. Details are compiled in Appendix B. The three heat-based distillation columns (i.e., SR1, SR2, and TD) were modelled using built-in RadFrac models with condenser and reboiler. The vacuum needed for the two vacuum solvent regeneration units (i.e., SR1 and SR2) was generated by ejectors which were driven by medium-pressure steam; these were modelled by expanders in Aspen, in the absence of ejectors. Their energy consumption and sizes were estimated based on the operating conditions from [21] and are summarised in Appendix B. The two LLE units should be two membrane contactors [21]. They were modelled as two extraction towers. Salt was assumed to be completely removed by a filter before the main stream entered LLE1. The local property method selected for both LLE units was the universal quasichemical functional-group activity coefficients with the Hayden-O'Connell equation of state for vapour phase properties (UNIFAC-HOC). Further modelling assumptions and details about the process are provided in Appendix B.

Heat was consumed or generated as utilities, such as low-pressure steam. The same type of utilities consumed and generated were subtracted. Note that heating was always a one-time process while cooling was staged. Furthermore, electricity was integrated.

The BESS and IRE profiles were not directly modelled in Aspen. Section 2.5 explains their integration with the process model.

Given the TRL of MES and membrane-based LLE, it is challenging to validate the simulation results of the whole process configuration without experiments or pilots. However, we carried out a sanity check at the unit level with the help of analogous literature, technology developers, and industrial experts. See more details in Appendix B.

2.2 Electricity supply profiles

Three electricity supply profiles were considered. One supplied constant grid electricity at the nominal electricity consumption rate of the MES plant ("J_o"; GJ/h). The other two were IRE profiles: 1) wind electricity from an onshore wind park, and 2) hybrid renewable electricity supply consisting of the same wind park together with an additional solar farm. The IRE profiles were generated on the basis of Rotterdam's wind speed and solar radiation data with an hourly interval over 2019 (8760 hours). The raw data was initially retrieved as hourly capacity factors from [41]. They were then converted into energy per hour by multiplying with the peak capacities of the selected wind park (Windpark Slufterdam, the Netherlands; 50.4 MWp) [42], and the solar farm (Shell Moerdijk, the Netherlands; 27 MWp) [43]. A direct line was assumed between the MES plant and the solar and wind farms. Furthermore, the solar and wind farms were built primarily to support the MES plant. With these assumptions, the renewable origin is guaranteed and the additionality condition is met following the latest regulations of the EU [44]. Also, it was assumed that the renewable electricity farm did not supply electricity to the MES plant as per demand. Instead, the intention was to explore how much available electricity from the renewable electricity farm the MES plant could consume. The electricity the plant could not consume was simply not used by the plant. The IRE profiles were represented by two datasets of 8760 data points each, "P_t^W" (GJ/h) for the wind power supply data and "P_t^H" (GJ/h) for the hybrid power supply data. The values were treated such that "P_t^W/J_o" and "P_t^H/J_o" have a precision of 1%. Details can be found in Appendix C.

The price of the constant grid electricity was assumed as the average electricity wholesale price for industrial use in the Netherlands in 2019, i.e., 25.56 €/GJ [45]. For the hypothetical future pricing scheme of renewable electricity, two three-tier load-following pricing schemes were assumed for the two IRE profiles, mimicking a power purchase agreement. The pricing scheme of the wind electricity profile is illustrated in Fig. 3.2. It was determined based on both load and time. Peak hours were assumed to be 30% of the time in a year when the capacity factor was the lowest. Off-peak hours were assumed to be 30% of the time in a year when the capacity factor was the highest. Mid-peak hours were assumed to be 40% of the time in a year when the capacity factor was in the middle. The off-peak, mid-peak, and peak prices were assumed to be 85%, 100% and 115% of that of the constant grid electricity, respectively [46]. The same rationale was applied to the hybrid renewable electricity profile. Furthermore, it was assumed that the electricity profiles and their pricing schemes were the same throughout the 30 years of the plant's lifetime. Details pertaining to the pricing are presented in Appendix C.

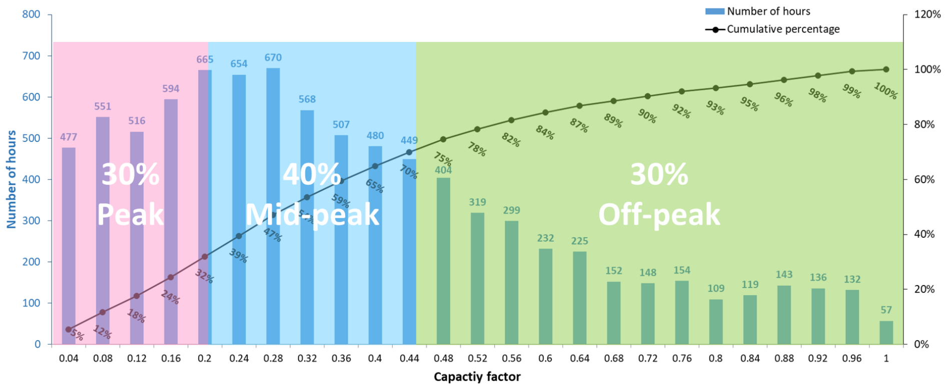

Fig. 3.2. Three-tier load-following pricing scheme used for wind electricity.

2.3 Operating schemes

Operating scheme 1 followed four rules specified for the hourly operation of the plant together with the BESS:

1) when the total electricity available from the IRE and the BESS does not reach the minimum tolerable throughput rate of the plant (how it was obtained is explained in section 2.5.1), shut down the production;
2) otherwise, ensure the minimum tolerable throughput rate of the plant, if needed, with the backup electricity from the BESS;
3) if the BESS is not fully charged and not used for production, charge it;
4) if the BESS is fully charged, increase the production of the plant using IRE directly.

Operating scheme 2 proposed that:

1) when the total electricity available from the IRE and the BESS does not reach the minimum tolerable throughput rate of the plant, shut down the production;
2) otherwise, boost the production as much as possible, by using the backup electricity from BESS in addition to IRE;
3) if the BESS was not fully charged, only charge it during off-peak hours when the two prior rules were satisfied.

A critical assumption was that the ramping time was negligible. Details about the two operating schemes are schematically illustrated in Appendix B.

2.4 Cases

In total, seven cases were examined, as summarised in Table 3.1. In each case, the BESS implementation, electricity supply profile, and the operating scheme of the plant were specified if applicable.

Table. 3.1. Summary of cases the plant level considered in this chapter. BESS: battery energy storage system.

Case	Electricity supply profile	BESS implementation	Operating scheme
0	Grid	No	-
1	Wind	No	-
2	Hybrid	No	-
3	Wind	Yes	1
4	Hybrid	Yes	1
5	Wind	Yes	2
6	Hybrid	Yes	2

2.5 Volume flexibility estimation

To integrate the Aspen process model with the BESS, the electricity profiles, and the two operating schemes, Python scripts were created. They were used to extract mass and energy balances of the process model from Aspen at varying throughput rates and to assess techno-economic performances.

To design for or assess any type of flexibility, five elements have to be specified for the context, namely hierarchical level, target, range, time scale, and impacts [25]. As has been stated in section 1, this chapter focuses on the volume flexibility of the MES plant. However, to evaluate the volume flexibility at the plant level in Cases 1 to 6, we first need to understand the volume flexibility at the equipment level independent of any case. Hence, the five elements are specified for the volume flexibility at both the equipment and plant levels (see Table 3.2).

Table. 3.2. Definitions of volume flexibility used in this chapter, based on [25]. REC: range of effective capacities. LRR: load ratio range.

Element	Specification	
Hierarchy level	Equipment	Plant
Target (unit)	Fluctuating throughput rates (kg/h)	Fluctuating electricity supply (GJ/h)
Range (unit)	REC (%)	LRR (%)
Time scale	Hourly	Hourly
Impacts/conditions	1. Meeting the product requirements	1. Fully consuming electricity available from wind and/or solar farm
	2. Not damaging the equipment	2. Meeting the product requirements
		3. Not damaging the equipment

At the equipment level, volume flexibility is defined as the ability of the equipment to operate within a range of flow rates while meeting the product and design requirements. It was characterised by the range of effective capacities (REC), which is elaborated on in section 2.5.1.

At the plant level, volume flexibility is represented by the range of electricity available from the renewable electricity farm that the plant could fully consume while meeting product requirements without damaging the equipment. It was characterised by the load ratio range (LRR). LRR is impacted by REC. Moreover, LRR is also associated with other factors such as electricity supply profiles and operating schemes of the plant. LRR is further detailed in section 2.5.2.

Additionally, the precision of both REC and LRR was set as 1% in this chapter.

2.5.1. Equipment level

REC^i, as calculated by Equation 3.1, represents the minimum "$\dot{m}^i_{min}$" and maximum "$\dot{m}^i_{max}$" tolerable throughput rates a piece of equipment "i" could handle. Values are normalised to the nominal value "$\dot{m}^i_o$" [25]. The larger the range, the higher the flexibility of the equipment, i.e., the larger the range of throughput rates at which each piece of equipment operates safely while satisfying the designed recovery yield and purity of hexanoic acid. The limits were detected by failures to meet product requirements, temperature requirements for heat exchangers, or experiencing unstable hydraulics of tower trays. In this chapter, the assessment of volume flexibility at the equipment level focused on three heat-based distillation columns (i.e., SR1, SR2 and TD) because their operating conditions, such as temperature and pressure are more complex and stringent. The rest of the equipment was assumed to be fully flexible without loss in performance or penalty in energy consumption.

$$REC^i = [\frac{\dot{m}^i_{min}}{\dot{m}^i_o}, \frac{\dot{m}^i_{max}}{\dot{m}^i_o}] \tag{3.1}$$

To determine REC^i, the throughput rates should be varied while the dimensions of the columns were fixed at the nominal conditions in the Aspen model. Nonetheless, in Aspen, equipment is, by default, automatically resized when the throughput rate varies. In a built-in RadFrac model with an integrated condenser and reboiler, the dimension of a column can be manually fixed by specifying the tray diameter, tray spacing, etc. However, the dimensions of the integrated condenser and reboiler cannot be fixed and hence change with variations in throughput rates. To address this issue, the distillation columns were modified using a single-tower RadFrac model (without integrated condenser or reboiler) with a separate condenser and reboiler (heat exchangers, namely HeatX) as well as two splitters to recirculate the streams to the columns. This new combination is called the "decomposed model" in this chapter. The areas "A" of the condensers and reboilers of SR1, SR2 and TD could thus be fixed in the HeatX model at their nominal capacities according to Equations 3.2 and 3.3 [47]. Heat duty "Q" and log-mean temperature difference "$LMTD$" were obtained at the nominal conditions. The overall heat transfer coefficient "U" was estimated following heuristics, based on the temperatures and liquid properties [48]. The details are summarised in Appendix B.

$$Q = U * A * LMTD \tag{3.2}$$

$$LMTD = \frac{(Temp_{in} - temp_{out}) - (Temp_{out} - temp_{in})}{ln\frac{Temp_{in} - temp_{out}}{Temp_{out} - temp_{in}}} \tag{3.3}$$

After the decomposed models were constructed, the flowrates were varied. At different rates, split ratios between the reflux and distillate streams, as well as between the boilup and bottom streams, were adjusted to keep the purity and recovery yield of hexanoic acid in the outlet streams at the nominal conditions (deviation < 0.01%). The utility usage was controlled by Design Specs. Here, it was assumed that for each piece of equipment driven by electricity, its input flow rate was always proportional to its electricity consumption rate. Therefore, the minimum and maximum electricity consumption of the plant without any BESS (i.e., "J_{min}" and "J_{max}") could also be obtained, calculated as in Equations 3.4 and 3.5. They will be used in the evaluation of Cases 3 to 6.

$$J_{min} = \max_i \frac{\dot{m}^i_{min}}{\dot{m}^i_o} * J_o \tag{3.4}$$

$$J_{max} = \max_i \frac{\dot{m}^i_{max}}{\dot{m}^i_o} * J_o \tag{3.5}$$

To assist volume flexibility at the equipment level, the energy consumption (GJ/h) of the three columns was evaluated.

2.5.2. Plant level

Case 0

Since Case 0 was powered by constant grid electricity, it did not need a BESS to buffer the fluctuations in the electricity supply. Moreover, it essentially corresponds to the nominal conditions of the MES plant. Hence, volume flexibility is not applicable to Case 0.

Cases 1 and 2

In Cases 1 and 2, no BESS was deployed. As mentioned, for each equipment driven by electricity, its flow rate was assumed to be always linear to its electricity consumption rate. Therefore, in Cases 1 and 2, the volume flexibility of the plant could be the frontier depicted by the most limiting RECs (see Equation 3.6).

$$LRR^k = REC^{SR1} \cap REC^{SR2} \cap REC^{TD} \tag{3.6}$$

Cases 3 to 6

In Cases 3 to 6, since a BESS was installed in the plant, the plant as a whole could consume extra electricity in addition to its nominal electricity consumption, or consume electricity when the production was off. Hence, the operating profile of the plant changed, and the "LRR^k" was quantified differently from using Equation 3.6. Its boundaries were determined using Equation 3.7, which was linked to the plant's operating profile and, thus, the IRE profile. The operating profile consisted of the electricity stored in the BESS "Jin_t^k", the electricity discharged from the BESS "$Jout_t^k$", and the electricity directly used for production "J_t^k" (see the illustration in Fig. 3.3). For the IRE profile, we use "P_t^H" for explanation here, while the same rationale applies to "P_t^W" as well.

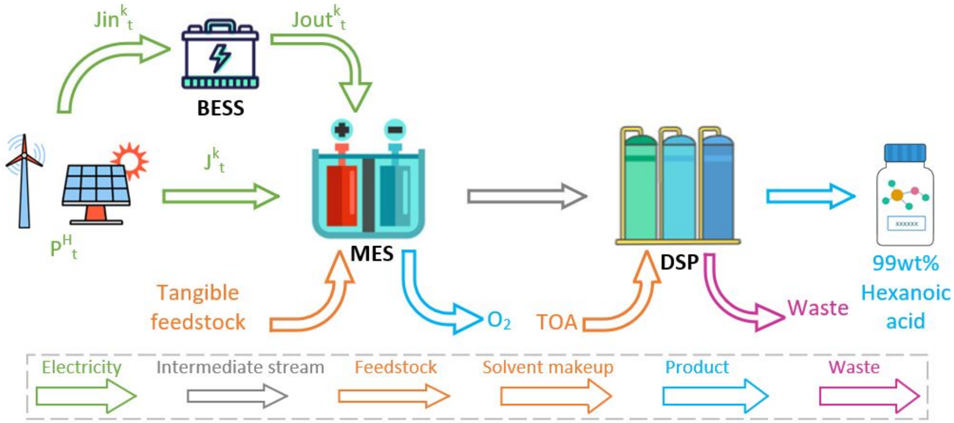

Fig. 3.3. Illustration of the operating profiles in Cases 3 to 6.

The lower boundary of "LRR^k" is defined as $\min V_{LB}^k$. It is the minimum "v/J_o" among the vector "V_{LB}^k". "v" is an available electricity power generated by the hybrid renewable electricity farm, which is time-independent. "J_o" is the hourly nominal electricity consumption of the MES plant. "V_{LB}^k" is composed of continuous "v/J_o" ratios (with a precision of 1%) that the "v" is equal to or smaller than the minimum electricity consumption of the MES plant without any BESS "J_{min}" while the "C_v^k" equals to 100%. "C_v^k" represents the percentage of hours in a year the plant can fully consume the available electricity from the hybrid renewable electricity farm "$Jin_t^k + J_t^k = v = P_t^H$" as well as produce hexanoic acid "$J_t^k + Jout_t^k \geq J_{min}$" over the hours when the "P_t^H" equals to a specific "v". To count the hours when this happens, the Iverson bracket "$[\![\Phi]\!]$" is used. If the statement Φ inside the bracket is true, the value is 1; otherwise, it is 0. "C_v^k=100%" means that the plant can fully consume the available electricity from the hybrid renewable electricity farm and produce hexanoic acid whichever hour this electricity power "v" is generated by the hybrid renewable electricity farm "P_t^H" in a year.

The upper boundary of "LRR^k" is defined as $\min V_{UB}^k$. It is the maximum "v/J_o" among the vector "V_{UB}^k". "V_{UB}^k" consists of a continuous range of "v/J_o" ratios (with a precision of 1%) that the "v" is equal to or larger than the maximum electricity consumption of the MES plant without any BESS "J_{max}" while the "C_v^k" equals to 100%. Note that applying Equation 3.7 to Cases 1 and 2 would get the same results as with Equation 3.6.

$$LRR^k = [\min V_{LB}^k, \max V_{UB}^k] \tag{3.7}$$

s.t.

$$T = [1, 8760] \cap \mathbb{Z}$$

$$C_v^k = \frac{\sum_{t \in T} [\![Jin_t^k + J_t^k = v = P_t^H, J_t^k + Jout_t^k \geq J_{min}]\!]}{\sum_{t \in T} [\![P_t^H = v]\!]} \quad \forall v \in P_T^H$$

$$V_{LB}^k = \{ \frac{v}{J_o} | v \leq J_{min}, C^k_{\forall v^* \in [v, J_{min}]} = 100\% \}$$

$$V_{UB}^k = \{ \frac{v}{J_o} | v \geq J_{max}, C^k_{\forall v^* \in [J_{max}, v]} = 100\% \}$$

To assist volume flexibility at the plant level, the shutdown time (h/y) and production quantity of hexanoic acid (kt/y) were also assessed. Shutdown time counts when "J_t^k+$Jout_t^k$=0".

2.6 Economic assessment

Capital expenditure (CAPEX), operating expense (OPEX), and levelised production cost of hexanoic acid ($\mathrm{LPC_{C6A}}$) were used to assess the economic performance of the plant's inside battery limits (i.e., process facility). The CAPEX was calculated as the sum of direct capital costs (i.e., purchase equipment cost), indirect capital costs (e.g., construction, supervision), and working capital costs. The purchase costs of equipment were either obtained from the Aspen Process Economic Analyzer v12, retrieved from vendors (e.g., ejectors), or estimated based on literature (e.g., MES). The direct costs and indirect costs were estimated using factors (e.g., a percentage of purchased equipment cost) available in references [47, 49, 50]. A CAPEX flow might differ due to the replacement of BESS and LLE units at the end of year 15 as well as the salvage value of the whole plant at the end of its life, while the OPEX remains the same every year (assuming constant price of raw materials and utilities).

The OPEX includes costs for feedstock "F", electricity "E", utilities "UT", operation and maintenance "$O\&M$", and waste treatment "WT". Feedstock costs were calculated using the mass balance and feedstock's prices. Electricity and utility costs were calculated based on the energy balance of the plant and local energy prices. All the prices and assumptions to quantify CAPEX and OPEX can be found in Appendix B.

The $\mathrm{LPC_{C6A}}$ in all seven cases was calculated using Equation 3.8. An economic allocation was applied between hexanoic acid and oxygen following Equation 3.9. Thirty years of the plant's lifetime at a discount rate "r" of 8% were assumed [6]. The salvage value of the plant was assumed to be 3.3% of the initial CAPEX [6, 51].

$$LPC_{C6A}^k = AF_{C6A} \frac{\sum_{y=1}^{n} (CAPEX_y^k + O\&M^k + F^k + UT^k + WT^k + E^k)}{\sum_{y=1}^{n} \dot{M}_{C6A}^k} \tag{3.8}$$

$$AF_{C6A} = \frac{\dot{M}_{C6A}^0 \theta_{C6A}}{\dot{M}_{C6A}^0 \theta_{C6A} + \dot{M}_{O_2}^0 \theta_{O_2}} \tag{3.9}$$

3 Results and discussion

3.1 Process modelling at the nominal conditions

Table 3.3 summarises the techno-economic results of the MES plant without a BESS at the nominal conditions, i.e., results of Case 0. The production of hexanoic acid requires much more electric energy than energy from the hot utilities. This is not surprising given the electricity consumption of the electrolyser, which is at the core of the concept. Among the hot utilities, low-pressure steam yielded a negative value, indicating that there was more generation of this utility than consumption. The net amount of this utility was partially used for the low-low-pressure steam demand and partially used outside the plant without profit. The annual consumption of CO_2 was 23 kt/y. Therefore, the electricity required to convert a tonne of CO_2 into hexanoic acid was 24.7 GJ/t (= 6.9 MWh/t). Detailed utilities and electricity consumption and a complete stream table can be found in Appendix C.

Among all the items contributing to the OPEX, the annual electricity cost was the highest, accounting for 36%, followed by operations and maintenance costs (22%) and feedstock (20%). The levelised production cost of hexanoic acid, $\mathrm{LPC}^0_{\mathrm{C6A}}$ was estimated at 4.0 €/kg, which was 33% higher than the assumed market price (i.e., 3 €/kg for 2019), but still fell within the range of current market prices of hexanoic acid (i.e., 2.5-4.2 €/kg) [5].

Table. 3.3. Techno-economic results in Case 0 (prices in 2019).

Technical indicators	**Value**[1]
Utilities	
Low-low-pressure steam - TJ/y	3.7
Low-pressure steam - TJ/y	-20.1
Hot oil - TJ/y	217.4
Medium-pressure steam - TJ/y	11.2
Chilled water - TJ/y	61.7
Cooling water - TJ/y (kt/y)	144 (2302)
Electricity consumption - TJ/y (=GWh/y)	**600 (=167)**
Economic indicators	**Value**
CAPEX - M€	**93**
Fixed capital investment - M€	79
Working capital - M€	14
OPEX - M€/y	**34**
Operations and maintenance - M€/y	9.5
Feedstock - M€/y	6.7
Electricity - M€/y	15.4
Utilities (incl. cooling water) - M€/y	0.9
Waste treatment - M€/y	1.6
Levelised production cost of hexanoic acid, $\mathrm{LPC}^0_{\mathrm{C6A}}$ - €/kg	**4.0**

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[1] A negative value indicates that there is more production of this utility than consumption.

3.2 Volume flexibility

3.2.1. Equipment level

Table 3.4 summarises the REC of the three process columns and pinpoints the bottlenecks for reference. The bottlenecks were the pieces of equipment that limit the minimum and maximum values of throughput rate for each distillation column; these were the condenser and the tower (the tray's hydraulic performance was affected).

Table. 3.4. Summary of volume flexibility limits at equipment level and its bottlenecks. REC: range of effective capacity. SR: solvent regeneration. TD: dehydration column.

Equipment	REC	Lower boundary bottleneck	Higher boundary bottleneck
SR1	[56%, 100%]	Condenser oversized	Condenser undersized
SR2	[65%, 100%]	Tray's hydraulic performance	Condenser undersized
TD	[70%, 100%]	Tray's hydraulic performance	Condenser undersized

The dimensions of condensers were fixed at the nominal conditions. During the test to estimate volume flexibility at a lower throughput rate, the reflux and boilup ratios were adjusted to maintain the same temperature profile inside the tower as under nominal conditions (to obtain the targeted product streams). The resulting throughput rate of the condenser declined, and the value of Q decreased. Since the U, A, and the conditions of utilities were fixed (e.g., inlet and outlet temperature, steam ratio), $LMTD$ was forced to be reduced gradually. It would eventually reach the minimum temperature difference and thus the minimum heat duty limited by the initial design. Moreover, according to Equation 3.3, the decrease of $LMTD$ marks a reduction in the Tempout of the condenser, which might affect the operating conditions of the next unit. Therefore, to allow a lower throughput rate, an extra heater should be installed to amend the deviation of Tempout in avoidance of possible failure of subsequent unit operations. At a larger throughput rate, the distillate stream cannot be fully condensed. In a future design, overdesigning the condensers is an option to perform for larger ranges of throughput rates. More explicitly, the overdesign factor allowed for a heat exchanger in the industry is normally within 20% to avoid fouling [52, 53]. Another option is to increase the initial temperature difference between the target cooling or heating stream and the utility used.

The performance of the tray's hydraulics also appeared as a bottleneck. It was reported as having a low loading rate in Aspen. The loading rate in the tower is calculated as the rate of liquid that is split from the condensed overhead stream, and that is sent back to the tower, which is associated with the reflux ratio. The internal geometry of the tower imposes a minimum threshold loading rate for the trays. When the inlet flow rate keeps declining, it eventually results in a low loading rate. The liquid was held up on the upper stages by the gas, leading to undesired operating conditions.

Operating the distillation columns at lower throughput rates than the nominal rate results in an increase in energy consumption per tonne of hexanoic acid produced. The highest increase occurs in the final dehydration column TD. At the point when its throughput rate reaches the lowest possible value of 70% of its nominal rate, its energy consumption per tonne of hexanoic acid produced increased maximally: 8% compared to its nominal conditions. This finding coheres to the reality in industry, which usually reports higher variations. However, in this chapter, compared to the total energy consumption, the variation can be considered negligible. Refer to Appendix B for further details.

3.2.2. Plant level

Cases 1 and 2

The volume flexibility results of Cases 1 and 2 are presented in Table 3.5. No BESS was implemented in these two cases, so the plant had to be shut down for 44% and 31% of the nominal operating time per year (i.e., 8760 h/y), respectively. The resulting production quantity of hexanoic acid was 47% and 34% lower than the nominal production target. Case 2 performed better because it was coupled with the hybrid electricity profile, which supplies more electricity throughout the year. In terms of volume flexibility, in both cases, the plant could fully consume available electricity and operate safely while satisfying the product purity and recovery yield when the available electricity was 70% and 100% of the plant's nominal electricity consumption. Below 70%, the plant always had to be shut down.

Table. 3.5. Results of Cases 1 and 2.

	Case 1	Case 2
Shutdown time (h/y)	3837	2678
Production quantity (kt/y)	5.4	6.7
LRR^k	[70%, 100%]	[70%, 100%]

Cases 3 to 6

A BESS was installed in the MES plant in Cases 3 to 6. To reflect the impact of operating schemes, Cases 3 and 5 or 4 and 6 are compared in Fig. 3.4. As the deployed capacity of BESS increased, the shutdown time was reduced, and the production quantity increased more rapidly under operating scheme 1. Moreover, under scheme 1, the results indicate that to completely avoid shutting down the plant by covering all the long periods of electricity shortage, a minimum BESS capacity of 12.5 TJ/h (=3.5 GW) would be required in Case 3 and of 1.7 TJ/h (=0.47 GW) in Case 4 (note these numbers are not plotted in the figure). The corresponding values would be higher under scheme 2.

As for the impact of a BESS on volume flexibility, the lower boundary of LRR^k could only be slightly expanded as the BESS capacity increased under scheme 1. Therefore, the improvement in volume flexibility was insignificant. This result implies that in this context, selected BESS capacities and operating schemes could not expand the range of available electricity that can be fully consumed by the plant while safely producing hexanoic acid that satisfied the product purity and recovery requirements. On the other hand, to provide more details regarding how shortage hours were partially covered with the help of a BESS, an example is provided to demonstrate the conditions of coverage percentage of shortage hours "C_v^k" versus electricity power generated by the renewable electricity farm over nominal electricity consumption of the reference process "v/J_o". For instance, in Case 4 (see Fig. 3.5), at a BESS capacity of 20 GJ/h (=5.6 MW), the MES plant could partially cover shortage hours "100%>C_v^4>0" when the available electricity power was between 40% and 69% of its nominal electricity consumption rate "69%≥v/J_o≥40%". This partial coverage accounted for the decrease in shutdown time and the increase in production quantity.

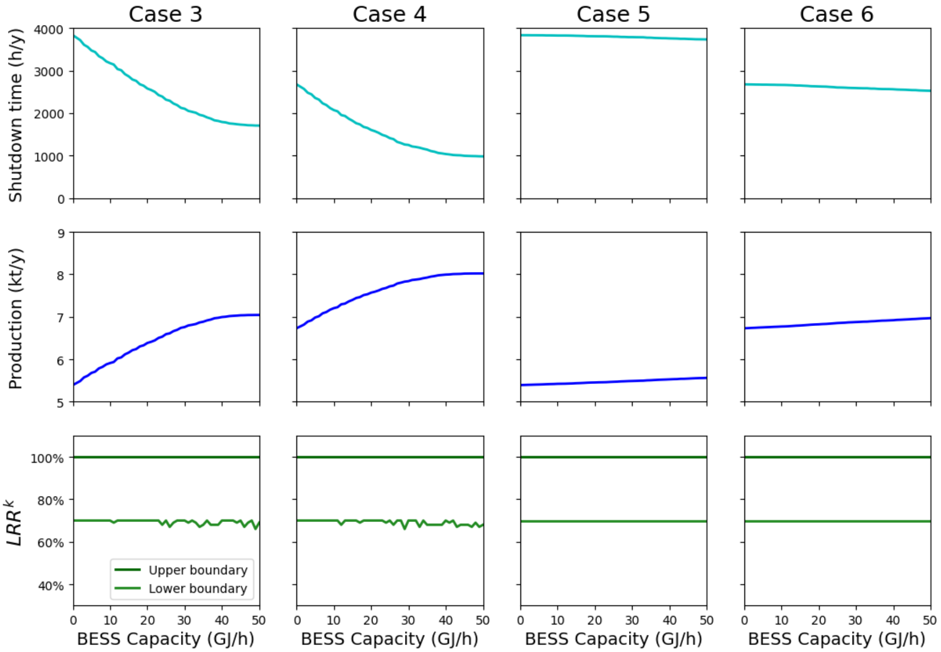

Fig. 3.4. Shutdown time, production quantity of hexanoic acid, and loa ratio range (LRR) in Cases 3 to 6.

Another common trend between shutdown time and production quantity under scheme 1, was that the decreasing or increasing trend plateaued locally as the BESS capacity approached 50 GJ/h. This indicates the existence of a hurdle for deploying BESS at a certain point. This is essentially related to the long periods of electricity shortage. A BESS installation of 50 GJ/h was only enough to cover short periods of electricity shortage. Moreover, under operating scheme 1, little extra electricity was taken in by the plant equipped with a BESS. This is confirmed by the right part of Fig. 3.5. When the "v/J_o" was above 100%, meaning when there was extra electricity, the "C_v^4" was small. Regarding operating scheme 2, it performed worse in any of the three indicators.

To summarise, an operating scheme where the BESS could be charged at peak hours

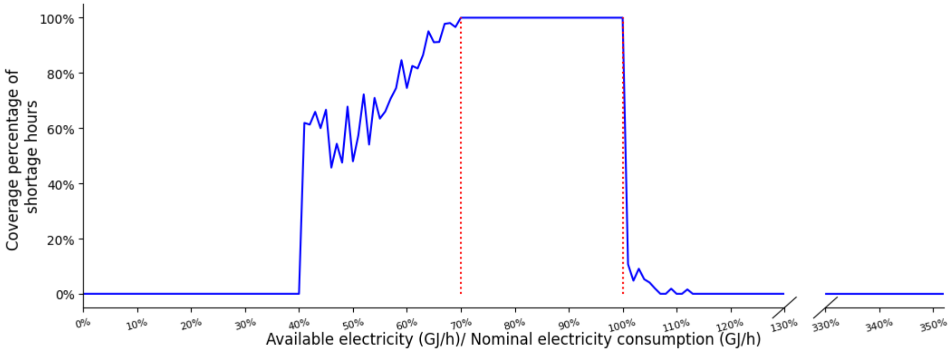

Fig. 3.5. Coverage percentage of shortage hours "C_{v}^{4}" versus available electricity over nominal electricity consumption of the reference process "v/J_o". An example of Case 4 with a BESS of 20 GJ/h. Red dashed lines: boundaries of LRR^4 with a BESS of 20 GJ/h.

and used to cover electricity shortage periods was more effective in improving overall production quantity, when compared to an operating scheme where the BESS can only be charged at off-peak hours and used for increasing the production as soon as possible. However, even under the first operating scheme, the benefits from a BESS will eventually plateau locally when its capacity increases, due to the long periods of electricity shortage.

As for the impact of different electricity profiles on technical performances, Cases 3 and 4 or Cases 5 and 6 can be compared. Undoubtedly, the cases where hybrid electricity was supplied performed better, as the hybrid electricity profile consists of solar and wind electricity, which renders a higher average capacity. Otherwise, the trends were the same for all technical indicators.

3.3 Economic performance

The economic results of Cases 1 to 6 are shown in Fig. 3.6. Comparing Cases 1 and 2 to Case 0, the levelised production cost of hexanoic acid ($\mathrm{LPC}^{\mathrm{k}}_{\mathrm{C6A}}$) was penalised by 34% and 19%, respectively, owing to the reduced production quantity and therefore less revenue. In both cases, the shares related to capital goods (i.e., O&M and CAPEX) increased while the shares relevant to daily operation decreased (i.e., the rest).

To compare the impact caused by different operating schemes, Cases 3 and 5 or Cases 4 and 6 should be compared to each other. Under operating scheme 1 (i.e., Cases 3 and 4), initially, the BESS contributed to decrease the $\mathrm{LPC}_{\mathrm{C6A}}$. In Case 3, the $\mathrm{LPC}^{3}_{\mathrm{C6A}}$ went down to 5.1 €/kg when the capacity of BESS was 29 GJ/h (=8.1 MW), leading to an improvement of 4% compared to Case 1. In Case 4, the lowest $\mathrm{LPC}^{4}_{\mathrm{C6A}}$ reached was 4.7 €/kg with a BESS of 12 GJ/h (=3.3 MW), which was improved by less than 1% upon Case 2. Compared to $\mathrm{LPC}^{0}_{\mathrm{C6A}}$, the penalty in production cost was 28% in Case 3 and 18% in Case 4. Meanwhile, the shares of CAPEX and O&M costs first declined and then increased along with the increase in the BESS capacity. This trend points out that a

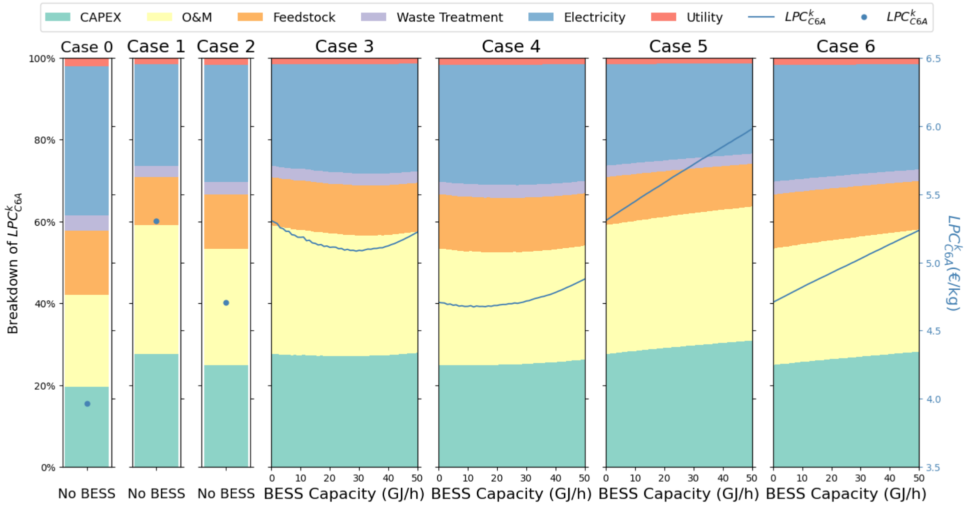

Fig. 3.6. Levelised production cost of hexanoic acid and its breakdown versus a range of BESS capacities.

higher BESS capacity does not guarantee a lower LPC_{C6A}. This was due to the fact that the extra production of hexanoic acid was not always linear to the BESS capacity, as visualised in Fig. 3.4. Therefore, at a certain point, the increased capital investment in BESS could not be paid back by the limited extra revenue. Under operating scheme 2 (see Cases 5 and 6), the LPC^5_{C6A} and LPC^6_{C6A} as well as the shares of CAPEX and O&M costs raised proportionally to the BESS capacity, which suggests that the installation of BESS did not enhance the economic viability under this scheme. The reason was that the use of the BESS was restricted, which is capital intensive and thereby resulting in a high sunk cost. This finding is in line with other similar studies [4, 30]. Moreover, similar to the technical performances, different electricity profiles did have an impact on the values but not on the trends.

4 Conclusions

The current chapter conducts an ex-ante assessment of a novel MES process for synthesising hexanoic acid under IRE supply. This chpater aims to (i) contribute to volume flexibility estimation, (ii) elucidate the impact of intermittency on the techno-economic performance of a MES plant, (iii) and understand the use of batteries as a strategy to improve the performance of the plant.

At the equipment level, the sizing of condensers and the internal geometrical design of the tower were identified as bottlenecks in the volume flexibility of the separation columns. To enhance the volume flexibility of condensers, three options are recommended: 1) deploy condensers and reboilers that allow a smaller minimum heat duty; 2) overdesign, or 3) increase the initial temperature difference between the target cooling or heating stream and utility stream. Moreover, operating the equipment below its nominal rates penalises the utility consumption. Regarding the internal design of the tower and trays, a better design of column's internal geometry or a higher reflux ratio could enhance their volume flexibility. Eventually, based on the results at the equipment level, in this chapter, column TD restricted the volume flexibility of the entire plant.

At the plant level and nominal conditions (i.e., Case 0), the levelised production cost of hexanoic acid ($\mathrm{LPC}^{0}_{\mathrm{C6A}}$) was 4.0 €/kg, which is competitive in today's market. When the electricity source was switched from constant grid electricity to IRE without implementing flexibility strategies (i.e., Cases 1 and 2), the $\mathrm{LPC}_{\mathrm{C6A}}$ was penalised by 34% and 19%, respectively. It was a consequence of shutting down the plant for 44% and 31% of the time per year due to electricity shortage. Batteries could help to reduce the penalties in production quantity. However, under an operating scheme where the batteries can be charged during peak hours and primarily used to cover the shortage (i.e., Cases 3 and 4), the penalties in $\mathrm{LPC}_{\mathrm{C6A}}$ was not exaggerated only when short periods of electricity shortage were covered. Otherwise, the capital investment in batteries became too large to be compensated by the revenue obtained from the increase in hexanoic acid production. Moreover, under the operating scheme where the batteries can only be charged during off-peak hours (i.e., Cases 5 and 6), the batteries were not used enough owing to the stringent operating scheme. Consequently, the batteries barely increased the production time, and the limited additional revenue could not pay back the capital investment. In any case, coupling the MES plant with IRE is not economically viable in this context.

For future work, along with the development of the MES technology, more details of the technologies should be included, such as more realistic assumptions and estimations. Also, it should be highlighted that the solvent regeneration and distillation unit operations should be validated by experiments or pilots in the future. Moreover, novel extraction technologies for dilute VCAs, such as electrodialysis, can be considered and incorporated into the simulation model when they become more mature. Other design strategies to improve volume flexibility can also be studied. In addition, operating schemes, namely the scheduling of the plant, can be optimised while maximising production. Importantly, the environmental performance should also be assessed to understand the impact and potential of the technology.

References

[1] IPCC. Climate change 2022: Impacts, adaptation and vulnerability. IPCC, 2022. DOI: `10.1017/9781009325844`.

[2] S. Morgenthaler, W. Kuckshinrichs, and D. Witthaut. “Optimal system layout and locations for fully renewable high temperature co-electrolysis”. Applied Energy. 260. 2020. P. 114218. DOI: `10.1016/j.apenergy.2019.114218`.

[3] M. Del Pilar Anzola Rojas, M. Zaiat, E. R. Gonzalez, H. De Wever, and D. Pant. “Effect of the electric supply interruption on a microbial electrosynthesis system converting inorganic carbon into acetate”. Bioresource Technology. 266. 2018. Pp. 203–210. DOI: `10.1016/j.biortech.2018.06.074`.

[4] A. Prevoteau, J. M. Carvajal-Arroyo, R. Ganigue, and K. Rabaey. “Microbial electrosynthesis from CO_2: forever a promise?” Current Opinion in Biotechnology. 62. 2020. Pp. 48–57. DOI: `10.1016/j.copbio.2019.08.014`.

[5] P. Dessi et al. “Microbial electrosynthesis: Towards sustainable biorefineries for production of green chemicals from CO_2 emissions”. Biotechnology Advances. 46. 2021. P. 107675. DOI: `10.1016/j.biotechadv.2020.107675`.

[6] L. Jourdin, J. Sousa, N. van Stralen, and D. P. B. T. B. Strik. “Techno-economic assessment of microbial electrosynthesis from CO_2 and/or organics: An interdisciplinary roadmap towards future research and application”. Applied Energy. 279. 2020. P. 115775. DOI: `10.1016/j.apenergy.2020.115775`.

[7] E. C. Canapi, Y. T. V. Agustin, E. A. Moro, E. Pedrosa, and M. L. J. Bendano. “Coconut Oil”. Bailey’s Industrial Oil and Fat Products. F. Shahidi. Vol. 1-6. 2005. John Wiley & Sons. Chap. Coconut Oil. Pp. 123–147. DOI: `10.1002/047167849X`.

[8] R. J. Whitehead. 2017. El Nino disruption causes palm kernel prices to double. URL: `https://www.foodnavigator-asia.com/Article/2017/01/16/El-Nino-disruption-causes-palm-kernel-prices-to-double`. (Access date: 10 Aug 2022).

[9] The Dollar Business Bureau. 2017. India lifts 9-year ban on bulk export of certain edible oils. URL: `https://www.thedollarbusiness.com/news/india-removes-ban-on-bulk-export-of-certain-edible-oils/49790`. (Access date: 10 Aug 2022).

[10] W. D. Cavalcante, R. C. Leitao, T. A. Gehring, L. T. Angenent, and S. T. Santaella. “Anaerobic fermentation for -caproic acid production: A review”. Process Biochemistry. 54. 2017. Pp. 106–119. DOI: `10.1016/j.procbio.2016.12.024`.

[11] N. A. Huq et al. “Toward net-zero sustainable aviation fuel with wet waste-derived volatile fatty acids”. PNAS. 11813. 2021. e2023008118. DOI: `10.1073/pnas.2023008118`.

[12] J. H. Miller, G. R. Hafenstine, H. H. Nguyen, and D. R. Vardon. “Kinetics and Reactor Design Principles of Volatile Fatty Acid Ketonization for Sustainable Aviation Fuel Production”. Industrial & Engineering Chemistry Research. 618. 2022. Pp. 2997–3010. DOI: `10.1021/acs.iecr.1c04548`.

[13] Z. Chen, X. Wang, and L. Liu. “Electrochemical Reduction of Carbon Dioxide to Value-Added Products: The Electrocatalyst and Microbial Electrosynthesis”. The Chemical Record. 197. 2019. Pp. 1272–1282. DOI: `10.1002/tcr.201800100`.

[14] P. De Luna, C. Hahn, D. Higgins, S. A. Jaffer, T. F. Jaramillo, and E. H. Sargent. “What would it take for renewably powered electrosynthesis to displace petrochemical processes?” Science. 3646438. 2019. eaav3506. DOI: `10.1126/science.aav3506`.

[15] T. Zhang and P.-L. Tremblay. “Possible Industrial Applications for Microbial Electrosynthesis From Carbon Dioxide”. Microbial Electrochemical Technology. 2019. Elsevier. Pp. 825–842. DOI: `10.1016/b978-0-444-64052-9.00034-0`.

[16] S. Aghapour Aktij, A. Zirehpour, A. Mollahosseini, M. J. Taherzadeh, A. Tiraferri, and A. Rahimpour. “Feasibility of membrane processes for the recovery and purification of bio-based volatile fatty acids: A comprehensive review”. Journal of Industrial and Engineering Chemistry. 81. 2020. Pp. 24–40. DOI: `10.1016/j.jiec.2019.09.009`.

[17] M. Atasoy, I. Owusu-Agyeman, E. Plaza, and Z. Cetecioglu. “Bio-based volatile fatty acid production and recovery from waste streams: Current status and future challenges”. Bioresource Technology. 268. 2018. Pp. 773–786. DOI: `10.1016/j.biortech.2018.07.042`.

[18] R. J. Jones, J. Massanet-Nicolau, and A. J. Guwy. “A review of carboxylate production and recovery from organic wastes”. Bioresource Technology Reports. 16. 2021. P. 100826. DOI: `10.1016/j.biteb.2021.100826`.

[19] L. Valentino and A. Alejandre. “Capacitive Deionization for the Extraction and Recovery of Butyrate”. Acs Sustainable Chemistry & Engineering. 1116. 2023. Pp. 6385–6394. DOI: `10.1021/acssuschemeng.3c00221`.

[20] H. C. Woo and Y. H. Kim. “Eco-efficient recovery of bio-based volatile C2-6 fatty acids”. Biotechnol Biofuels. 12. 2019. P. 92. DOI: `10.1186/s13068-019-1433-8`.

[21] P. O. Saboe et al. “In situ recovery of bio-based carboxylic acids”. Green Chemistry. 208. 2018. Pp. 1791–1804. DOI: `10.1039/c7gc03747c`.

[22] E. A. Benalcazar, B. G. Deynoot, H. Noorman, P. Osseweijer, and J. A. Posada. “Production of bulk chemicals from lignocellulosic biomass via thermochemical conversion and syngas fermentation: a comparative techno-economic and environmental assessment of different site-specific supply chain configurations”. Biofuels, Bioproducts and Biorefining. 115. 2017. Pp. 861–886. DOI: `10.1002/bbb.1790`.

[23] A. N. Ajah and P. M. Herder. “Addressing flexibility during process and infrastructure systems conceptual design: Real options perspective.” International Conference on Systems, Man and Cybernetics, Vol 1-4, Proceedings. 2005. Pp. 3711–3716. DOI: `10.1109/ICSMC.2005.1571723`.

[24] I. E. Grossmann and R. W. H. Sargent. “Optimum Design of Chemical-Plants with Uncertain Parameters”. AIChE Journal. 246. 1978. Pp. 1021–1028. DOI: `10.1002/aic.690240612`.

[25] J. Luo, J. Moncada, and A. Ramirez. “Development of a Conceptual Framework for Evaluating the Flexibility of Future Chemical Processes”. Industrial & Engineering Chemistry Research. 619. 2022. Pp. 3219–3232. DOI: `10.1021/acs.iecr.1c03874`.

[26] X. Christodoulou and S. B. Velasquez-Orta. “Microbial Electrosynthesis and Anaerobic Fermentation: An Economic Evaluation for Acetic Acid Production from CO_2 and CO”. Environmental Science & Technology. 5020. 2016. Pp. 11234–11242. DOI: `10.1021/acs.est.6b02101`.

[27] S. Gadkari, B. H. Mirza Beigi, N. Aryal, and J. Sadhukhan. “Microbial electrosynthesis: is it sustainable for bioproduction of acetic acid?” RSC Advances. 1117. 2021. Pp. 9921–9932. DOI: `10.1039/d1ra00920f`.

[28] J. Sadhukhan et al. “A critical review of integration analysis of microbial electrosynthesis (MES) systems with waste biorefineries for the production of biofuel and chemical from reuse of CO_2”. Renewable and Sustainable Energy Reviews. 56. 2016. Pp. 116–132. DOI: `10.1016/j.rser.2015.11.015`.

[29] M. Shemfe et al. “Life cycle, techno-economic and dynamic simulation assessment of bioelectrochemical systems: A case of formic acid synthesis”. Bioresource Technology. 255. 2018. Pp. 39–49. DOI: `10.1016/j.biortech.2018.01.071`.

[30] J. C. Wood et al. “Strategies to improve viability of a circular carbon bioeconomy-A techno-economic review of microbial electrosynthesis and gas fermentation”. Water Research. 201. 2021. P. 117306. DOI: `10.1016/j.watres.2021.117306`.

[31] X. Christodoulou, T. Okoroafor, S. Parry, and S. B. Velasquez-Orta. “The use of carbon dioxide in microbial electrosynthesis: Advancements, sustainability and economic feasibility”. Journal of CO_2 Utilization. 18. 2017. Pp. 390–399. DOI: `10.1016/j.jcou.2017.01.027`.

[32] M. del Pilar Anzola Rojas et al. “Microbial electrosynthesis (MES) from CO2 is resilient to fluctuations in renewable energy supply”. Energy Conversion and Management. 177. 2018. Pp. 272–279. DOI: `10.1016/j.enconman.2018.09.064`.

[33] R. Mateos, A. Escapa, M. I. San-Martin, H. De Wever, A. Sotres, and D. Pant. “Long-term open circuit microbial electrosynthesis system promotes methanogenesis”. Journal of Energy Chemistry. 41. 2020. Pp. 3–6. DOI: `10.1016/j.jechem.2019.04.020`.

[34] L. C. Bree et al. “Techno-Economic Comparison of Flexibility Options in Chlorine Production”. Industrial & Engineering Chemistry Research. 5926. 2020. Pp. 12186–12196. DOI: `10.1021/acs.iecr.0c01775`.

[35] C. Chen and A. D. Yang. “Power-to-methanol: The role of process flexibility in the integration of variable renewable energy into chemical production”. Energy Conversion and Management. 228. 2021. P. 113673. DOI: `10.1016/j.enconman.2020.113673`.

[36] A. Huesman. “Integration of operation and design of solar fuel plants: A carbon dioxide to methanol case study”. Computers & Chemical Engineering. 140. 2020. P. 106836. DOI: `10.1016/j.compchemeng.2020.106836`.

[37] O. Osman, S. Sgouridis, and A. Sleptchenko. “Scaling the production of renewable ammonia: A techno-economic optimization applied in regions with high insolation”. Journal of Cleaner Production. 271. 2020. P. 121627. DOI: `10.1016/j.jclepro.2020.121627`.

[38] M. Qi, J. Park, R. S. Landon, J. Kim, Y. Liu, and I. Moon. “Continuous and flexible Renewable-Power-to-Methane via liquid CO_2 energy storage: Revisiting the techno-economic potential”. Renewable and Sustainable Energy Reviews. 153. 2022. P. 111732. DOI: `10.1016/j.rser.2021.111732`.

[39] G. Wang, A. Mitsos, and W. Marquardt. “Renewable production of ammonia and nitric acid”. AIChE Journal. 666. 2020. e16947. DOI: `10.1002/aic.16947`.

[40] S. Gadkari, M. Shemfe, J. A. Modestra, S. V. Mohan, and J. Sadhukhan. “Understanding the interdependence of operating parameters in microbial electrosynthesis: a numerical investigation”. Physical Chemistry Chemical Physics. 2120. 2019. Pp. 10761–10772. DOI: `10.1039/c9cp01288e`.

[41] I. Staffell and S. Pfenninger. “Using bias-corrected reanalysis to simulate current and future wind power output”. Energy. 114. 2016. Pp. 1224–1239. DOI: `10.1016/j.energy.2016.08.068`.

[42] Eneco. 2022. Windpark Slufterdam. URL: `https://www.eneco.nl/over-ons/wat-we-doen/duurzame-bronnen/windpark-slufterdam/`. (Access date: 11 Nov 2022).

[43] Shell. 2019. Shell opens solar park at Shell Moerdijk chemicals site in the Netherlands. URL: `https://www.shell.com/business-customers/chemicals/media-releases/2019-media-releases/shell-moerdijk-solar-farm.html`. (Access date: 11 Nov 2022).

[44] European Commission. Commission Delegated Regulation (EU) 2023/1184 of 10 February 2023. 2023. URL: `http://data.europa.eu/eli/reg_del/2023/1184/oj`.

[45] Statista. 2022. Prices of electricity for non-household consumers in the Netherlands. URL: `https://www.statista.com/statistics/596254/electricity-industry-price-netherlands/#:~:text=The%5C%2010.51%5C%20euro%5C%20cents%5C%20per,towards%5C%20the%5C%20middle%5C%2Drange%5C%20of`. (Access date: 11 Nov 2022).

[46] M. McNamara, V. Plutshack, J. Phillips, and N. Poindexter. 2022. Can Time-of-Use Tariffs Increase the Financial Viability of Mini-Grids? URL: `https://dukespace.lib.duke.edu/dspace/bitstream/handle/10161/26572/can-time-of-use-tariffs-increase-financial-viability.pdf?sequence=2`. (Access date: 11 Nov 2022).

[47] G. Towler and R. Sinnott. Chemical engineering design: principles, practice and economics of plant and process design. 2nd. Amsterdam: Butterworth-Heinemann, 2021.

[48] C. R. Branan. Rules of thumb for chemical engineers. 3rd. USA: Gulf Publishing Company, 1998.

[49] S. P. Max, D. T. Klaus, and E. W. Ronald. Plant design and economics for chemical engineers. 5th. Boston: McGraw-Hill Companies, 2003.

[50] W. Sieder, J. Seader, and D. Lewin. Product and process design principles. 3rd. USA: John Wiley & Sons, 2004.

[51] T. H. Kwan, Y. Z. Hu, and C. S. K. Lin. "Techno-economic analysis of a food waste valorisation process for lactic acid, lactide and poly(lactic acid) production". Journal of Cleaner Production. 181. 2018. Pp. 72–87. DOI: `10.1016/j.jclepro.2018.01.179`.

[52] J. E. Berryman and D. M. Himmelblau. "Influence of Stochastic Inputs and Parameters on Heat Exchanger Design". Industrial & Engineering Chemistry Process Design and Development. 122. 2002. Pp. 165–171. DOI: `10.1021/i260046a007`.

[53] R. K. Shah and D. P. Sekulic. Fundamentals of Heat Exchanger Design. 1st. USA: John Wiley & Sons, 2003. DOI: `10.1002/9780470172605`.

4

Battery use or chemical storage for intermittent renewable electricity? A comparison for a microbial CO_2 electrolysis plant

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This chapter is based on a manuscript that has been submitted to a journal.

Chapter-specific symbols

Symbols

C_v	Yearly coverage percentage of shortage hours at an available electricity power v, %
Lin_t	Intermediate chemicals stored into the storage tank at time t, m^3/h
$Lout_t$	Intermediate chemicals sent to the DSP units from the storage tank at time t, m^3/h
L_t	Intermediate chemicals directly sent to the DSP from the MES at time t, m^3/h
Jin_t	Electricity stored in the BESS at time t, GJ/h
$Jout_t$	Electricity discharged from the BESS at time t, GJ/h
J_t	Electricity consumption immediately used for hexanoic acid production at time t, GJ/h
P_t^H	Available electricity from the hybrid farms (i.e., wind and solar) at time t, GJ/h
T	Time vector, 1-8760 h
V	Vector of hourly available electricity over hourly nominal electricity consumption (for intermediate calculation), %
X_t	Production of hexanoic acid at time t, kt/h
γ_t	Binary variable
E	Electricity price, M€/y
F	Feedstock price, M€/y
J	Electricity consumption, GJ/h
$\dot{M}$	Mass flow rate at plant level, kt/y
m	Total number of equipment
n	Plant lifetime, years
r	Discount rate, %
UT	Utility price at plant level, M€/y
v	Available electricity power generated by the wind and/or solar farm (time-independent), GJ/h
v^*	Available electricity power generated by the wind and/or solar farm (time-independent; for intermediate calculation), GJ/h
WT	Waste treatment price, M€/y
$\mathbb{Z}$	Integers
θ	Price, €/kg
φ	Annuity factor
Φ	Statement inside the Iverson bracket
α	Constant
β	Constant
λ	Constant
η	Constant
ω	Constant
ϵ	Constant

Superscripts

i	Type of equipment
k	Case number, from A to F

Subscripts

$C6A$	Hexanoic acid
LB	Lower boundary
max	Maximum value
min	Minimum value
o	Nominal value
O_2	Oxygen
t	Time, h
UB	Upper boundary
y	Year
xa	Extra available
xr	Extra required

Acronyms

AF	Allocation factor, %
ANP	Annualised net profit, M€/y
CAPEX	Capital expenditure, M€/y
EAC	Equivalent annualized price, M€/y
EC	Electricity consumption, %
LPC	Levelised production cost, €/kg
LRR	Load ratio range, %
O&M	Operation and maintenance price, M€/y
OPEX	Operating expenditure, M€/y
WC	Working capital, M€

Abstract

CO_2 electroreduction driven by intermittent renewable electricity is promising for defossilising the chemical industry, but intermittency challenges the performance of downstream processing units. This chapter aims to understand the impacts of intermittency in the design, volume flexibility, and scheduling of a microbial electrosynthesis plant that converts CO_2 into hexanoic acid. A battery and a storage tank were considered to buffer the intermittency. In explorative case studies, there was no economic advantage when using the battery. A storage tank with optimised size combined with optimal scheduling improved the plant's volume flexibility by 10%. The carbon footprint became almost 3 times lower when switching from grid to renewable electricity, but the levelised production cost of hexanoic acid ($\mathrm{LPC_{C6A}}$) increased. Hence, coupling with renewable electricity was not economically but environmentally favourable, and the use of the tank compared to not using any storage unit allowed for a 7% decrease in the $\mathrm{LPC_{C6A}}$.

1 Introduction

To mitigate anthropogenic global warming, accelerating energy transitions is crucial in many industrial sectors, including the chemical sector [1, 2]. To reduce CO_2 emissions in the chemical sector, fossil-based feedstock and fuels are expected to be replaced by cleaner alternatives. For instance, fossil-based carbon sources can be replaced by CO_2 captured from the air or exhaust gas, while fossil-based electricity can be substituted by renewable energy such as solar and wind. Therefore, the electroreduction of CO_2 to value-added chemicals with renewable electricity is a promising alternative in the chemical sector. Among the different CO_2 electroreduction technologies, microbial electrosynthesis (MES) is an emerging technology that can convert CO_2 into useful chemicals through electricity-driven microbial reactions, such as into hexanoic acid [3, 4]. High-purity hexanoic acid has a high market value and is, hence, an attractive product. It is currently produced by fractional distillation of coconut or palm kernel oil, mainly exported by Indonesia or Malaysia [5, 6]. As a result, this product is constrained by the origins and availability of raw materials, whereas the MES route would allow for more flexible supply chains and upscaling. Up to now, both fundamental research and ex-ante techno-economic assessments of low-temperature direct CO_2 electroreduction technologies, focus on the synthesis of commodity chemicals or fuels such as methane, methanol, or ethylene [7]. Their downstream recovery and purification processes are challenging because of the low concentration of the targeted products and the type of impurities. However, downstream processing (DSP) is often overlooked in ex-ante techno-economic assessments [8]. MES produces hexanoic acid in a dilute aqueous environment. Hexanoic acid has a longer carbon chain and can form an azeotrope with water. As a result, the reported separation trains cannot easily recover it to a high degree of purity [9–11]. Moreover, the intrinsic variability in renewable electricity and consequent fluctuations in the throughput rate of the MES unit further exacerbate the challenge in the DSP design.

In the previous chapter [12], we proposed and modelled a MES plant producing high-purity hexanoic acid at a design capacity of ca. 10 kt/y and consuming 602 TJ/y of electricity. The DSP technologies selected to purify the hexanoic acid stream were liquid-liquid extraction (LLE), solvent regeneration (SR), and distillation. We assessed the plant's volume flexibility (understood as the ability of the plant to operate over a range of electricity loads while meeting product requirements and not damaging the equipment [13]) for different intermittent renewable electricity (IRE) profiles and storage strategies with batteries. According to our modelling results, the MES plant without a battery energy storage system (BESS) could be operated between 70% and 100% of its nominal capacity. The major bottleneck was the last heat-based distillation unit in the process. Below 70%, the plant must be shut down. The results suggested that covering short periods of electricity shortage by a BESS increased the product quantity synthesised yearly, though the reduction in the production cost was insignificant (e.g. with a BESS size under 14 MW). On the other hand, covering long periods of electricity shortage was too capital-intensive; the capital investment in the BESS soared because of the substantial capacity required, whereas limited extra revenue was obtainable. For instance, to avoid all shutdown periods, a BESS of nearly 500 MW would have been needed. Based on the outcome of the previous chapter [12], which investigated different predefined sizes and operating schemes of the BESS (discrete cases), we argued that if a capital-intense flexibility strategy is not used efficiently, it can lead to a high sunk cost. Optimising the sizes of the buffering units, the use of the buffering units and the operating loads of the MES plant was deemed necessary. In contrast to the expensive BESS, a cheaper buffering option, storage tanks (ST), has been advised in literature to decouple the more from the less flexible sections of a process to buffer the fluctuations in flow rates caused by intermittent renewable electricity in Power-to-Chemicals plants [14–19].

Operation scheduling has been primarily intended for meeting product demand and reducing capital and operating costs [20, 21]. However, in recent years, integrating IRE into the electricity grid while minimising operating costs has led to a considerable and growing number of studies, which have approached the IRE integration problem as a scheduling problem with a commonly used hourly resolution over a year [1, 19, 22–27]. Such a problem has usually been formulated as a mixed-integer linear programming (MILP) or a mixed-integer nonlinear programming (MINLP) problem.

In this chapter, we extend the previous chapter [12] by addressing two questions: i) how does hourly fluctuation in the electricity supply affect the sizing of the buffering units (i.e., BESS and ST) and scheduling of a MES plant? and ii) what are the subsequent trade-offs in terms of techno-economic performances and carbon emissions when the buffering units are installed, and the scheduling is optimised?

2 Methodology

This chapter started with building the system model, where the design considerations of the plant were specified, the process model was developed, and electricity profiles were selected (see section 2.1). Next, explorative case studies were conducted under predefined operating schemes and predefined buffering unit sizes (see section 2.2), which were the starting point of the optimisation problem. They helped to narrow the optimisation down, namely reducing several variables and nonlinearities, which eventually determined the use of a ST as the only buffering unit and confined the boundaries of variables. Section 2.3 elaborates on how these cases were characterised by various indicators. Next, a MINLP (i.e., mixed-integer quadratically constrained programming-MIQCP) problem was constructed and solved in Python (see section 2.4). The operating patterns of the MES-based plant and of the tank and the size of the tank were optimised to obtain a maximum annualised net profit (ANP). This optimised case was further evaluated using several indicators presented in section 2.3. In addition, the carbon footprint was calculated for the optimised case and compared with the cases with grid electricity and continuous operation, and with IRE but without buffering units (see section 2.5), revealing the impacts of IRE as well as of the optimal scheduling and buffering unit size on the carbon footprint. Last, sensitivity analyses were performed on the optimised case (see section 2.6).

Table 4.1 gives an overview of the six (reference, explorative, and optimisation) cases studied in this chapter (see details in section 2.2). For clarification, Cases A, B and C are the same as Cases 0, 2, and 4 in the previous chapter [12], respectively. Moreover, it summarises the various indicators used in this chapter for characterising the performances of the different cases (see details in section 2.3 and section 2.5).

Table. 4.1. Overview of the case studies. IRE: intermittent renewable electricity; BESS: battery energy storage system; ST: storage tank.

Case (k)	Reference		Explorative			Optimised
	A	B	C	D	E	F
Factors considered						
Electricity profile	Grid	IRE	IRE	IRE	IRE	IRE
Buffering units implemented	-	-	BESS	ST	BESS&ST	Depends
Predefined sizes of buffering units	-	-	Yes	Yes	Yes	-
Predefined operating scheme	-	-	Yes	Yes	Yes	-
Optimised scheduling	-	-	-	-	-	Yes
Optimised sizes of buffering units	-	-	-	-	-	Yes
Indicators used						
Production shutdown time per year (h/y)	-	Yes	Yes	Yes	-	Yes
Hexanoic acid production (kt/y)	-	Yes	Yes	Yes	-	Yes
Levelised production cost of hexanoic acid, LPC_{C6A}^{k} (€/kg)	Yes	Yes	Yes	Yes	-	Yes
Load ratio range, LRR^{k} (%)	-	Yes	Yes	Yes	-	Yes
Total electricity consumption EC_{ttl}^{k} (%)	-	Yes	Yes	Yes	-	Yes
Surplus electricity consumption EC_{spl}^{k} (%)	-	-	Yes	-	-	Depends
Extra production required, $\dot{M}_{C6A,xr}$ (kt/y)	-	-	-	-	Yes	-
Extra production available, $\dot{M}_{C6A,xa}$ (kt/y)	-	-	-	-	Yes	-
Carbon footprint (t CO_2eq/t C6A)	Yes	Yes	-	-	-	Yes

2.1 System model

2.1.1. Design considerations

The MES plant was assumed to be installed in the Port of Rotterdam and have a lifetime of 30 years. It produces 99 wt% hexanoic acid as the main product at a nominal production rate of ca. 10 kt/y (at a continuous operation, 8760 hours/y) and ca. 22 kt/y of compressed O_2 as a by-product. Its configuration is described in section 2.1.2.

2.1.2. Process description

Fig. 4.1 is a simplified block flow diagram of the MES plant. Demineralised H_2O is fed into the anode chamber of the MES, and the by-product, O_2, is produced. Demineralised H_2O, CO_2, $Ca(OH)_2$, and electrons are supplied to the cathode chamber, where carboxylates and corresponding carboxylic acids are generated. The stream is then sent to the DSP units for acidification, filtration, recovery via two LLE units with distillation-based SR, and final distillation-based dehydration to obtain the 99 wt% hexanoic acid.

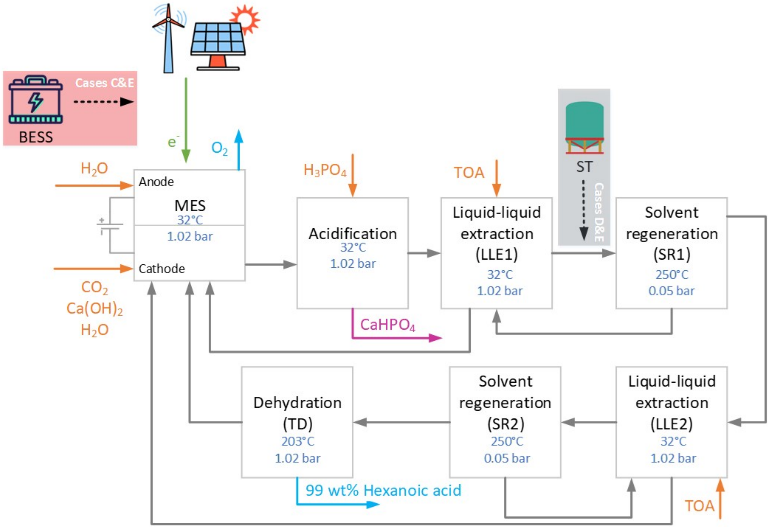

Fig. 4.1. (a) Block flow diagram of the process of hexanoic acid production via MES. MES: microbial electrosynthesis. BESS: battery energy storage system. LLE: liquid-liquid extraction. SR: solvent regeneration. TD: dehydration column. ST: storage tank. TOA: trioctylamine (solvent used for liquid-liquid extraction). (b) A simplified illustration of the operating patterns of the MES plant. Notice: the acidification unit was omitted in this figure. DSP: downstream processing.

2.1.3. Electricity profiles

Two electricity profiles were selected and used. One was constant grid electricity provided at the plant's nominal capacity. It was assumed to be sold to the MES plant at the average industrial electricity price in the Netherlands in 2019 [28]. The second profile was hybrid IRE, consisting of combined solar and wind power. This profile has an hourly resolution and was generated based on the wind speed and solar radiation in the region of Rotterdam in 2019. As a design condition, the average hourly capacity of the hybrid farms (i.e., solar and wind farms) was set 200% of the nominal hourly electricity consumption rate of the MES plant. Appendix B explains how the profile was generated and its corresponding pricing scheme.

2.2 Case specification

2.2.1. Case A

This is the first reference case where the plant was powered by constant grid electricity and operated at its nominal conditions, and no buffering unit was installed.

2.2.2. Case B

This is the second reference case where the plant was driven by hybrid IRE while no buffering unit was deployed. For the operation of the plant, it was assumed that when the available electricity from the hybrid farms could not enable the production at the plant's minimum tolerable throughput rate, which is 70% of its nominal capacity, the plant was shut down. On the other hand, if the available electricity was higher than the plant's maximum tolerable electricity load, which is 100% of its nominal capacity, the production was kept at its maximum capacity and the surplus electricity available (the amount of electricity that exceeds the plant's nominal electricity consumption rate) was not used.

2.2.3. Case C

This is an explorative case where the plant was driven by hybrid IRE, and a BESS was installed before the MES unit (see Fig. 4.1). The plant's operating scheme was predefined, and the BESS capacity was varied. Based on the range of tolerable capacities mentioned for Case B, at each BESS capacity studied, the plant's operating scheme was defined by the following sequential rules (schematically depicted in Appendix B):

1) when the total electricity available from the hybrid IRE and the BESS does not reach the minimum tolerable electricity power of the plant, which is 70% of its nominal capacity, shut down the production of hexanoic acid;
2) otherwise, ensure the production at the plant's minimum tolerable throughput rate, if needed, with the stored electricity from the BESS;
3) if the BESS is not fully charged and not used for production, charge it. It is possible that the BESS is charged while the production is off because of insufficient electricity to reach the plant's minimum tolerable throughput rate;
4) if the BESS is fully charged, increase the production of hexanoic acid using hybrid IRE directly up to the plant's maximum throughput rate, which is 100% of its nominal capacity;
5) electricity that cannot be consumed (because the BESS is fully charged and the plant is working at 100% of its nominal capacity) is not used by the MES plant.

Moreover, we assumed that 1) at the start of operation (t=1), the BESS was already fully charged; 2) the BESS could be charged or discharged up to its full capacity within one hour; 3) in consistency with the previous chapter [12], for each equipment, the material flow rate was linear to the electricity consumption rate. As measured in the previous chapter [12], the consumption rate of utility (i.e., heating and chilling) was non-linear to the material flow rate due to the penalties for deviating from the nominal operating conditions.

2.2.4. Case D

In this explorative case, the plant was driven by the hybrid IRE and a ST was implemented in front of the SR1 (see Fig. 4.1) to decouple the more flexible section (i.e., units prior to the ST) from the less flexible section (i.e., units after the ST) of the process. This location was proposed based on the fact that the heat-based columns were limiting fluctuations handling, and SR1 is the first heat-based column in the plant [12]. The plant's operating scheme was predefined, and the ST size was varied.

Based on the range of tolerable capacities of Case B, at each ST size studied, the plant's operating scheme was specified by the sequential rules below (schematically depicted in Appendix B):

1) when the electricity available from the hybrid IRE and the intermediate chemicals stored in the ST together cannot enable the plant's minimum tolerable throughput rate, shut down the production;
2) otherwise, ensure the production at the minimum tolerable throughput rate of the plant, if needed, with the stored intermediate chemicals from the ST;
3) if the ST is not fully filled and the intermediate chemicals stored inside it are not used for production, fill it. It is possible that the production is off due to insufficient flow going to SR1, however, the MES can consume electricity and the intermediate chemicals produced are stored in the ST;
4) when the ST is fully filled, increase the production without using the stored chemicals from the ST until the plant's maximum throughput rate, which is 100% of its nominal capacity;
5) electricity that cannot be consumed (because the ST is fully filled, and the plant is working at 100% of its nominal capacity) is not used by the MES plant.

Note that the intermediate chemicals stored in the ST could essentially be seen as "stored electric energy", which was the electricity available from the hybrid farms previously and used by MES to generate product compounds and then stored in the chemical bonds.

Moreover, we assumed that 1) at the start of operation (t=1), the ST was already fully filled; 2) the ST could be filled or drained up to its full capacity within one hour; 3) same as the third assumption for Case C; 4) electricity was all consumed by the more flexible section of the process and utility was all consumed by the less flexible section of the process for simplicity, which was supported by the results in the previous chapter[12], where only 1.5% of electricity was consumed in the less flexible section and only 1% of the utility was used in the more flexible section. See Appendic C for the check of this hypothesis.

2.2.5. Case E

In this last case study, the plant was driven by hybrid IRE and a BESS and a ST were implemented at the same plant locations as in Cases C and D, respectively. This case study aimed to understand if the two buffering units would have synergies and further promote the production quantity of hexanoic acid and the economic performance of the plant. Since storage tanks are usually much cheaper than batteries, we explored the potential advantages of deploying a BESS in addition to a ST of the size that yielded the best economic performance in Case D, to assess if the BESS unit can enable extra hexanoic acid production to pay back its capital costs and even improve the operating income.

First, we calculated how much extra production of hexanoic acid was required per year "$\dot{M}_{C6A,xr}$" to pay back each GJ/h of BESS implemented when the ST was already in place. Then, we calculated how much extra production per year "$\dot{M}_{C6A,xa}$" was available per GJ/h of BESS implemented in addition to this ST (see equations in section).

The operating scheme when the BESS and ST were implemented concurrently was also predefined. This scheme was based on the assumption that the BESS should be used more frequently so it could consume more electricity (that otherwise will not be used) to boost the production of hexanoic acid [12]. At each BESS capacity studied, the plant's operating scheme followed the sequential rules below (schematically depicted in Appendix B):

1) when the electricity available from hybrid IRE, the stored electricity in the BESS, and the intermediate chemicals stored in the ST cannot enable together the plant's minimum tolerable throughput rate; the production is shut down;
2) otherwise, ensure the production at the plant's minimum tolerable throughput rate, if needed, with stored electricity from the BESS and/or the stored chemicals from the ST;
3) if the ST is not fully filled and the intermediate chemicals stored inside are not used for production, fill it. It is possible that the production is off due to insufficient flow going to SR1, however, the MES can still consume electricity and the intermediate chemicals produced can be stored into the ST. When the ST is full and the first rule still cannot be achieved, the BESS can be charged;
4) when the ST is fully filled, increase the production of hexanoic acid without using the stored chemicals from the ST until the plant reaches its maximum throughput rate, i.e., 100% of its nominal capacity. If the hybrid IRE does not reach 100% of the plant's nominal electricity load, stored electricity in the BESS shall be used. If the hybrid IRE is over 100% of the plant's nominal electricity load, and the BESS is not fully charged, charge the BESS;
5) electricity that cannot be consumed (because the BESS is fully charged, the ST is fully filled, and the plant is working at 100% of its nominal capacity) is not used by the MES plant.

The assumptions made are consistent with Cases C and D.

2.3 Techno-economic evaluation

The process model was first developed at nominal conditions and a continuous operation in Aspen Plus [12]. The mass and heat balances of the process at different throughput rates were retrieved from Aspen Plus and combined with a buffering unit, the hybrid IRE profile, and an operating scheme using Python scripts, where the indicators described in this section were calculated.

2.3.1. Levelised production cost

The levelised production cost of hexanoic acid ($\mathrm{LPC_{C6A}}$) is calculated using Equations 4.1-4.3. Costs include capital expenditure (CAPEX) and operating costs (OPEX). CAPEX of the plant is a sum of direct costs, indirect costs, and working capital. Direct costs are the purchase costs of all physical items, estimated based on the Aspen process model. Values were retrieved from Aspen Process Economic Analyzer v12, webpages, or literature. Indirect costs and working capital were estimated according to heuristics [29–31] expressed as a series of percentages of purchase costs. OPEX is classified into five categories: operation and maintenance, feedstock, utilities (i.e., heating and chilling), waste treatment, and electricity. Operation and maintenance costs are associated with the purchased costs as well as labour costs and were calculated according to the abovementioned heuristics. Feedstock and waste treatment costs were based on mass balances and material prices. Utilities and electricity prices were obtained for the Netherlands. A discount rate of 8% was assumed over the lifetime of 30 years. The plant would depreciate over 30 years, and a salvage rate of 3.3% of the initial CAPEX was considered. Since the plant has a salvage value and some equipment (i.e., LLE & BESS) will be replaced after 15 years, CAPEX varies over time. The construction of the plant was assumed to last for a year.

Considering that the by-product O_2 was produced at a higher quantity than hexanoic acid, an economic allocation between hexanoic acid and O_2 was applied to both indicators ("AF_{C6A}"). The selling prices of hexanoic acid and O_2 were based on literature [32, 33]. More details about economic inputs and heuristics used are provided in Appendix B.

$$LPC_{C6A}^{k} = AF_{C6A}\frac{\sum_{y=1}^{n}(CAPEX_{y}^{k} + O\&M^{k} + F^{k} + UT^{k} + WT^{k} + E^{k})}{\sum_{y=1}^{n}\dot{M}_{C6A}^{k}} \tag{4.1}$$

$$OPEX^{k} = O\&M^{k} + F^{k} + UT^{k} + WT^{k} + E^{k} \tag{4.2}$$

$$AF_{C6A} = \frac{\dot{M}_{C6A}^{A}\theta_{C6A}}{\dot{M}_{C6A}^{A}\theta_{C6A} + \dot{M}_{O_2}^{A}\theta_{O_2}} \tag{4.3}$$

2.3.2. Load ratio range

The load ratio range (LRR) was used to quantify volume flexibility at the plant level. It was defined in the previous chapter [12] as the amount of available electricity (unit: GJ/h) from the hybrid farms that the plant could fully consume while meeting product requirements (i.e., purity and recovery rate) without damaging the equipment, divided by the plant's nominal electricity consumption rate (unit: GJ/h). Hence, the boundaries of LRR are expressed in percentages, and a precision of 1% was used. The formulas for calculating the LRR (see Equation 4.4) were proposed in the previous chapter [12] and are slightly modified and briefly explained below with the help of Fig. 4.2.

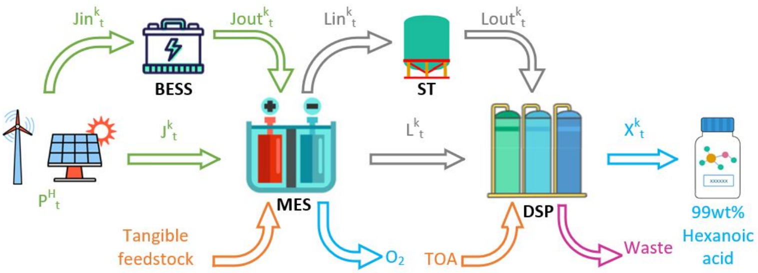

Fig. 4.2. A simplified illustration of the operating patterns of the MES plant. Notice: the acidification unit was omitted in this figure. DSP: downstream processing.

First of all, the LRR is calculated using the power profile and outcome operating profiles over a year with a time resolution of one hour (i.e., 8760 hours). In the first step, based on the annual power profile of the hybrid farms "P^H_T", at each power "v" generated by the farms, the total number of hours was counted together using an Iverson bracket (see Equation 4.4). Then, based on the resulting operating profiles of the plant, the number of hours were counted at each electricity power "v" if the plant met two expectations simultaneously: 1) fully consumed the available electricity "$Jin^k_t + J^k_t = v = P^H_t$" from the hybrid farms and 2) produced hexanoic acid "$X^k_t \geq 0.7X_o$" (0.7 is explained in the following paragraph). Next, at each electricity power, a percentage "C^k_v" was calculated using the two counts. This percentage represents how frequently the plant was operated with the two expectations met when the electricity power was "v". This percentage is denoted as the coverage percentage hereafter. If the coverage percentage is 100% at a particular "v", it means that the plant could always operate as expected when "v" was supplied from the hybrid farms. Finally, a continuous range of the electricity power was identified, where the corresponding coverage percentages were all 100%.

$$LRR^k = [\min V^k_{LB}, \max V^k_{UB}] \tag{4.4}$$

s.t.

$$T = [1, 8760] \cap \mathbb{Z}$$

$$C^k_v = \frac{\sum_{t\in T} \llbracket Jin^k_t + J^k_t = v = P^H_t, X^k_t \geq 0.7X_o \rrbracket}{\sum_{t\in T} \llbracket P^H_t = v \rrbracket} \quad \forall v \in P^H_T$$

$$V^k_{LB} = \{\frac{v}{J_o} | v \leq J_{min}, C^k_{\forall v^* \in [v, J_{min}]} = 100\%\}$$

$$V^k_{UB} = \{\frac{v}{J_o} | v \geq J_{max}, C^k_{\forall v^* \in [J_{max}, v]} = 100\%\}$$

The LRR of Cases A and B was [70%, 100%] based on the previous chapter [12]. It means that during any hour in which the available electricity from the hybrid farms was between 70% and 100% of the process's nominal electricity consumption, the plant could take in all the available electricity while safely producing hexanoic acid. Below 70%, there was an electricity shortage, and the plant had to be shut down. Above 100%, without a BESS or a ST, the surplus electricity available from the hybrid farms could not be used by the plant.

2.3.3. Total and surplus electricity consumption

Total and surplus electricity consumption were distinguished. Both are cumulative indicators and are expressed as percentages. During the calculation, both numerators and denominators were summed per annum or by a specific available electricity power generated by the hybrid farms. The detailed explanations are as follows. The total electricity consumption "EC^k_{ttl}" is the electricity taken in by the plant "$Jin^k_t + J^k_t$" divided by the available electricity power from the hybrid farms "P^H_t" (see Fig. 4.2). The surplus electricity consumption "EC^k_{spl}" focuses on the plant's surplus electricity consumption "$Jin^k_t + J^k_t - J_o$" and the surplus available electricity "$P^H_t - J_o$" from the hybrid farms. "J_o" is the nominal electricity load of the plant. Equations 4.5 and 4.6 show how these two indicators are summed by per annum "T", respectively. Equations 4.7 and 4.8 show how these two indicators can be summed by a specific available electricity power generated by the hybrid farms "v", respectively.

$$EC^k_{ttl} = \frac{\sum_{t \in T} Jin^k_t + J^k_t}{\sum_{t \in T} P^H_t}, T = [1, 8760] \cap \mathbb{Z} \tag{4.5}$$

$$EC^k_{spl} = \frac{\sum_{t \in T} (Jin^k_t + J^k_t - J_o) \llbracket P^H_t > J_o \rrbracket}{\sum_{t \in T} (P^H_t - J_o) \llbracket P^H_t > J_o \rrbracket} \tag{4.6}$$

$$EC^k_{ttl} = \frac{\sum_{t \in T} v \llbracket Jin^k_t + J^k_t = v \rrbracket}{\sum_{t \in T} v \llbracket P^H_t = v \rrbracket} \quad \forall v \in P^H_T \tag{4.7}$$

$$EC^k_{spl} = \frac{\sum_{t \in T} (v - J_o) \llbracket Jin^k_t + J^k_t = P^H_t = v > J_o \rrbracket}{\sum_{t \in T} (v - J_o) \llbracket P^H_t = v > J_o \rrbracket} \tag{4.8}$$

2.3.4. Extra production required and available

As mentioned in section 2.2.5, two extra indicators were specially used for Case E. The extra production required "$\dot{M}_{C6A,xr}$" was calculated using Equation 4.9. The capital cost of the BESS was annualised to the equivalent annualised cost (EAC) using Equations 4.10 and 4.11. The extra production available "$\dot{M}_{C6A,xa}$" was calculated based on the extra electricity the BESS can consume when the ST was already deployed. The extra electricity the BESS could consume from the hybrid IRE was calculated when applying the operating scheme in section 2.2.5. Then, it was translated into "$\dot{M}_{C6A,xa}$" using Equation 4.12.

$$\dot{M}_{C6A,xr} = \frac{EAC^{BESS} + O\&M^{BESS}}{\min LPC^{D}_{C6A} - \frac{F^A + WT^A + E^A + UT^A}{\dot{M}^A_{C6A}}} \tag{4.9}$$

$$EAC^i = \frac{CAPEX^i}{\varphi^i} \tag{4.10}$$

$$\varphi^i = \frac{1 - \frac{1}{(1+r)^{n^i}}}{r} \tag{4.11}$$

$$\dot{M}_{C6A,xa} = \frac{\text{Extra electricity consumed by the BESS}}{J_o} * \dot{M}^A_{C6A} \tag{4.12}$$

2.4 Optimisation problem

The MIQCP problem was coded in Pyomo [34, 35] and solved with Gurobi [36]. In light of the large problem size, a tolerance of 0.1% was imposed on the lower and upper bounds. The problem was solved in a high-performance computer [37]. A memory size of 1.2 TB was requested for this optimisation. It took ca. 18 hours to find the globally optimal solution.

2.4.1. Objective function

This optimisation aims to find a maximum ANP_{C6A} instead of the maximum LPC_{C6A} to circumvent the nonlinear form of the objective function. ANP_{C6A} is defined by the annual revenue upon hexanoic acid subtracted by the OPEX and EAC^{plant} allocated to hexanoic acid (see Equations 4.13-4.15). The annual revenue is the product of the yearly production quantity and market prices of the main product.

$$ANP_{C6A} = \theta_{C6A}\dot{M}_{C6A} - AF_{C6A}(EAC^{plant} + OPEX) \tag{4.13}$$

$$EAC^{plant} = \sum_{i=1}^{m} EAC^i + \frac{WC}{\varphi^{plant}} \tag{4.14}$$

$$\varphi^{plant} = \frac{1 - \frac{1}{(1+r)^{n^{plant}}}}{r} \tag{4.15}$$

The optimisation variables were the scheduling profile and the size of buffering units. The scheduling profile is composed of electricity stored into the BESS "Jin_t^F", electricity from the hybrid farms that is directly consumed by the plant excluding the BESS "J_t^F", intermediate chemicals stored into the ST "Lin_t^F", intermediate chemicals directly sent to the DSP from the MES "L_t^F", and intermediate chemicals sent to the DSP from the ST "$Lout_t^F$" (see in Fig. 4.2). The size of buffering units were "V_{BESS}" and "V_{ST}". Therefore, the objective function could be formulated based on Equation 4.13 as:

$$\max_{V_{BESS}, V_{ST}, Jin_t^F, J_t^F, Lin_t^F, L_t^F, Lout_t^F, X_t^F} \theta_{C6A} \sum_{t \in T} X_t^F - AF_{C6A}\left(EAC^{plant} + OPEX^F\right) \tag{4.16}$$

$$\forall v \in P_T^H, T = [1, 8760] \cap \mathbb{Z}$$

where all the variables are continuous.

2.4.2. Constraints

The electricity consumption rate (of the more flexible section of plant) "$J_t^F + Jout_t^F$" (GJ/h) was between 0 and its nominal rate "J_o" (GJ/h). The throughput rate of the DSP "$L_t^F + Lout_t^F$" (m^3/h) should be between 70% and 100% of its nominal rate "L_o" (m^3/h) or shut down the production "$L_t^F + Lout_t^F = 0$". Moreover, the electricity consumption rate of the whole plant "$J_t^F + Jin_t^F$" (GJ/h) cannot be larger than the power supply "P_t^H" (GJ/h) or the plant's nominal capacity "J_o" (GJ/h). Time spent for ramping, starting up and shutting down were neglected.

$$0 < J_t^F + Jout_t^F \leq J_o \quad \forall t \in T \tag{4.17}$$

$$0.7 \leq \frac{L_t^F + Lout_t^F}{L_o} \leq 1 \vee L_t^F + Lout_t^F = 0 \quad \forall t \in T \tag{4.18}$$

$$0 < J_t^F + Jin_t^F \leq P_t^H \quad \forall t \in T \tag{4.19}$$

Since Equation 4.18 is a disjunctive constraint that can increase computational demand, a binary variable γ_t was introduced to define this constraint, which is the only binary variable in this optimisation.

$$0.7\gamma_t \leq \frac{L_t^F + Lout_t^F}{L_o} \leq \gamma_t \quad \gamma_t \in \{0,1\} \quad \forall t \in T \tag{4.20}$$

Two adjacent equipment should have the same load ratio. Taking into account that for each equipment its throughput rate is linear to its electricity consumption rate, the equations can be written as:

$$\frac{J_t^F + Jout_t^F}{J_o} = \frac{L_t^F + Lin_t^F}{L_o} \quad \forall t \in T \tag{4.21}$$

$$\frac{L_t^F + Lout_t^F}{L_o} = \frac{X_t^F}{X_o} \quad \forall t \in T \tag{4.22}$$

Further, it was assumed that at t=1 the ST was full. Therefore, the cumulative quantity of the intermediate stream stored into or used from the ST at any time "t" should not exceed the maximum capacity of the ST "V_{ST}". The same rationale applied to the BESS.

$$-V_{ST} \leq \sum_{t=1}^{t} (Lin_t^F + Lout_t^F) \leq 0 \quad \forall t \in T \tag{4.23}$$

$$-V_{BESS} \leq \sum_{t=1}^{t} (Jin_t^F + Jout_t^F) \leq 0 \quad \forall t \in T \tag{4.24}$$

Moreover, filling "Lin_t^F" or draining "$Lout_t^F$" the ST could not occur simultaneously. The same applies to the BESS. Equations 4.25 and 4.26 exhibit nonlinearity. Usually, it can be avoided by introducing binary variables and combining them with the prefixed capacities of the buffering units [19]. However, the capacities of the BESS and ST were also variables in this context. Hence, the nonlinearity of Equations 4.25 and 4.26 was kept.

$$Lin_t^F Lout_t^F = 0 \quad \forall t \in T \tag{4.25}$$

$$Jin_t^F Jout_t^F = 0 \quad \forall t \in T \tag{4.26}$$

2.4.3. Cost functions

Equation 4.27 shows a general example of a cost function of storage tanks. Unlike "$CAPEX^{BESS}$", which is usually linear to the BESS capacity, "$CAPEX^{ST}$" presents a nonlinear relation to the size of the ST "V_{ST}" [29–31]. This eventually introduces a nonlinearity to the objective function. Therefore, underpinned by the results of the explorative case studies, the range of possible optimal sizes of ST could be narrowed down, and Equation 4.27 could be linearised to Equation 4.28. "α", "β", "λ", "η", "ω", and "ϵ" are constants; exact values can be found in Appendix B.

$$CAPEX^{ST} = \alpha(\beta + \lambda V_{ST}^{\eta}) \tag{4.27}$$

$$CAPEX^{ST} = \omega V_{ST} + \varepsilon \tag{4.28}$$

Moreover, for the "$OPEX^F$", as shown in the previous chapter [12], nonlinearities exist between the utility consumption and production rate of hexanoic acid because of the penalties in utility usage due to flexible operation. This non-linear relation would introduce another binary variable into the optimisation, enlarging the optimisation size and slowing down the calculation. Therefore, given that the penalties in utility consumption were negligible compared to the plant's total consumption, the utility cost was linearised to the production rate based on the plant's nominal conditions (see Equation 4.29).

$$OPEX^F = \left(E^A + F^A + WT^A + UT^A\right)\frac{\sum_{t\in T} X_t^F}{\sum_{t\in T} X_t^A} + O\&M^F \quad \forall t \in T \tag{4.29}$$

2.5 Carbon footprint accounting

2.5.1. Goal and scope definition

A cradle-to-gate system boundary was chosen. The global warming potential (GWP) was evaluated for Cases A, B (reference cases), and F (optimised case). Carbon emissions related to facility and infrastructure were neglected in this chapter, assuming that the capital goods only account for a small portion of carbon emissions [38].

2.5.2. Functional unit and allocation method

The functional unit selected was 1 tonne of hexanoic acid produced. As oxygen was also produced, and to be consistent with the techno-economic assessment, an economic allocation of emissions was used.

2.5.3. Product system

Fig. 4.3 depicts the product system. The foreground system comprises three activities: CO_2 capture, CO_2 transport and hexanoic acid production. The CO_2 capture activity was not simulated in this chapter. It was assumed that the MES plant was located in the Port of Rotterdam, which is the initiator of a CO_2 transport and storage project - Porthos. Additionally, the leading CO_2 emitter in the Porthos project is integrated oil refineries [39]. Hence, it was assumed that the CO_2 capture facility was placed at these emission points. CO_2 is separated from the post-combustion flue gas by chemical absorption using monoethylamine (MEA) [39]. Therefore, in the foreground system, the CO_2 capture activity consists of amine scrubbing, CO_2 compression, and waste treatment (non-recycled solvent and water). After CO_2 is purified and compressed at the emission points, CO_2 is transported using the CO_2 network in the Port of Rotterdam. It is assumed that the MES plant can source purified and compressed CO_2 on demand from the pipeline network. Emissions from pipeline transport of CO_2 were neglected. Moreover, it was assumed that the CO_2 conditions after transportation fulfilled MES unit requirements (i.e., no further CO_2 purification unit was needed in the plant) [40, 41].

The end use of the products and solid waste generated in the foreground system were outside the system boundaries of this study. The reason for making this assumption for the solid waste was that it is mainly $CaHPO_4$ and can be recycled and treated for biomedical applications [42]. Meanwhile, the background system consists of the production of the solvent, other chemicals, heating energy (incl. chilling), electricity, infrastructure, and transport. Note that emissions from the original source of CO_2 were not included, assuming that the carbon emissions incurred during the production of flue gas are 100% allocated to the target products of the oil refineries [43].

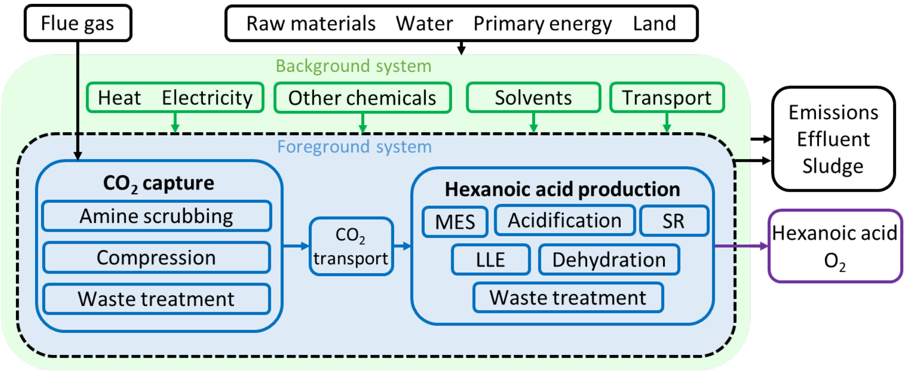

Fig. 4.3. Product system. MES: microbial electrosynthesis. SR: solvent regeneration. LLE: liquid-liquid extraction.

Process data of hexanoic production was taken from the resulting mass and energy balances of the Aspen process model. Process data of CO_2 capture was retrieved from [39, 44]. The emission data of the background system and elementary flows were retrieved from Ecoinvent [45] via SimaPro. Note that there is no data for $Ca(OH)_2$ and trioctylamine (TOA). Therefore, a similar chemical or solvent was used as an analogous. Complete process data and life cycle inventory data are presented in Appendix D.

2.6 Sensitivity analyses

In the economic sensitivity analysis, the influence of five parameters on the LPC_{C6A} was analysed for the optimised Case F, as listed in Table 4.2. A second sensitivity analysis was carried out to investigate the impact of the carbon intensity of the electricity grid and utility on the GWP in Cases A and F. It was assumed that the future electricity grid and utility would be defossilised by 90%. A third sensitivity analysis was done on the allocation method of GWP for Cases A, B and F. Mass allocation was applied.

Table. 4.2. Table showing different CAPEX values, selling price of hexanoic acid, and interest rate.

	Low	**High**
CAPEX of MES, $CAPEX^{MES}$ (M€)	×10%	×200%
CAPEX of LLE, $CAPEX^{LLE}$ (M€)	×10%	×200%
CAPEX of ST, $CAPEX^{ST}$ (M€)	×10%	×200%
Selling price of hexanoic acid, θ_{C6A} (€/kg)	-1	+1
Interest rate, r	-0.05	+0.05

3 Results and discussion

3.1 Reference cases

The annual production in Case A was 10 kt/y, and the resulting LPC_{C6A} was ca. 4.0 €/kg. In Case B (see Table 4.3), as no storage was deployed, the plant's volume flexibility remained as [70%, 100%]. As a result, the plant was shut down for 2678 hours. The drop in annual production was over 30%, and the LPC_{C6A} was penalised by 19%.

Table. 4.3. Results of Cases A to D. BESS: battery energy storage system. ST: storage tank. LPC_{C6A}: levelised production cost of hexanoic acid. EC_{ttl}: cumulative electricity consumption. EC_{spl}: surplus electricity consumption.

	A	B
LRR^k	-	[70%, 100%]
Production shutdown time per year (h/y)	0	2678
Hexanoic acid production (kt/y)	10.12	6.73
Levelised production cost of hexanoic acid LPC^k_{C6A} (€/kg)	3.96	4.70
	C (plant with a BESS)	D (plant with a ST)
Buffering capacity to fully eliminate shutdown	1666 GJ/h (=463 MW)	1964 m^3
Hexanoic acid production when no shutdown (kt/y)	8.43	8.02
LPC^k_{C6A} when no shutdown (€/kg)	21.10	4.74
minLPC^k_{C6A} (€/kg)	4.67	4.38
Sizes of buffering unit	12 GJ/h (=3.3 MW)	43 m^3
Production shutdown time (h/y)	1954	989
Hexanoic acid production (kt/y)	7.30	8.01
EC^k_{ttl} per annum	65%	72%
EC^k_{spl} per annum	<0.01%	-

3.2 Explorative case studies

3.2.1. Cases C and D

The key results are summarised in Table 4.3 and Fig. 4.4. In Case C, where a BESS was implemented, a capacity of 1666 GJ/h (=463 MW) was sufficient to manage the periods with electricity shortage (Case B), implying a LRR of [0%,100%] for the whole plant during a year. The resulting production of hexanoic acid was 8.43 kt/y. This corresponds to 83% of the amount produced in Case A. In Case D, where a ST was installed, a size of 1964 m^3 was necessary to enable production without shutting down the plant. The resulting production of hexanoic acid was 8.02 kt/y, 80% of the nominal production. The difference between 8.43 kt/y in Case C and 8.02 kt/y in Case D was caused by the fact that batteries can store surplus electricity to promote the overall production (electricity consumptions higher than the equivalent to 100% plant load) while storage tanks are limited by the 100% plant load. According to the LPC_{C6A} results, the plant with a ST was economically favoured even though it produced less hexanoic acid. This was due to the big difference in the CAPEX between a ST and a BESS.

Furthermore, compared to Case A (see Table 4.3), the LPC_{C6A} of Cases C and D were still considerably higher.

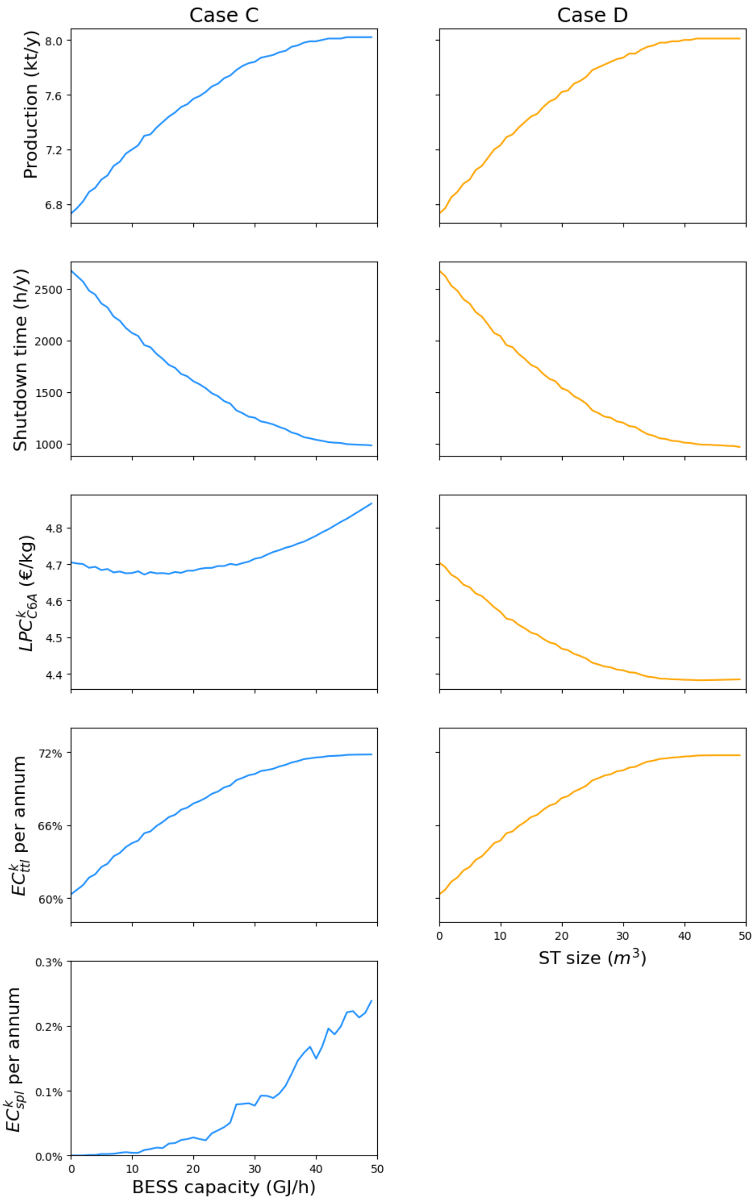

Fig. 4.4. Results of the MES plant with a BESS and a ST individually (i.e., Cases C and D, respectively) in production quantity of hexanoic acid, shutdown time, levelised production cost of hexanoic acid "LPC^k_{C6A}", total electricity consumption, "EC^k_{ttl}" per annum, and surplus electricity consumption "EC^k_{spl}" per annum.

The trends and values of annual production, annual shutdown hours, and cumulative electricity consumption per annum as the sizes of both buffering units increase were similar between Cases C and D (see Fig. 4.4). The increase or decrease of these three indicators plateaued when the size of buffering units was around 40 GJ/h (=11 MW) or 40 m^3, respectively. The plateaued production quantity was about 8 kt/y, 80% of the nominal production and close to the production generated when the shutdown time was fully eliminated. The annual shutdown hours were reduced from 2678 to nearly 1000. The total electricity consumption per annum reached nearly 72% of the total electricity available from the hybrid farms. In Case C, see Fig. 4.4, the lowest LPC^{C}_{C6A} achieved using a BESS was slightly lower than 4.7 €/kg, with a corresponding BESS capacity of 12 GJ/h. In contrast, in Case D, the lowest LPC^{D}_{C6A} achieved using a ST was 4.4 €/kg, with a corresponding ST volume of 43 m^3. It can be seen that, even when the installed capacity of BESS was 50 GJ/h, the value of surplus electricity consumption was less than 0.3%. This result showed that the BESS was hardly used for storing surplus electricity, which should have been its advantage over a ST.

It can be concluded that a ST was a less expensive and equally effective buffering choice over a BESS. With optimised scheduling, a ST should be used more efficiently to boost the production, the range of the variable "V_{ST}" in the optimisation problem being smaller than 43 m^3, as shown in Fig. 4.4.

3.2.2. Case E

Using the results in Case D as a starting point, Fig. 4.5 shows the extra production of hexanoic acid required to pay back the cost of the BESS installed when a ST of 43 m^3 was installed. It was clear in Fig. 4.5 that when such a ST was operated following the schemes explained in section 2.2.5, making the BESS larger would not generate enough extra production to pay back its capital cost. According to the resulting operating profile of the BESS, the BESS was charged for 694 hours and discharged for 716 hours in a year. For the rest of the time, the BESS was not used. This could be a particular result of the electricity profile selected in the Rotterdam area and the farms' size used in this case study, together with the size of the MES plant and BESS. Hence, in this context, the attempt to use BESS as much as possible to boost production failed; we could not equal 100% of the plant's load during the whole year.

3.3 Optimised case - Case F

Underpinned by the results of the explorative case studies, the optimisation problem focused on the sizing and scheduling of the use of the ST only, and the BESS-related components (i.e., "Jin^{F}_{t}", "$Jout^{F}_{t}$", and "V_{BESS}") were not considered in the optimisation.

The obtained optimal size of the storage tank was 35 m^3. The techno-economic results of the optimised case (i.e., Case F) are summarised in Table 4.4. Cases A, B, D-ST35 and D-ST43 were used for comparison. D-ST35 is the subcase of Case D when the ST is 35 m^3, while D-ST43 is another subcase of Case D when the ST is 43 m^3. The following paragraphs compare and discuss these cases per indicator.

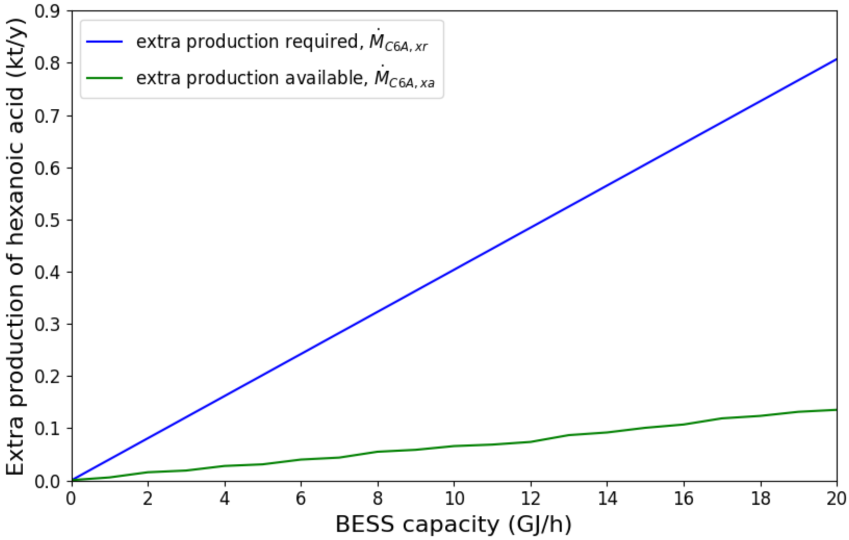

Fig. 4.5. Extra production of hexanoic acid required to pay back the annualised capital investment in BESS versus extra production of hexanoic acid available per GJ/h of BESS installed in addition to a ST of 43 m^3.

Table. 4.4. Comparison of cases. LRR: load ratio range. LPC_{C6A}: levelised production cost of hexanoic acid. EC_{ttl}: total electricity consumption.

	A	B	D-ST35	D-ST43	F
Shutdown time per year (h/y)	0	2678	1075	989	1135
Hexanoic acid production (kt/y)	10.12	6.73	7.96	8.01	8.00
LPC^k_{C6A} (€/kg)	3.96	4.70	4.39	4.38	4.37
LRR^k	-	[70%,100%]	[70%,100%]	[67%,100%]	[60%,100%]
EC^k_{ttl} per annum	100%	60.3%	63.8%	66.4%	66.0%

3.3.1. Shutdown time and production quantity

In Case F, the plant's production shutdown time was 1152 hours per year, which was more than halved upon Case B but still noticeably longer than in Case D-ST43 and especially Case D-ST35. However, the production quantity in Case F was slightly improved upon Case D-ST35. This result proved that, under the investigated conditions, longer production shutdown time does not necessarily lead to less product or revenue. This finding can be explained by Fig. 4.6 and electricity consumption conditions discussed in section 3.3.3. Fig. 4.6 is a snapshot of 24 hours showing the available electricity from the hybrid farms and how Cases D-ST35 and F consumed the electricity for hexanoic acid production. The Y-axis values for Cases D-ST35 and F represent the sum of available electricity directly from hybrid farms and "stored electric energy" consumed in that specific hour (i.e., corresponding x-axis value). What is different between the two cases was that, in Case F, the production was more often promoted as soon as possible instead of being kept at 70% of the nominal production rate.

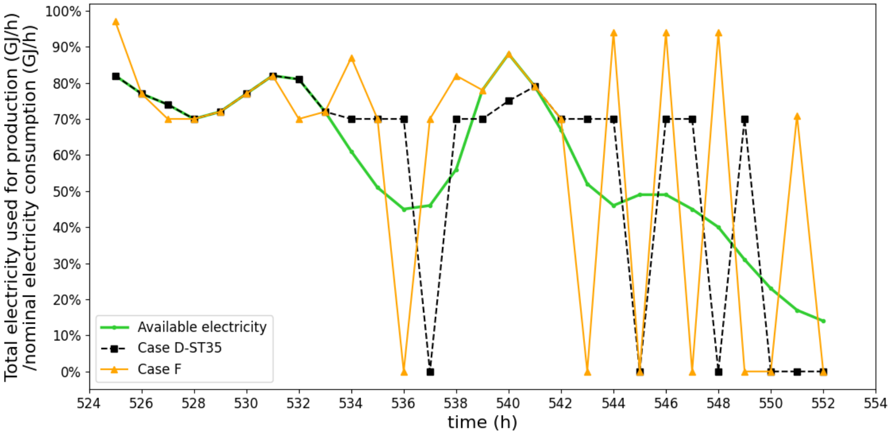

Fig. 4.6. Illustration of production promotion by the optimised scheduling. A snapshot of a day.

3.3.2. Load ratio range

Fig. 4.7a shows the results of coverage percentage - how frequently the plant can be operated while consuming all the electricity supplied by the hybrid farms and producing hexanoic acid when the power supply from the hybrid farms is below 70% of the plant's nominal electricity consumption rate. The red dashed line marks the lower boundary of LRR. Left to this line, the plant cannot always use all the electricity supplied while producing hexanoic acid at the same time. In Case F, when the electricity supplied from the hybrid farms was between 60% and 100% of the plant's nominal electricity consumption rate, the plant could always use all the electricity supplied while safely producing hexanoic acid that meets requirements. The lower boundary of the LRR for Case F was lower than for Cases D-ST35 and D-ST43. This was related to the steep slope in Case F when the electricity power was between 53% and 60% of the plant's nominal electricity consumption rate (see X-axis), and the coverage percentage dropped from 100% to 53% (see the left Y-axis). Given that in Fig. 4.7b, the electricity consumption conditions for the three cases were similar when electricity power was between 53% and 60% of the plant's nominal electricity consumption rate, the slope in Case F shown in Fig. 4.7a indicates that the plant shut down production more frequently than kept producing by using the intermediate chemicals stored in the ST. Such a slope was not found in either Cases D-ST35 or D-ST43, where the operating scheme was predetermined. This suggests that strategically shutting down production when facing larger shortages and bridging smaller shortages would enhance the volume flexibility of the plant.

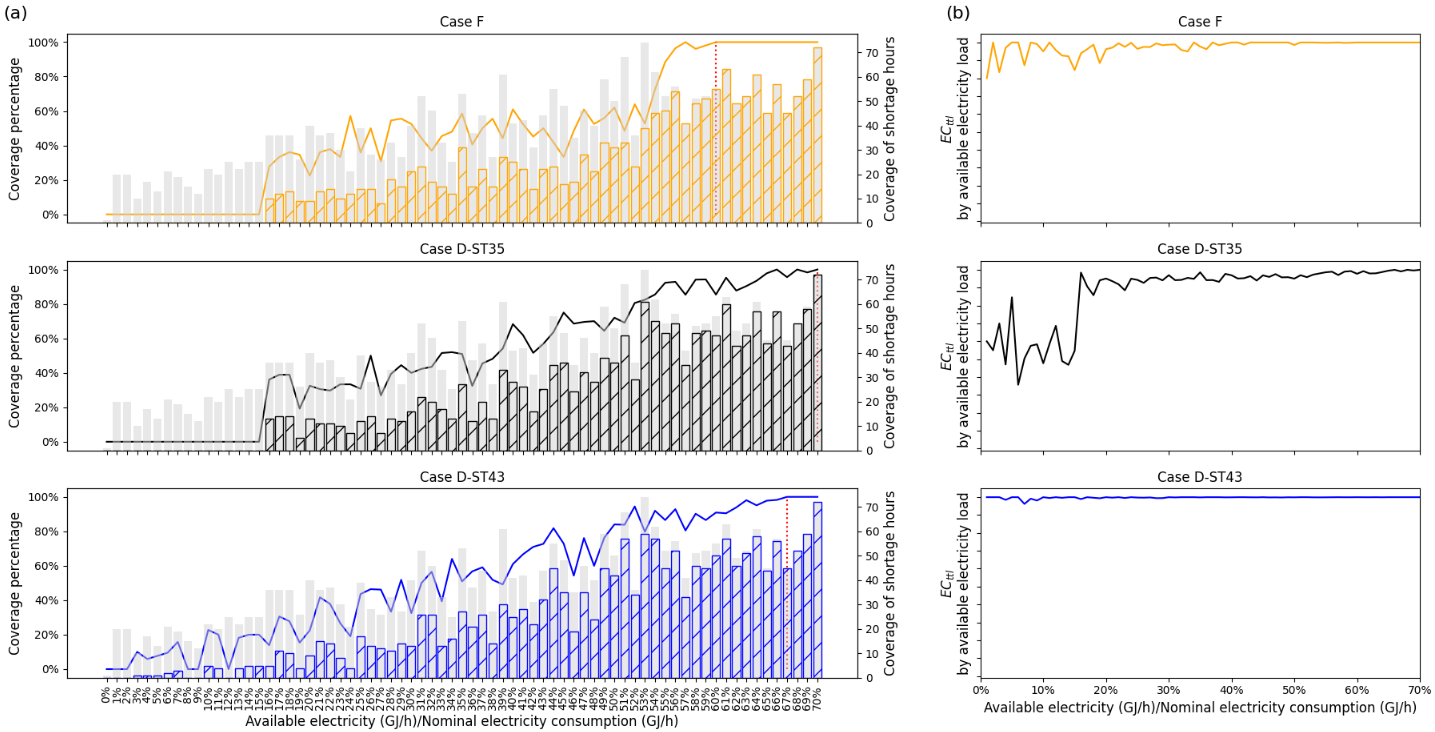

Fig. 4.7. (a) Coverage percentage at an electricity power generated by the hybrid farms over the nominal electricity consumption. Gray bars: number of hours in a year at an electricity power generated by the hybrid farms. Hatched bars: number of hours operated while meeting the expectations at an electricity power generated by the hybrid farms. Solid line: coverage percentage. Red dashed line: lower boundary of the LRR. (b) Total electricity consumption by an available electricity load generated by the hybrid farms.

3.3.3. Electricity consumption

In Case F, the total electricity consumption per annum was 66%. Compared to Case D-ST35, it was enhanced by 2.2%. Meanwhile, it was only 0.4% lower than in Case D-ST43, which is an insignificant decrease. Since the plant with a ST would never consume electricity beyond its nominal electricity load, the difference in total electricity consumption resulted from the consumption when the ratio of available electricity from the hybrid farms and nominal electricity consumption was below 70%. The total electricity consumption summed by different electricity loads below 70% is shown in Fig. 4.7b. It can be deduced that a smaller ST with better scheduling could perform reasonably well compared with a larger ST operating under a specific predefined operating scheme, which was an educated guess based on the results of volume flexibility of the reference case. Since the production quantity was highly associated with the electricity consumption conditions, the results here confirm the finding in section 3.3.1 that a longer production shutdown did not necessarily result in lower production.

3.3.4. Levelised production cost

The LPC^{F}_{C6A} is 4.4 €/kg, which is lower than in Case B but is higher than in Case A as well as the current market price of hexanoic acid (i.e., 2.5-4.2 €/kg [32]). Unexpectedly, the LPC^{F}_{C6A} is similar to the LPC^{D-ST43}_{C6A} and LPC^{D-ST35}_{C6A}. The reasons are the minor increment in production quantity and the moderate decrease in the storage tank size. The breakdown of LPC^{A}_{C6A}, LPC^{B}_{C6A}, and LPC^{F}_{C6A} is shown in Fig. 4.8a. When Cases B and F are compared with Case A, the total amount of capital cost-related items (i.e., CAPEX and O&M) increased while the total amount of operation-related items (i.e., the rest items) decreased. The trend was reversed when comparing Case F to Case B. This indicates that shifting from constant electricity supply to hybrid IRE leads to less output and, thus, less revenue and, eventually, a higher sunk cost in the capital items. Implementing a ST helped reduce the impact, though to a minor extent.

3.3.5. Carbon footprint

As can be seen in Fig. 4.8b, Cases B and F exhibit similar GWPs, around 5.3 t CO_2eq/t C6A, which indicates that the impact of linearisation of utility consumption on GWP is negligible. Moreover, Fig. 4.8b shows that the GWP of Case F was 2.8 times lower than that of Case A, which is credited to the coupling between the MES plant and hybrid IRE.

In all three cases, the CO_2 capture process led to an emission of 1.0 t CO_2eq/t C6A. Since the CO_2 used for hexanoic acid production as feedstock was 2.2 t CO_2/t C6A, the carbon intensity of capturing CO_2 is up to 0.4 t CO_2eq/t CO_2 captured. However, in Case A, the CO_2 capture process was only responsible for 7% of total emissions, while in Cases B and F, it constituted 19% of the total emissions as a result of the change in

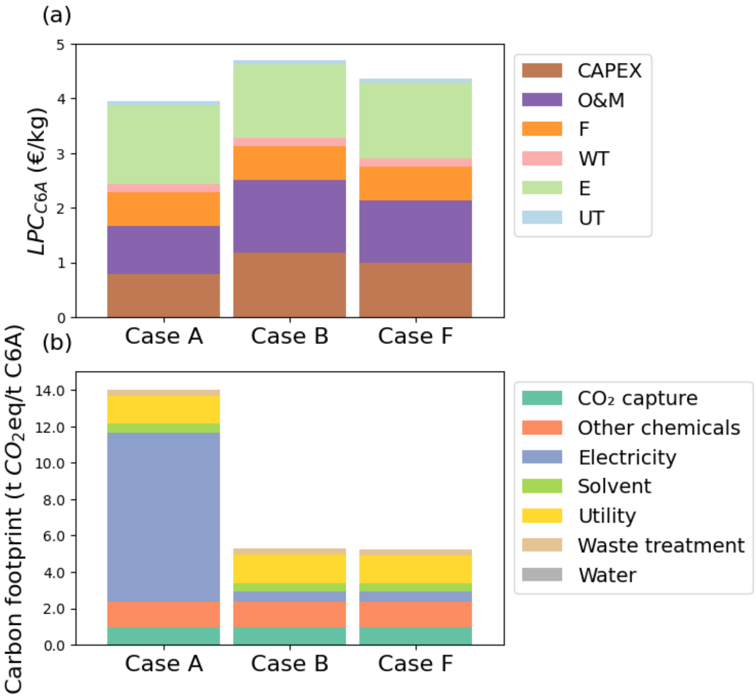

Fig. 4.8. (a) Breakdown of the levelised production cost of hexanoic acid in Cases A, B, and F. CAPEX: capital expenditure. O&M: operation and maintenance. F: feedstock. WT: waste treatment. E: electricity. UT: utility. (b) Carbon footprint and their breakdown for Cases A, B and F with an economic allocation.

electricity source. In Case A, the highest share of emissions was attributed to electricity generation, utilities' generation, and other chemicals' syntheses. In both Cases B and F, the three largest contributors were utilities generation, production of other chemicals, and electricity generation. This was due to the energy-intensive nature of the DSP and the use of fossil-based chemicals and solvents.

3.3.6. Sensitivity analyses

Economic

The results of the economic sensitivity analysis are shown in Fig. 4.9a. The impact of changes in parameters on LPC^{F}_{C6A} was almost linear to the changes in the variables, except for the $CAPEX^{MES}$ and θ_{C6A}. This is caused by the resulting positive operating income and consequent tax. $CAPEX^{MES}$ makes up for 50% of the CAPEX of all equipment. Therefore, lowering its cost not only reduced the initial capital expenditures of the plant but also the annual O&M. This, in turn, increased the annual operating income, which became positive. It was similar for the θ_{C6A}. The original θ_{C6A}

was not sufficient for the plant to make a positive operating income. As the selling price increased and thus the revenue increased, the plant's operating income turned positive. In both situations, the resulting operating income fell in the high-tax range in the Netherlands (see Appendix B for tax details). As a result, the operating costs increased, and the LPC^F_{C6A} became higher than expected. This change induced by tax did not occur to the $CAPEX^{LLE}$, because its decrease was not enough to enable a positive operating income.

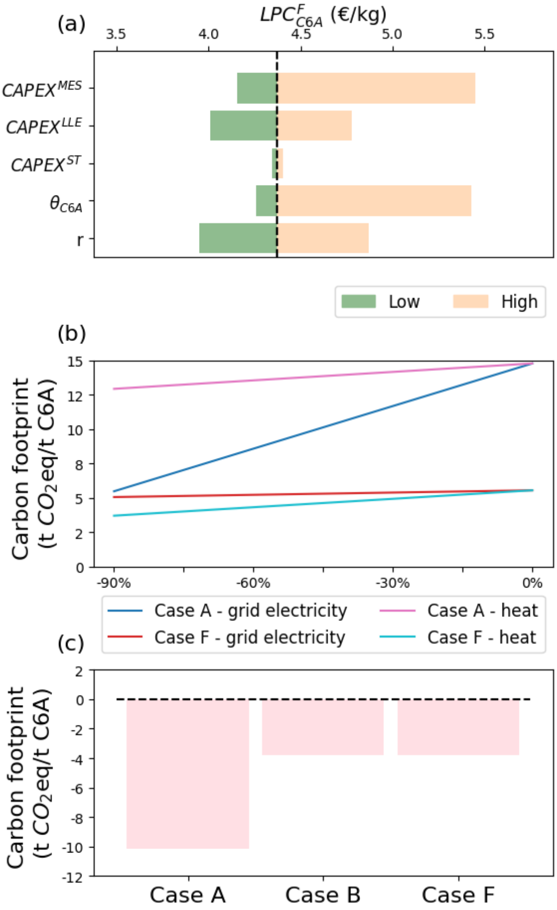

Fig. 4.9. (a) Results of the economic sensitivity analysis. $CAPEX^{MES}$: capital cost of the microbial electrosynthesis unit. $CAPEX^{LLE}$: capital cost of the liquid-liquid extraction units. $CAPEX^{ST}$: capital cost of the storage tanks. θ_{C6A}: selling price of hexanoic acid. r: interest rate. (b) Sensitivity analysis on the carbon intensity of grid electricity and utility (incl. chilling energy). (c) Change in carbon footprint from original results that used economic allocation versus using mass allocation.

Carbon footprint

The results of sensitivity analysis on the emission intensity of grid electricity and utility in Cases A and F are shown in Fig. 4.9b. Case A was more sensitive to the changes in emission intensity of grid electricity, while Case F was more sensitive to that of utility energy. In Case A, only grid electricity was supplied throughout the supply chain, which was the highest emitter. Hence, it makes sense that decarbonising the grid electricity posed a higher impact. In Case F, utility, which was generated from natural gas, emitted the most. Electricity consumed in the MES plant was already from renewables and thus provided less opportunity for further decarbonisation. Therefore, the observation from this sensitivity analysis, again, suggested that electricity should no longer be seen as a defossilising focus if further defossilisation is expected for a MES plant coupled with hybrid IRE.

Regarding allocation, using mass allocation instead of economic allocation lowered the GWP by two-thirds based on the GWP obtained with economic allocation (see Fig. 4.9c). In Case F, the GWP allocated to liquid oxygen would change from 0.3 t CO_2eq/t O_2 to 1.7 t CO_2eq/t O_2. Note that the current GWP per tonne of liquid oxygen generated by an air separation unit in Europe is around 0.6 t CO_2eq/t O_2 [45]. Usually, with mass allocation, the technical improvement of the technologies or processes that lead to an increased mass ratio of the main products is more visible [46]. Nonetheless, in the MES plant, the mass ratio between hexanoic acid and oxygen always remains the same. Therefore, this advantage of mass allocation does not apply in this context. On the other hand, mass allocation is more reliable when the market price of the (by)products changes over time [46]. Therefore, the employment of mass allocation will be sensible if the amount of oxygen produced via MES becomes much more indispensable in the market or the prices of the two products become more volatile over time.

4 Conclusion

This chapter has investigated how intermittency affects the sizing of the buffering units and scheduling of a novel MES plant designed to produce 10 kt/y at continuous and full load and what the trade-offs are in terms of economic performance and carbon emissions. Firstly, explorative case studies were conducted to simplify the optimisation problem. Then, a MIQCP problem was proposed to optimise the scheduling profiles and the size of a ST, seeking the maximum ANP_{C6A}. Last, techno-economic and environmental performances of the optimised case, compared to relevant explorative case studies, were assessed.

Concluding from the explorative studies, a ST was found to be more economical than a BESS to buffer fluctuations in available electricity from the hybrid farms when the load was between 0 and 100% of the plant's nominal consumption rate. A BESS had a limited advantage in consuming surplus electricity when the available electricity supply from the hybrid farms was over 100% of the MES's plant nominal capacity. Additionally, the deployment of BESS had a high impact on the CAPEX of the plant when its capacity was larger than 12 GJ/h (=3.3 MW). Hence, a ST was in a better position to foster the economic potential of the MES plant. With the help of a ST of 43 m^3, available electricity that was below 100% of the plant's nominal consumption rate could be nearly completely used by the MES plant while the levelised production cost of hexanoic acid was lowered compared to the ST-free case. As a result, this chapter only considered the ST in the optimisation. The resulted optimal size of the ST was 35 m^3.

When compared to the case where the operating scheme of the ST was predefined, the optimal scheduling profile suggested 1) the plant stops producing hexanoic acid and store the intermediate chemicals when the available electricity from the hybrid farms was below 60% of the plant's nominal electricity consumption and 2) the intermediate chemicals stored to promote production should be used as soon as possible. This practice also enhanced the volume flexibility, expanding the load ratio range from [70%, 100%] to [60%, 100%]. However, the levelised production cost was not significantly reduced because both the reduction in CAPEX and increase in revenue were marginal.

Even with an optimal size of ST and an optimal scheduling profile, the MES plant powered with the selected hybrid IRE was less economically viable compared to the case when it was powered by constant grid electricity. From an environmental point of view, the MES plant running on the hybrid IRE outperformed the MES plant on constant grid electricity. The cradle-to-gate carbon emissions became 2.8 times lower, as the substantial amount of electricity the MES demanded was replaced by hybrid renewable IRE. The results show that using grid electricity is not an option unless it is further decarbonised. Moreover, the impact of penalties on energy consumption induced by flexible operation was minor.

The results also show that in the MES plant powered by hybrid IRE, utility energy, solvent and other chemicals were the major CO_2 emitters. To further defossilise the MES-based system, utilities, solvents, and other chemicals would need to be produced from non-fossil sources.

As for limitations, this study did not include ramping, starting-up, and shutting-down procedures, and the assumed charging and discharging rates of the BESS were highly optimistic. Taking these factors into account may affect the results for the BESS because the stored electricity could possibly be used to prevent the plant from being completely shut down. The low potential for BESS was also compounded by the fact that the electricity profile and pricing scheme were highly specific, though reasonable. Perhaps the advantage of BESS would be more visible under other pricing schemes [19] or electricity profiles with a more alternating pattern. To enable a more efficient optimisation, the nonlinearities could be linearised to avoid the large memory demand. Given the low technology readiness level of the technology, many hypotheses were considered in the plant modelling. As the technology advances, the proposed model of the MES unit and the plant should be updated, also to incorporate operation under a variable electricity profile; validation of operation under IRE in a lab or pilot plant setup would be needed. Moreover, with the possibility to scale up the global market of hexanoic acid due to future applications such as blends for sustainable aviation fuels [47], it is important to investigate the environmental burdens of the full value chain. A comprehensive life cycle assessment should be performed to understand the environmental performances from a broader perspective.

References

[1] O. Osman, S. Sgouridis, and A. Sleptchenko. “Scaling the production of renewable ammonia: A techno-economic optimization applied in regions with high insolation”. Journal of Cleaner Production. 271. 2020. P. 121627. DOI: `10.1016/j.jclepro.2020.121627`.

[2] C. Breyer et al. “On the role of solar photovoltaics in global energy transition scenarios”. Progress in Photovoltaics. 258. 2017. Pp. 727–745. DOI: `10.1002/pip.2885`.

[3] A. Prevoteau, J. M. Carvajal-Arroyo, R. Ganigue, and K. Rabaey. “Microbial electrosynthesis from CO_2: forever a promise?” Current Opinion in Biotechnology. 62. 2020. Pp. 48–57. DOI: `10.1016/j.copbio.2019.08.014`.

[4] L. Jourdin et al. “High Acetic Acid Production Rate Obtained by Microbial Electrosynthesis from Carbon Dioxide”. Environmental Science & Technology. 4922. 2015. Pp. 13566–74. DOI: `10.1021/acs.est.5b03821`.

[5] E. C. Canapi, Y. T. V. Agustin, E. A. Moro, E. Pedrosa, and M. L. J. Bendano. “Coconut Oil”. Bailey’s Industrial Oil and Fat Products. F. Shahidi. Vol. 1-6. 2005. John Wiley & Sons. Chap. Coconut Oil. Pp. 123–147. DOI: `10.1002/047167849X`.

[6] Y. Basiron. “Palm oil”. Bailey’s Industrial Oil and Fat Products. F. Shahidi. Vol. 1-6. 2005. John Wiley & Sons. Chap. 2.8 Palm Oil.

[7] M. Jouny, W. Luc, and F. Jiao. “General Techno-Economic Analysis of CO Electrolysis Systems”. Industrial & Engineering Chemistry Research. 576. 2018. Pp. 2165–2177. DOI: `10.1021/acs.iecr.7b03514`.

[8] J. B. Greenblatt, D. J. Miller, J. W. Ager, F. A. Houle, and I. D. Sharp. “The Technical and Energetic Challenges of Separating (Photo)Electrochemical Carbon Dioxide Reduction Products”. Joule. 23. 2018. Pp. 381–420. DOI: `10.1016/j.joule.2018.01.014`.

[9] N. Savla et al. “Techno-economical evaluation and life cycle assessment of microbial electrochemical systems: A review”. Current Research in Green and Sustainable Chemistry. 4. 2021. P. 100111. DOI: `10.1016/j.crgsc.2021.100111`.

[10] P. A. Hernandez et al. “Selective Extraction of Medium-Chain Carboxylic Acids by Electrodialysis and Phase Separation”. ACS Omega. 611. 2021. Pp. 7841–7850. DOI: `10.1021/acsomega.1c00397`.

[11] L. T. Angenent et al. “Chain Elongation with Reactor Microbiomes: Open-Culture Biotechnology To Produce Biochemicals”. Environmental Science & Technology. 506. 2016. Pp. 2796–810. DOI: `10.1021/acs.est.5b04847`.

[12] J. Luo, M. Perez-Fortes, P. Ibarra-Gonzalez, A. J. J. Straathof, and A. Ramirez. “Impact of intermittent electricity supply on a conceptual process design for microbial conversion of CO_2 into hexanoic acid”. Chemical Engineering Research and Design. 205. 2024. Pp. 364–375. DOI: `10.1016/j.cherd.2024.04.005`.

[13] J. Luo, J. Moncada, and A. Ramirez. “Development of a Conceptual Framework for Evaluating the Flexibility of Future Chemical Processes”. Industrial & Engineering Chemistry Research. 619. 2022. Pp. 3219–3232. DOI: `10.1021/acs.iecr.1c03874`.

[14] L. S. Layritz et al. “The potential of direct steam cracker electrification and carbon capture & utilization via oxidative coupling of methane as decarbonization strategies for ethylene production”. Applied Energy. 296. 2021. P. 117049. DOI: `10.1016/j.apenergy.2021.117049`.

[15] E. Moioli, A. Wotzel, and T. Schildhauer. “Feasibility assessment of small-scale methanol production via power-to-X”. Journal of Cleaner Production. 359. 2022. P. 132071. DOI: `10.1016/j.jclepro.2022.132071`.

[16] M. Qi, J. Park, R. S. Landon, J. Kim, Y. Liu, and I. Moon. “Continuous and flexible Renewable-Power-to-Methane via liquid CO_2 energy storage: Revisiting the techno-economic potential”. Renewable and Sustainable Energy Reviews. 153. 2022. P. 111732. DOI: `10.1016/j.rser.2021.111732`.

[17] F. Salomone, E. Giglio, D. Ferrero, M. Santarelli, R. Pirone, and S. Bensaid. “Techno-economic modelling of a Power-to-Gas system based on SOEC electrolysis and CO methanation in a RES-based electric grid”. Chemical Engineering Journal. 377. 2019. P. 120233. DOI: `10.1016/j.cej.2018.10.170`.

[18] M. Van Dael et al. “Techno-economic assessment of a microbial power-to-gas plant - Case study in Belgium”. Applied Energy. 215. 2018. Pp. 416–425. DOI: `10.1016/j.apenergy.2018.01.092`.

[19] L. C. Bree et al. “Techno-Economic Comparison of Flexibility Options in Chlorine Production”. Industrial & Engineering Chemistry Research. 5926. 2020. Pp. 12186–12196. DOI: `10.1021/acs.iecr.0c01775`.

[20] A. P. Barbosa-Povoa and S. Macchietto. “Detailed design of multipurpose batch plants”. Computers & Chemical Engineering. 1811-12. 1994. Pp. 1013–1042. DOI: `10.1016/0098-1354(94)e0015-f`.

[21] T. V. Thomaidis and E. N. Pistikopoulos. “Optimal-Design of Flexible and Reliable Process Systems”. Ieee Transactions on Reliability. 442. 1995. Pp. 243–250. DOI: `10.1109/24.387378`.

[22] S. Schulte Beerbuhl, M. Frohling, and F. Schultmann. “Combined scheduling and capacity planning of electricity-based ammonia production to integrate renewable energies”. European Journal of Operational Research. 2413. 2015. Pp. 851–862. DOI: `10.1016/j.ejor.2014.08.039`.

[23] Q. Zhang, M. Martin, and I. E. Grossmann. “Integrated design and operation of renewables-based fuels and power production networks”. Computers & Chemical Engineering. 122. 2019. Pp. 80–92. DOI: `10.1016/j.compchemeng.2018.06.018`.

[24] A. Sanchez and M. Martin. “Optimal renewable production of ammonia from water and air”. Journal of Cleaner Production. 178. 2018. Pp. 325–342. DOI: `10.1016/j.jclepro.2017.12.279`.

[25] C. Varela, M. Mostafa, and E. Zondervan. “Modeling alkaline water electrolysis for power-to-x applications: A scheduling approach”. International Journal of Hydrogen Energy. 4614. 2021. Pp. 9303–9313. DOI: `10.1016/j.ijhydene.2020.12.111`.

[26] H. Teichgraeber and A. R. Brandt. “Optimal design of an electricity-intensive industrial facility subject to electricity price uncertainty: Stochastic optimization and scenario reduction”. Chemical Engineering Research & Design. 163. 2020. Pp. 204–216. DOI: `10.1016/j.cherd.2020.08.022`.

[27] A. Huesman. “Integration of operation and design of solar fuel plants: A carbon dioxide to methanol case study”. Computers & Chemical Engineering. 140. 2020. P. 106836. DOI: `10.1016/j.compchemeng.2020.106836`.

[28] Statista. 2022. Prices of electricity for non-household consumers in the Netherlands. URL: `https://www.statista.com/statistics/596254/electricity-industry-price-netherlands/#:~:text=The%5C%2010.51%5C%20euro%5C%20cents%5C%20per,towards%5C%20the%5C%20middle%5C%2Drange%5C%20of`. (Access date: 11 Nov 2022).

[29] G. Towler and R. Sinnott. Chemical engineering design: principles, practice and economics of plant and process design. 2nd. Amsterdam: Butterworth-Heinemann, 2021.

[30] S. P. Max, D. T. Klaus, and E. W. Ronald. Plant design and economics for chemical engineers. 5th. Boston: McGraw-Hill Companies, 2003.

[31] W. Sieder, J. Seader, and D. Lewin. Product and process design principles. 3rd. USA: John Wiley & Sons, 2004.

[32] P. Dessi et al. "Microbial electrosynthesis: Towards sustainable biorefineries for production of green chemicals from CO_2 emissions". Biotechnology Advances. 46. 2021. P. 107675. DOI: `10.1016/j.biotechadv.2020.107675`.

[33] Intratec. 2022. Oxygen Price | Current and Forecast. URL: `https://www.intratec.us/chemical-markets/oxygen-price`. (Access date: 20 Sept 2022).

[34] W. E. Hart, J. P. Watson, and D. L. Woodruff. "Pyomo: modeling and solving mathematical programs in Python". Mathematical Programming Computation. 33. 2011. Pp. 219–260. DOI: `10.1007/s12532-011-0026-8`.

[35] M. L. Bynum et al. Pyomo-Optimization Modeling in Python. Third. Vol. 67. Springer Optimization and Its Applications. Springer, 2021. DOI: `10.1007/978-3-030-68928-5`.

[36] Gurobi Optimization. Gurobi Optimizer Reference Manual. 2023. URL: `https://www.gurobi.com`.

[37] DHPC. DelftBlue Supercomputer (Phase 1). 2022. URL: `https://www.tudelft.nl/dhpc/ark:/44463/DelftBluePhase1`.

[38] M. Z. Hauschild, R. K. Rosenbaum, and S. I. Olsen. Life Cycle Assessment. Switzerland: Springer, 2018. DOI: `10.1007/978-3-319-56475-3`.

[39] IEAGHG. Understanding the Cost of Retrofitting CO_2 capture in an Integrated Oil Refinery. IEAGHG, 2017. URL: `http://documents.ieaghg.org/index.php/s/2cCda5q0bnYhsvo`.

[40] L. Jourdin and J. Luo. Personal cummunication. 2023.

[41] Porthos. 2021. Porthos CO_2 specifications. URL: `https://www.porthosco2.nl/wp-content/uploads/2021/09/CO2-specifications.pdf`. (Access date: 05 Jan 2023).

[42] F. Tamimi, Z. Sheikh, and J. Barralet. "Dicalcium phosphate cements: brushite and monetite". Acta Biomater. 82. 2012. Pp. 474–87. DOI: `10.1016/j.actbio.2011.08.005`.

[43] European Commission. LCA4CCU-Guidelines for life cycle assessment of carbon capture and utilisation. European Commission, 2020. DOI: `10.2833/161308`.

[44] IEAGHG. Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS. IEAGHG, 2017. URL: `https://ieaghg.org/component/content/article/49-publications/technical-reports/784-2017-02-smr-based-h2-plant-with-ccs`.

[45] G. Wernet, C. Bauer, B. Steubing, J. Reinhard, E. Moreno-Ruiz, and B. Weidema. "The ecoinvent database version 3 (part I): overview and methodology". International Journal of Life Cycle Assessment. 219. 2016. Pp. 1218–1230. DOI: `10.1007/s11367-016-1087-8`.

[46] S. H. Pishgar-Komleh and T. Vellinga. Evaluation of allocation methods in beef and pork production at slaughterhouse level. Wageningen Livestock Research, 2022. DOI: `10.18174/576774`.

[47] U.S. Department of Energy. Sustainable Aviation Fuel: Review of Technical Pathways. U.S. Department of Energy, 2020. DOI: `10.2172/1660415`.

5

Life cycle assessment of hexanoic acid production via microbial electrosynthesis and renewable electricity: Future opportunities

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This chapter is based on a manuscript that has been submitted to a journal.

Abstract

Microbial electrosynthesis (MES) is a novel carbon utilisation technology aiming to contribute to a circular economy by converting CO_2 and renewable electricity into value-added chemicals. This chapter presents a life cycle assessment of hexanoic acid (C6A) production via MES for current uses as a food additive, precursor to lubricant, and antimicrobial in pharmaceuticals and for future upgrading to a potential neat sustainable aviation fuel (SAF). On a cradle-to-gate basis, MES-based C6A exhibits a carbon footprint at 5.5 t CO_2eq/t C6A, similar to fermentation- and plant-based C6A. However, its direct land use is more than one order of magnitude lower than plant-based C6A. On a cradle-to-grave basis, MES-based neat SAF emits 325 g CO_2eq/MJ neat SAF, which is significantly higher than the counterparts from currently certified routes and conventional petroleum-derived jet fuel. However, its negligible indirect land use change emissions might potentially make it competitive against neat SAFs originating from first-generation biomass.

1 Introduction

Direct electrochemical conversion of CO_2 to chemicals powered by renewable electricity can play a key role in the energy transition in the chemical sector. Some studies have investigated the environmental impacts of small-molecule products, which are usually commodity chemicals with a low market price, such as chlorine [1], methane, ethanol, and ethylene [2]. Insight into the potential for converting CO_2 to larger molecules is currently limited. In recent years, the conversion of CO_2 to carboxylic acids (e.g., propionic acid, butyric acid, valeric acid, and hexanoic acid [3]) with a longer carbon chain via microbial electrosynthesis (MES) has caught the attention of researchers [4, 5]. These chemicals do not only have a higher economic value as compared to shorter C-chain chemicals but can also be used as a platform chemical and for synthesising fuels [6, 7]. Among the carboxylic acids that MES can produce, hexanoic acid (C6A), also known as caproic acid, has the highest market price between 2.5-4.2 €/kg [8] and is used, among others, as a food additive, precursor to lubricants, and antimicrobial in pharmaceuticals [9]. Therefore, some researchers are particularly interested in producing C6A from CO_2 via either MES [8] or biofermentation [10]. Production of C6A from CO_2 through MES has three key advantages:

I. MES can be driven by renewable electricity and converts CO_2 into a valuable product, thereby fitting with the need to defossilise chemical production [11, 12].

II. C6A can be catalytically upgraded to n-alkanes via ketonisation and subsequent hydrodeoxygenation [13, 14]. On average, n-alkanes make up about 20 wt% of current Jet A fuel [15, 16]. Synthetic n-alkanes can be potentially blended with petroleum-derived jet fuel to a maximum of 50 vol% [15, 17], denoted as neat sustainable aviation fuel (SAF) [18] or neat synthetic kerosene [19]. SAFs are an essential option for defossilising jet fuels, with a market size estimated at 230 billion gallons (equivalent to 870 million m^3) in 2050 [15, 20]. The ideal carbon chain length for aviation fuels is between 8 and 16 [15, 21], with an average carbon number of 11.4 [13, 14]. The ketonisation has experimentally converted 98 wt% of C6A to C_8-C_{16} n-alkanes [14], with an average carbon chain length of 11 [14] or 11.3 [13]. These characteristics could potentially qualify n-alkanes from C6A as a neat SAF. Adoption of the ketonisation route for neat SAF would, however, require a massive increase in C6A production. As a reference, C6A is projected to reach a global market of ca. 100 kt/y in 2027 [22] (see Appendix D for details).

III. The current commercial production method of C6A is the fractional distillation of coconut or palm kernel oil [9] where C6A is a by-product accounting for less than 1 wt% of the products. Hence, it is subject to limited resources [6] (e.g., exporting bans on plant oils as recently occurred in Indonesia) and sustainability concerns [23].

The sustainability of hexanoic acid will play an important role in its further use in new markets. In chapter 3, we designed a process model for MES-based C6A in Aspen Plus and assessed its techno-economic performance integrated with an intermittent source of electricity [24].

To date, there is limited information on the potential environmental impact of C6A production via MES. Sadhukhan, Gadkari, and Muazu [3] evaluated the global warming potential of the production of a range of carboxylic acids (incl. C6A) at an equipment level, the results of which are directly visualised at `https://tesarrec.web.app/sustainability/mes`. In [25], the authors carried out a carbon footprint of C6A from fermentation at a plant level, however, within a gate-to-gate scope. This chapter aims to provide a better understanding of the environmental footprint of producing C6A via MES to supply the current market and as a potential feedstock for neat SAF.

2 Methodology

To identify and assess the potential environmental impacts, a life cycle assessment (LCA) was conducted, assuming two future deployment scenarios for C6A. The details are further explained in this section.

2.1 Production of hexanoic acid

Fig. 5.1 provides an overview of the production of C6A via MES. In the anode chamber of the MES reactor, water is converted into H^+ and O_2. O_2 leaves the reactor via the headspace, while H^+ permeates the membrane to reach the cathode chamber. In there, CO_2 is fed as a carbon source while $Ca(OH)_2$ is dosed to control the pH. Microbial cells attached to the cathode convert the CO_2 with electrons and H^+ to produce aqueous hexanoate via acetate and butyrate. After the MES unit, the hexanoate is acidified to C6A by H_3PO_4. Next, C6A is recovered by liquid-liquid extraction (LLE) using trioctylamine (TOA), followed by solvent regeneration (SR). Finally, the stream is dehydrated to reach the market purity requirement of 99 wt%.

In this chapter, we depart from a process model of C6A production via MES developed in chapter 3 [24]. A nominal capacity of 10 kt/y of purified C6A was assumed. According to the reaction stoichiometry, O_2 was produced as a by-product at about 22 kt/y, and it was compressed to 80 bar. The plant was designed for continuous operation (8760 h/y). It is assumed to be situated in the Port of Rotterdam (the Netherlands) and powered by renewable electricity from dedicated wind and solar farms nearby (see Appendix D for additional information). To reduce the impact of fluctuations, a storage tank (ST) was used as a buffer. The ST was placed before the first solvent regeneration column (see Fig. 5.1). In chapter 4 [26], the tank's size and the scheduling of the entire plant were optimised to reach a maximum annualised net profit under the pre-selected hybrid renewable electricity profile on an hourly basis. This resulted in an ST size of 35 m^3, which allows to produce ca. 8 kt of C6A per year. Specifications of the MES reactor and heat and mass balances of the plant are summarised in Appendix B and Appendix D, respectively.

Two scenarios were studied to understand the potential environmental impacts of MES-based C6A:

- Scenario I: MES-C6A would fulfil the market demand of current applications.
- Scenario II: MES-C6A would be used to produce neat SAF, which is a potential new application.

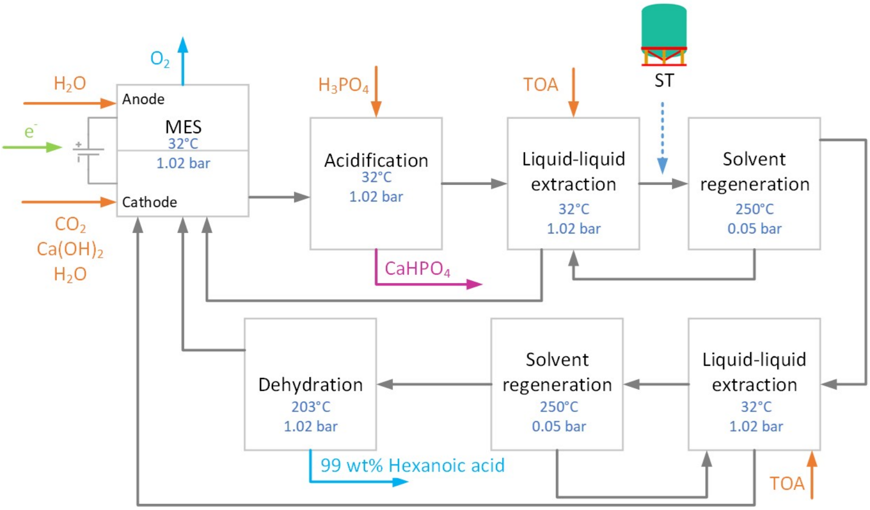

Fig. 5.1. Simplified block flow diagram of producing hexanoic acid via microbial electrosynthesis (MES). ST: storage tank. TOA: trioctylamine.

2.2 Life cycle assessment

An ex-ante LCA was performed for a hypothetical Nth-of-a-kind plant, following ISO 14044 [27]. We used SimaPro 9.6 and the databases Ecoinvent 3.8 [28] and Agri-footprint 5.0 [29]. The method selected for the life cycle impact assessment (LCIA) was ReCiPe Midpoint H. The environmental impacts from infrastructure were not included in this study as their contribution is expected to be marginal [30].

As indicated in Fig. 5.1, the plant produces both hexanoic acid and oxygen, with the amount of oxygen being twice that of hexanoic acid. The multifunctionality due to O$_2$ co-production was treated in two ways: 1) economic allocation and 2) system expansion with substitution in the manner of subtraction (referred to as substitution hereafter).

2.2.1. Scenario I

2.2.1.1 System boundary

In this scenario, the MES-based C6A would displace the counterfactual C6A, and it is assumed to have the same product functionality (same chemical composition), the system boundary was set as cradle-to-gate. The foreground system focuses on the activities that are specific to this study and includes CO_2 capture (solvent used: monoethanolamine-MEA), CO_2 transport, and C6A production, as shown in Fig. 5.2. The source of CO_2 is assumed to be the flue gas of a point source. The flue gas is therefore considered a waste stream, and therefore, following ISO guidelines, 100% of resources and emissions are allocated to the products of the point source [31]. This implies that the emissions allocated to the systems are only those of the CO_2 capture unit. The background system includes heat, chilling, and electricity generation, solvents and other chemicals production, and transportation, as outlined in Fig. 5.2.

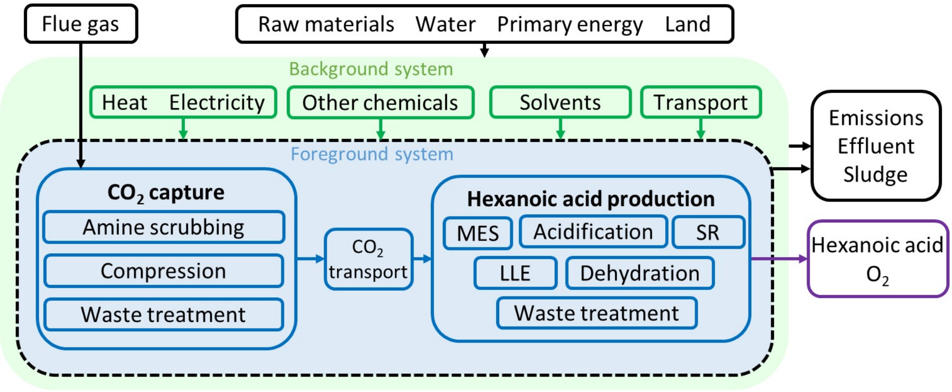

Fig. 5.2. System boundary of MES-based hexanoic acid in Scenario I. MES: microbial electrosynthesis. SR: solvent generation. LLE: liquid-liquid extraction.

2.2.1.2 Functional unit and indicators

The selected functional unit was one tonne of produced C6A. In this scenario, three impact categories are addressed. Since MES is a carbon utilisation technology, global warming potential (GWP; t CO_2eq/t C6A) was selected as the first indicator. The second indicator was land use change (LUC; m^2a crop eq/t C6A) because it is a key bottleneck for the current production pathway, and the MES plant requires dedicated solar and wind farms, which can require a significant amount of land for their installation. LUC can be decomposed into direct land use change (dLUC) and indirect land use change (iLUC). dLUC occurs when cropland is converted for production or service [32]. iLUC happens when changes in the use of existing cropland for production or service would result in those goods or services (e.g., food) being produced on another (crop)land [33]. Although iLUC emissions (t CO_2eq/t C6A) are important, there is a lack of data due to the challenges in quantification. Hence, they are not incorporated into the GWP calculation in SimaPro but are discussed separately in this study. Direct land occupation decoupled from the time factor (DLO; m^2) was estimated for the renewable electricity farms and the MES plant based on their capacities. Finally, water consumption (m^3/t C6A) was included as it is a key reactant for the MES and is also used as a cooling utility (i.e., make-up cooling water), and it is a key concern for plant-based C6A production. Water consumption refers to "freshwater withdrawals which are evaporated, incorporated into products and waste, transferred to different watersheds, or disposed into the land or sea after usage" [34].

2.2.1.3 Reference system and comparison to other studies

For the reference system, a coconut oil production route was selected. the system boundary is depicted in Fig. 5.3. In the foreground system are crude coconut oil (CCO) production, CCO transport, and C6A production. the CCO was assumed to be imported from Southeast Asia to Europe to produce C6A. Data obtained from Ecoinvent was used for these activities. As C6A is a by-product in the CCO route (accounting for less than 1 wt%), the emissions were allocated between C6A and other fatty acids using economic allocation.

As mentioned in section 2.1, the MES system also produces oxygen as a by-product. In the reference system, it was assumed that O_2 is produced using an air separation unit (ASU). The data was obtained from Ecoinvent and was used for substitution.

Finally, for comparison purposes, GWP data for fermentation-based hexanoic acid produced from waste, an alternative production route, was gathered from [25], and the DLO of the pilot plant based on this fermentation route was used for discussion (`http://www.chaincraft.nl/`).

2.2.1.4 Life cycle inventory

Life cycle inventories (LCI) of the MES and coconut routes are provided in Appendix D. For the MES route, except for the electricity used to directly power the MES plant (scope 1), emissions from other utilities were accounted for in scope 2 and based on natural gas. The electricity used to regenerate cooling water belonged to scope 2 utilities and was also assumed to have originated from natural gas. From here onward, electricity refers to electricity consumed on site; utilities refer to the rest scope 2 utilities. For the reference coconut route, utilities were from a mix of fossil and non-fossil fuels, as reported in Ecoinvent. Although it can be expected that in the future, the background systems will entirely rely on renewable sources, we decided to keep the background system as of today to better explore the impact of changes in the foreground versus the background system.

Regarding solvents (i.e., MEA and TOA) and other chemicals (i.e., $Ca(OH)_2$ and H_3PO_4), since TOA and $Ca(OH)_2$ were not available in Ecoinvent, analogous compounds (i.e., triethylamine and $Al(OH)_3$, respectively) were used in the LCI.

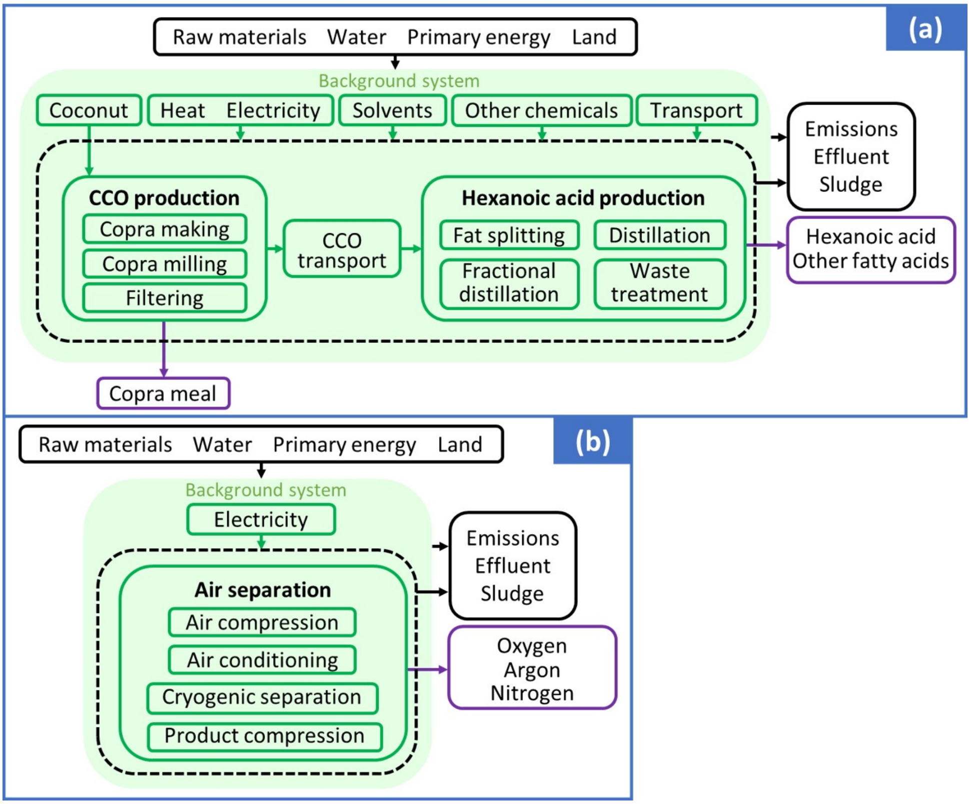

Fig. 5.3. System boundary of the reference system: (a) coconut-based hexanoic acid; (b) O_2 from an air separation unit. CCO: crude coconut oil.

2.2.1.5 Sensitivity analysis

To assess the impacts of changes in the background system, for the MES route, the impact of the carbon footprint from utilities on the GWP per functional unit was assessed via one-at-a-time sensitivity analyses.

In addition, since coconut is used in the reference system, we compared the relevant data in two different databases: Ecoinvent 3.8 and Agri-footprint 5.0. We could not directly compare the environmental metrics for hexanoic acid between these two databases owing to the lack of any fatty acid data in Agri-footprint. Thus, we used the impacts allocated to CCO production for comparison and analysed between both databases.

2.2.2. Scenario II

2.2.2.1 System boundary

In this explorative scenario, the system boundary includes the transport of C6A to the neat SAF production plant (which was assumed to be 200 km away from the MES plant) and the production of neat SAF (see Fig. 5.4). The mass balance and emissions for the conversion of C6A to neat SAF were collected from literature [13, 14].

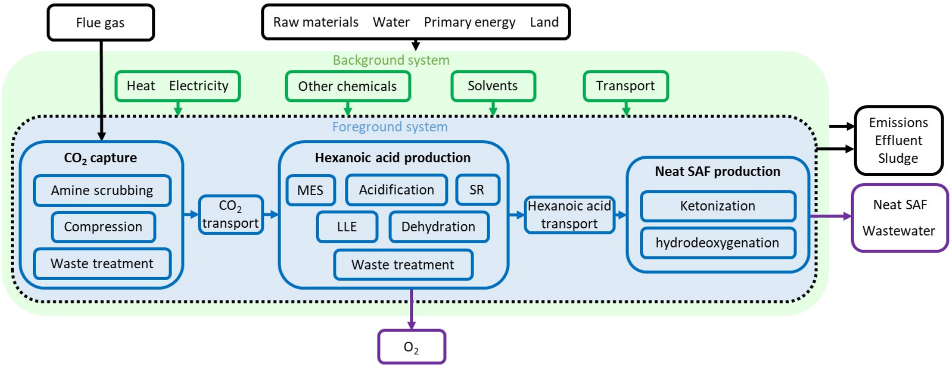

Fig. 5.4. System boundary of MES-based hexanoic acid in Scenario II. MES: microbial electrolysis. SR: solvent regeneration. LLE: liquid-liquid extraction. SAF: sustainable aviation fuel.

2.2.2.2 Functional unit and comparison to other studies

The functional unit was one MJ of neat SAF produced. It was calculated from the stoichiometry of converting C6A to neat SAF using the ratio 2.22 kg C6A:1 kg neat SAF [13, 14] and the calorific value of average jet fuels, i.e., 43.4 MJ/kg [13, 35] (check Appendix D for details).

In this scenario, we focus on only one indicator, global warming potential (GWP; g CO_2eq/MJ neat SAF).

In contrast to scenario I, no reference system was explicitly modelled in scenario II. Instead, the results of the current analysis were compared to the GWP of alternative neat SAFs produced from biomass, which were retrieved from the literature [21, 36–38]. Since the referencing data might have different system boundaries, in the discussion (see section 3.2.1), we included the final combustion emissions of conventional jet fuel for the neat SAF, which is 74 g CO_2eq/MJ [39] in addition to its cradle-to-gate system boundary to obtain a rough approximation of the cradle-to-grave direct GHG emissions, while recognising that emissions will be underestimated as transport of the product and any additional processes (e.g., storage) are not included. To the best of our knowledge, data on the LUC and iLUC emissions are not available for specific neat SAFs. For biofuels, the LUC and resulting iLUC emissions data are usually based on the biomass feedstock type, and data on converting the biomass feedstock to bioethanol or biodiesel is available in the literature [33, 40]. This data was used for discussion

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purposes (see Appendix D for details). Note that the neat SAF discussed in this chapter, neither MES- nor biomass-based SAF necessarily meets the regulated specifications. For the purpose of this study, it is assumed that they do.

2.2.2.3 Life cycle inventory

In addition to the LCI described in section 2.2.1.4, data on C6A transport and neat SAF production were added to the LCI (see Appendix D). Specifically, according to Huq et al. [13], the emissions of neat SAF production activity are 15 g CO_2eq/MJ neat SAF.

3 Results and discussion

The LCA results are presented in Table 5.1. The results are discussed in the following sections.

Table. 5.1. Cradle-to-gate life cycle assessment results in Scenario I and II. SAF: sustainable aviation fuel.

Scenario I	Global warming potential t CO_2eq/t C6A	Direct land use change m^2a crop eq/t C6A	Water consumption m^3/t C6A
MES route			
with economic allocation	5.5	416	122
with substitution	4.6	407	61
Coconut route			
with economic allocation	5.0	9,335	1,202
Scenario II	**Global warming potential g CO_2eq/MJ neat SAF**		
MES route			
with economic allocation	297		
with substitution	251		

3.1 Scenario I

3.1.1. Global warming potential

On a cradle-to-gate basis and when the economic allocation was applied, a tonne of C6A produced via MES generated about 5.5 t CO_2eq (see Table 5.1). Among the three activities (i.e., CO_2 capture, CO_2 transport and C6A synthesis) (see Fig. 5.5), C6A production played a major role, accounting for 82% of the total emissions. The top three emitters were utility generation, synthesis of other chemicals (i.e., H_3PO_4 and $Ca(OH)_2$), and electricity. It should be noted that even though renewable electricity has a lower carbon intensity than Dutch grid electricity, due to the large consumption in the C6A plant, the total emissions related to it were still considerable. As for the CO_2 capture activity, it contributed 18% to the total carbon footprint, where utilities (steam) were the major emitter. The emissions resulting from short-distance CO_2 transport via pipeline were negligible in this study.

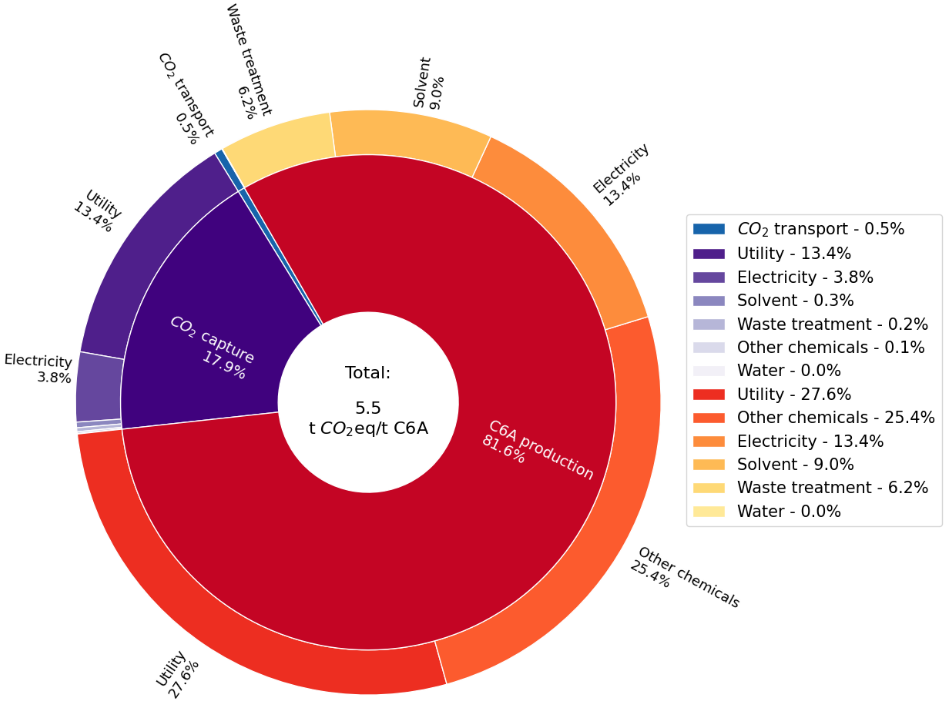


Fig. 5.5. Breakdown of the GWP and (b) dLUC of the MES route with economic allocation. Small values are hidden from the pie chart but shown in the legend.

Table 5.1 also shows the importance of allocation on the final results, with substitution resulting in a lower GWP (16%) than economic allocation. This difference represents the emissions saved by producing O_2 in the MES process instead of producing the same amount of O_2 in an ASU.

A comparison of the GWP of the MES route with the reference system and literature data. Table 5.1 shows that coconut-based C6A has a GWP at a similar level to the MES-based counterpart. We also compared the results to an alternative route (fermentation-based C6A). Three data points were found in [25]. They modelled the processes using a similar downstream processing configuration as in this chapter, namely LLE and SR. Their process used organic solid wastes at the lab and pilot scales. Two key differences in the LCA should be noted. First, the authors used gate-to-product system boundaries (equivalent to gate-to-gate), and second, they used mass allocation. The emissions ranged from 8.7 to 14.9 t CO_2eq/t C6A, with the pilot scale rendering the lowest emission. Note that in their work [25], only the feedstock (i.e., organic solid wastes) was of non-fossil origin. The values of emissions of MES- and fermentation-based hexanoic acid are close. Considering the current technology readiness level of this MES (i.e., 2-3), differences in system boundaries, and differences in allocation methods, although MES seems to perform better, it is hard to assess which route outperforms the other regarding the GWP.

3.1.2. Land use

Fig. 5.6 shows the importance of other chemicals and electricity in the land footprint of the MES route. Note that H_3PO_4 alone made up 50% of the share. In contrast to GWP, the allocation method did not have a significant impact on the results. When using substitution instead of allocation, the change in dLUC appeared insignificant. According to Ecoinvent's documentation for O_2 from an ASU in Europe, the dLUC is dominated by a small fraction of its electricity consumption that originates from combusting wood chips. Compared to the reference case, the dLUC of coconut-based C6A is 9,335 m^2a crop eq/t C6A, which is 20-fold higher than the MES-based plant. According to Alouw and Wulandari [41], the large land footprint of the reference might result from the low productivity of coconut in major exporting countries such as Indonesia and Malaysia.

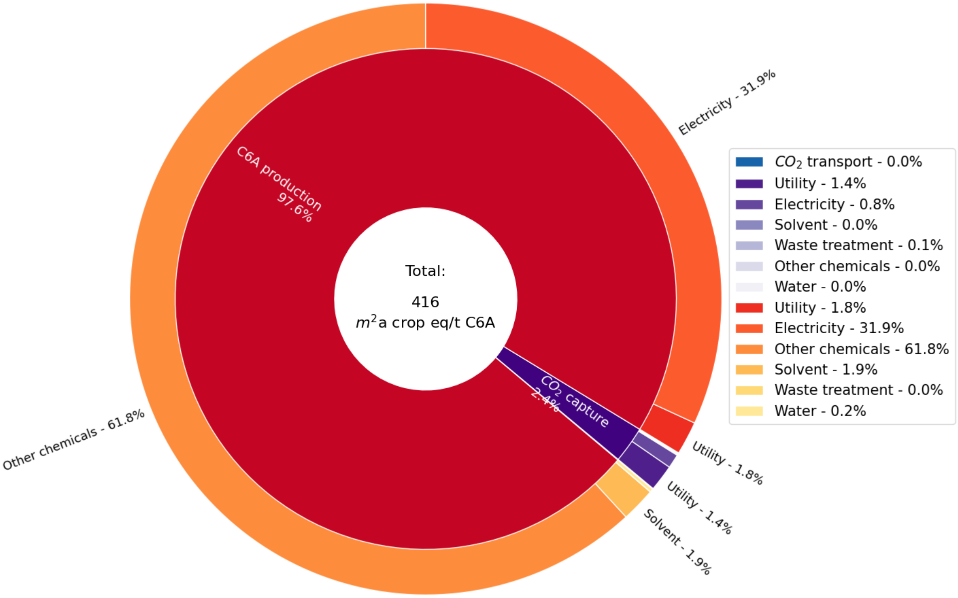


Fig. 5.6. Breakdown of the dLUC of the MES route with economic allocation. Small values are hidden from the pie chart but shown in the legend.

As discussed previously, wind and solar farms can lead to iLUC. Fthenakis and Kim [42] reported 7.5~18.4 m^2a/GWh for ground-mounted photovoltaic (PV) systems and 1.8~5.5 m^2a/GWh for onshore wind farms. These values would correspond to 0.03~0.07 and 0.04~0.11 m^2a/t C6A, respectively. Both values are, however, insignificant when compared to the dLUC (i.e., 416 m^2a crop eq/t C6A).

The iLUC emissions in the MES system could also originate from wind and solar farms. According to Agostini et al. [43], iLUC emissions associated with ground-mounted PV systems are less than 0.4 g CO_2eq/MJ electricity [44]. Converting it to our functional unit, it is equivalent to 6 10^{-3} t CO_2eq/t C6A, which is negligible compared to the direct GHG emissions (i.e., 5.5 t CO_2eq/t C6A). iLUC emission data on onshore wind farms are scarce. However, one could argue that iLUC emissions would be negligible as well because wind turbines must be installed with large spacings, and the free lands could be used [42].

To estimate the DLO of the MES plant, we used the combined DLO of a membrane electrolysis facility for chlorine production [45] and an ethanol plant that captures CO_2 from the flue gas of an adjacent steel plant and produces ethanol via fermentation [46]. The chloralkali plant has a capacity of 200 MW and occupies 0.32 km^2 of land (see Appendix D for calculation details). The ethanol plant is also equipped with downstream separation and purification units. It has a volumetric capacity of 80,000 m^3/y and occupies a land area of ca. 0.14 km^2 (see Appendix D for calculation details). The MES plant has a nominal electricity capacity of 19 MW and a volumetric capacity of 10,900 m^3/y. This rough calculation indicated that the DLO of the MES plant could remain below 1 km^2. Meanwhile, the DLO of the existing dedicated wind and solar farms in this scenario is estimated to be ca. 2.9 and 0.47 km^2, respectively (see Appendix D for calculation details). Therefore, the land for the MES plant is smaller than the land needed for renewable electricity farms. In total, MES and electricity generation DLO is around 4 km^2. The fermentation route is operated at a pilot scale, and it is reported to occupy an area of 0.01 km^2 for 2 kt/y of >98 wt% medium-chain carboxylic acids (see Appendix D for calculation details).

3.1.3. Water consumption

When using economic allocation, the MES system consumes about 122 m^3/t C6A (see Fig. 5.7). H_3PO_4 contributed two-thirds of the total water consumption. The production of all the other chemicals made up about 70% of total water consumption. The generation of renewable electricity accounted for 14%. When substitution was applied, the results showed 50% less water consumption. This can be explained because 50% less water is consumed in the MES system to produce the same amount of O_2 from an ASU. Note that coconut-based C6A uses 1,202 m^3 /t C6A produced, equivalent to 10 times the water footprint of MES-based C6A. This point is further discussed in section 3.1.4.

3.1.4. Sensitivity analysis

Given the importance of the utilities' contribution to the GWP, one-at-a-time sensitivity analyses on electricity and heat energy (incl. chilling) were performed (see Appendix D). If the carbon intensity of the grid electricity (consumed in the CO_2 capture and cooling water regeneration activities) were reduced by 90%, the MES system's GWP could be lowered by 9%. This is because electricity from the grid only accounts for 13% of the GWP in the plant (the electricity used by the electrolyser is mainly provided by a renewable plant). With a similar reduction in carbon intensity in the heat source (incl.

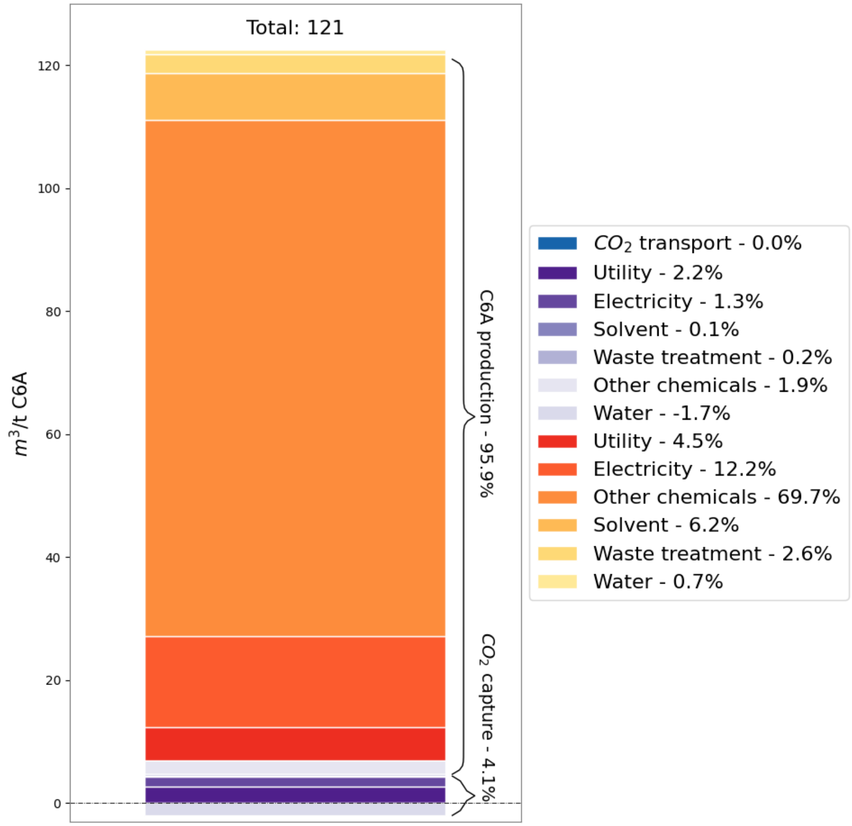


Fig. 5.7. Breakdown of water consumption of the MES route with economic allocation.

chilling), the GWP could be lowered by 32%. This indicates that defossilising the heat (incl. chilling) supply remains important in this kind of system.

The results of the sensitivity analysis on the carbon intensity of solvents and other chemicals show that changes in their carbon intensity are less significant. A 50% change in the triethylamine's carbon intensity can lead to a 7% variation in the final GWP, while the same change in the $Al(OH)_3$ carbon intensity can cause a 4% variation (see Appendix D).

Beyond the MES plant, it is important to highlight the large range of values found in literature, affecting the overall results. CCO has a GWP of 3.3 t CO_2eq/t CCO in Ecoinvent, while it is 6.7 t CO_2eq/t CCO in Agri-footprint. The difference gets even larger for other impacts. For instance, dLUC is 6,510 m^2a crop eq/t CCO in Ecoinvent and 20,000 m^2a crop eq/t in Agri-footprint, while water consumption is reported as 840 m^3/t CCO in Ecoinvent and 4.6 m^3/t CCO in Agri-footprint. Based on Ecoinvent's documentation, the differences in water consumption could be linked to the quantity of irrigation water used and the allocation methods. Therefore, based on the information provided in the literature, pinpointing the cause of the differences was not possible, making a robust comparison of the technologies' relative performance difficult.

3.2 Scenario II

3.2.1. Global warming potential

The cradle-to-gate GWP of the neat SAF produced is significantly higher than that of the conventional route. This is independent of the allocation method used (297 g CO_2eq/MJ neat SAF when using economic allocation and 251 g CO_2eq/MJ neat SAF when using substitution). These values are 26-fold higher than conventional jet fuel (i.e., 9.6 g CO_2eq/MJ [39]). If we include the final combustion emissions of conventional jet fuel for the neat SAF, 74 g CO_2eq/MJ [39], the cradle-to-grave emissions will increase to 371 g CO_2eq/MJ neat SAF using economic allocation while 325 g CO_2eq/MJ neat SAF using substitution.

Since, according to Huq et al. [13], the neat SAF production activity, converting C6A to n-alkanes, only emits 15 g CO_2eq/MJ neat SAF, the total cradle-to-gate emissions remained dominated by the production of C6A (see Fig. 5.8).

A comparison with literature data ([21] and references therein) on the GWP of different production routes of neat SAFs was performed. When neglecting the iLUC emissions and using substitution, the cradle-to-grave GWP of neat SAF produced through MES appears at least 3 times larger than most of its counterparts from alternative routes. Only when peatland rainforest or tropical forest is transformed into orchards that grow certain first-generation biomass (e.g., soybean oil and palm oil), will the substantial emissions caused by dLUC make the GWP of the neat SAFs produced from the first-generation biomass higher than the MES-based neat SAF [38]. The comparison with literature data is, however, not straightforward. For instance, using the guidelines for assessing emissions in the biofuel industry [47], avoided emissions can be counted as negative emissions, while the GHGs are not truly removed from the atmosphere. If the subtraction is significant, the impression can be given that the biofuel has a lower carbon footprint on a cradle-to-gate basis [48]. This point has been reported elsewhere, for example, [13]. Second, the choice of the system boundary and the treatment of multifunctionality are not harmonised in the literature. Ng, Farooq, and Yang [21], for instance, estimated the CO_2eq emissions of a neat SAF derived from woody residues based on the emission data provided in [49]. This study only considered scope 1 emissions and did not include utilities or other activities on the supply chain. The same approach was used to estimate the emissions in [50]. Finally, in several cases, it is impossible to trace back how data was generated. Pavlenko, Searle, and Christensen [36], for instance, reported a carbon intensity of neat SAFs generated from municipal wastes at 14.8 g CO_2eq/MJ, which is only 40% of the 37.5 g CO_2eq/MJ reported in the original source used for the estimation [48]. This points out a problem that goes well beyond the scope of this chapter regarding the harmonisation of system boundaries and allocation methods used in SAF literature.

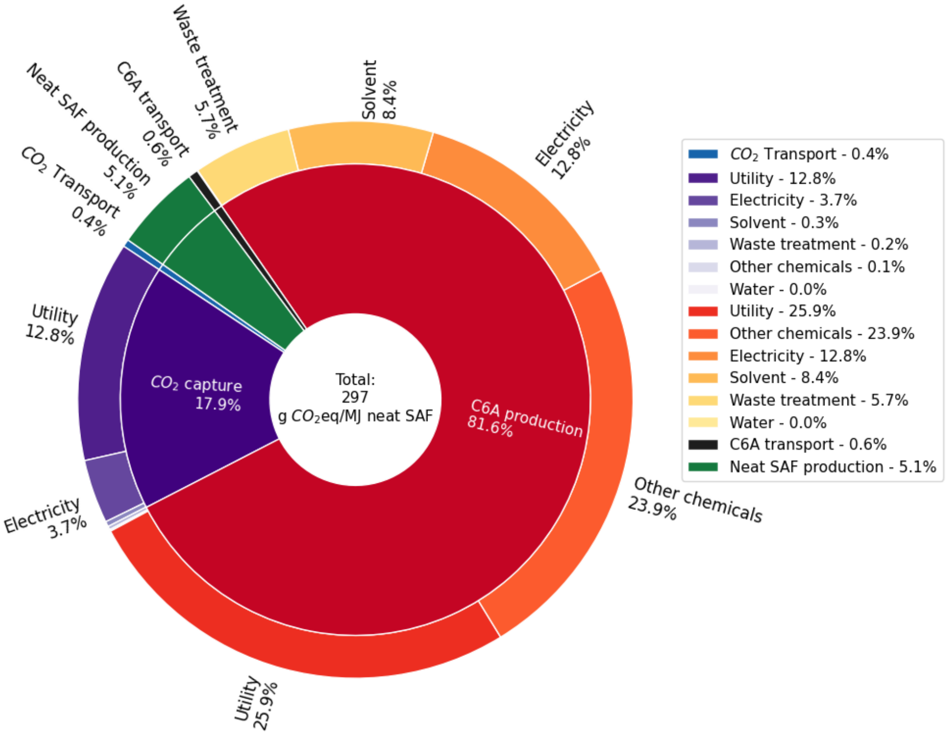


Fig. 5.8. Breakdown of the cradle-to-gate GWP and of the MES-based neat SAF with economic allocation. Small values are hidden from the pie chart but shown in the legend.

3.2.2. Land use

The dLUC of the MES-based neat SAF is around 0.02 m^2a crop eq/MJ. The iLUC of wind and solar farms is negligible compared to the dLUC. dLUC and iLUC data for alternative non-SAF biofuels originating from various feedstock types can be found in [33, 40] (see also Appendix D). Among the studies in literature, the total LUC of the biofuel derived from agricultural residues is around 0.025 m^2a crop eq/MJ biofuel (= 2.5 ha/TJ) for agricultural residues, which is hence comparable to the MES-based neat SAF.

Regarding emissions from iLUC, as previously discussed in section 3.1.2, the iLUC emissions of the MES route in Scenario I are likely to have limited impact. In Scenario II, although iLUC data on the upgrading process is lacking, it can be assumed to have a minor impact due to its efficient DLO and no use of biomass. Our reasoning for an efficient DLO is: 1) the upgrading reactions feature high yields and purities; 2) according to the process proposed by Huq et al. [13], there are only seven unit operations involved, making it a relatively simple process route. Reported iLUC emissions of alternative biofuels can be found in [33, 40] (see also Appendix D). Bioethanol can be produced from different categories of biomass and has iLUC emissions in the range of 0-50 g CO_2eq/MJ. Biodiesel produced from energy crops and first-generation crops were assessed for iLUC emissions in both reports. According to Valin et al. [33], biodiesel derived from switchgrass, miscanthus, and willow/poplar can even lead to negative emissions at the gate. After the biodiesel is combusted, the carbon will be released, resulting in carbon neutrality at best but not carbon negativity. For other feedstock, their iLUC emissions are above 50 g CO_2eq/MJ. Values are higher for neat SAFs from first-generation biomass, reaching up to 250 g CO_2eq/MJ. If these values are used as an indication for the iLUC emissions of alternative neat SAFs, the direct GHG plus iLUC emissions of neat SAF produced from first-generation biomass (e.g., palm oil and soybean oil) via the up-to-date most industrialised route (hydroproccessed esters and fatty acids-HEFA) can exceed 300 g CO_2eq/MJ on a cradle-to-grave basis. Thus, the neat SAF derived from MES-based C6A might be competitive.

4 Conclusion

This chapter assessed the environmental impacts of C6A produced via MES and renewable electricity and its derivative neat SAF and compared the results with other production routes. Cradle-to-gate assessments were performed to quantify global warming potential, land use, and water consumption of production systems. Both economic allocation and substitution were applied to examine the multifunctionality of the MES production system.

When an economic allocation was applied, the results showed that the GWP of C6A produced from CO_2 via MES is comparable to the GWP of C6A produced from coconut oil via fractional distillation and from organic solid wastes via fermentation. Factors that would reduce the carbon footprint of the MES route are defossilising heat and chilling utilities used in energy-intensive downstream processing as well as using less carbon-intensive chemicals.

The results also highlight the advantage of MES in terms of land use, as it is 20 times lower than the reference case (coconut-based hexanoic acid). Additionally, the direct land occupation of the renewable electricity farms is likely larger than the MES plant itself. The major shares in both land use and water consumption of the MES route are due to the vast consumption of renewable electricity in the C6A production activity and the chemicals used in the C6A production activity, especially H_3PO_4, for its large consumption of fossil resources. The overall picture indicates that the MES-based C6A has a lower environmental impact than the coconut-based C6A.

If C6A produced via MES is further upgraded to produce neat SAF, the GWP of this route does not seem to outperform alternative routes, with the exception of iLUC emissions. A reliable comparison with published LCA studies on biomass-based SAF production is currently difficult due mainly to differences in system boundaries. Nonetheless, considering the direct CO_2eq emissions and iLUC emissions together, neat SAF derived from MES-based C6A might be competitive with counterparts that use first-generation biomass. However, there are alternative neat SAFs with a lower carbon intensity being developed and industrialised. Finally, for future research, the conversion of C6A produced via MES to other chemicals, such as adipic acid, should be explored.

References

[1] B. Nilges, C. Burghardt, K. Roh, C. Reinert, and N. von der Assen. "Comparative life cycle assessment of industrial demand-side management via operational optimization". Computers & Chemical Engineering. 177. 2023. P. 108323. DOI: `10.1016/j.compchemeng.2023.108323`.

[2] K. Roh et al. "Early-stage evaluation of emerging CO_2 utilization technologies at low technology readiness levels". Green Chemistry. 2212. 2020. Pp. 3842–3859. DOI: `10.1039/c9gc04440j`.

[3] J. Sadhukhan, S. Gadkari, and R. I. Muazu. "Technoeconomic analysis and life cycle assessment methodologies for microbial electrochemical systems". Material-Microbes Interactions. 2023. Elsivier. Pp. 409–423. DOI: `10.1016/b978-0-323-95124-1.00015-2`.

[4] J. Sadhukhan et al. "A critical review of integration analysis of microbial electrosynthesis (MES) systems with waste biorefineries for the production of biofuel and chemical from reuse of CO_2". Renewable and Sustainable Energy Reviews. 56. 2016. Pp. 116–132. DOI: `10.1016/j.rser.2015.11.015`.

[5] S. Gadkari, M. Shemfe, J. A. Modestra, S. V. Mohan, and J. Sadhukhan. "Understanding the interdependence of operating parameters in microbial electrosynthesis: a numerical investigation". Physical Chemistry Chemical Physics. 2120. 2019. Pp. 10761–10772. DOI: `10.1039/c9cp01288e`.

[6] N. Chu et al. "Microbial Electrosynthesis for Producing Medium Chain Fatty Acids". Engineering. 16. 2022. Pp. 141–153. DOI: `10.1016/j.eng.2021.03.025`.

[7] R. Morya, A. Sharma, A. Pandey, I. S. Thakur, and D. Pant. "Microbial electrosynthesis systems toward carbon dioxide sequestration for the production of biofuels and biochemicals". Biomass, Biofuels, Biochemicals. 2022. Elsevier. Pp. 279–297. DOI: `10.1016/b978-0-12-823500-3.00004-2`.

[8] P. Dessi et al. "Microbial electrosynthesis: Towards sustainable biorefineries for production of green chemicals from CO_2 emissions". Biotechnology Advances. 46. 2021. P. 107675. DOI: `10.1016/j.biotechadv.2020.107675`.

[9] E. C. Canapi, Y. T. V. Agustin, E. A. Moro, E. Pedrosa, and M. L. J. Bendano. "Coconut Oil". Bailey's Industrial Oil and Fat Products. F. Shahidi. Vol. 1-6. 2005. John Wiley & Sons. Chap. Coconut Oil. Pp. 123–147. DOI: `10.1002/047167849X`.

[10] M. T. Agler, C. M. Spirito, J. G. Usack, J. J. Werner, and L. T. Angenent. "Development of a highly specific and productive process for n-caproic acid production: applying lessons from methanogenic microbiomes". Water Science & Technology. 691. 2014. Pp. 62–8. DOI: `10.2166/wst.2013.549`.

[11] L. Jourdin, J. Sousa, N. van Stralen, and D. P. B. T. B. Strik. "Techno-economic assessment of microbial electrosynthesis from CO_2 and/or organics: An interdisciplinary roadmap towards future research and application". Applied Energy. 279. 2020. P. 115775. DOI: `10.1016/j.apenergy.2020.115775`.

[12] M. Omidi et al. "From Electricity to Products: Recent Updates on Microbial Electrosynthesis (MES)". Top Catal. 2021. Pp. 1–18. DOI: `10.1007/s11244-021-01503-3`.

[13] N. A. Huq et al. "Toward net-zero sustainable aviation fuel with wet waste-derived volatile fatty acids". PNAS. 11813. 2021. e2023008118. DOI: `10.1073/pnas.2023008118`.

[14] J. H. Miller, G. R. Hafenstine, H. H. Nguyen, and D. R. Vardon. “Kinetics and Reactor Design Principles of Volatile Fatty Acid Ketonization for Sustainable Aviation Fuel Production”. Industrial & Engineering Chemistry Research. 618. 2022. Pp. 2997–3010. DOI: `10.1021/acs.iecr.1c04548`.

[15] U.S. Department of Energy. Sustainable Aviation Fuel: Review of Technical Pathways. U.S. Department of Energy, 2020. DOI: `10.2172/1660415`.

[16] J. T. Edwards. “Reference Jet Fuels for Combustion Testing”. 55th AIAA aerospace sciences meeting. 2017. DOI: `10.2514/6.2017-0146`.

[17] M. Kaltschmitt and U. Neuling. Biokerosene. SpringerLink, 2018. DOI: `10.1007/978-3-662-53065-8`.

[18] ICAO. ICAO environmental report 2019: destination green: the next chapter. ICAO, 2019. URL: `https://digitallibrary.un.org/record/3837917?ln=en`.

[19] G. Quante, N. Bullerdiek, S. Bube, U. Neuling, and M. Kaltschmitt. “Renewable fuel options for aviation - A System-Wide comparison of Drop-In and non Drop-In fuel options”. Fuel. 333. 2023. P. 126269. DOI: `10.1016/j.fuel.2022.126269`.

[20] U.S. EIA. 2020. Annual Energy Outlook 2020. URL: `https://www.eia.gov/outlooks/aeo/data/browser/#/?id=57-AEO2020%5C&cases=ref2020%5C&sourcekey=0`. (Access date: 16 May 2023).

[21] K. S. Ng, D. Farooq, and A. Yang. “Global biorenewable development strategies for sustainable aviation fuel production”. Renewable & Sustainable Energy Reviews. 150. 2021. P. 111502. DOI: `10.1016/j.rser.2021.111502`.

[22] S. Agnihotri et al. “A Glimpse of the World of Volatile Fatty Acids Production and Application: A review”. Bioengineered. 131. 2022. Pp. 1249–1275. DOI: `10.1080/21655979.2021.1996044`.

[23] M. Yani, D. Toruan, T. Puspaningrum, M. Sarfat, and C. Indrawanto. “Life cycle assessment of coconut oil product”. Earth and Environmental Science. 2022. P. 012017. DOI: `10.1088/1755-1315/1063/1/012017`.

[24] J. Luo, M. Perez-Fortes, P. Ibarra-Gonzalez, A. J. J. Straathof, and A. Ramirez. “Impact of intermittent electricity supply on a conceptual process design for microbial conversion of CO_2 into hexanoic acid”. Chemical Engineering Research and Design. 205. 2024. Pp. 364–375. DOI: `10.1016/j.cherd.2024.04.005`.

[25] W. Chen, D. Strik, C. J. N. Buisman, and C. Kroeze. “Production of Caproic Acid from Mixed Organic Waste: An Environmental Life Cycle Perspective”. Environmental Science & Technology. 5112. 2017. Pp. 7159–7168. DOI: `10.1021/acs.est.6b06220`.

[26] J. Luo, M. Perez-Fortes, A. J. J. Straathof, and A. Ramirez. “Understanding the flexibility challenges of a plant for microbial CO_2 electroreduction with hexanoic acid recovery”. submitted to a journal. 2024.

[27] ISO. Environmental management: life cycle assessment; requirements and guidelines. 2006.

[28] G. Wernet, C. Bauer, B. Steubing, J. Reinhard, E. Moreno-Ruiz, and B. Weidema. “The ecoinvent database version 3 (part I): overview and methodology”. International Journal of Life Cycle Assessment. 219. 2016. Pp. 1218–1230. DOI: `10.1007/s11367-016-1087-8`.

[29] B. Durlinger, M. Tyszler, J. Scholten, R. Broekema, and H. Blonk. “Agri-footprint; A life cycle inventory database covering food and feed production and processing”. The 9th International Conference on Life Cycle Assessment in the Agri-Food Sector. American Center for Life Cycle Assessment. 2014.

[30] M. Z. Hauschild, R. K. Rosenbaum, and S. I. Olsen. Life Cycle Assessment. Switzerland: Springer, 2018. DOI: `10.1007/978-3-319-56475-3`.

[31] European Commission. LCA4CCU-Guidelines for life cycle assessment of carbon capture and utilisation. European Commission, 2020. DOI: `10.2833/161308`.

[32] C. Malins, S. Searle, and A. Baral. A Guide for the Perplexed to the Indirect Effects of Biofuels Production. ICCT, 2014. URL: `https://theicct.org/wp-content/uploads/2021/06/ICCT_A-Guide-for-the-Perplexed_Sept2014.pdf`.

[33] H. Valin et al. The land use change impact of biofuels consumed in the EU - Quantification of area and greenhouse gas impacts. Ecofys Netherlands BV, 2015. URL: `https://energy.ec.europa.eu/system/files/2016-03/Final%5C%2520Report_GLOBIOM_publication_0.pdf`.

[34] Franklin Associates. Cradle-to-Gate Life Cycle Analysis of Olefins. American Chemistry Council Plastics Division, 2020. URL: `https://www.americanchemistry.com/better-policy-regulation/plastics/resources/cradle-to-gate-life-cycle-analysis-of-olefins`.

[35] A. Bauen, N. Bitossi, L. German, A. Harris, and K. Leow. “Sustainable Aviation Fuels Status, challenges and prospects of drop-in liquid fuels, hydrogen and electrification in aviation”. Johnson Matthey Technology Review. 643. 2020. Pp. 263–278. DOI: `10.1595/205651320x15816756012040`.

[36] N. Pavlenko, S. Searle, and A. Christensen. The cost of supporting alternative jet fuels in the European Union. ICCT, 2019. URL: `https://theicct.org/sites/default/files/publications/Alternative_jet_fuels_cost_EU_20190320.pdf`.

[37] S. de Jong et al. “Life-cycle analysis of greenhouse gas emissions from renewable jet fuel production”. Biotechnol Biofuels. 10. 2017. P. 64. DOI: `10.1186/s13068-017-0739-7`.

[38] R. Stratton, H. M. Wong, and J. Hileman. Life cycle greenhouse gas emissions from alternative jet fuels. Partnership for Air Transportation Noise and Emissions Reduction, 2010. URL: `http://web.mit.edu/aeroastro/partner/reports/proj28/partner-proj28-2010-001.pdf`.

[39] L. Jing et al. “Understanding variability in petroleum jet fuel life cycle greenhouse gas emissions to inform aviation decarbonization”. Nature Communications. 131. 2022. P. 7853. DOI: `10.1038/s41467-022-35392-1`.

[40] K. Overmars, R. Edwards, M. Padella, A. G. Prins, and L. Marelli. Estimates of indirect land use change from biofuels based on historical data. 2015. DOI: `10.2790/3647`.

[41] J. C. Alouw and S. Wulandari. “Present status and outlook of coconut development in Indonesia”. 1^{st} International Conference on Sustainable Plantation (1^{st} Icsp 2019). 418. 2020. P. 012035. DOI: `10.1088/1755-1315/418/1/012035`.

[42] V. Fthenakis and H. C. Kim. “Land use and electricity generation: A life-cycle analysis”. Renewable & Sustainable Energy Reviews. 136-7. 2009. Pp. 1465–1474. DOI: `10.1016/j.rser.2008.09.017`.

[43] A. Agostini et al. “Environmentally Sustainable Biogas? The Key Role of Manure Co-Digestion with Energy Crops”. Energies. 86. 2015. Pp. 5234–5265. DOI: `10.3390/en8065234`.

[44] A. Agostini, M. Colauzzi, and S. Amaducci. “Innovative agrivoltaic systems to produce sustainable energy: An economic and environmental assessment”. Applied Energy. 281. 2021. P. 116102. DOI: `10.1016/j.apenergy.2020.116102`.

[45] Vattenfall. 2021. Flexible chlorine production contributes to grid stability. URL: `https://group.vattenfall.com/press-and-media/newsroom/2021/flexible-chlorine-production-contribute-to-grid-stability`. (Access date: 24 June 2023).

[46] ArcelorMittal. 2023. ArcelorMittal and LanzaTech announce first ethanol samples from commercial flagship carbon capture and utilisation facility in Ghent, Belgium. URL: `https://corporate.arcelormittal.com/media/news-articles/arcelormittal-and-lanzatech-announce-first-ethanol-samples-from-commercial-flagship-carbon-capture-and-utilisation-facility-in-ghent-belgium#:~:text=The/%5C%20ethanol/%5C%20will/%5C%20be/%5C%20jointly,total/%5C%20current/%5C%20demand/%5C%20in/%5C%20Belgium.`. (Access date: 24 June 2023).

[47] ICAO. Sustainable Aviation Fuels Guide. ICAO, 2017. URL: `https://www.icao.int/environmental-protection/knowledge-sharing/Docs/Sustainable%5C%20Aviation%5C%20Fuels%5C%20Guide_vf.pdf`.

[48] S. Unnasch. Life Cycle GHG Emissions For Fulcrum Sierra BioFuels, LLC's MSW-to-Fischer Tropsch Fuel Production Process. John A. Volpe National Transportation Systems Center (US), 2015. URL: `https://ww2.arb.ca.gov/sites/default/files/classic//fuels/lcfs/2a2b/apps/ful-ftd-rpt-123015.pdf`.

[49] J. Tarud and S. Phillips. Techno-economic comparison of biofuels: ethanol, methanol, and gasoline from gasification of woody residues. NREL, 2011. URL: `https://permanent.fdlp.gov/gpo15468/52636.pdf`.

[50] A. Dutta, J. A. Schaidle, D. Humbird, F. G. Baddour, and A. Sahir. "Conceptual Process Design and Techno-Economic Assessment of Ex Situ Catalytic Fast Pyrolysis of Biomass: A Fixed Bed Reactor Implementation Scenario for Future Feasibility". Topics in Catalysis. 591. 2015. Pp. 2–18. DOI: `10.1007/s11244-015-0500-z`.

6

Conclusion

1 Overview

This dissertation explored the impact of intermittency of renewable electricity on the design and upscaling of a novel CO_2 electrochemical plant. We first developed a conceptual framework for designing and assessing future novel flexible chemical processes against various uncertainties. Then, we used a case study on hexanoic acid production via microbial electrosynthesis (MES) as a representative of novel CO_2 electrochemical conversion technologies to explore the impacts of intermittency on the design and performance of a CO_2 electrochemical plant and design strategies for improving its flexibility and evaluating its economic and environmental performances.

This chapter first summarises the research outcomes and answers the main research question proposed in **chapter 1**. Then, analyses and discusses the limitations of this research, followed by the recommendations for future research.

2 Research outcomes

This dissertation aims to understand:

which process designs and conditions could facilitate the upscaling of a novel CO_2 electrochemical plant under intermittent renewable electricity supply

To reach this aim, three research sub-questions were proposed. Below is a quick background recap for each research sub-question, followed by results and conclusion. Then, an overall conclusion is made to the main research question covering technical, economic, and environmental aspects.

Sub-question 1: What does flexibility mean when designing flexible novel chemical processes?

Designing for flexibility has been extensively studied in process system engineering (PSE). However, it has mostly focused on well-understood processes equipped with a control system. In recent years, the possibility to shift toward alternative carbon sources (e.g., biomass and CO_2) and alternative energy sources (e.g., renewable electricity) have increased uncertainties regarding feedstock quality and/or quantity fluctuations in chemical processes. Not only a growing number of novel flexible technologies are being considered to cope with the fluctuations, but innovative plant configurations are also being developed to enable flexible operations. Nonetheless, a framework (understanding a framework as a guideline) for designing and assessing such flexible designs for novel technologies was missing. Moreover, the terminology used in case studies focusing on flexibility is confusing, making it harder to compare results and draw insights.

To address these knowledge gaps, in **chapter 2**, a systematic literature review on flexibility was conducted. The review covered the period 1990 to 2020. The background of flexibility was revisited, and a conceptual framework for defining, designing, and evaluating flexibility for novel flexible chemical processes was proposed.

Flexibility has been historically part of operability and represents the static boundaries the physical equipment can guarantee independent of any control system. It is a comparative characteristic for processes facing uncertainties that designers know and allow.

In **chapter 2**, we propose that to define flexibility, five elements of flexibility should be specified in advance, based on the design requirements: target, range, hierarchical level, time scale, and impact (see Table 6.1). Using these elements, flexibility can be defined as "the ability of [a hierarchical level] to operate over [a range of operating conditions] on [a certain time scale basis] to cope with [a target] with acceptable [impact]". The definition of flexibility for a specific case allows us to identify the type of flexibility that a process design needs to enable. In literature, there are five types of flexibility: feedstock, product, volume, scheduling, and production (see Table 6.2). For each type, we identified several design strategies (listed in Table 6.2) that can be used to enable or improve flexibility. Finally, a selection of indicators was proposed to evaluate the different flexibility types (see Table 2.4 in **chapter 2**).

Table. 6.1. Elements of flexibility.

Element	Explanation
Target	A target can be derived from the sources of uncertainties and elaborates the content of a flexibility type (e.g., fluctuating electricity supply).
Range	A range indicates how many options are available once the operating conditions deviate from the nominal ones. A range is derived from the boundaries of uncertainties. They can be a series of continuous values (e.g., 30-50 kg/h) or a set of discrete criteria (e.g., product types such as biofuel or hydrogen).
Hierarchical level	The hierarchical level reflects the degree of detail a design needs to reach in order to meet the design requirements derived from the flexibility needs. The hierarchical levels also reflect at which level the flexibility needs to be assessed for a given purpose. The amount of data and requirements decreases with the level of aggregation. The hierarchical level can be equipment, process, plant, etc.
Time scale	Uncertainties are time-dependent. A unit time period can be a second, an hour, a day, a season, a production cycle, or others.
Impact	Designing for flexibility often results in impacts when compared to a reference design. Such impacts concern, for example, technical performance (e.g., conversion efficiency, product purity), economic performance (e.g., net present value, payback time), human resources (e.g., time, effort) and/or environmental performance (e.g., global warming potential, acidification). Impacts can be either positive or negative (i.e., penalties). Impacts are often quantified by comparing the performance of the (relatively more) flexible design to the performance of a reference design.

For designing future flexible chemical processes, designers and stakeholders should first determine the types of uncertainties to incorporate. Then, the corresponding flexibility types can be defined based on case-specific conditions and expectations using the five elements identified in this dissertation. Finally, the flexibility types can be quantified separately using the corresponding indicators proposed in **chapter 2** to compare different candidate designs. It is important to note that the list of indicators is not exhaustive, it can be modified, or new indicators can be proposed. Moreover, during the design phase, it might be found that a flexibility type might trigger another type, and in such a case, the design would be modified. Additionally, designers or technology developers might find that the evaluated impacts are unacceptable and changes to the design need to be made. Therefore, the design procedure might iterate. In the end, the framework allows users to get a general idea of what technologies, locations, configurations, operating conditions and other relevant system conditions the processes should have and how the processes should run.

Table. 6.2. Classification of flexibility and their definition as well as design strategies.

Feedstock	The ability to handle changes in quantities and/or qualities of inflow materials	(i) Implement different production schemes to produce different product types (ii) Blend different types of feedstocks (iii) Select and/or design the equipment that can deal with variations in feedstock quality (iv) Install buffer unit(s) to regulate fluctuations in feedstock quality.
Product	The ability to change the qualities of outflow materials	(i) Select synthetic pathways that inherently produce multiple products (ii) Implement different production schemes
Voume	The ability to vary throughput	(i) Select and/or design (function-wise) equipment that can deal with variations in throughput (ii) Select and/or oversize equipment (capacity-wise) that meet wide load requirements (iii) Install buffer units to decouple units with variations in throughput from steadily operated units (iv) Install parallel units or process lines (v) Robust scheduling
Scheduling	The ability to adjust resources allocation for different production cycles	(i) Oversize equipment (ii) Install parallel same units or process lines
Production	The ability to switch to exercise another production scheme	(i) Select and/or design equipment that can handle inflow materials with different qualities and/or produce outflow materials with different qualities (ii) Select and/or design production schemes and equipment that can be switched on/off at request

Sub-question 2: How does intermittency affect the techno-economic and environmental performances of a novel CO_2 electrochemical plant?

Researchers have been investigating the concept of coupling intermittent renewable electricity and novel CO_2 electrochemical conversion technologies (and of water electrolysers and electrified units, among others), but only a limited number of works has studied the impact of intermittency on the technical design at an industrial scale. Novel CO_2 electrochemical conversion technologies, especially low-temperature ones, produce a wide range of products but in a dilute stream, while the products are sold at a high purity. Hence, downstream processing (DSP) technologies are paramount to recover and purify the products to meet market requirements. An intermittent electricity supply impacts the throughput rate of the whole plant, therefore, how the DSP technologies respond to intermittent renewable electricity is worth studying. The subsequent trade-offs in the techno-economic and environmental performances of an electrochemical plant should also be understood for its future development.

In **chapter 3**, we modelled an electrochemical plant cantered on (MES) producing hexanoic acid, at an industrial scale (i.e., 10 kt/y), in Aspen Plus (see the block flow diagram in Fig. 3.1 in **chapter 3**). To estimate the volume flexibility of the downstream processes, the dimensions of the distillation columns were fixed and the flow rates were varied. To fix the dimensions that are always automatically adjusted by Aspen Plus as the flow rate changes, we decomposed an integrated distillation column equipped with a reboiler and condenser into a tower with two separate heat exchangers. Additionally, introducing fluctuations inherent within IRE to technologies or equipment not intended for flexible operation might result in undesired product quality and or cause damage to the equipment and, subsequently, hazards to process safety. Hence, during the estimation, we stopped varying the flow rates once hazard signals appeared, such as when the tray's hydraulics were unstable, or the column's overhead steam could not be condensed.

Then, it was observed that the temperature and pressure profiles inside the distillation tower had to remain unchanged to ensure the same recovery rate and product purity as the nominal conditions. Our results indicate that the maximum condensing capacity of the condenser restricted the maximum tolerable flow rate of all the distillation columns at their nominal value, while the tray's hydraulic stability of the distillation column restricted the minimum tolerable flow rate. In the design under study, the last distillation column, which is the final step needed to reach the product's purity, had the highest minimum tolerable flow rate compared to other columns and thus limited the volume flexibility of the entire plant to no lower than 70% of its nominal throughput rate. Eventually, the volume flexibility of the plant was [70%, 100%].

To assess the impact of intermittency on the performance of the plant, the plant simulation was run using different electricity profiles (i.e., solely wind power and hybrid power consisting of both solar and wind power). Not surprisingly, intermittency had a significant impact on the operation of the plant. With a wind electricity supply, the intermittency resulted in a total shutdown time of 3837 hours and an increase in the levelised production cost of hexanoic acid (LPC_{C6A}) of 34%. With a hybrid electricity supply, the intermittency resulted in a total shutdown time of 2678 hours and an increase in the LPC_{C6A} of 19%. The results show that when using profiles with higher levels of intermittency (i.e., only wind power) and, subsequently, more often under the threshold power needed for production, the plant had to be shut down more frequently, which resulted in less production and higher LPC_{C6A}. To minimise the impact of intermittency, the model was then run using pre-defined operating schemes with and a battery energy storage system (BESS) (in **chapter 3** and **chapter 4**) and a storage tank (ST) (in **chapter 4**) as buffer units, with pre-selected sizes. See in Table 6.3, a BESS of 8.1 MW led to the lowest LPC_{C6A} when the plant was powered by wind electricity; the penalty caused by intermittency was reduced by 7%. Under a hybrid electricity supply, a BESS of 3.3 MW led to the lowest LPC_{C6A}, which reduced the penalty caused by intermittency by merely 2%. This implies that the BESS was more useful when the intermittency level was higher (i.e., wind electricity).

The LPC_{C6A} did not always improve as the BESS capacity increased. The extra

Table. 6.3. Techno-economic results of the MES plant driven by different electricity profiles.

	Hybrid electricity	Wind electricity
Lowest LPC_{C6A} (€$_{2019}$/kg)	4.67	5.08
Corresponding BESS capacity (GJ/h)	12 (=3.3 MW)	29 (=8.1 MW)
Shutdown time (h/y)	1954	2124
Hexanoic acid production (kt/y)	7.30	6.74

production of hexanoic acid enabled by the BESS could not always offset the capital costs. With the largest capacity of BESS that the resulting LPC_{C6A} was still lower than without this BESS, the load ratio range (LRR) of the plant could not be enhanced under any investigated level of intermittency. Therefore, the use of a BESS is not advised based on the investigated conditions.

In **chapter 4**, a ST was installed to store the intermediate (liquid) chemical stream prior to the first solvent regeneration column to buffer the fluctuations that were caused by intermittency in the electricity supply. At the same capital cost, a ST showed a higher equivalent storing capability than a BESS. As a result, when the resulting LPC_{C6A} remained lower than the LPC_{C6A} obtained without a buffering unit, in addition to increasing the production quantity and LPC_{C6A}, a ST could also slightly enhance the volume flexibility (i.e., from [70%, 100%] to [67%, 100%]) by bridging more periods of electricity shortage. The volume flexibility could be further expanded by optimising the scheduling of the plant, reaching a range of [60%, 100%]. However, despite the use of buffer units (i.e., BESS or ST) and the optimised scheduling, coupling the MES plant to intermittent renewable energy (IRE) resulted in penalties of about 20% in production quantity and 10% in LPC_{C6A} compared to the case where the MES plant was powered by constant grid electricity.

In **chapter 4**, we also assessed the impact of intermittency in the cradle-to-gate carbon footprint of hexanoic acid. As expected, using renewable energy sources instead of the electricity from the Dutch grid (year 2019), resulted in a substantial decrease in the GWP (from 15 to 5 t CO_2eq/t C6A). This was due to the current carbon footprint of the grid mix, which still contains a high share of fossil sources.

To answer question 2, although electrolysers might be flexible to IRE supply, the thermal-based downstream processing (DSP) can become a bottleneck because of their operating conditions for ensuring the quality and recovery rate of the product. Therefore, flexibility should be incorporated when selecting technologies or designing equipment. Furthermore, with the increase in electricity fluctuations, the shutdown time increases, and the subsequent production quantity reduces, resulting in an increase in the LPC_{C6A}. This points out the fact that the capital costs incurred based on continuous operation are not being used enough to generate sufficient revenue. This phenomenon, namely sunk cost, is a prominent problem for the flexible operation of capital-intensive equipment.

Introducing buffering units can, to a certain extent, enable operation and production when the available electricity is under the plant's threshold electricity consumption rate, thus increasing the production quantity and lowering the levelised production cost, compared to the case where the plant is operated under intermittent conditions without buffering units. Additionally, if an expensive buffering unit (e.g., batteries) is not used sufficiently to generate enough extra revenue, its capital cost cannot be paid back, causing an unacceptable sunk cost. Furthermore, optimising the scheduling of the entire plant equipped with a buffering unit was necessary.

Sub-question 3: What factors can potentially influence the competitiveness of a novel electrochemical technology powered by renewable electricity against its market competitor?

Currently, hexanoic acid is commercially produced as a byproduct from the fractional distillation of coconut or palm kernel oil. For the future development of and investment in MES, it is essential to understand how competitive it can be in today's and tomorrow's markets. Another promising pathway is bio-fermentation based on ethanol or shorter carboxylic acids via chain elongation, which has been operated at a pilot scale [1]. Hexanoic acid has a small market, but researchers have been investigating the feasibility of synthesising n-alkanes from hexanoic acid to produce "neat sustainable aviation fuel" (neat SAF), which can be blended with conventional jet fuels.

In this thesis, we assessed the techno-economic and environmental performance of producing hexanoic acid via MES and compared it to today's production route based on plant oils and a bio-fermentation route. In **chapter 3** and **chapter 4**, the economic evaluation of hexanoic acid produced via MES was conducted. When the plant was powered by constant grid electricity, the LPC_{C6A} was around 4 €$_{2019}$/kg, which is near the upper boundary of today's market price (i.e., 2.5 to 4.2 €$_{2019}$/kg [2]) and comparable to the production cost of bio-fermentation route (i.e., 3.2 and 8.0 €$_{2019}$/kg [3]). When coupled with IRE, the lowest LPC_{C6A} that could be achieved was 4.4 €$_{2019}$/kg when using a ST and optimised scheduling. Though this figure is higher than the upper boundary of today's market price, it can be deemed competitive. The largest shares of LPC_{C6A} were capital costs and operation and maintenance costs, collectively accounting for 49%. Electricity consumption was responsible for 32% of the costs. Among the capital costs, the MES reactor and liquid-liquid extraction (LLE) membrane contactors were the most expensive due to: 1) the large number of MES stacks driven by the low productivity of MES, 2) the large number of LLE membrane contactors due to the low concentration of hexanoic acid in the product stream of the MES, and 3) the high costs of novel technologies such as the MES stacks and LLE membrane contactors.

In **chapter 5**, the life cycle impacts of the supply chains for MES-based and coconut-based hexanoic acid were compared (see Table 6.4). The CO_2 supplied to the MES plant was assumed to come from flue gas in integrated refineries. In the first scenario, it was also assumed that the end use of hexanoic acid from both routes was the same and therefore, cradle-to-gate boundaries were used (see Fig. 6.1).

The MES-based hexanoic acid had a global warming potential (GWP) of 5.5 t CO_2eq/t C6A, at the same level of the coconut-base counterpart (5.0 t CO_2eq/t C6A) and fermentative counterpart (8.0 to 15.0 t CO_2eq/t C6A [4]). On the value chain of MES-based hexanoic acid (i.e., CO_2 capture, CO_2 transport, and C6A production), C6A

Table. 6.4. Life cycle assessment results of the MES and coconut routes on a cradle-to-gate basis using economic allocation.

Economic allocation	Global warming potential t CO_2eq/t C6A	Direct land use m^2a crop eq/t C6A	Water consumption m^3/t C6A
MES route	5.5	416	121
Coconut route	5.0	9,335	1,202

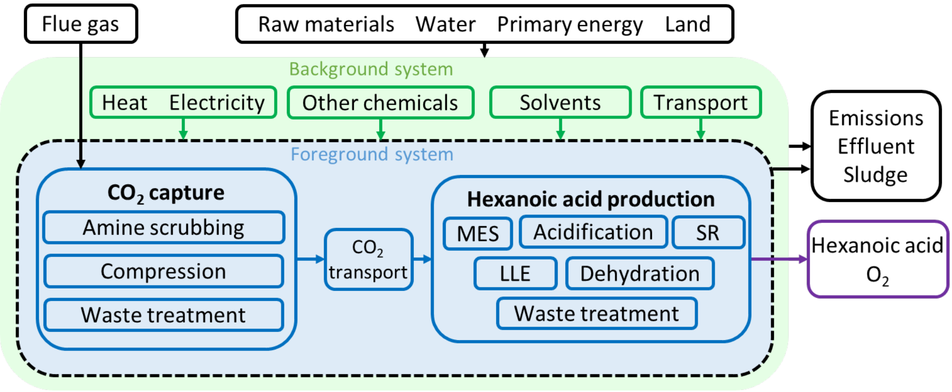


Fig. 6.1. Product system. MES: microbial electrosynthesis. SR: solvent regeneration. LLE: liquid-liquid extraction.

production activity played a major role, accounting for 82% of the total emissions. The top three subcategorised emitters on the entire value chain were fossil-based utility generation (41%), synthesis of other fossil-based chemicals (26%), and generation of the renewable electricity used in the MES plant (13%). In terms of direct land use (dLUC) and water consumption, MES-based hexanoic acid exhibited an impact of 416 m^2a crop eq/t C6A, which is more than one order of magnitude lower than the coconut-based counterpart (9,335 m^2a crop eq/t C6A) due to the low productivity of coconut in its major exporting countries such as Indonesia and Malaysia [5]. Among all the activities, C6A production alone made up 98% of the dLUC. The largest contributor to the dLUC of MES-based hexanoic acid was the synthesis of other fossil-based chemicals (62%), followed by the generation of the renewable electricity used in the MES plant (32%). The water footprint of MES-based hexanoic acid was 121 m^3/t C6A. C6A production activity accounted for 96% in total. Among the subcategories, the synthesis of other fossil-based chemicals (72%) and the generation of the renewable electricity used in the MES plant (12%) were the hotspots. The reference product, coconut-based hexanoic acid, had a water footprint one order of magnitude higher than the MES-based counterpart (1,202 m^3/t C6A), which remains questionable due to the conflicting data provided in different life cycle inventory (LCI) databases.

From the results in **chapter 5**, the neat SAF upgraded from MES-based hexanoic acid had cradle-to-gate emissions of 297 g CO_2eq/MJ neat SAF when using economic allocation and 251 g CO_2eq/MJ neat SAF when using substitution. The corresponding cradle-to-grave emissions were around 371 and 325 g CO_2eq/MJ neat SAF, respectively. Benefiting from its negligible indirect land change (iLUC) emissions, the MES-based neat SAF could be environmentally competitive against some neat SAFs that are produced from the 1st-generation biomass (e.g., palm oil and soybean oil) via the currently most industrialised route: hydroproccessed esters and fatty acids (HEFA), of which the direct CO_2eq emissions and iLUC emissions can collectively exceed 300 g CO_2eq/MJ neat SAF. However, given the growing development and deployment of other neat SAFs with a carbon intensity lower than the conventional jet fuel (<89 g CO_2eq/MJ [6]) on a cradle-to-grave basis (e.g., neat SAFs originating from agricultural and municipal solid wastes), upgrading hexanoic acid to n-alkanes might not be the route to follow from an environmental point of view.

From the results and analysis presented above, some key hurdles of the feasibility of novel CO_2 conversion technologies powered by renewable electricity have been identified via the case study of MES, which can be translated into the core attributes of their competitiveness. From a technical perspective, and in contrast to the competing technologies, the novel electrolysers have not yet reached a high yield or a highly concentrated product stream. Therefore, intensive DSP for separating and purifying the target product is needed, requiring inputs of utilities, chemicals, and solvents. Moreover, DSP (because of their operating principles and heat exchangers, dimensioned for steady-state operation) can require stringent operating conditions and thus possibly restrict the flexibility of the entire plant's operation. From an economic perspective, as employing novel and thus costly equipment, high CAPEX can be a hotspot that reduces their current/short-to-medium term competitiveness towards more established production pathways. Additionally, given the large quantity of electricity consumption, economics will strongly rely on the electricity price. From an environmental perspective, the use of renewable electricity can greatly lower greenhouse gas (GHG) emissions, but it still notably contributes to other environmental impacts. Another environmental bottleneck can be the DSP technologies selected, where a large quantity of fossil-based utilities, solvents, and other chemicals are consumed. Furthermore, without using biomass as feedstock, CO_2 conversion technologies can avoid considerable direct and indirect land use and corresponding emissions. Last but not least, the end product of novel CO_2 conversion technologies coupled with renewable electricity, which involves market development, should be carefully determined, taking into account also future competitors based on alternative raw materials and processes.

Main question: What process designs and conditions could facilitate the upscaling of a novel CO_2 electrochemical plant under intermittent renewable electricity supply?

Technical aspect

First of all, regardless of whether continuous or intermittent electricity supply is used, the productivity and product concentration of the electrolysers should be improved. Otherwise, complex DSP technologies and purification trains could be required, which can indirectly restrict the flexibility of the plant. For example, in the MES plant, two cycles of liquid-liquid extraction and solvent regeneration with stringent operating conditions heightened the chance of decreasing the volume flexibility of the plant. Additionally, more utilities and chemicals can be consumed in the DSP to recover and purify the products. On the other hand, this suggests that electrolysis technologies with low productivity and a dilute product stream can better aim for potential applications where less concentrated products are required.

When IRE is coupled, though electrolysers might be flexible in terms of throughput rate, the DSP technologies might still be subject to stringent operating conditions. Their inflexibility would significantly affect the production time and quantity, thus the economic outcomes. Therefore, designers should stress the choice of flexible technologies for the entire plant, including DSP. In addition, consciously sizing equipment to accommodate expected fluctuations is important; the volume flexibility of all the equipment in the entire plant should match. Furthermore, buffering units can smoothen the intermittency by decoupling the less flexible units from the more flexible units. Their sizing and scheduling as how much and when to store or drain, can also impact the plant's volume flexibility. Lastly, installing smaller parallel units instead of one larger unit can keep the production ongoing when the electricity supply is relatively low by shutting down part of the parallel units.

The pattern of electricity profiles also matters. When the available electricity is more often below the minimum required load for production or above the maximum tolerable load of the plant, the available electricity is more likely not used, leading to less production. The peaks and valleys in IRE profiles are never perfectly alternating, so the extra electricity available in the previous hour cannot always be stored and used for compensating electricity shortage in the next hour. Sometimes, the electricity shortages are too long, and it will be cost-prohibitive to install buffering units such as storage tanks to fill the gap. Therefore, choosing less intermittent electricity profiles in the first place and implementing design strategies to counteract the fluctuations can be helpful.

Economic aspect

When the novel electrochemical plant is driven by constant grid electricity, its product might be competitive but not advantageous in today's market due to the high CAPEX of the specific equipment and the operating costs of electricity consumption. With intermittency, the sunk cost appears to further worsen. Therefore, the technology has to be enhanced and is indeed under continuous improvement such that equipment costs become much lower. Moreover, a cheaper electricity deal should be made between the plant and renewable electricity suppliers. Cheap buffering units, such as storage tanks, can enhance the plant's volume flexibility by smoothening the intermittency and hence promoting production quantity while improving the economic outcomes. Optimising the scheduling of the plant, in addition to implementing buffering units, can further promote volume flexibility, production, and hence economic performances. The aim is to minimally invest in their capital costs while using them to maximally promote production. On the other hand, the product can also have a chance in the market if its market price increases in the future, implying 1) a soaring demand for the product in general, 2) competing but less sustainable production routes being charged significantly for waste generation, 3) a collapse in its production via other cheaper pathways, or 4) a striking change in consumer's behaviour.

Environmental aspect

Coupling electrolysis with renewable electricity exhibits lower environmental impacts than with current grid electricity. However, it is not necessarily cleaner than its market competitors. The possible fossil-based utilities, solvents, and/or other chemicals used in the DSP can be a bottleneck, which is essentially linked to the DSP technologies selected. Moreover, the carbon intensity of the CO_2 feedstock stream also matters, as the CO_2 might not be biogenic or atmospheric, and the capture process consumes energy, solvent, and/or chemicals.

3 Limitations

This dissertation performed an ex-ante assessment of a novel technology, which required the use of several assumptions. In this section, the major assumptions and limitations in methodologies are discussed.

3.1 Assumptions

An important limitation of this work is that ramping rates were not considered. This work was conducted as a first exploration of flexibility in a novel plant (TRL 3). Introducing ramping rates would require experimental data. The results obtained in this dissertation are therefore optimistic and it can be expected that additional penalties both in production quantity and utility consumption would occur. Furthermore, the advantages of batteries might become more apparent in preventing the shutdown of production.

Regarding the flexibility of the DSP units, apart from the three distillation columns, other equipment was assumed to be fully flexible, meaning they could operate no matter what flow rate it was and, meanwhile, were not subject to any loss in performance or safety hazards. This was done because other units have less stringent operating conditions. Also, within the volume flexibility range of the three columns, the efficiency of other units is limitedly impacted according to industrial experience. In reality, it's important to note that their efficiency would not always remain the same as the nominal conditions, and their operational safety should not be overlooked.

In **chapter 4**, when a ST was implemented in the MES plant, it was hypothesised that electricity was all consumed by the more flexible section of the process and utility was all consumed by the less flexible section of the process for simplicity, which was supported by the results in **chapter 3**, where only 1.5% of electricity was consumed in the less flexible section and only 1% of the utility was used in the more flexible section. Though this assumption caused negligible changes in the production quantity, the results of the volume flexibility range would significantly change if this assumption was not made. When the intermediate chemicals were stored in the ST, the DSP did not use the corresponding quantity of electricity required to convert the intermediate chemicals to final products. As a result, even though the available electricity was equal to or higher than the plant's nominal electricity consumption rate, the process would not be available to consume electricity at the nominal rate.

Regarding the supply chain, it was also ideally assumed that the renewable electricity plant would always prioritise the needs of the MES plant, which made them dedicated to the MES plant. According to the EU regulations, if the renewable electricity plants are new, then the additionality is guaranteed. Otherwise, apart from in-house renewable electricity farms, any existing renewable electricity farm should not be dedicated to a specific customer [7]. In this dissertation, data from two existing renewable electricity farms were used as references, although our intention was to establish a power purchase agreement with new renewable electricity plants. Electricity shortage caused by insufficient allocation would hamper the MES production and, consequently, the levelised production cost. Moreover, it was assumed that CO_2 used in the MES plant was at a constant quality and could be supplied on demand. In this way, no CO_2 pre-treatment was considered in the MES plant. Therefore, extra pre-treatment and storage units for CO_2 should be considered in further work.

Regarding the economic parameters, assumptions were made regarding the purchase costs of the MES and BESS units. However, not all assumed data inputs underwent a sensitivity analysis since the main investigated variable was the intermittency level. All in all, the investigated conditions and assumptions in this dissertation are highly specific. The methods used in this work can be applied to other studies, but the results or trends should not be directly generalised to other similar Power-to-Chemicals concepts without rigorous reasoning.

3.2 Selection of downstream processing

The two main DSP technologies used in this dissertation were membrane-based LLE and vacuum distillation. Membrane-based LLE requires preceding acidification of carboxylates and the use of a solvent, while vacuum distillation consumes a great deal of medium-pressure steam and hot oil. The possibility that they would impact the environmental performances was already known before the modelling. Indeed, the LCA results showed that the acid used for the acidification was the reason why "other chemicals" were among the major contributors to the environmental impacts. The hot oil made "utilities" another bottleneck.

They were still selected for several reasons. First, they have been applied to recover and purify hexanoic acid by others [8]. Second, distillation is a mature technology and is used by competing processes [4, 9]. There are alternative emerging and possibly cleaner technologies promising for separating and purifying carboxylic acids, such as reverse osmosis, electrodialysis, and anion exchange with carbon dioxide expanded methanol desorption [10]. However, models of those technologies are not directly available in Aspen Plus, and at the time of writing this work there was insufficient data to even model these technologies as a black box. One can certainly create models in Aspen

Custom Modeler based on their thermodynamic and kinetic data, if any, and import them into Aspen Plus. However, this is not the focus of this PhD thesis, and therefore, it was decided to select more conventional units.

3.3 Process simulation

This dissertation designed and modelled the chemical process at steady state in Aspen Plus. The MES unit was treated as a black box due to the lack of its thermodynamics and kinetics. In the following research, Aspen Custom Modeler could be employed. Moreover, as the design was the first attempt, the equipment was not sized to match their volume flexibility. Additionally, the reference design was finished with some inherent flexibility. If it had been optimised for steady-state operation, its CAPEX would have been lower. Finally, in Aspen Plus simulation, heat was consumed or generated as utilities, such as low-pressure steam and hot oil. The same type of utilities consumed and generated were subtracted. More costs would have been incurred to implement extra heat exchangers for the heat integration. Lastly, regarding the validation of simulation, the work performed in this thesis is an ex-ante assessment for a design that it is not yet deployed (the technology is at TRL 3). A formal validation of results would require a pilot or demonstration unit that would produce experimental data to validate the results. Instead, we only performed a sanity check at the equipment level using data from literature from analogous processes and expert opinions. Experiments or pilots should be performed to validate the results in the future.

3.4 Indicator for volume flexibility

In this dissertation, the design of the indicator for volume flexibility at the plant level, LRR, also took into account demand response (DR). Therefore, LRR emphasised how much available electricity from the renewable electricity farms could be fully consumed by the plant. In terms of production of hexanoic acid, LRR only indicated if hexanoic acid was produced without detailing the precise production quantity. In some cases, when the production quantity was improved, LRR was not improved, hence creating an incomplete picture. Furthermore, as mentioned in section 3.1, the apparent improvement in LRR when a ST was installed, and the scheduling was optimised mainly relied on the assumption made that the more flexible part of the process consumed all the electricity. Otherwise, the formulas defining LRR should be modified.

3.5 Optimisation

The optimisation problem in **chapter 4** was solved as a one-layer mixed-integer quadratically constrained programming (MIQCP) problem, which requested substantial computational power and time. One quadratic constraint was formulated to prevent the ST from filling and draining simultaneously. Normally, this nonlinearity could be reduced by adapting the one-layer MIQCP problem to a two-layer mixed-integer linear programming (MILP) problem. The outside layer can loop the capacity of the ST as an integer variable. Meanwhile, the nested layer treats the capacity of the ST as a constant parameter and introduces another two binary variables to confine the filling and draining variables of the ST using linear inequalities with a constant ST capacity. We benefited from the DelftBlue supercomputer, which was powerful enough to directly solve the one-layer MIQCP problem. If there is no access to such powerful computers, the abovementioned method is suggested.

3.6 Treatment of multifunctionality

Economic allocation and system expansion with substitution were used to address the multifunctionality of the system during the LCA. System expansion without substitution was not performed owing to the complex product portfolio resulting from the fractional distillation of plant oils. If MES-based hexanoic acid is able to replace current plant-based hexanoic acid in the future, system expansion with substitution and consequential LCA should be performed to provide a more comprehensive understanding of the environmental impacts.

4 Recommendations

4.1 Microbial electrosynthesis

It is recommended that the MES's tolerance of impurities in the CO_2 feed stream should be investigated by the technology developers. Moreover, kinetic data of the MES operated under intermittency should be studied at a lab scale to enable dynamic modelling of the plant. And undoubtedly, the productivity and efficiency of the MES should be largely enhanced. As informed by Dr. Ludovic Jourdin, at the end of my PhD journey, the productivity of this MES electrolyser has been enhanced three-fold as compared to what was assumed in this dissertation, though the purity of the product stream has not been notably improved.

Furthermore, today's hexanoic acid has a niche market owing to its current commercial production method. Just replacing the current market of plant-based hexanoic acid with MES-based hexanoic acid can be challenging. First, plant-based hexanoic acid is much cheaper as it is a by-product. Additionally, hexanoic acid from the bio-fermentation route is also highly competitive given its higher TRL and similar LPC_{C6A}. Therefore, creating more demand to expand the market of hexanoic acid and/or its derivatives is necessary. This thesis indicates that upgrading hexanoic aid to n-alkanes is not attractive from an environmental perspective unless significant changes in the process occur. Other options, such as adipic acid, could be explored.

4.2 Renewable electricity and volume flexibility

The pattern of IRE profiles is essentially a geographical factor. Therefore, back-engineering, as what pattern of (hybrid) IRE profiles is ideal to enable a feasible production, can also be studied. This information can help with plant siting, renewable electricity sourcing, plant scheduling, etc. However, it should be noted that this practice should not exacerbate the imbalance of the local grid network. Moreover, the pricing of renewable electricity could also play a role in the hourly operation of the plant, which is recommended for further investigation.

In this thesis, we only looked at one design strategy to cope with intermittency (use of buffers). Other design strategies for volume flexibility can be investigated, such as deploying more flexible DSP technologies or modularising the units. If other flexibility types are also desired for the plant (as defined in **chapter 2**), the interaction between different flexibility types should also be studied. Maybe an indicator for overall flexibility needs to be proposed if justifiable.

This dissertation has shown that the electrochemical plants would face significant economic penalties if they operate flexibly rather than at a steady state, and if the electricity and equipment are available at current market prices. These economic penalties would possibly discourage the electrochemical plants from participating in DR. Then the question comes as to why the electrochemical plants should take the risks alone. The industrial sector, together with the power supplier, should make a joint effort so that the deployment of electricity-based chemical processes can make a significant contribution to the defossilisation of the industrial sector.

References

[1] M. T. Agler, C. M. Spirito, J. G. Usack, J. J. Werner, and L. T. Angenent. “Development of a highly specific and productive process for n-caproic acid production: applying lessons from methanogenic microbiomes”. Water Science & Technology. 691. 2014. Pp. 62–8. DOI: `10.2166/wst.2013.549`.

[2] P. Dessi et al. “Microbial electrosynthesis: Towards sustainable biorefineries for production of green chemicals from CO_2 emissions”. Biotechnology Advances. 46. 2021. P. 107675. DOI: `10.1016/j.biotechadv.2020.107675`.

[3] P. Debergh and M. Van Dael. “Production of caproic acid from acetate and ethanol through microbial chain elongation: A techno-economic assessment”. Bioresource Technology Reports. 18. 2022. P. 101055. DOI: `10.1016/j.biteb.2022.101055`.

[4] W. Chen, D. Strik, C. J. N. Buisman, and C. Kroeze. “Production of Caproic Acid from Mixed Organic Waste: An Environmental Life Cycle Perspective”. Environmental Science & Technology. 5112. 2017. Pp. 7159–7168. DOI: `10.1021/acs.est.6b06220`.

[5] J. C. Alouw and S. Wulandari. “Present status and outlook of coconut development in Indonesia”. 1st International Conference on Sustainable Plantation (1st Icsp 2019). 418. 2020. P. 012035. DOI: `10.1088/1755-1315/418/1/012035`.

[6] L. Jing et al. “Understanding variability in petroleum jet fuel life cycle greenhouse gas emissions to inform aviation decarbonization”. Nature Communications. 131. 2022. P. 7853. DOI: `10.1038/s41467-022-35392-1`.

[7] European Commission. Commission Delegated Regulation (EU) 2023/1184 of 10 February 2023. 2023. URL: `http://data.europa.eu/eli/reg_del/2023/1184/oj`.

[8] P. O. Saboe et al. “In situ recovery of bio-based carboxylic acids”. Green Chemistry. 208. 2018. Pp. 1791–1804. DOI: `10.1039/c7gc03747c`.

[9] E. C. Canapi, Y. T. V. Agustin, E. A. Moro, E. Pedrosa, and M. L. J. Bendano. “Coconut Oil”. Bailey’s Industrial Oil and Fat Products. F. Shahidi. Vol. 1-6. 2005. John Wiley & Sons. Chap. Coconut Oil. Pp. 123–147. DOI: `10.1002/047167849X`.

[10] C. Fernando-Foncillas, C. I. Cabrera-Rodriguez, F. Caparros-Salvador, C. Varrone, and A. J. J. Straathof. “Highly selective recovery of medium chain carboxylates from co-fermented organic wastes using anion exchange with carbon dioxide expanded methanol desorption”. Bioresource Technology. 319. 2021. P. 124178. DOI: `10.1016/j.biortech.2020.124178`.

A

Appendix A: Literature search and mapping

A.1 Searching criteria for the literature search performed on Scopus

Table. A1. Searching criteria for the literature search performed on Scopus.

Boolean operator	Search item	Field
	English	Language
AND	"chemical industry" OR "chemical plant" OR "process industry" OR "process engineering" OR "chemical process" OR "biochemical industry" OR biorefinery OR biorefineries	Article title, Abstract, Keywords
AND	flexible OR flexibility	Article title, Abstract, Keywords
AND	chemical OR biochemical OR biotechnology OR renewable OR biofuel*	All fields
AND NOT	human OR nonhuman OR animal* OR microelectronic OR optical OR genetic* OR ceramic* OR "metal-organic framework" OR MOF* OR "glass transition" OR "tensile strength" OR graphene* OR nanocomposite* OR nanoparticle*	Article title, Abstract, Keywords
AND NOT	article OR "priority journal" OR "conference paper"	Keywords
AND NOT	"flexible electronic" OR "flexible electronics" OR "flexible foam" OR "flexible substrate" OR "flexible bone" OR "flexible surface" OR "flexible device"	Article title, Abstract, Keywords
AND NOT	"polymer international" OR optical OR "polymer reviews" OR "ink world"	Source title
AND NOT	"surface modification" OR spectroscopy	Article title, Abstract, Keywords
AND NOT	polyurethane OR "flexible packaging" OR "flexible textile" OR "flexible film" OR yarn OR "flexible fiber" OR carbontube OR nanotube	All fields
Date range	1990 - present (July 2020)	
Document types	All	
Access types	All	

A.2 Details on mapping parameters of the bibliometric graphs in VOSviewer

The keyword maps were created based on bibliographic data exported from Scopus decade by decade. Co-occurrence was chosen to be the type of analysis, and the unit of analysis was all keywords. The counting method was full counting. Keywords shown on the maps had a minimum number of occurrences of 5. However, to avoid sheltering other keywords caused by some popular generic keywords, keywords listed in the table below were unselected from the keywords list in VOSviwer and hence invisible on the maps. Other specific parameters for mapping can be found in the table below as well.

Table. A2. Mapping parameters in VOSviewer.

Unselected keywords	"chemical industry", "chemical engineering", "chemical plant", "chemical plants", "chemical process", "chemical processes", "flexibility", "process industry", and "process engineering"
Normalization method	Associate strength
Resolution	300%

B

Appendix B: Supporting information for process design and techno-economic assessment

B.1 Technical specifications of microbial electrosynthesis

Technical specifications of the microbial electrolysis (MES) technology used in this dissertation are specified in Tables B1-B4. "input assumptions" are approved by Dr. Ludovic Jourdin and Dr. Adrie Straathof at Delft University of Technology based on Dr. Jourdin's previous work [1] and references therein.

Table. B1. MES performance settings

MES performance settings			Note
Current density (A/m^2 effective area)		1000	input assumption
Total e^- uptake rate [mole e^-/(m^2 active area*h)]		37	calculated
Total faradaic efficiency into products (incl. biomass & H_2) (%)		100	input assumption
Total e^- uptake rate (mole e^-/h)		382336	calculated
Carbon selectivity (carbon for production and biomass growth, excl. pH control)			
	C into caproate (%)	80	input assumption
	C into butyrate (%)	10	input assumption
	C into acetate (%)	10	input assumption
	C into biomass	0	input assumption
Cell voltage (V)		1.80	input assumption
CO_2 conversion efficiency (%)		100	input assumption
H^+ membrane crossover efficiency (%)		90	input assumption
Temperature influent (°C)		32	experimental conditions [1]
Temperature effluent (°C)		32	experimental conditions [1]
Reactor temperature (°C)		32	experimental conditions [1]
Pressure inside the electrolyser (bar)		1.02	experimental conditions [1]
Cathode pH		5.8	experimental conditions [1]
Anode pH		2	experimental conditions [1]
Electricity consumption (TJ/y)		582	calculated

Table. B2. Material balance

Material balance		Note
Required mole e^- for caproate per mole C outcome	4.3	calculated
Required mole e^- for butyrate per mole C outcome	0.50	calculated
Required mole e^- for acetate per mole C outcome	0.40	calculated
Required e^- per mole C outcome	5.2	calculated
e^- into caproate (%)	0.83	calculated
e^- into butyrate (%)	0.10	calculated
e^- into acetate (%)	0.08	calculated
e^- into biomass (%)	0	calculated
Caproate productivity (mol/m^2 effective area/h)	0.96	calculated
Butyrate productivity (mol/m^2 effective area/h)	0.18	calculated
Acetate productivity (mol/m^2 effective area/h)	0.36	calculated
Total faradaic efficiency into products (excl. biomass) (%)	1	input assumption
H^+ needed in all cathode chambers for the production of organics (kmol/h)	382	calculated
H^+ produced in all anode chambers (kmol/h)	382	calculated
H^+ crossed over (kmol/h)	344	calculated
H^+ needed for production from catholyte because of non-100% H^+ transfer efficiency (kmol/h)	38	calculated
H^+ for H_2 production (kmol/h)	0	calculated
OH^- needed to neutralise the acids (kmol/h)	14	calculated
OH^- generated because of extra H^+ consumption in cathode (kmol/h)	38	calculated
CO_2 addition to neutralise OH^- to keep pH@5.8 (kmol/h)	24	calculated
H_2O produced in all cathode chambers (kmol/h)	117	calculated
H_2O reacted in all anode chambers (kmol/h)	191	calculated
O_2 produced (kmol/h)	96	calculated
e^- required incl. all(mol/m^2 active area/h)	37	calculated
e^- required for production excl. biomass growth (mol/m^2 active area/h)	37	calculated
CO_2 for production excl. biomass growth (kmol/m^2 active area/h)	0.0072	calculated
CO_2 total consumption for production (kmol/h)	74	calculated

Table. B3. Hexanoic acid (C6A) production parameters - plant level

C6A Production parameters - plant level (some deviation from simulation results)		Note
C6A production target (t/y)	10040	input assumption
Nominal effective operating time (h/y)	8760	input assumption
C6A production rate (kg/h) - in product stream	1146	calculated
Caproate production rate (kmol/h)	10	calculated
Butyrate production rate (kmol/h)	1.85	calculated
Acetate production rate (kmol/h)	3.7	calculated
Caproate production rate (kg/h)	1136	calculated
Butyrate production rate (kg/h)	161	calculated
Acetate production rate (kg/h)	218	calculated
Carboxylates max purity in the MES (kg/m^3)	10	input assumption
Water out from cathode (kmol/h)	8420	calculated
Water into cathode (kmol/h)	8303	calculated
Water flowrate into anode (kmol/h)	191	calculated
Caproate productivity (kg/m^2 active area/day)	2.66	input assumption

Table. B4. Scaling up MES - plant level

Scaling up MES - plant level		Note
Total active area (m^2)	10247	calculated
Active area of a single cathode (m^2)	2.5	input assumption
# of cells/cathode chambers	4099	calculated
Total volume of real total cathode chamber (m^3)	128	calculated
Caproate flowrate per cathode chamber (g/h)	277	calculated
Caproate flowrate per cathode chamber (mol/h)	2.4	calculated
Butyrate flowrate per cathode chamber (mol/h)	0.45	calculated
Acetate flowrate per cathode chamber (mol/h)	0.90	calculated
Biomass flowrate per cathode chamber (mol/h)	0	calculated
Butyrate flowrate per cathode chamber (g/h)	39	calculated
Acetate flowrate per cathode chamber (g/h)	53	calculated

B.2 Details of the process route

Fig. B1 illustrates the process route. The microbial electrosynthesis (MES) stacks were operated at 32°C and 1.02 bar [1]. The anode compartments of the MES stacks were fed with demineralised H_2O, and O_2 was produced. Renewable pure decompressed CO_2 (e.g., CO_2 stripped from flue gas, compressed to 100 bar) and demineralised H_2O fed into the cathode compartments. The faradaic efficiency of the products was assumed to be 100%. The conversion efficiency of dissolved CO_2 was assumed to be 100% in this process. The carbon selectivity was assumed to be 10% in acetate and acetic acid, 10% in butyrate and butyric acid, and 80% in caproate and hexanoic acid (C6A) [2]. Biomass growth was assumed to be inhibited [3]. Due to the maximum limit of carboxylic acids on microbial cells' activity, the titre of the carboxylates and corresponding acids was assumed to be 10 g/L. 100% of H^+ generated in the anode chamber crossed from the to the cathode chamber over the cation exchange membrane. The pH value of the cathode compartment was maintained at 5.8 by dosing $Ca(OH)_2$. pH buffer chemicals and nutrients were neglected. The outlet stream of the cathode compartments is further acidified with H_3PO_4 solution in preparation for later purification and commercialisation. In the acidification unit, $CaHPO_4$ was generated and partially precipitated. The first purification unit is a set of liquid-liquid extraction based membrane contactor stacks (LLE1), operated at 1.02 bar [4]. Tri-octylamine (TOA) was supplied to the extent that 99.95% of the C6A was extracted. The raffinate stream was recycled to the MES unit after 2% of purging. The following vacuum solvent regeneration column (SR1) was operated at 0.05 bar. The column had 5 stages with the third stage being the feed stage. Two operating variables (i.e., reflux ratio and bottoms to feed ratio) were employed to control two Design Specifications of the column: (i) a recovery rate of 99.94% for C6A and (ii) a mass purity of 0.02% for TOA in the distillate. Its distillate stream was fed into another LLE-based membrane contactor set (LLE2) operated at 1.02 bar. TOA was supplied to the extent that 99.93% of the C6A was extracted. The raffinate stream was recycled to the MES unit after 2% of purging. The extract stream was sent to another solvent regeneration column (SR2), which was operated at 0.05 bar. This column had 4 stages with the second stage being the feed stage. Two operating variables (i.e., reflux ratio and bottoms rate) were employed to control two Design Specifications of the column: (i) a recovery rate of 99.87% for C6A and (ii) a mass purity of 1.7 10^{-5} for TOA in the distillate. Its distillate stream was fed to a dehydration column (TD) operated at 1.02 bar. This column had 20 stages, with the 19th stage being the feed stage. Two operating variables (i.e., reflux ratio and bottom rate) were employed to control two Design Specifications of the column: (i) a recovery rate of 15.77% for butyric acid in the bottom stream and (ii) a mass purity of 99% for C6A in the bottom stream. The bottom stream was the product stream and was cooled down to a storage temperature of 25°C and centrifuged to remove the last hint of $CaHPO_4$ precipitate. The final product stream was then C6A at a purity of 99 wt% in liquid form. It was assumed that all the $CaHPO_4$ precipitate was removed with a moisture content of 8%. The process flowsheet and stream table are provided in Appendix C.

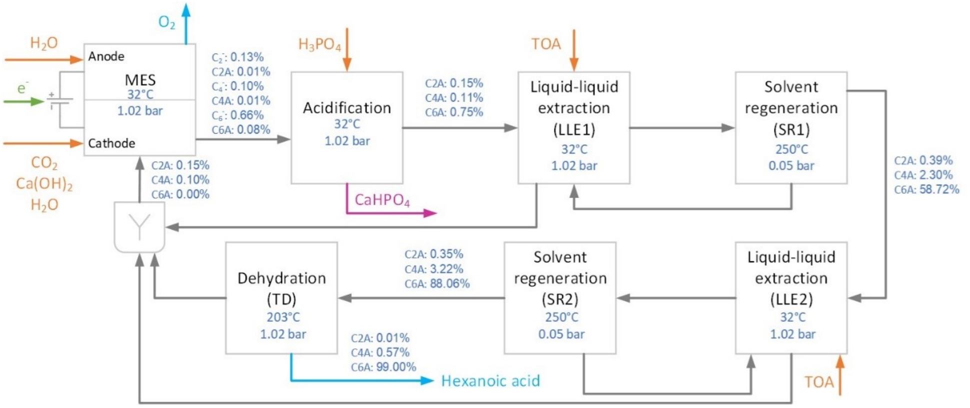


Fig. B1. Block flow diagram with operating conditions of key unit operations and mass purity of carboxylates and carboxylic acids of key streams, if any. MES: microbial electrosynthesis. LLE: liquid-liquid extraction. SR: solvent regeneration. TD: dehydration column. TOA: tri-octylamine. $C2^-$: acetate. C2A: acetic acid. $C4^-$: butyrate. C4A: butyric acid. $C6^-$: hexanoate. C6A: hexanoic acid.

B.3 Decomposed models for distillation columns

The built-in trayed RadFrac column integrated with reboiler and condenser was initially selected to represent the three distillation columns (i.e., SR1, SR2, and TD) in the process. However, when estimating the volume flexibility of the three distillation columns, the size of the reboilers and condensers could not be fixed within the integrated models. Therefore, decomposed columns were created by adapting the integrated RadFrac column. The default integrated reboiler and condenser were selected as none in the RadFrac settings. Instead, two HeatX and two splitters were added adjacent to the distillation tower, representing the total reboiler and total condenser (as shown in Fig. B2).

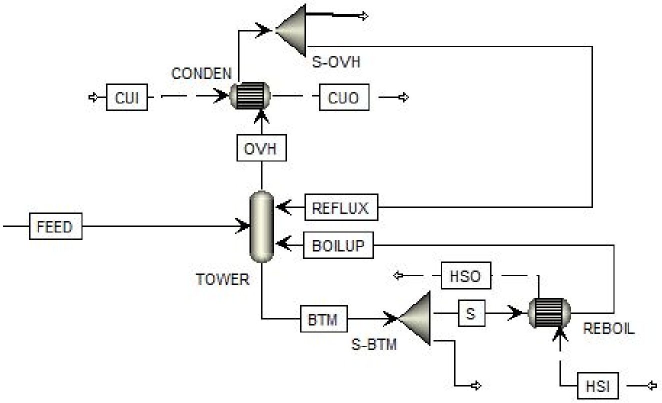
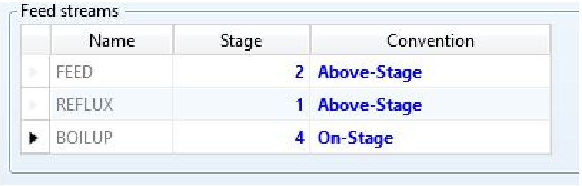


Fig. B2. An example of a decomposed distillation column. CUI/CUO: cold utility in/out. HSI/HSO: heating stream in/out. S-BTM: bottom stream. S-OVH: overhead stream.

B.3.1 Distillation tower

The internal dimension of the distillation tower could be fixed by specifying the number of stages, the spacing between stages, the tray details, etc. Details of the internal dimensions and settings of the three distillation columns are summarised in Appendix C. It should be noticed that combining two isolated HeatX with a single distillation tower changed how feed streams should be sent to the column, accordingly, the RadFrac settings should be adjusted. Fig. B3 is an example of the feed-in convention settings for the decomposed column. Apart from the original feed stream, reflux and boilup streams were also supposed to be sent back to the column. Within the integrated RadFrac model (see Fig. B4), the reflux stream is sent to the column above the first tray, and the boilup stream is above the last stage (i.e., the reboiler). In a decomposed model, the reflux stream could be managed the same as the feed-in convention. As for the boilup stream, the intuitive option was to send it on the second last stage (i.e., the last tray), which meant that the second last stage was not used for gas-liquid interaction. As a result, the quality of its product stream would not meet the expectations. On the other hand, it implies that to replicate the desired results as that of the integrated RadFrac column, an additional tray had to be added below the original last tray. This practice would increase the total stages and, thus, the height of the tower. However, the hydraulic behaviours were monitored for the heightened tower. With proper adjustment, the additional try did not impact the hydraulic behaviour of the above ones. Moreover, the initial integrated RadFrac column was used for economic analysis. With the heightened tower, there were two feed-in conventions. For the first option, the boilup stream could be fed on the last tray, where the product stream flows out. Alternatively, the boilup stream could be sent below the last tray, so the last tray was used for the interaction between the liquid and steam. However, the product stream could only come out on/above the last tray, and the stream quality was not desired. Therefore, this option was discarded.



Feed streams

Name	Stage	Convention
FEED	2	Above-Stage
REFLUX	1	Above-Stage
BOILUP	4	On-Stage

Fig. B3. An example of the feed-in convention settings for the decomposed column.

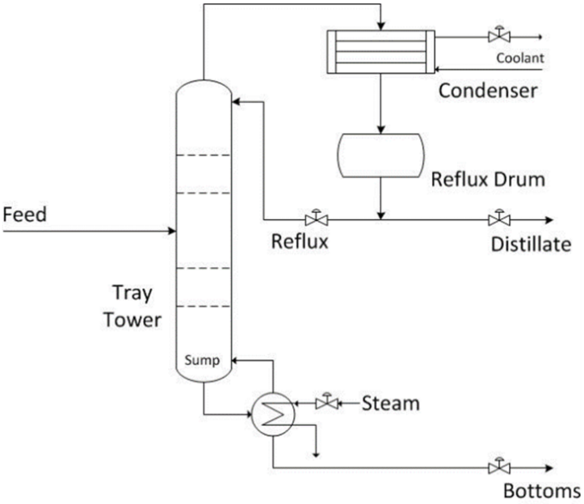


Fig. B4. A schematic illustration of the feed-in convention of an integrated trayed RadFrac column. The reflux stream is sent to the column above the second stage (i.e., the first tray). The boilup stream is sent below the second last stage (i.e., the last tray) [5].

B.3.2 Heat exchanger

The reboiler and condenser were modelled by two HeatX units. The size of the HeatX was fixed considering 100% the nominal throughput rate. First, the Model Fidelity was selected as "Shortcut" and the Calculation Method as "Design". Then, the outlet vapour fraction was specified as 0 for the hot utility stream in a condenser or 1 for the cold stream in a reboiler. The minimum temperature approach was set to 5°C for condensers or 10°C for reboilers. Second, the cold and hot utilities were specified as material streams. The usage of the two utility streams was controlled by Design Specs. Third, the split fractions of the two splitters in the decomposed RadFrac column could be estimated by copying the reflux and boilup ratios in the result page of the initial integrated RadFrac column. Fine-tuning of the splitting fractions might be required to reach the same results as that of the integrated RadFrac column. Fourth, the process model was run, and the thermal results (e.g., heat duty "Q", stream temperatures, log-mean temperature difference "LMTD") were recorded. Fifth, the Calculation

Method was changed to the Simulation Method where the overall heat transfer coefficient "U" and overall heat exchange area "A" were to be specified. The "U" Method was specified with a "U" value, which was estimated according to the heuristics provided by Sieder, Seader, and Lewin [6]. With the "Q" and "LMTD" obtained in the previous step, "A" could be determined with the application of Equation B1. The decomposed column was then set up and ready for the estimation of volume flexibility. Specifications of the heat exchangers are summarised in Table B5.

$$Q = U * A * LMTD \tag{B1}$$

$$LMTD = \frac{(Temp_{\text{in}} - temp_{out}) - (Temp_{out} - temp_{in})}{\ln\left(\frac{Temp_{in} - temp_{out}}{Temp_{out} - temp_{in}}\right)}$$

where,
Q, heat duty, kJ/s
U, overall heat transfer coefficient, kJ/(s*m^2*K)
$LMTD$, log-mean temperature difference, K
A, heat exchange surface area, m^2
$Temp_{in}$, inlet temperature of the hot stream, K
$Temp_{out}$, outlet temperature of the hot stream, K
$temp_{in}$, inlet temperature of the cold stream, K
$temp_{out}$, outlet temperature of the cold stream, K

Table. B5. Specification of heat exchangers.

	U (kJ/s*m^2*K)	A (m^2)	Temp$_{\text{in}}$ (°C)	Temp$_{\text{out}}$ (°C)	Utility
TD condenser	0.11	37.31	105.15	100.62	Cooling water
SR1 condenser	2.27	11.96	96.90	30.06	Chilled water
SR2 condenser	2.83	1.89	114.13	32.11	Chilled water
	U (kJ/s*m^2*K)	A (m^2)	temp$_{\text{in}}$ (°C)	temp$_{\text{out}}$ (°C)	Utility
TD reboiler	0.57	5.57	195.73	203.01	Hot oil
SR1 reboiler	1.14	83.38	247.76	250.48	Hot oil
SR2 reboiler	1.14	2.02	133.61	221.78	Hot oil
Sources	[7]	Aspen model (i.e., the results of the process at nominal conditions, unless otherwise stated)			

B.4 Validation of the process model

Given the technology readiness level of MES and membrane-based LLE, it is challenging to validate the simulation results of the whole process configuration without experiments or pilots. However, we carried out a sanity check at the unit level with the help of analogous literature, technology developers and industrial experts. Specifically:

MES unit

The MES was scaled up based on the input assumptions approved by Dr. Ludovic Jourdin and Dr. Adrie Straathof, based on their experimental work and projection for near-future performances of this specific MES unit.

LLE units

The LLE modelled in Aspen Plus was based on the experimental work of [4]. The purities of carboxylic acids they had were 100 g/L acetic acid, 100 g/L butyric acid, and 100 g/L hexanoic acid. They tested a range of organic phase to aqueous phase volume ratios for their first cycle of extraction (equivalent to LLE1 in our block flow diagram): 0.03-4.00. Their results showed that when the volume ratio was 0.10, the first extraction led to a caproic acid recovery rate of 90%. After the second cycle of extraction, the recovery rate of hexanoic acid reached 99%. These values were used as an indication for our units LLE1 and LLE2.

We first calibrated the Aspen Plus models by testing the range of volume ratios (i.e., 0.03-4.00) using carboxylic acids' purities studied in [4] (i.e., 100 g/L acetic acid, 100 g/L butyric acid, and 100 g/L hexanoic acid). A LLE unit was modelled in Aspen Plus using an extraction tower with the property method UNIF-HOC. When the volume ratio was 0.09, a 90% recovery rate was obtained. When switching to the composition derived from our simulated MES unit (i.e., 1.5 g/L acetic acid, 1 g/L butyric acid, and 7.5 g/L hexanoic acid), 90% of hexanoic acid was recovered using a volume ratio of 0.07.

Next, we adapted the volume ratios of our two extraction towers (i.e., LLE1 and LLE2), because we aimed to recover hexanoic acid as much as possible considering that we also designed a purging rate of 2% when the raffinate streams were recycled. For LLE1, the feed stream was dilute ((i.e., 1.5 g/L acetic acid, 1 g/L butyric acid, and 7.5 g/L hexanoic acid); the volume ratio had to reach 0.42 to yield a recovery rate of 99.95%. For LLE2, since the carboxylic acids in the feed stream were more concentrated (i.e., 3.9 g/L acetic acid, 23.0 g/L butyric acid, and 587 g/L hexanoic acid), a volume ratio of 0.12 led to a recovery rate of 99.93%.

SR units

The vacuum solvent regeneration was modelled following the Aspen Plus simulation model in [4]. Their simulation model was based on experimental work. According to their experiment, 76% and 90% of hexanoic acid were recovered after their first and second cycles of solvent regeneration, respectively. Note that they focused on acetic acid, and they obtained a 100% recovery rate of acetic acid after the first cycle already. For their simulation model, they used the Winn-Underwood-Gilliland method in the Aspen Plus DSTWU shortcut distillation model. They specified a recovery rate of 99.5% and 0.001% for acetic acid and TOA in the distillate stream, respectively. They controlled the vacuum such that the boiling point of the bottom stream was less than 250°C. After obtaining the reflux ratio and column stages, they switched to a RadFrac model.

For our two SR units (i.e., SR1 and SR2 in our block flow diagram), we also first used DSTWU shortcut models and then changed to RadFrac models. However, since we focused on hexanoic acid, our operating conditions were specified differently in DSTWU models. For SR1, 99.94% recovery rate of hexanoic acid and 0.02 wt% of TOA in the distillate stream were specified. The boiling point of the bottom stream was controlled around 256°C at 0.05 bar. For SR2, 99.87% recovery rate of hexanoic acid and 1.75 10^{-5} wt% of TOA in the distillate stream were specified.

Dehydration

The ambient distillation (i.e., TD in our block flow diagram) was modelled following the Aspen Plus simulation model in [4]. However, no relevant experiment was conducted by them. They used the DSTWU shortcut model, which we followed. We specified a recovery rate of 15.77% for butyric acid and (ii) a mass purity of 99% for hexanoic acid in the bottom stream.

Decomposed models

When designing the decomposed models for SR1, SR2, and TD, we followed heuristics in [6–10] and also consulted industrial experts regarding the design of column internals and heat exchangers.

Sanity check

Finally, we did a sanity check with similar simulation work [4, 11]. First, they reached a high purity of carboxylic acids (>98 wt%). Note that their focus was not hexanoic acid. Second, our total heating duties (in MJ/kg carboxylic acid) for condensers and reboilers of the entire downstream processing (i.e., SR1, SR2, and TD) are comparable to the heat duties for the condensers and reboilers of their entire downstream processing. Woo and Kim [11] reported 36 MJ/kg of volatile fatty acid (without heat integration). Saboe et al. [4] obtained around 28 MJ/kg acetic acid (high-water case with heat integration). In our simulation, we obtained 29 MJ/kg hexanoic acid for condensers and reboilers (with heat integration).

B.5 Inputs for techno-economic assessment

B.5.1 Feedstock, products and waste treatment

Table. B6. Prices of inlet and outlet streams of the MES plant.

Item	Price (€$_{2019}$/t)	Source
CO_2	50	[12]
H_2O	0.4	[1]
$Ca(OH)_2$	155	[13]
H_3PO_4	362	[14]
TOA	1000	[15]
Hexanoic Acid (C6A)	3000	[16]
O_2	76	[17]
Wastewater	0.1	[18]
Conventional solid/liquid waste	23	[18]
Hazardous solid/liquid waste	150	[19]

B.5.2 Utility

Table. B7. Specifications of utilities.

Utility	Inlet state variables	Value	Inlet pressure (bar)	Outlet state variables	Value	Outlet pressure (bar)
Chilled water	Temperature (°C)	5	1.02	Temperature (°C)	7.5	1.02
Cooling water		25	1.02		40	1.02
Hot oil		330	1.02		310	1.02
Low-low-pressure steam (LLPS)	Vapour fraction	1	3.9	Vapour fraction	0	3.9
LLPS-generation		0	3.9		1	3.9
Low-pressure steam (LPS)		1	5.5		0	5.5
LPS-generation		0	5.5		1	5.5
Medium pressure steam (MPS)		1	21		0	21
Source	Aspen Plus (i.e., embedded information provided by AspenTech [20]), [21]					

Table. B8. Prices of utilities.

Utility	Price (€$_{2019}$/GJ)
Chilled water	2.4
Cooling water	0.19
Hot oil	3.1
Low-low-pressure steam (LLPS)	1.7
LLPS-generation	1.7
Low-pressure steam (LPS)	1.7
LPS-generation	1.7
Medium pressure steam (MPS)	2.0
Source	[20, 22]

B.5.3 Tax

Table. B9. Specifications of company tax in the Netherlands in 2019.

	Value
High-tax threshold in the Netherlands 2019 (€/y)	200,000
Low tax rate	15%
High tax rate	25%
Source	[23]

B.5.4 Operation and maintenance

Table. B10. Percentages for estimation operation and maintenance costs [8].

Category	Feature	Factor	Basis
Labour costs	Operating supervision	0.15	of operating labour
	Laboratory charges	0.15	of operating labour
Maintenance costs	Maintenance	0.06	of fix capital investment
	Operating supplies	0.15	of maintenance
Fixed & general costs	Taxes	0.02	of fix capital investment
	General costs	0.2	of labour, supervision and maintenance
Plant overhead	Plant overhead	0.6	of labour, supervision and maintenance
Wage per person		55,000 €/y	

B.5.5 Microbial electrosynthesis unit

Table. B11. Economic specifications of the MES [1].

Total cathode area (m^2)	10,247
Single cathode area (m^2)	2.5
Active factor	0.8
Cathode cost (€/m^2)	155
Cathode CAPEX (M€)	2.0
Anode area (m^2)	10,247
Anode cost (€/m^2)	500
Anode CAPEX (M€)	6.4
Cathode chamber thickness (m)	0.01
Anode chamber thickness (m)	0.01
Membrane area (m^2)	10,247
Membrane cost (€/m^2)	10
Membrane CAPEX (M€)	0.13
Single cell volume (m^3)	0.06
Total volume (m^3)	256
Frame cost (€/m^3)	4,000
Frame CAPEX (M€)	1.0
MES CAPEX (M€)	9.5

B.5.6 Membrane-based liquid-liquid extraction unit

The two LLE units should be two sets of membrane contactors [4]. They were modelled as two extraction towers, and the property method selected was UNIFAC-HOC.

B.5.6.1. Dimensioning

Their dimensions were estimated based on Equation B2 [4] and parameters retrieved from different sources (see Table B12).

$$\text{Productivity} * V_F = \text{Area} * \text{Product flux} \tag{B2}$$

where,
V_F, volume of the previous vessel, L

Table. B12. Parameters for quantifying the dimensions of the two membrane-based LLE units.

	Productivity (g/(h*L))	V_F (L)	Product flux (g/(h*m^2))
LLE1	9.85	155441	10
LLE2	575	2084	
Source	Aspen model		[4]

B.5.6.2. Dimensions and costs

Table. B13. Dimensions and costs of the two membrane-based LLE units.

	A single LLE stack	LLE1	LLE2	Lifetime (y)
Area (m^2)	560	153109	119797	15
Number of stacks	1	273	214	
Cost (€)	7200	1968549	1540246	-
Source	[24, 25]			[26]

B.5.7 Battery energy storage system (BESS)

Table. B14. A summary of the techno-economic assumptions for BESS [27–29].

Material	Installed cost (M€/GJ)	Efficiency	Lifetime (y)	Salvage rate	Self-discharge	Response time
Lithium	0.33	0.9	15	0.05	negligible	negligible

B.5.8 Storage tank

Pumps around the storage tank (ST) were neglected. The following formula can be used for calculating the capital costs of a storage tank that is larger than 1 m^3. Parameters α, β, η, and λ are assumed based on [10, 30].

$$CAPEX^{ST} = \alpha(\beta + \lambda V_{ST}^{\eta}) \tag{B3}$$

where,
$CAPEX^{ST}$, capital costs of a storage tank, M€
α, installed CAPEX factor based on the purchase cost, 4.31 10^{-6}
β, constant, 58000
λ, constant, 16000
V_{ST}, volume of the storage tank in m^3
η, constant, 0.7

B.5.9 Ejectors

The vacuum for the two vacuum solvent regeneration units (i.e., SR1 and SR2) should be generated by medium-pressure steam-powered ejectors. However, due to the absence of built-in ejector models in Aspen Plus, they were modelled by expanders.

B.5.9.1. MPS consumption

The following Equation B4 [4] and date in Table B15 and Table B16 can calculate the energy consumption of the two ejectors.

$$w_{in} = \left(\frac{1}{\eta_C}\right)\left(\frac{kRT_1}{k-1}\right)\left[\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} - 1\right] \tag{B4}$$

where,
w_{in}, vacuum pump net work of evacuated gas, kJ/mol
η_C, pump efficiency
k, heat capacity ratio (C_p/C_v)
R, ideal gas constant, kJ/(mol*K)
T_1, temperature at the inlet of the vacuum pump, K
P_2, pressure at the inlet vacuum pump, bar
P_1, discharge pressure of the vacuum pump, bar

Table. B15. Processing parameters of the two ejectors.

	Ejector 1	Ejector 2	Source
T_1 (°C)	32.14	55.95	Aspen model
k	1.15	1.07	Aspen model
R (J/mol*K)	8.31	8.31	-
P_1 (bar)	0.05	0.05	Aspen model
P_2 (bar)	1.02	1.02	Aspen model
Pump efficiency η_C	0.5	0.5	[4]
Processing vapour flow rate @100% load (L/h)	502316	136149	Aspen model
Processing mass flow rate @100% load (kg/h)	1950.91	1299.89	Aspen model
Processing molar flow rate @100% load (kmol/h)	52.27	16.44	Aspen model

Table. B16. Heating value the medium-pressure (MPS) steam.

MPS heating value (MJ/kg)	Source
1.87787	[20]

B.5.9.2. Cost

Based on the flow rates of the two ejectors, their costs were estimated.

Table. B17. Estimation of the costs of the two ejectors,

	Ejector 1	Ejector 2
Cost (€/piece)	6000	4000
Source	[31]	

B.5.10 Centrifuges

Table. B18. Dimension of centrifuges.

	Processing throughput rate @100% load (m^3/h)	Unit energy consumption (MJ/m^3)
Centrifuge 1	157	5
Centrifuge 2	64	
Centrifuge 3	1.67	
Centrifuge 4	1.5	
Source	Aspen model	[32]

Table. B19. Cost of centrifuges.

	Centrifuge 1	Centrifuge 2	Centrifuge 3	Centrifuge 4
Cost (€)	160000 Alfa Laval CH 900 & 700	90000 Alfa Laval CH 300 & 600	20000 Alfa Laval AlfaPure S2	20000 Alfa Laval AlfaPure S2
Source	[33]			

B.5.11 Additional heaters

The additional three heaters were installed after SR1, SR2, and TD, respectively. The maximum energy consumption required for these heaters to correct the temperature of the stream flowing into the next unit can be calculated by Equation B5 and data in Table B20 and Table B21. Then, they were sized in Aspen Plus based on their conditions in the two tables. Finally, their costs were estimated by Aspen Process Economic Analyzer based on their sizes. Note that the temperature that was to be corrected was measured during the estimation of volume flexibility at the equipment level.

$$Q = \dot{m} c_p \Delta T \tag{B5}$$

where,
Q, energy consumption, J/h
$\dot{m}$, mass flow rate, kg/h
c_p, specific heat, J/(kg*K)
ΔT, temperature difference, K

Table. B20. Parameters for quantifying maximum energy used by the additional heaters.

	Mass flow rate @100% load (kg/h)	c_p (J/(kg*K))	ΔT (K)
Heater 1	1950.91	3501.32	14.78
Heater 2	1299.89	2460.82	15.46
Heater 3	144.19	3758.79	22.63
Source	Aspen model		

Table. B21. Heating value of low-low-pressure (LLPS) steam.

Heating value of LLPS (MJ/kg)	Source
2.14	[20]

B.5.12 Capital expenditures (CAPEX)

Table. B22. Percentages for estimating CAPEX based on purchased equipment [8].

Purchased equipment	Percentage of purchased equipment
Direct Costs	
Purchased equipment installation	0.39
Instrumentation and Controls (installed)	0.43
Piping (installed)	0.31
Electrical systems (installed)	0.1
Buildings (including services)	0.15
Yard improvements	0.12
Service facilities (installed)	0.55
Total Direct	**2.05**
Indirect Costs	
Engineering and supervision	0.32
Construction expenses	0.34
Legal expenses	0.04
Contractor’s fee	0.19
Contingency	0.37
Total Indirect	**1.26**
Working capital	**0.75**

B.5.13 Chemical Engineering Plant Cost Index

Table. B23. Chemical Engineering Plant Cost Index (CEPCI) [34].

Year	CEPCI
2019	607.5
2018	60.3.1
2017	567.5
2016	541.7

B.5.14 Labour requirements

Table. B24. Estimation of labour requirements for the MES plant.

Type of equipment	Workers/unit/shift	Source	MES plant
Blowers and compressors	0.1	[8]	7
Centrifugal separator	0.3		4
Heat exchanger	0.1		23
Process towers	0.5		3
Reactor, continuous	0.5		1
Electrified stacks	1	assumed	3
Total		10	

B.6 Operating schemes

B.6.1 Operating scheme 1 in chapter 3 (Case C in chapter 4)

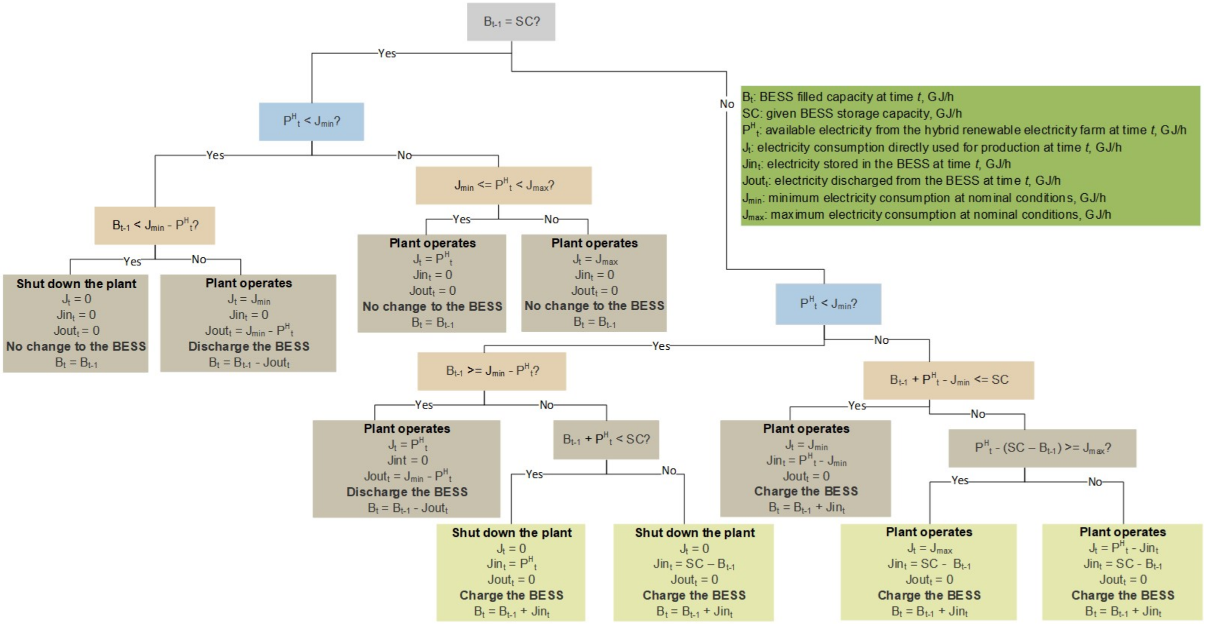


Fig. B5. Decision tree of the operating scheme 1 in chapter 3 (i.e., Case C in chapter 4).

B.6.2 Operating scheme 2 in chapter 3

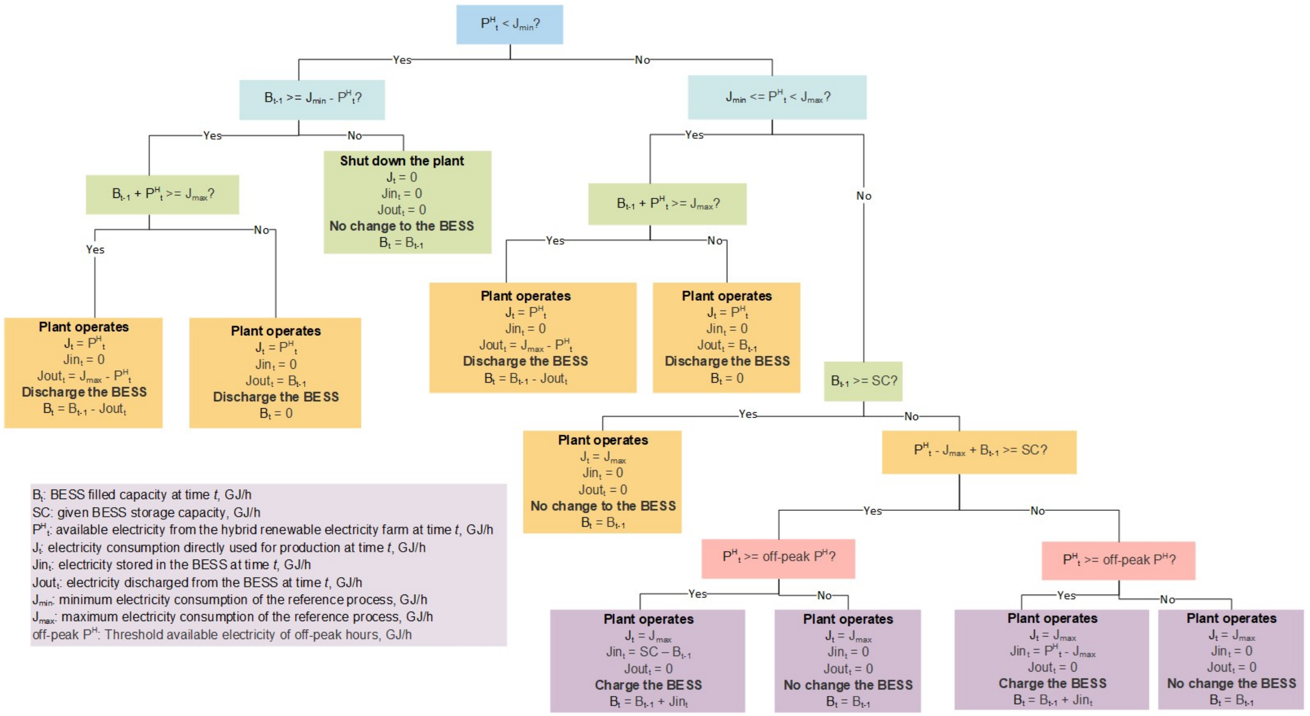


Fig. B6. Decision tree of the operating scheme 2 in chapter 3.

B.6.3 Operating scheme in Case D in chapter 4

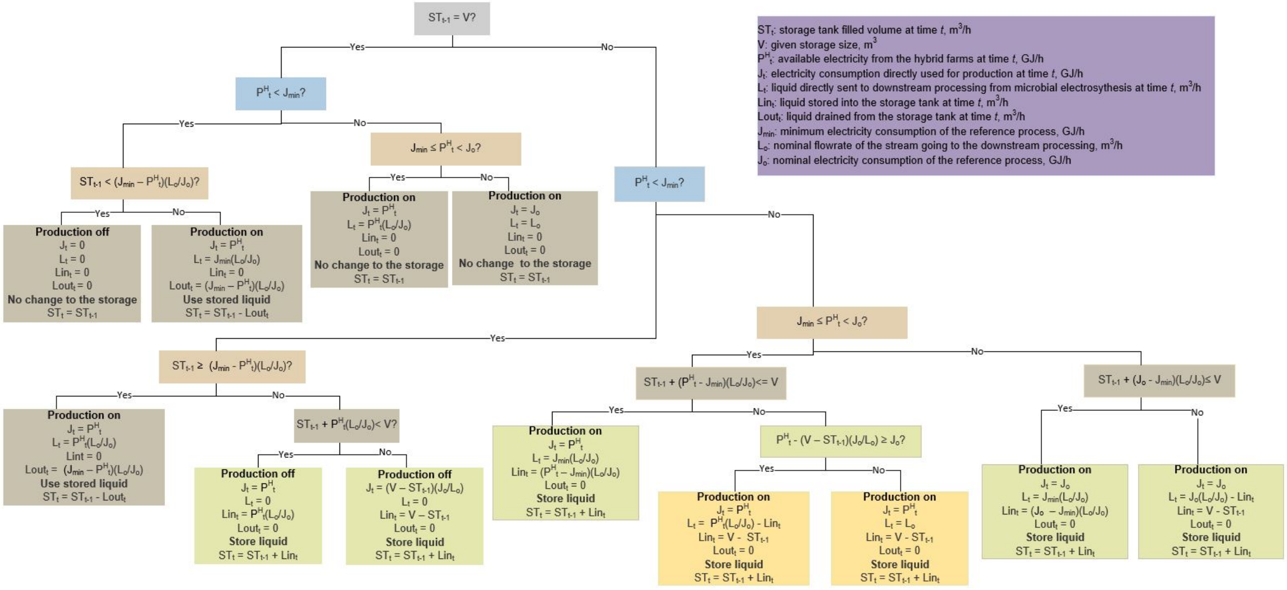


Fig. B7. Decision tree of the operating scheme in Case D in chapter 4.

B.6.4 Operating scheme in Case E in chapter 4

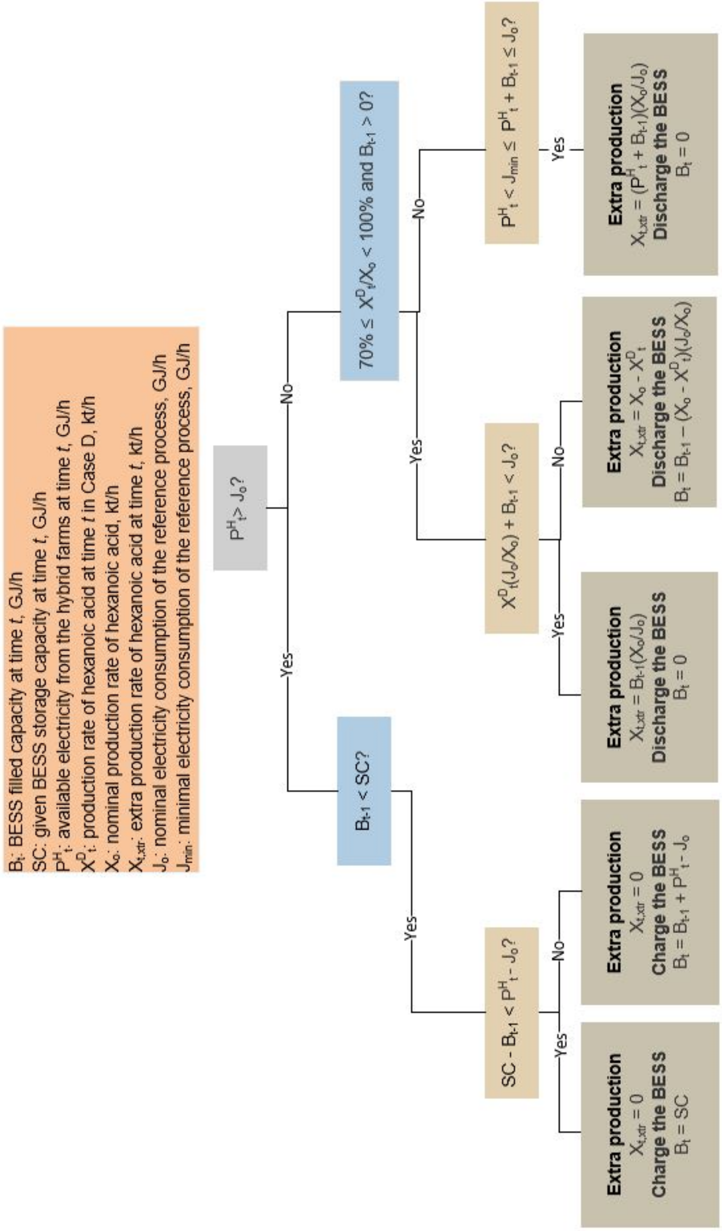


Fig. B8. Decision tree of the operating scheme in Case E in chapter 4.

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B.7 Energy consumption at the equipment level

Fig. B9 shows the impact on the dehydration column (TD) when operating the plant at a lower production rate than the nominal rate on the energy consumption of the column, where the condenser and reboiler were distinguished. The x-axis corresponds to the range of operable throughput rates, which are normalised to the nominal throughput rate. It is obvious that the deviation of energy consumption from the nominal condition increases steadily as the flow rate is farther away from the nominal flow rate. For column TD, at the lowest tolerable flow rate, the deviation ratio of energy consumption of its condenser reached the highest among all the heat exchangers of the three columns, almost 8% of the nominal condition. The energy consumption behaviour of the heat exchangers of the other two separation columns had the same fashion (see Fig. B10 and Fig. B11). However, their highest deviation ratio was smaller. The results revealed that more energy was spent per unit mass of the product if the process route was operated below its nominal throughput rate, elucidating the penalty in energy efficiency.

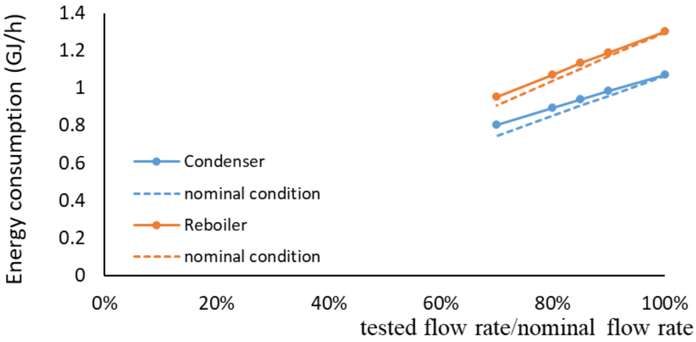

Fig. B9. Energy consumption of the condenser and reboiler of the dehydration column TD.

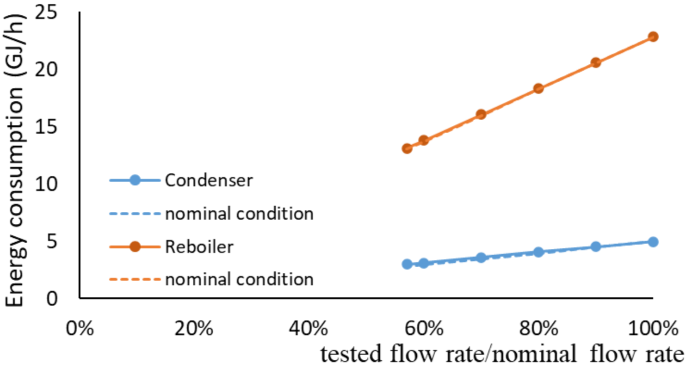

Fig. B10. Energy consumption of the condenser and reboiler of the solvent regeneration column SR1.

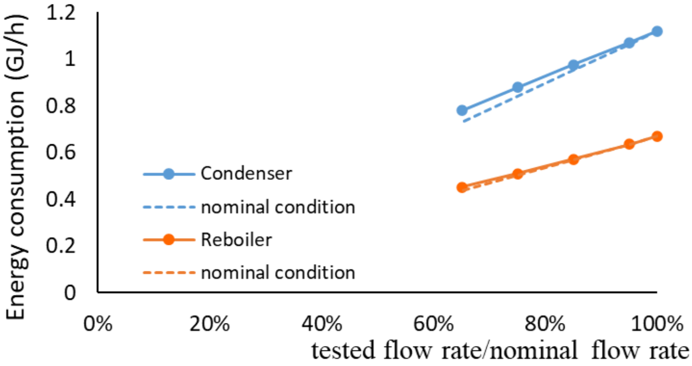

Fig. B11. Energy consumption of the condenser and reboiler of the solvent regeneration column SR2.

Table. B25. Summary of the impact on energy consumption at the equipment level.

Column	Heat exchanger	Maximum deviation from the nominal conditions
TD	Condenser	7.61%
	Reboiler	4.46%
SR1	Condenser	5.37%
	Reboiler	0.56%
SR2	Condenser	7.22%
	Reboiler	3.45%

B.8 Hypothesis check

In chapter 4, for cases where a ST was installed, it was assumed that the whole electricity was consumed by the more flexible part of the process (upstream of the ST) and that the whole heat was consumed by the downstream units after the ST, which was based on our calculations in chapter 3, where 98.5% of the electricity consumption was allocated to the more flexible part, and 99% of the utility consumption was allocated to the less flexible part. This hypothesis was reflected in Equations 4.17 and 4.21 in chapter 4.

An error check was done to investigate how much product quantity would have been reduced if the assumption had not been made. We used Case D-ST35 as an example. The reduction in product quantity was less than 1%.

References

[1] L. Jourdin, J. Sousa, N. van Stralen, and D. P. B. T. B. Strik. "Techno-economic assessment of microbial electrosynthesis from CO_2 and/or organics: An interdisciplinary roadmap towards future research and application". Applied Energy. 279. 2020. P. 115775. DOI: `10.1016/j.apenergy.2020.115775`.

[2] M. T. Agler, C. M. Spirito, J. G. Usack, J. J. Werner, and L. T. Angenent. "Chain elongation with reactor microbiomes: upgrading dilute ethanol to medium-chain carboxylates". Energy & Environmental Science. 58. 2012. Pp. 8189–8192. DOI: `10.1039/c2ee22101b`.

[3] O. Cabau-Peinado, A. J. J. Straathof, and L. Jourdin. "A General Model for Biofilm-Driven Microbial Electrosynthesis of Carboxylates From CO_2". Frontiers in Microbiology. 12. 2021. P. 669218. DOI: `10.3389/fmicb.2021.669218`.

[4] P. O. Saboe et al. "In situ recovery of bio-based carboxylic acids". Green Chemistry. 208. 2018. Pp. 1791–1804. DOI: `10.1039/c7gc03747c`.

[5] MathWorks. c1994-2022. Design and Cosimulate Control of High-Fidelity Distillation Tower with Aspen Plus Dynamics. URL: `https://www.mathworks.com/help/mpc/ug/design-and-cosimulate-control-of-high-fidelity-distillation-tower-with-aspen-plus-dynamics.html`. (Access date: 11 Aug 2022).

[6] W. Sieder, J. Seader, and D. Lewin. Product and process design principles. 3rd. USA: John Wiley & Sons, 2004.

[7] C. R. Branan. Rules of thumb for chemical engineers. 3rd. USA: Gulf Publishing Company, 1998.

[8] S. P. Max, D. T. Klaus, and E. W. Ronald. Plant design and economics for chemical engineers. 5th. Boston: McGraw-Hill Companies, 2003.

[9] B. Peters et al. "XDEM multi-physics and multi-scale simulation technology: Review of DEM-CFD coupling, methodology and engineering applications". Particuology. 44. 2019. Pp. 176–193. DOI: `10.1016/j.partic.2018.04.005`.

[10] G. Towler and R. Sinnott. Chemical engineering design: principles, practice and economics of plant and process design. 2nd. Amsterdam: Butterworth-Heinemann, 2021.

[11] H. C. Woo and Y. H. Kim. "Eco-efficient recovery of bio-based volatile C2-6 fatty acids". Biotechnol Biofuels. 12. 2019. P. 92. DOI: `10.1186/s13068-019-1433-8`.

[12] S. Akerboom, S. Waldmann, A. Mukherjee, C. Agaton, M. Sanders, and G. J. Kramer. "Different This Time? The Prospects of CCS in the Netherlands in the 2020s". Frontiers in Energy Research. 9. 2021. P. 644796. DOI: `10.3389/fenrg.2021.644796`.

[13] Intratec. 2022. Calcium Hydroxide Price | Current and Historical. URL: `https://www.intratec.us/chemical-markets/calcium-hydroxide-price`. (Access date: 17 Oct 2022).

[14] Intratec. 2022. Phosphoric Acid Price | Current and Historical. URL: `https://www.intratec.us/chemical-markets/phosphoric-acid-price`. (Access date: 17 Oct 2022).

[15] Guidechem. 2022. Tri-n-octylamine products price,suppliers. URL: `https://www.guidechem.com/cas/1116-76-3.html`. (Access date: 17 Oct 2022).

[16] P. Dessi et al. “Microbial electrosynthesis: Towards sustainable biorefineries for production of green chemicals from CO_2 emissions”. Biotechnology Advances. 46. 2021. P. 107675. DOI: `10.1016/j.biotechadv.2020.107675`.

[17] M. Gotz et al. “Renewable Power-to-Gas: A technological and economic review”. Renewable Energy. 85. 2016. Pp. 1371–1390. DOI: `10.1016/j.renene.2015.07.066`.

[18] J. Moncada, I. V. Gursel, W. J. J. Huijgen, J. W. Dijkstra, and A. Ramirez. “Techno-economic and ex-ante environmental assessment of C6 sugars production from spruce and corn. Comparison of organosolv and wet milling technologies”. Journal of Cleaner Production. 170. 2018. Pp. 610–624. DOI: `10.1016/j.jclepro.2017.09.195`.

[19] G. D. Ulrich and P. T. Vasudevan. “How to estimate utility costs”. Chemical Engineering. 1134. 2006. Pp. 66–69.

[20] AspenTech. Aspen Plus v12. URL: `https://www.aspentech.com/en/products/engineering/aspen-plus`.

[21] Tebodin. Veiligheidsrapport - Gesterde delen Lyondell Chemie Nederland B.V. locatie Maasvlakte Deel 0 en 1. Lyondell Chemie Nederland B.V., 2017. URL: `https://www.commissiemer.nl/projectdocumenten/00002667.pdf`.

[22] European Central Bank. 2022. Euro foreign exchange reference rates. URL: `https://www.ecb.europa.eu/stats/policy_and_exchange_rates/euro_reference_exchange_rates/html/eurofxref-graph-usd.en.html`. (Access date: 17 Oct 2022).

[23] Consultants International. 2019. The Netherlands - Tax Changes 2019 - Corporate Income Tax. URL: `https://www.tax-consultants-international.com/news/the-netherlands-tax-changes-2019-corporate-income-tax#:~:text=does%5C%20not%5C%20apply.-,Reduction%5C%20the%5C%20Dutch%5C%20corporate%5C%20income%5C%20tax%5C%20rate,taxable%5C%20profits%5C%20exceeding%5C%20%5C%E2%5C%82%5C%AC%5C%20200%5C%2C000.`. (Access date: 17 Oct 2022).

[24] Lenntec. 2022. 3M membrane contactors. URL: `https://www.lenntech.com/products/membrane/liqui-cel.htm`. (Access date: 17 Oct 2022).

[25] SGProjects. 2022. Gas transfer membranes. URL: `https://sgprojectsstore.it/en/10-gas-transfer-membranes`. (Access date: 17 Oct 2022).

[26] T. Kuramochi, A. Ramirez, W. Turkenburg, and A. Faaij. “Techno-economic prospects for CO capture from distributed energy systems”. Renewable & Sustainable Energy Reviews. 19. 2013. Pp. 328–347. DOI: `10.1016/j.rser.2012.10.051`.

[27] J. Liu, C. Hu, A. Kimber, and Z. Wang. “Uses, Cost-Benefit Analysis, and Markets of Energy Storage Systems for Electric Grid Applications”. Journal of Energy Storage. 32. 2020. P. 101731. DOI: `10.1016/j.est.2020.101731`.

[28] G. J. May, A. Davidson, and B. Monahov. “Lead batteries for utility energy storage: A review”. Journal of Energy Storage. 15. 2018. Pp. 145–157. DOI: `10.1016/j.est.2017.11.008`.

[29] B. Sun et al. “Economic analysis of lithium-ion batteries recycled from electric vehicles for secondary use in power load peak shaving in China”. Journal of Cleaner Production. 276. 2020. P. 123327. DOI: `10.1016/j.jclepro.2020.123327`.

[30] Matches. 2014. Tank Cost Estimate. URL: `http://www.matche.com/equipcost/Tank.html`. (Access date: 11 Aug 2022).

[31] Alibaba. 2022. Single Stage Ejectors for Gas Mixing and Dilution with Condensers. URL: `https://www.alibaba.com/product-detail/Single-Stage-Ejectors-for-Gas-Mixing_1600198491615.html?spm=a2700.galleryofferlist.normal_offer.d_image.14b340edUGBaoF`. (Access date: 17 Oct 2022).

[32] Alfa Laval. 2022. Separators. URL: `https://www.alfalaval.com/products/separation/centrifugal-separators/separators/`. (Access date: 17 Oct 2022).

[33] Indiamart. 2022. Alfa Laval centrifugal pumps. URL: `https://dir.indiamart.com/search.mp?ss=alfa+laval+centrifugal+pumps%5C&stype=attr=1%5C&res=RC4`. (Access date: 17 Oct 2022).

[34] Chemical Engineering. The Chemical Engineering Plant Cost Index. URL: `https://www.chemengonline.com/pci-home`. (Access date: 17 Oct 2022).

C

Appendix C: Supporting information in other types of files

This appendix directs readers to the supporting information that is not possible to be presented within this book but can be accessed online at `https://doi.org/10.4121/d7c9c167-c04b-4b6b-83cd-3d2da3790736`. The contents included are specified as follows:

1. Aspen Plus process flowsheets
2. Excel sheets containing inputs for process modelling and economic assessments and process modelling and techno-economic results
3. Python scripts

D

Appendix D: Supporting information for environmental assessment

D.1 Energy and mass balances

The following mass and energy information of the MES route and additional assumptions in Table D1 were used to construct the life cycle inventory (LCI) table.

Table. D1. Process information of the MES route - results of chapter 4. C6A: hexanoic acid.

Streams	**Value**	**Unit**	**Note**
Feedstock streams			
Captured CO_2	2272	kg/t C6A produced	
Demineralised water	3201	kg/t C6A produced	
$Ca(OH)_2$	473	kg/t C6A produced	
H_3PO_4	708	kg/t C6A produced	
Solvent-trioctylamine	214	kg/t C6A produced	
Heat (by natural gas)	22.6	GJ/t C6A produced	
Product streams			
Hexanoic acid	8.00	kt/y	
O_2	17.6	kt/y	
Waste streams			
Solid waste ($CaHPO_4$ sludge)	821	kg/t C6A produced	
Wastewater	2629	kg/t C6A produced	
Waste solvent	213	kg/t C6A produced	
Utility			
Chilling energy (by natural gas)	6.09	GJ/t C6A produced	
Hot oil (by natural gas)	21.5	GJ/t C6A produced	*
Medium-pressure steam (by natural gas)	0.92	GJ/t C6A produced	*
Cooling water	227,470	kg/t C6A produced	**
Renewable electricity			
Wind electricity	68.9	GJ/t C6A produced	
Solar electricity	14.1	GJ/t C6A produced	

* Heat energy in the LCI table is composed of hot oil and medium-pressure steam.

** Cooling water was supplied externally, and hence, it was a scope 2 stream. For the mass balance, it was counted as one-time consumption. In the life cycle assessment (LCI), it was recycled and regenerated by the supplier. Only 10% of it was supplemented due to evaporation or leak. It was assumed that the cooling water was regenerated by heat exchange with seawater. The electricity consumption was calculated using Equations D1 and D2 and information in Table D2:

$$P = \frac{\rho g \dot{V} H}{\eta} \tag{D1}$$

where,
P, pump work, W
ρ, density, kg/m^3
g, acceleration of gravity, 9.81 m/s2
$\dot{V}$, volumetric flow rate, m^3/s
H, pump head, m
η, pump efficiency

$$Q = \dot{m} c_p \Delta T \tag{D2}$$

where,
Q, heat flow rate, J/s
$\dot{m}$, mass flow rate, kg/s
c_p, specific heat, J/(kg*K)
ΔT, temperature different, K

Table. D2. Information needed to calculate the pump work for regenerating the cooling water.

	ρ	$\dot{V}$		ΔT	c_p
		Amine scrubbing	C6A production		
Cooling water	997	1.56	0.073	25	4189
Seawater	1030	To be calculated	To be calculated	1	3930

D.2 Life cycle inventory

D.2.1 MES route

Table. D3. LCI of the MES-based hexanoic acid route. MEA: Monoethanolamine. GLO: global. RER: Europe. NL: Netherlands. AP: Aspen Plus. TOA: trioctylamine. BE: Belgium.

Input	Quantity	Unit	Source	Ecoinvent data source
CO_2 capture				
Solvent - MEA	2.32	kg/t CO_2 captured	[1]	Monoethanolamine | market for GLO
Electricity - grid (for process incl. compression)	0.57	GJ/t CO_2 captured	[1]	Electricity, medium voltage | market for NL
Water - tap (for process)	1000	kg/t CO_2 captured	[1]	Tap water | market group for RER
Other chemicals - NaOH	2	kg/t CO_2 captured	assumed [2] [a]	Sodium hydroxide, without water, in 50% solution state | market for GLO
Utility - heat (by natural gas)	3.72	GJ/t CO_2 captured	[1]	Heat, district or industrial, natural gas | market group for RER
Utility - grid electricity (for regenerating cooling water)	0.81	GJ/t CO_2 captured	[3]	Electricity, medium voltage | market for NL
Utility - cooling water	68.3	kg/t CO_2 captured	[3]	Tap water | market group for RER
Waste treatment - sludge (incl. waste solvent)	2.32	kg/t CO_2 captured	assumed [2][b]	Refinery sludge Europe without Switzerland | treatment of refinery sludge, hazardous waste incineration, with energy recovery
Waste treatment - wastewater	1000	kg/t CO_2 captured	assumed [1][c]	Wastewater, average Europe without Switzerland | market for wastewater, average
CO_2 compression loss	0%		assumed	
CO_2 transport				
Transport - pipeline	200	km	assumed [d]	Transport, pipeline, onshore, long distance, natural gas RER| market for transport, pipeline, offshore, long distance, natural gas
Hexanoic acid production - MES				
Captured CO_2	2272	kg/t C6A produced	AP simulation [e]	

Continue on next page

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[a] The weight ratio between NaOH and captured CO_2 was 1:1 in the reference, but we assumed it to be 2:1.

[b] It was assumed in the reference that the weight ratio between the monoethanolamine and sludge disposal was 1:1.

[c] It was calculated based on the process data provided in the reference and made a slightly optimistic approximation.

[d] It was assumed that the plant was 200 km within the CO_2 pipeline network in Port of Rotterdam.

[e] Aspen simulation refers to the results from chapter 4.

Input	Quantity	Unit	Source	Ecoinvent data source
Hexanoic acid production - MES				
Water - demineralised (for process)	3686	kg/t C6A produced	AP simulation	Water, completely softened RER| market for water, completely softened
Other chemicals - $Ca(OH)_2$	473	kg/t C6A produced	AP simulation	Aluminium hydroxide | market for GLO
Other chemicals - H_3PO_4	708	kg/t C6A produced	AP simulation	Phosphoric acid, industrial grade, without water, in 85% solution state | market for GLO
Solvent - TOA	213	kg/t C6A produced	AP simulation	Trimethylamine | market for RER
Electricity - wind (for process)	68.9	GJ/t C6A produced	AP simulation	Electricity, high voltage NL| electricity production, wind, >3MW turbine, onshore
Electricity - solar (for process)	14.1	GJ/t C6A produced	AP simulation	Electricity, low voltage BE| electricity production, photovoltaic, 570kWp open ground installation, multi-Si
Utility - heat (by natural gas)	22.6	GJ/t C6A produced	AP simulation	Heat, district or industrial, natural gas | market group for RER
Utility - cooling water	228	kg/t C6A produced	AP simulation	Tap water | market group for RER
Utility - chilling energy (by natural gas)	6.09	GJ/t C6A produced	AP simulation	Cooling energy | market for GLO
Utility - grid electricity (for regenerating cooling water)	0.041	GJ/t C6A produced	AP simulation	Electricity, medium voltage | market for NL
Waste treatment -sludge	824	kg/t C6A produced	AP simulation	Waste gypsum Europe without Switzerland | treatment of waste gypsum, inert material landfill
Waste treatment - wastewater	2629	kg/t C6A produced	AP simulation	Wastewater from vegetable oil refinery | market for GLO
Waste treatment - spent solvent	213	kg/t C6A produced	AP simulation	Spent solvent mixture Europe without Switzerland | market for spent solvent mixture

D.2.2 Coconut route

Table. D4. LCI of the coconut-based hexanoic acid. RER: Europe.

Input	**Quantity**	**Unit**	**Source**	**Ecoinvent data source**
Hexanoic acid production - from coconut oil				
Fatty acid	1000	kg/t C6A	[4]	Fatty acid RER | fatty acid production, from coconut oil

D.2.3 Crude coconut oil production

Table. D5. LCI data of the crude coconut oil production. RER: Europe. GLO: global.

Database	Data source
Agri-footprint	Crude coconut oil, mart mix, at regional storage RER
Ecoinvent	Coconut oil, crude | market for GLO

D.2.4 Sustainable aviation fuel

Table. D6. LCI of the upgrade of hexanoic acid to n-alkanes.

Input	Quantity	Unit	Source	Ecoinvent data source
Hexanoic acid transport				
Transport-truck	200	km	assumed [1]	Transport, freight, lorry 16-32 metric ton, euro6 RER | market for transport
Upgrading to neat SAF				
Hexanoic acid	2.22	kg/kg neat SAF	[5, 6]	
Emissions (gate-to-gate)	15	g CO_2eq/MJ neat SAF	[5]	

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[1] It was assumed that the neat SAF plant was 200 km away from the MES plant.

D.3 Sensitivity analyses

D.3.1 Heat energy (incl. chilling) and grid electricity

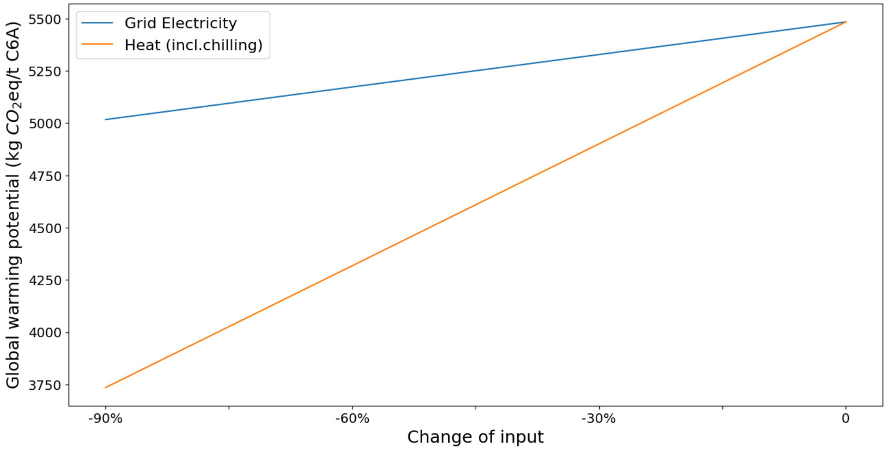

Fig. D1. Sensitivity analysis results - the impact of reduced carbon intensity of grid electricity and heat energy (incl. chilling) on the global warming potential per tonne hexanoic acid produced.

D.3.2 Solvent and other chemicals

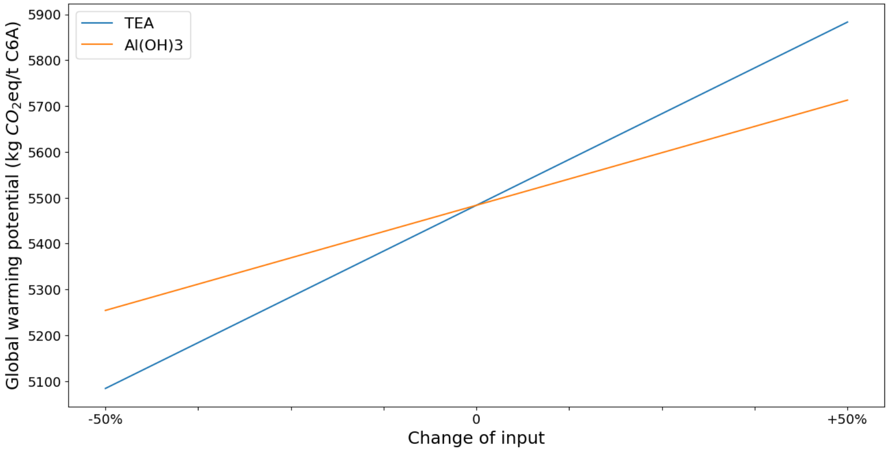

Fig. D2. Sensitivity analysis results - the impact of the carbon intensity of substituting solvent and chemical on the global warming potential per tonne hexanoic acid produced. TEA: triethylamine.

D.4 Information on alternative SAFs

The emission data of alternative neat SAFs from bio-sources are abundant in the literature. Ng, Farooq, and Yang [7] reviewed the CO_2eq emissions of bio-based neat SAFs, focusing on the major four out of the six production routes of biojet fuels that have been certified by the American Society for Testing and Materials (ASTM). These neat SAFs that can be blended with conventional jet fuels are Fischer-Tropsch synthetic paraffinic kerosene (FT-SPK), hydroprocessed esters and fatty acids (HEFA), alcohol-to-jet synthetic paraffinic kerosene (ATJ-SPK), and hydroprocessing of fermented sugars - synthetic iso-paraffins (HFS-SIP). For each route, multiple authors include data points from other studies, by either directly retrieving others' results or calculating based on process data presented in others' work. The CO_2eq emissions mainly tend to cover the direct greenhouse gas (GHG) emissions and sometimes indirect land use change (iLUC) emissions. In this work, with a focus on direct GHG emissions, we used the values directly reported in the references, which are plotted in Fig. D3.

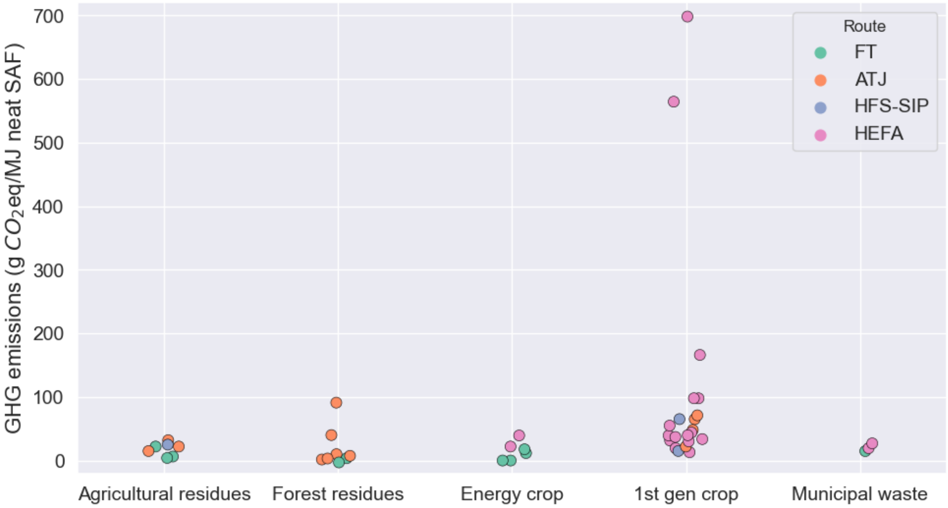

Fig. D3. GHG emissions of neat SAFs via four reference routes. This figure is made based on the data presented in [7–9]. GHG: greenhouse gas. SAF: sustainable aviation fuel. FT: Fischer-Tropsch. ATJ: Alcohol-to-jet. HFS-SIP: Hydroprocessing of fermented sugars. HEFA: Hydroprocessed esters and fatty acids. 1st gen: the first generation.

D.5 Information on alternative biofuels

As current neat SAFs are mostly biofuels and the comparable and available data from literature stress on biofuels (i.e., bioethanol and biodiesel), for indirect land use and its induced emissions in regard to alternative neat SAFs, we used data in biofuel-focused studies [10, 11], which are visualised in Fig. D4.

Overmars et al. [10] first calculated net direct LUC (dLUC) for each type of feedstock based on their gross dLUC following two allocation methods (i.e., Renewable Energy Directive (RED) and economic value). Then they applied two area contribution approaches (i.e., local and exporting regions) to quantify indirect LUC (iLUC) based on net dLUC. Next, they applied two models (i.e., Integrated Model to Assess the Global Environment (IMAGE) and Cropland Spatial Allocation Model (CSAM)) to estimate the emission factors based on iLUC. Then they multiply the factors by the iLUC. Here, we discuss their best estimates of iLUC and iLUC emissions. The best estimates are weighted averages of the two area contribution approaches, which were calculated by Overmars et al. [10]. Please refer to their work for calculating details.

Valin et al. [11] computed two values that sum the dLUC and iLUC Global Biosphere Management Model (GLOBIOM) and following the RED allocation method. One for cropland, and the other for agricultural land. Here, we stick to the cropland. By employing the same set of methods, Valin et al. [11] also obtained emissions consisting of dLUC and iLUC emissions for each type of feedstock. They performed Monte Carlo Simulation for uncertainty analyses, and they reported an average emission value for each type of feedstock.

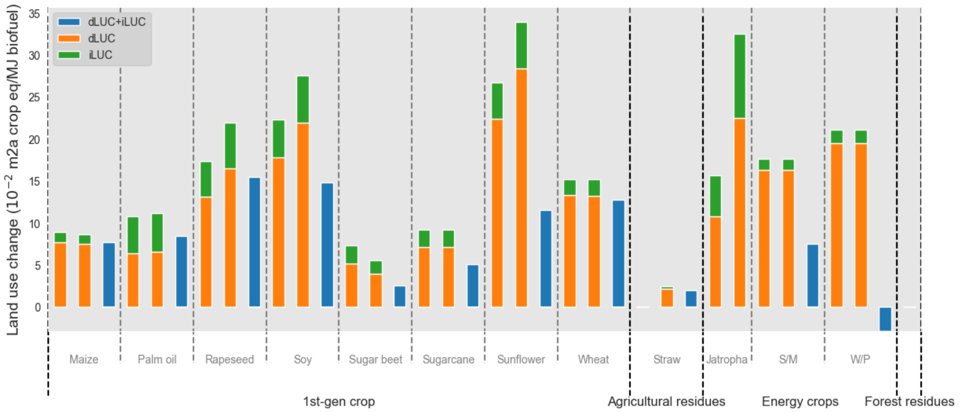

Fig. D4. Direct and indirect land use change of reference biofuels (i.e., bioethanol and biodiesel). This figure is produced based on results obtained by [10, 11]. dLUC: direct land use change. iLUC: indirect land use change. 1st-gen: the first generation. S/M: switchgrass or miscanthus. W/P: willow or poplar.

D.6 Relevant hypothesis

D.6.1 Global market of hexanoic acid

The global market for caproic acid is projected to reach 252.8 million US dollars by 2027 [12]. The market price of hexanoic acid is around 2.5-4.2 k€/t [13]. Therefore, its global production capacity has been estimated at around 100 kt/y in 2027.

D.6.2 Renewable electricity profile

The hybrid renewable electricity profile was generated based on Rotterdam's wind speed and solar radiation data on an hourly basis over 8760 hours in the year 2019. The raw data was initially retrieved as hourly capacity factors from [14]. They were then converted into energy per hour by multiplying with the peak capacities of the selected wind park (Windpark Slufterdam, the Netherlands; 50.4 MWp) [15], and the solar farm (Shell Moerdijk, the Netherlands; 27 MWp) [16]. This electricity profile is the same as the one used in chapters 4 and 3.

D.6.3 Upgrade of hexanoic acid to neat SAF

The conventional jet fuel is composed of alkanes, among which, the n-alkanes range from C_8 to C_{18} and have an average carbon number of 11.3-11.4 [5, 6, 17]. Jet fuel has a calorific value of 43.4 MJ/kg [5, 18].

Hexanoic acid can be self-ketonised and subsequently hydrodeoxygenised to n-alkanes. Which can be used as a blend for conventional jet fuel. Hexanoic acid has 6 carbons, and the resulting average carbon number of n-alkanes from its self-ketonisation is 11. Self-ketonisation of hexanoic acid can reach a yield of 98% [6] while hydrodeoxygenation can reach 95% [5] based on experimental data. The overall yield was reported between 79% and 82% based on simulation data [5]. Therefore, we assumed that the yield of converting hexanoic acid to C_8 - C_{18} n-alkanes (denoted as neat SAF in this work) with an average carbon number of 11.3 was 85%. Consequently, the reaction stoichiometry between hexanoic acid and neat SAF was 2.22 kg hexanoic acid:1 kg neat SAF.

D.6.4 Direct land occupation calculation

The land occupation of the Rotterdam-based chloralkali plant [19], the Ghent-based Steelanol plant [20], the Rotterdam-based wind park [15], the Amsterdam-based fermentative carboxylic acids plant (https://chaincraft.com/), and the Rotterdam-based solar farm [16] were estimated by the Google Maps Area Calculator Tool on https://www.daftlogic.com/.

D.7 Data support for figures

Table. D7. Breakdown of global warming potential of MES-based hexanoic acid, with an economic allocation. Unit: kg CO_2eq/t C6A. Data supporting Fig. 5.5 in chapter 5.

	CO_2 capture	CO_2 transport	C6A production
Utility	736.8		1513.4
Electricity	211.1		733.9
Other chemicals	5.9		1393.3
Solvent	17.0		493.2
Water	0.7		1.1
Waste treatment	12.3		339.7
Transport		25.2	

Table. D8. Breakdown of direct land use change of MES-based hexanoic acid, with an economic allocation. Unit: m^2a crop eq/t C6A. Data supporting Fig. 5.6 in chapter 5.

	CO_2 capture	CO_2 transport	C6A production
Utility	6.0		7.6
Electricity	3.2		132.8
Other chemicals	0.2		257.3
Solvent	0.2		7.8
Water	0.0		0.0
Waste treatment	0.2		0.8
Transport		0.2	

Table. D9. Breakdown of water consumption of MES-based hexanoic acid, with an economic allocation. Unit: m^3/t C6A. Data supporting Fig. 5.7 in chapter 5.

	CO_2 capture	CO_2 transport	C6A production
Utility	2.68		5.38
Electricity	1.57		14.76
Other chemicals	0.16		84.05
Solvent	0.26		7.53
Water	2.28		3.10
Waste treatment	-2.02		0.81
Transport		0.02	

Table. D10. Breakdown of cradle-to-gate global warming potential of MES-based neat SAF, with an economic allocation. Unit: g CO_2eq/MJ neat SAF. Data supporting Fig. 5.8 in chapter 5.

	CO_2 capture	CO_2 transport	C6A production	C6A transport	Neat SAF production
Utility	37.7		77.4		
Electricity	10.8		37.5		
Solvent	0.9		25.2		
Waste treatment	0.6		17.4		
Other chemicals	0.3		71.3		
Water	0.0		0.1		
Transport		1.3		1.7	
Upgrading					15.0

References

[1] IEAGHG. Understanding the Cost of Retrofitting CO_2 capture in an Integrated Oil Refinery. IEAGHG, 2017. URL: `http://documents.ieaghg.org/index.php/s/2cCda5q0bnYhsvo`.

[2] M. Biermann, C. Langner, S. Roussanaly, F. Normann, and S. Harvey. "The role of energy supply in abatement cost curves for CO_2 capture from process industry - A case study of a Swedish refinery". Applied Energy. 319. 2022. P. 119273. DOI: `10.1016/j.apenergy.2022.119273`.

[3] IEAGHG. Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS. IEAGHG, 2017. URL: `https://ieaghg.org/component/content/article/49-publications/technical-reports/784-2017-02-smr-based-h2-plant-with-ccs`.

[4] G. Wernet, C. Bauer, B. Steubing, J. Reinhard, E. Moreno-Ruiz, and B. Weidema. "The ecoinvent database version 3 (part I): overview and methodology". International Journal of Life Cycle Assessment. 219. 2016. Pp. 1218–1230. DOI: `10.1007/s11367-016-1087-8`.

[5] N. A. Huq et al. "Toward net-zero sustainable aviation fuel with wet waste-derived volatile fatty acids". PNAS. 11813. 2021. e2023008118. DOI: `10.1073/pnas.2023008118`.

[6] J. H. Miller, G. R. Hafenstine, H. H. Nguyen, and D. R. Vardon. "Kinetics and Reactor Design Principles of Volatile Fatty Acid Ketonization for Sustainable Aviation Fuel Production". Industrial & Engineering Chemistry Research. 618. 2022. Pp. 2997–3010. DOI: `10.1021/acs.iecr.1c04548`.

[7] K. S. Ng, D. Farooq, and A. Yang. "Global biorenewable development strategies for sustainable aviation fuel production". Renewable & Sustainable Energy Reviews. 150. 2021. P. 111502. DOI: `10.1016/j.rser.2021.111502`.

[8] S. de Jong et al. "Life-cycle analysis of greenhouse gas emissions from renewable jet fuel production". Biotechnol Biofuels. 10. 2017. P. 64. DOI: `10.1186/s13068-017-0739-7`.

[9] R. Stratton, H. M. Wong, and J. Hileman. Life cycle greenhouse gas emissions from alternative jet fuels. Partnership for Air Transportation Noise and Emissions Reduction, 2010. URL: `http://web.mit.edu/aeroastro/partner/reports/proj28/partner-proj28-2010-001.pdf`.

[10] K. Overmars, R. Edwards, M. Padella, A. G. Prins, and L. Marelli. Estimates of indirect land use change from biofuels based on historical data. 2015. DOI: `10.2790/3647`.

[11] H. Valin et al. The land use change impact of biofuels consumed in the EU - Quantification of area and greenhouse gas impacts. Ecofys Netherlands BV, 2015. URL: `https://energy.ec.europa.eu/system/files/2016-03/Final%5C%2520Report_GLOBIOM_publication_0.pdf`.

[12] S. Agnihotri et al. "A Glimpse of the World of Volatile Fatty Acids Production and Application: A review". Bioengineered. 131. 2022. Pp. 1249–1275. DOI: `10.1080/21655979.2021.1996044`.

[13] P. Dessi et al. "Microbial electrosynthesis: Towards sustainable biorefineries for production of green chemicals from CO_2 emissions". Biotechnology Advances. 46. 2021. P. 107675. DOI: `10.1016/j.biotechadv.2020.107675`.

[14] I. Staffell and S. Pfenninger. "Using bias-corrected reanalysis to simulate current and future wind power output". Energy. 114. 2016. Pp. 1224–1239. DOI: `10.1016/j.energy.2016.08.068`.

[15] Eneco. 2022. Windpark Slufterdam. URL: `https://www.eneco.nl/over-ons/wat-we-doen/duurzame-bronnen/windpark-slufterdam/`. (Access date: 11 Nov 2022).

[16] Shell. 2019. Shell opens solar park at Shell Moerdijk chemicals site in the Netherlands. URL: `https://www.shell.com/business-customers/chemicals/media-releases/2019-media-releases/shell-moerdijk-solar-farm.html`. (Access date: 11 Nov 2022).

[17] U.S. Department of Energy. Sustainable Aviation Fuel: Review of Technical Pathways. U.S. Department of Energy, 2020. DOI: `10.2172/1660415`.

[18] A. Bauen, N. Bitossi, L. German, A. Harris, and K. Leow. "Sustainable Aviation Fuels Status, challenges and prospects of drop-in liquid fuels, hydrogen and electrification in aviation". Johnson Matthey Technology Review. 643. 2020. Pp. 263–278. DOI: `10.1595/205651320x15816756012040`.

[19] Vattenfall. 2021. Flexible chlorine production contributes to grid stability. URL: `https://group.vattenfall.com/press-and-media/newsroom/2021/flexible-chlorine-production-contribute-to-grid-stability`. (Access date: 24 June 2023).

[20] ArcelorMittal. 2023. ArcelorMittal and LanzaTech announce first ethanol samples from commercial flagship carbon capture and utilisation facility in Ghent, Belgium. URL: `https://corporate.arcelormittal.com/media/news-articles/arcelormittal-and-lanzatech-announce-first-ethanol-samples-from-commercial-flagship-carbon-capture-and-utilisation-facility-in-ghent-belgium#:~:text=The/%5C%20ethanol/%5C%20will/%5C%20be/%5C%20jointly,total/%5C%20current/%5C%20demand/%5C%20in/%5C%20Belgium..` (Access date: 24 June 2023).

Curriculum Vitæ

Jisiwei Luo, also known as Jessie, was born on Jan 2, 1996 in Luzhou, China. In 2017, She obtained her bachelor’s degree in Applied Chemistry (Engineering) from Tianjin University in China. During her bachelor’s study, she exchanged and finished her bachelor’s thesis at the University of Queensland in Brisbane, Australia. In 2019, she graduated from Delft University of Technology with a master’s degree in Chemical Engineering. In the same year and at the same university, she started pursuing a PhD in the section Energy & Industry at the Department of Energy System and Services at the Faculty of Technology, Policy, and Management. Between 2021 and 2023, she was a member/chairman of the faculty's PhD council.

List of Publications and Conference Appearances

Publications

J. Luo, J. Moncada, and A. Ramirez, Development of a Conceptual Framework for Evaluating the Flexibility of Future Chemical Processes. Industrial & Engineering Chemistry Research. 61 (2022) 3219-3232 3219, DOI: 10.1021/acs.iecr.1c03874.

J. Luo, M. Pérez-Fortes, P. Ibarra-Gonzalez, A.J.J. Straathof, and A. Ramirez, Impact of intermittent electricity supply on a conceptual process design for microbial conversion of CO2 into hexanoic acid. Chemical Engineering Research and Design. 205 (2024) 364-375, DOI: 10.1016/j.cherd.2024.04.005.

J. Luo, M. Pérez-Fortes, A.J.J. Straathof, and A. Ramirez, Understanding the flexibility challenges of a plant for microbial CO_2 electroreduction with hexanoic acid recovery. 2024. submitted to a journal.

J. Luo, M. Pérez-Fortes, A.J.J. Straathof, and A. Ramirez, Life cycle assessment of hexanoic acid production via microbial electrosynthesis and renewable electricity: Future opportunities. 2024. submitted to a journal.

Conference appearances

2023, July, 18th Netherlands Process Technology Symposium (NPS2023), Enschede, Netherlands. "Optimal scheduling and sizing for a microbial electrosynthesis plant integrated with renewable electricity " (Oral)

2023, July, 11th International Conference on Industrial Ecology (ISIE2023), Leiden, Netherlands. "Understanding the performance of a novel technology to produce hexanoic acid from CO_2 and renewable electricity" (Oral)

2022, June, 32nd European Symposium on Computer Aided Process Engineering (ESCAPE32), Toulouse, France. "Assessing the volume flexibility of a bio-electrochemical process" (Poster)

Acknowledgements

During my master's, I swore many times that I would NEVER do a PhD! Out of the question! Well, as what you are reading right now, I have completed my PhD dissertation. What happened back then? When my master's approached the end, I was looking for jobs in entirely different fields – finance and business. However, it all changed when I was handed a brochure full of e-Refinery PhD vacancies. Captivating words like "novel", "renewables", "sustainability", and "reduce carbon emissions" leapt into my eyes and successfully attracted the young and perhaps naive me – a curious chemical engineer who had been doubting if the so-called sustainable technologies were sustainable. Soon afterwards, my dreadful but, after all, fun and rewarding PhD journey started. I can write another book about my PhD life, but I prefer not to waste your extra time or patience, given that this one is already hard to digest.

Undoubtedly, I could not have arrived at this point without help from others, and I have always been grateful to those who have supported me throughout the past years. I apologise in advance that I cannot mention everyone's name here for privacy reasons. I remember everyone who has been in my life. So, please do not be frustrated if you do not find your name here; your face and voice are forever in my head.

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相知无远近，万里尚为邻。感谢我身边的以及五湖四海的中国朋友们给予我的关怀与鼓励。

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路漫漫其修远兮，吾将上下而求索。

— 屈原