University of Antwerp

Faculty of Business and Economics

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Dissertation

A Techno-Economic and Environmental Life Cycle Assessment of Plasma Catalysis for the Conversion of CO_2

Towards the design of a novel Carbon Capture and Utilization technology in an uncertain future

Thesis submitted for the degree of Doctor of Applied Economics at the University of Antwerp to be defended by

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Antwerp, September 2023

Deze thesis wordt voorgedragen voor het behalen van de titel “Doctor in de toegepaste economische wetenschappen” aan de Universiteit Antwerpen.

Een Techno-Economische en Levenscyclusanalyse van Plasma Katalyse voor de Omzetting van CO_2:

Op weg naar het design van een nieuwe technologie voor Carbon Capture & Utilization in een onzekere toekomst

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ISBN: 9789057288074
Wettelijk depot D/2023/12.293/31

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Publications

This thesis is based on the following research papers:

Lamberts-Van Assche, H., & Compernolle, T. (2021). Economic feasibility studies for Carbon Capture and Utilization technologies: a tutorial review. Clean Technologies and Environmental Policy, 24(2), 467-491. doi:10.1007/s10098-021-02128-6 **(Chapter 2)**

Lamberts-Van Assche, H., Thomassen, G., & Compernolle, T. (2022). The early-stage design of plasma for the conversion of CO_2 to chemicals: A prospective techno-economic assessment. Journal of CO_2 Utilization, 64, 102156. doi:10.1016/j.jcou.2022.102156 **(Chapter 3)**

Lamberts-Van Assche, H., Buyle, M., & Compernolle, T. (n.d.). The early-stage design of plasma for the conversion of CO_2 to chemicals: A prospective life cycle assessment. *Working paper*. **(Chapter 4)**

Seynnaeve, B., Bossier, S., Lamberts-Van Assche, H., Compernolle, T., Van Der Voort, P., Lauwaert, J., Meynen, V., & Verberckmoes, A. (n.d.). The controversial impact of catalytically activated packing materials on conversion in dry reforming of methane in a dielectric barrier discharge reactor. *Working paper.* **(Chapter 4)**

Lamberts-Van Assche, H., & Compernolle, T. (2022). Using Real Options Thinking to Value Investment Flexibility in Carbon Capture and Utilization Projects: A Review. Sustainability, 14(4), 2098. Retrieved from https://www.mdpi.com/2071-1050/14/4/2098 **(Chapter 5)**

Lamberts-Van Assche, H., Lavrutich, M., Compernolle, T., Thomassen, G., Thijssen, J.J., & Kort, P.M. (n.d.). CO_2 storage or utilization? A real options analysis under market and technological uncertainty. *Under revision at the Journal of Environmental Economics and Management*. **(Chapter 6)**

Acknowledgements

After four years (and one month), the curtain now falls on my PhD journey.

People often think that writing a PhD is a lonely task, an assignment you have to fulfil on your own. While there were indeed many solo efforts along the PhD journey, this thesis is also the outcome of collaborations with many skilled researchers, talks at the coffee machine (both work- and non-work related), engaging encounters at conferences, and – at least as important – the support of friends and family.

First and foremost, I have to thank my promoter, Professor Dr. Tine Compernolle, for several reasons. First of all, it is thanks to Tine that I embarked on this PhD journey. While writing my master's thesis under her supervision, it was Tine who informed me of a vacant PhD position at the Environmental Economics research group, on the topic of 'Carbon Capture and Utilization'. After reading two sentences of the job description, my mind was already set on this PhD. And so it happened: on the 1st of September 2019, I started as a PhD researcher at the Environmental Economics research group of the University of Antwerp. Second, Tine has been the best guide I could wish for during my PhD. Giving feedback whenever needed, always approachable, never unkind. During our meetings, she was often able to present (pragmatic) solutions for issues I had been struggling with for several days. Her honest, constructive feedback has contributed to numerous improvements in this thesis. Finally, I want to thank Tine for her continued belief in me and for finding ways to let me continue my career as a researcher at the University of Antwerp.

I also want to acknowledge the partners from the PlasMaCatDESIGN project, especially those with whom I collaborated closely. Sander Bossier, thank you for exchanging your experimental datasets with me, for helping me unravel the Excel files and for helping me understand the plasma-catalytic process a bit better each time. Professor Dr. Annemie Bogaerts & Professor Dr. Vera Meynen, thank you for your reflections on my work during the PlasMaCatDESIGN meetings, for your suggestions, and for your crash courses on plasma catalysis, that helped me understand the technical conditions of this fascinating technology bit by bit.

Furthermore, I want to express my gratitude towards all the researchers that I was lucky enough to collaborate with over the past four years. Dr. Gwenny Thomassen, Professor Dr. Jacco Thijssen, Professor Dr. Maria Lavrutich, Dr. Matthias Buyle and Professor Dr. Peter Kort: thank you, for sharing your expertise with me and always giving feedback when needed.

A special thank you goes out to Professor Dr. Maria Lavrutich, for giving me the opportunity to visit her at the Norwegian University of Science and Technology (NTNU) in Trondheim and for working together on an exciting research paper. Collaborating with Maria felt very natural, and I want to thank her for sharing so much of her Real Options expertise with me in only four weeks. Trondheim has become my home away from home, and I will always cherish my time there.

If Trondheim is my home away from home, Antwerp is the base camp I always return to. The friendly atmosphere at our Environmental Economics research group – EnvEcon for the insiders – is something to treasure. Our research group has expanded massively since I started in September 2019. It has been a privilege to see our research group grow, to watch others defend their PhD successfully, to see new researchers start their PhD track, and to be a part of this international community. It is needless to say the past four years were also quite eventful for our research group. We had to endure several lockdowns due to COVID-19, shortly followed by a fire that destroyed our offices at the City Campus.

And yet, we managed to keep up the good spirit. Thank you guys, for all the fun lunch breaks, the coffee talks, the advice on how to survive a PhD, and the support during the past months while I was finishing my dissertation. This thesis would not have been the same with you.

This thesis could not have been written without the support of my family and friends.

I want to thank all of my friends for their support, for their 'good luck'-messages, and for helping me unwind when needed. To my friends from the fanfare: maybe next year, I can finally find the time to join you on that trip to Scherpenheuvel (but this is not a promise). To enFIN: thank you for being part of my life since 2012. I cannot believe we already passed the 10th anniversary of our friendship, and hope to be reunited with you all soon, in various parts of Europe. To my 'handelsingenieur'-friends: you made studying at the University of Antwerp so comfortable and so much fun, that I wanted to extend my stay at the University by another 4 years. That says enough, right?

I also want to express an enormous amount of gratitude to my family, who were there during the whole PhD journey and had to deal with my various stages of stress the last couple of months. Sara, moeke, vake, thank you for your support and patience over the past four years. From now on, I will hopefully have (a bit) more time to join you for Friday night dinners, to come along on trips to Middelkerke, to go cheer for our favourite Belgian athletes and to attend concerts of varying artists.

Last but not least, I need to find the words to express my gratitude to my favourite person in the world. The person who spent so many hours working alone in our house (soon-to-be home), because I was in Trondheim, at a conference, or simply working on my thesis at weekends. The person who took me on date nights to relax, who cooked the most delicious dinners to have some quality time together, and who flew to Trondheim to visit me for just a couple of days. To the person whose love has been so unconditional for the past 8 years, I can only say: thank you. Glenn, schat, you are the world to me.

And so, it seems, writing a PhD is not so lonely after all.

Thank you all, for being part of this wonderful journey.

Hanne Lamberts-Van Assche

Kapelle-op-den-Bos, September 2023

Summary

While the effects of climate change are becoming more and more obvious each year, our efforts to reduce these CO_2 emissions have increased as well. Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU) are recognized worldwide as key technologies in the transition to net-zero emissions. Despite the growing share of renewable energy, increasing energy efficiency and increased use of recycled materials, there will be a part of CO_2 emissions that cannot be avoided or reduced directly. In the chemical, cement and steel industries, in particular, CO_2 emissions are proven much harder to reduce. For those remaining hard-to-abate CO_2 emissions, CCS and CCU present ground-breaking technologies to remove carbon from the atmosphere.

The capture of CO_2 emissions is part of the EU's strategy to reach carbon neutrality by 2050. Carbon Capture and Storage (CCS) aims to capture the CO_2 from an industrial plant or even directly from the air, transport captured CO_2 by ship or via pipelines and permanently store CO_2 in deep geological formations. Despite the urgent call to reduce CO_2 emissions, the uptake of CCS on a larger scale remains slow. The high costs to capture CO_2 and the low CO_2 prices in the EU Emission Trading System (ETS) in the past have hampered investments in CCS. The absence of an attractive business case has raised the attention of Carbon Capture and Utilization (CCU). Instead of storing the CO_2 underground, the captured CO_2 is now utilized as an input to produce other valuable products, such as chemicals, fuels or building materials (IEA, 2022a),. Hence, CCU indeed offers a way to valorise the captured CO_2.

However, there is one major bottleneck for CCU: CO_2 is a very stable molecule. As a result, a lot of energy is needed to break the bonds of the molecule and convert CO_2 into other products. The high stability of the CO_2 molecule, which results in high energy needs, is perhaps the greatest challenge to overcome to make CCU an attractive solution in the future. There is one technology that may have the right features to conquer the high stability of the CO_2 molecule: plasma catalysis. In this dissertation, the feasibility and desirability of plasma catalysis as a novel CCU technology is analysed.

Plasma is often called the 'fourth state of matter', besides the three well-known states of matter (solid, liquid and gas). Plasma is an ionized gas, and it includes a mix of both ions and neutral species, such as atoms, electrons or molecules. All these different species can interact with each other in the plasma, creating a highly reactive chemical mixture. Different plasma technologies exist, but the most versatile technology is the Dielectric Barrier Discharge (DBD) reactor. The most interesting feature of a DBD reactor is that it can be filled with packing beads. These packing beads can have catalytic properties, and help to steer the conversion towards the desired products. The combined effect of plasma and catalysts results in a new process that is called plasma catalysis. Plasma catalysis brings together the reactivity of the plasma, to enable reactions which are normally unfavourable, and the selectivity of the catalysts, to steer the conversion of the gas towards the desired products.

The PlasMaCatDESIGN project brings together researchers from different universities and varying disciplines to help define the design rules for the catalyst that can make the conversion of CO_2 in plasma more selective and energy-efficient. Within this project, multiple rounds of experiments were performed in the laboratory to investigate systematically how variations in the design of the DBD reactor and the chosen catalyst affect the plasma-catalytic conversion of CO_2 (and CH_4). These experiments deliver data on how effectively the CO_2 is converted (CO_2 conversion), how much energy is consumed (energy efficiency) and which end-products are produced (product mix) for variations in the design of the DBD reactor and the chosen catalyst.

In this dissertation, this experimental dataset is used to assess how variations in the design of plasma catalysis affects its economic feasibility and environmental desirability as potential CCU technology, for the conversion of CO_2 into chemicals.

First, the economic feasibility of plasma catalysis for the conversion of CO_2 into chemicals is evaluated in a Techno-Economic Assessment. The results show that plasma catalysis, based on the experiments in the laboratory, is not profitable today. The plasma-catalytic conversion of CO_2 requires a high amount of energy, resulting in high energy expenditures. The revenues, created by converting CO_2 into chemicals, remain too low to cover all the costs. The revenues should be raised in the future, by increasing the conversion rate and by improving the selectivity towards higher-value chemicals, such as dimethyl ether.

Second, the environmental impacts of plasma catalysis over the CCU value chain are also analysed in a Life Cycle Assessment. The results indicate that the energy consumption of the CO_2 conversion process also dominates the environmental impact, based on the performance of the technology in the laboratory. When technological improvements are assumed in future technology development scenarios, it is shown that other processes become increasingly important, such as the capture of CO_2. When the avoided impacts of the conventional production processes are included as a credit, net negative environmental impacts can even be realized in a future technology development scenario. In particular, the conversion of CO_2 into chemicals in plasma catalysis can create a net negative impact in terms of fossil resource scarcity. This result highlights the potential of CCU technologies to reduce our dependency on fossil fuels in industrial processes.

Since the PlasMaCatDESIGN project is focused on the search for the most optimal catalyst, the performance of the different packing materials is evaluated extensively in the Techno-Economic and Life Cycle Assessments. Based on the results from the Techno-Economic and Life Cycle Assessment, recommendations are formulated for the most optimal design of the DBD reactor. Building on the insights from the experiments in the laboratory, a DBD reactor with a gap size of 4.44 mm, fed with a mix of CO_2 and CH_4, and filled with γ-Al_2O_3 or CuO@γ-Al_2O_3 packing beads, is recommended.

The final part of this thesis focuses on the uncertainty that is present when making investment decisions for novel CCU technologies. In the final chapter of this dissertation, the investment decision in the novel CCU technology is not evaluated as a stand-alone decision. Besides the possibility to invest in CCU, firms might also be interested to invest in CCS to reduce their CO_2 emissions. As CCS technologies are already more advanced than most CCU technologies, this might be an attractive alternative for firms to invest in. Moreover, investment decisions in emerging technologies are typically characterised by a high level of uncertainty. To tackle these uncertainties, firms tend to delay their investment decision and wait for more information to become available in the next period. The decision to invest in CCUS technologies is affected by two main sources of uncertainty: technological uncertainty, i.e. the innovation pace of the CCU technology, and market uncertainty, i.e. the unknown future evolution of the CO_2 price in the EU ETS. The optimal timing to invest in CCS, CCU or CCUS is identified, while taking into account these uncertainties, by applying the Real Options Theory. Real options analysis acknowledges the fact that decision-makers can delay investment decisions in practice and presents a tool to value this flexibility in investment decisions. The results of the real options analysis reveal that firms will delay their investment in CCS and CCU, due to the uncertainty in the CO_2 price. The higher the uncertainty, the higher the threshold to invest in CCS and CCU. The results also demonstrated that CCS and CCU are not necessarily competitive technologies. The expected development of a profitable CCU technology in the future, even if it's more profitable than the existing CCS, does not necessarily delay the investment in CCS today.

Samenvatting

Terwijl de gevolgen van de klimaatverandering ieder jaar duidelijker worden, nemen ook onze inspanningen om CO_2 emissies te verminderen gestaag toe.

Carbon Capture & Storage (CCS) en Carbon Capture & Utilization (CCU) worden wereldwijd erkend als cruciale technologieën om de doelstelling van een koolstofneutrale maatschappij te behalen. Ondanks het toenemende aandeel van hernieuwbare energie, de stijgende energie efficiëntie en het toenemend gebruik van gerecycleerde materialen, zal er altijd nog een deel van de CO_2 emissies niet rechtstreeks kunnen vermeden worden. Voor de chemische, cement en staalindustrie in het bijzonder blijkt het veel moeilijker om CO_2 emissies te vermijden. CCS en CCU zijn baanbrekende technologieën om ook die resterende CO_2 emissies te kunnen verminderen.

Het opvangen van CO_2 emissies maakt deel uit van de strategie van de EU om een klimaatneutraal continent te zijn tegen 2050. CCS technologieën vangen de CO_2 op bij een industriële installatie of zelfs rechtstreeks vanuit de atmosfeer, transporteren vervolgens die opgevangen CO_2 per schip of via pijpleidingen en slagen de CO_2 vervolgens op in de diepe ondergrond. Ondanks de urgentie die vandaag heerst om CO_2 emissies te verminderen, blijft de invoering van CCS installaties op grotere schaal nog steeds beperkt. De hoge kosten die gepaard gaan met het opvangen van de CO_2 en de lage prijzen voor CO_2 in het EU-emissiehandelssysteem in het verleden hebben de investeringen in CCS afgeremd. Door het uitblijven van een winstgevend business model voor CCS, is de focus verschoven naar CCU. CCU gebruikt de opgevangen CO_2 als een waardevolle grondstof en zet die CO_2 om in verhandelbare producten (bv. brandstoffen, chemicaliën of bouwmaterialen), die extra opbrengsten creëren. In plaats van de CO_2 permanent ondergronds op te slaan, wordt de CO_2 gebruikt als input voor andere producten. Op die manier biedt CCU een manier om de opgevangen CO_2 te valoriseren.

Er is echter één belangrijk knelpunt voor de verdere ontwikkeling van CCU: CO_2 is een zeer stabiele molecule. Dit betekent dat er heel wat energie nodig is om de verbindingen van de molecule te breken en de CO_2 om te zetten in andere producen. Deze hoge stabiliteit van de CO_2-molecule en de resulterend hoge vraag naar energie is waarschijnlijk de grootste uitdaging om van CCU een aantrekkelijke oplossing te maken in de toekomst. Er is één technologie die heel wat interessante kenmerken heeft om de hoge stabiliteit van CO_2 te overwinnen: plasma katalyse. In dit proefschrift zal de haalbaarheid van plasma katalyse als nieuwe CCU technologie beoordeeld worden.

Plasma wordt ook vaak de vierde aggregatietoestand genoemd, naast de vaste, vloeibare en gasvormige aggregatietoestand. Plasma is een geïoniseerd gas, en het bestaat uit een mix van zowel ionen als neutrale elementen, zoals atomen, elektronen en moleculen. Al deze verschillende elementen interageren met elkaar in het plasma, wat ervoor dat plasma een zeer reactief mengsel is. Er bestaan verschillende plasma technologieën, maar de meest veelzijdige is de Dielectric Barrier Discharge (DBD) reactor. Het meest interessante kenmerk van de DBD reactor is dat deze gevuld kan worden met zogenaamde ‘packing beads’ of ‘packing materials’. Deze packing beads kunnen katalytische eigenschappen hebben, wat kan helpen om de reactie te sturen naar de gewenste eindproducten. De combinatie van plasma (in de DBD reactor) en de katalyse (packing beads) creëert een nieuw proces dat plasma katalyse wordt genoemd. Plasma katalyse combineert de hoge reactiviteit van het plasma, om reacties te laten doorgaan die anders niet zouden kunnen

plaatsvinden, met de selectiviteit van de katalysatoren, om de omzetting van CO_2 te kunnen sturen zodat de gewenste eindproducten gevormd worden.

Het PlasMaCatDESIGN project brengt onderzoekers van verschillende universiteiten en disciplines samen om het meest optimale design te vinden voor de katalysator die de omzetting van CO_2 in plasma selectiever en energie-efficiënter kan laten gebeuren. In het kader van dit project werden meerdere experimenten uitgevoerd in het laboratorium, om te onderzoeken hoe verschillende opstellingen van de DBD reactor presteren voor de omzetting van CO_2 in plasma katalyse. Dankzij deze experimenten wordt een dataset gecreëerd met parameters die aangeven hoe efficiënt de CO_2 wordt omgezet, hoeveel energie geconsumeerd wordt en welke eindproducten geproduceerd worden voor verschillende opstellingen van de DBD reactor.

Deze dataset wordt gebruikt in dit proefschrift om te onderzoeken hoe variaties in het design van plasma katalyse de economische haalbaarheid en milieu-impact van deze potentiële CCU technology, voor de omzetting van CO_2 in chemicaliën, beïnvloeden.

Ten eerste, de economische haalbaarheid van plasma katalyse voor de omzetting van CO_2 in chemicaliën wordt geëvalueerd in een Techno-Economische Analyse. De resultaten hiervan tonen aan dat plasma katalyse nog niet winstgevend is, gebaseerd op de prestatie van de technologie in het labo. De plasma katalyse verbruikt ook nog steeds veel energie, wat resulteert in hoge uitgaven voor elektriciteit. De opbrengsten, die gecreëerd worden door CO_2 om te zetten in chemicaliën, blijven vooralsnog te laag om de kosten te dekken. De opbrengsten moeten verhoogd worden in de toekomst, door de conversiegraad en de selectiviteit naar hoogwaardige chemicaliën te verhogen, zoals dimethylether.

Ten tweede, de milieu-impact van de plasma katalyse over de ganse CCU waardeketen wordt geanalyseerd in een Levenscyclusanalyse. De resultaten geven aan dat de energieconsumptie van de plasmakatalyse ook hier de milieu-impact domineert, gebaseerd op de prestatie van de technologie in het labo. Wanneer verbeteringen aan de technologie worden verondersteld in toekomstige technologische ontwikkelingsscenario's, wordt ook de impact van andere processen in de CCU waardeketen belangrijker, zoals bv. de scheidingsstap. Rekening houdend met de negatieve milieu-impact, voor de vermeden productie van deze chemicaliën in de conventionele, fossiele productieprocessen, kunnen zelfs netto negatieve milieu-impacten gerealiseerd worden in de toekomst. De omzetting van CO_2 in andere chemicaliën in de plasma katalyse kan in het bijzonder een negatieve impact creëren in termen van 'fossil resource scarcity'. Dit resultaat benadrukt het potentieel van CCU om onze afhankelijkheid van fossiele brandstoffen in industriële processen te verminderen.

Het PlasMaCatDESIGN project is gericht op de zoektocht naar de meest optimale katalysator voor de omzetting van CO_2. Daarom wordt steeds de prestatie van verschillende packing materialen vergeleken en uitgebreid geëvalueerd in de Techno-Economische en Levenscyclusanalyse. Op basis van de resultaten van de Techno-Economische en Levenscyclusanalyse worden aanbevelingen geformuleerd voor de meest optimale opstelling van de DBD reactor. Op basis van de inzichten van deze analyses, wordt een DBD reactor aanbevolen met een afmeting van 4.44 mm voor de gap, die gevoed wordt met een mengeling van CO_2 en CH_4, en waarin γ-Al_2O_3 or CuO@γ-Al_2O_3 packings worden toegevoegd als katalysatoren.

Tot slot focust het laatste deel van dit proefschrift op de onzekerheid die aanwezig is bij het maken van investeringsbeslissingen voor CCU technologieën die nog in ontwikkeling zijn. In het laatste hoofdstuk van dit proefschrift wordt de investeringsbeslissing in de nieuwe CCU technologie niet geëvalueerd als een losstaande beslissing. Naast de mogelijkheid om te investeren in CCU, heeft het bedrijf namelijk ook nog steeds de mogelijkheid om te investeren in CCS om de CO_2 emissies te verminderen. CCS technologieën zijn al verder ontwikkeld dan de meeste CCU technologieën, waardoor CCS een interessant alternatief kan zijn. Bovendien zijn investeringsbeslissingen in nieuwe technologieën vaak getypeerd door een hoge mate van onzekerheid. Om met die onzekerheid om te gaan, zullen bedrijven vaak hun investeringsbeslissing uitstellen om te wachten op meer informatie. De beslissing om te investeren in CCUS technologieën wordt beïnvloed door twee bronnen van onzekerheid: technologische onzekerheid, nl. de snelheid waarmee CCU verder ontwikkeld wordt, en marktonzekerheid, nl. de onbekende CO_2 prijs in de toekomst. Om hiermee om te gaan, wordt in het laatste hoofdstuk van dit proefschrift Real Options Theory toegepast. Het optimale moment om te investeren in CCS, CCU of CCUS wordt bepaald met behulp van Real Options Theory. Reële optie analyse erkent dat investeerders hun beslissing kunnen uitstellen in de praktijk en geeft ons een tool om die flexibiliteit te gaan waarderen in investeringsbeslissingen. De resultaten van de reële optie analyse tonen aan dat de bedrijven de investering in CCS en CCU uitstellen, omwille van de onzekerheid over de CO_2 prijs. Hoe hoger die onzekerheid is, hoe hoger de drempel om te investeren in CCS en CCU. Daarnaast tonen de resultaten ook aan dat CCS en CCU niet noodzakelijk concurrerende technologieën hoeven te zijn. De verwachte komst van een winstgevende CCU technologie in de toekomst, die meer winstgevend is dan de huidige CCS technologie, zorgt er niet noodzakelijk voor dat de investering in CCS vandaag uitgesteld wordt.

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List of Abbreviations

ACCR	Annual Capital Charge Ratio
CAPEX	Capital Expenditures
CBA	Cost-Benefit Analysis
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
CCUS	Carbon Capture Utilization and Storage
CFPP	Coal-fired power plant
CO_2-EOR	CO_2-Enhanced Oil Recovery
CoE	Cost of Electricity
CTL	Coal-to-liquid
DBD	Dielectric Barrier Discharge
DMC	Dimethyl carbonate
DME	Dimethyl ether
DP	Dynamic programming
DPBP	Discounted Payback Period
EOR	Enhanced Oil Recovery
ETEA	Environmental and Techno-Economic Assessment
EU ETS	EU Emission Trading System
FA	Formic Acid
FCOP	Fixed Costs of Production
FFP	Fossil Fuel Potential
FRS	Fossil Resource Scarcity
GA	Gliding Arc
GBM	Geometric Brownian Motion
GHG	Greenhouse Gas
GW	Global Warming
GWP	Global Warming Potential
IEA	International Energy Agency
IRR	Internal Rate of Return
ISBL	Inside Battery Limits
LC	Learning curve
LCA	Life Cycle Assessment
LCC	Life Cycle Costing
LCOP	Levelized Cost of Product
LSMC	Least-Squares Monte Carlo
M&EB	Mass & Energy Balances
MAC	Maximum Acceptable Cost
MAI	Maximum Acceptable Impact
MC	Monte Carlo
MeOH	Methanol
moMILP	multi-objective Mixed Integer Linear Program
MSP	Minimum Selling Price
MW	Microwave
NG	Natural Gas
NPV	Net Present Value
NTP	Non-Thermal Plasma

OPEX	Operational Expenditures
OSBL	Outside Battery Limits
OT	Optimal timing
OU	Ornstein-Uhlenbeck
PBP	Payback Period
PDE	Partial Differential Equation
PFD	Process Flow Diagram
RM	Raw Material
ROA	Real Options Analysis
ROI	Return on Investment
ROT	Real Options Theory
SA	Sensitivity analysis
SEI	Specific Energy Input
SMR	Steam methane reforming
ST	Space time
TEA	Techno-Economic Assessment
TFCI	Total Fixed Capital Investment
TPC	Total Production Cost
TRL	Technology Readiness Level
UA	Uncertainty Analysis
VCOP	Variable Costs of Production
VF	Valuing flexibility
VOC	Volatile Organic Compounds
WoS	Web of Science

1

Introduction

Fossil fuels have shaped our modern way of living.

Cars allow us to work further away from home, travel independently and even go on solo trips in camper vans. Planes take us on journeys around the world, from the stunning nature of New Zealand to the vibrant city life in New York. Plastic packaging allows us to preserve food longer, eliminating the need to go for daily groceries. Electricity created light, enabling us to stay up longer and get up earlier, independent of sunrise and sunset.

Our daily life would not look the same without fossil fuels. However, we pay a high price for these embedded habits. The burning of fossil fuels is the number one cause of rising temperatures on Earth (CO_2 Value Europe, 2023).

The Intergovernmental Panel on Climate Change (IPCC) published their first report in 1990, stating that human activities largely contributed to the increasing greenhouse gas (GHG) emissions and that this increasing concentration of GHG emissions in the atmosphere resulted in a warming of the Earth's surface, also called global warming (IPCC, 1990). Since the 1990s, awareness of climate change has raised considerably and this has led to the development of many innovative technologies.

Fuel cars are more and more being replaced by electric cars, biofuels are being developed as sustainable aviation fuels, plastic bags are simply being banned, a growing number of packaging-free shops appear in the street scene, and renewable energy sources such as wind and solar are replacing fossil fuels at an increasing pace. In 2021, the share of renewables in global electricity generation rose to 28%. The importance of renewables is growing ever faster: in the next five years, the renewable energy capacity will be expanded just as much as it did in the last 20 years (IEA, 2023).

In heavy industries, however, the use of fossil fuels is much harder to avoid. In the cement industry, for example, about two-thirds of the CO_2 emissions are deemed to be unavoidable (IEA, 2019b). Despite their fossil-based character, the chemical, cement and steel industries also have a critical role to play in the transition to renewable energy. The steel industry, for example, provides the steel necessary for wind turbines and the chemical industry the necessary plastics for solar panels (IEA, 2020b). This continuously increasing demand for materials produced by the steel, chemical and cement industries makes it even more challenging to achieve large emissions reductions.

Nevertheless, even these heavy industries will need to find a way to reduce their emissions, as the public awareness of climate change grows and the European policy framework to reduce emissions becomes increasingly stringent.

The European Union (EU) aims to be one of the frontrunners in the transition to a carbon-neutral world. In 2005, the EU launched the world's very first Emissions Trading System (ETS), allowing the trade of emission allowances between various countries (European Commission, 2023d). The EU ETS is based on a 'cap-and-trade' system. A cap is set on the total amount of emissions that can be produced annually by the installations under the EU ETS. Within this cap, the installations can trade

emission allowances with one another, depending on their needs. The price of the emission allowances, often referred to as the carbon price or CO_2 price, gives an incentive for installations covered by the EU ETS to reduce their emissions. The EU ETS has been shaped gradually, in four phases, since its establishment in 2005. With each phase, the EU ETS regulations were changed to strengthen the EU ETS further, e.g. extending the ETS to new sectors or reducing the cap set on emissions. In the early years of the EU ETS, the CO_2 price remained at a low level, giving very little incentive for firms to reduce their emissions. Reforms in recent years, e.g. the introduction of the Market Stability Reserve, have driven the CO_2 price up. In 2023, the CO_2 price even surpassed the symbolic threshold of € 100 per tonne of CO_2.

The launch of the EU ETS in 2005 marks the start of many climate actions by the European Commission.

In 2019, the EU launched the Green Deal: a roadmap for Europe to become the first climate-neutral continent. In this roadmap, the European Commission has set the target to emit 55% less GHG emissions (in comparison to 1990 levels) by 2030 and by 2050, the EU should reach net-zero GHG emissions (European Commission, 2023e). To achieve these ambitious goals, the Green Deal bets on a portfolio of green technologies and behavioural changes, including – but not limited to – an increasing share of renewable energy, a growing number of electric vehicles, investments in public transport to promote a more sustainable way of travelling, exploring the use of hydrogen as a green energy carrier and raising awareness to reduce our overall energy and resource consumption.

These proposed solutions do not yet offer an answer to all the challenges that will come with the transition to a carbon-neutral society. While the lion's share of greenhouse gas (GHG) emissions can be mitigated with these conventional technologies, a small part of the GHG emissions cannot easily be abated. Heavy industries – steel, cement and chemicals manufacturing – account today for almost 20% of global CO_2 emissions and are known for their so-called hard-to-abate emissions. For those emissions that cannot be avoided or reduced immediately, carbon removal technologies are needed to offer relief. This is where Carbon Capture Utilisation and Storage (CCUS) could make a difference.

1.1 The proposed solution for the hard-to-abate emissions

The International Energy Agency (IEA) claims that achieving goals of net-zero CO_2 emissions will be virtually impossible without CCUS (IEA, 2019b) and the EU also recognizes a role to play for CCUS technologies in their path to a net-zero economy (Thielges et al., 2022). Nevertheless, CCUS technologies remain largely unknown to the broader public. Hence, a brief introduction to CCUS is appropriate. CCUS refers to a suite of technologies, covering both Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU).

1.1.1 Carbon Capture and Storage

Carbon Capture and Storage (CCS) is the set of technologies that aim to capture, transport and permanently store CO_2 in deep geological formations. The CO_2 can be captured from large point sources, e.g. fossil-fired power plants, or can be directly captured from the atmosphere. In their most recent report, the IPCC recognizes CCS as an indispensable part of the pathway to net-zero CO_2 emissions in the industry (Pathak et al., 2022). The IPCC estimates the mitigation potential of directly capturing CO_2 from the air and then storing it underground (DACCS) at 5 to 40 Gt CO_2 per year, which is higher than e.g. the estimated mitigation potential of reforestation. Although the potential of DACCS is very large, its estimated annual deployment remains limited. Even in scenarios that limit global warming below 2 °C, DACCS would only reach 0.02 Gt CO_2 per year in 2030 (Babiker et al., 2022). Direct air capture (DAC) is one of the more costly and energy-intensive capture technologies, explaining the

low estimates for the deployment of DACCS. In addition to the numbers for DACCS specifically, the IPCC report also provides estimates of the reduction potential in different sectors for CCS in general. By 2030, CCS would reduce 0.54 Gt CO_2 per year in the energy sector and 0.15 Gt CO_2 in the industry. Global CO_2 emissions from the burning of fossil fuels and industrial processes amounted to more than 37 Gt of CO_2 in 2021, by comparison (Ritchie, Roser, & Rosado, 2020b). Other estimates for the potential of CO_2 capture can be found in the 'Net Zero by 2050' roadmap, prepared by the IEA for the global energy sector. In this roadmap, the IEA estimates that 1.67 Gt of CO_2 will be captured globally in 2030, rising further to 7.6 Gt of CO_2 in 2050 (IEA, 2021b). These amounts represent 4.5% and 20.5% respectively of the global CO_2 emissions in 2021. These numbers illustrate the potential role that CCS can play in the transition to net-zero emissions.

The EU also foresees a role for CCS in its climate policies. In its vision towards a Clean Planet for All, the European Commission acknowledges the need for CCS to tackle the remaining CO_2 emissions, especially in energy-intensive industries (European Commission, 2018a). In the Net-Zero Industry Act, launched in March 2023, the EU recognizes CCS as one of the strategic technologies for meeting the EU's climate goals, based on its Technology Readiness Level (TRL) and its contribution to decarbonisation (European Commission, 2023f). The Net-Zero Industry Act is part of the Green Deal and aims at promoting investment in those technologies that will help us reach net-zero emissions by 2050. To stimulate the development of CCS projects particularly, the Act has set a target of reaching an annual CO_2 storage capacity of 50 million tonnes of CO_2 by 2030. It remains to be seen how these policy initiatives will affect the development of CCS.

Although CCS was already deemed technically feasible on a commercial scale in 2008 (Gibbins & Chalmers, 2008), the uptake of CCS remains slow until today. The main obstacles that hinder the deployment of CCS are the high costs for CO_2 capture and a lack of policy support to incentivize CCS investments (Bruhn, Naims, & Olfe-Kräutlein, 2016; Gibbins & Chalmers, 2008). The costs for CO_2 capture vary greatly, depending on the CO_2 source, the CO_2 purity and the selected capture technology. The capture costs can go as low as 15 € per tonne of CO_2 to capture CO_2 from highly concentrated CO_2 streams, e.g. from natural gas processing facilities or bioethanol plants, and reach a maximum of 340 € per tonne of CO_2 to capture CO_2 directly from the air (DAC) (IEA, 2019b). Moreover, the costs for safe transport and storage of CO_2 are also case-specific, dependent on the transport distance, type of transport and the CO_2 volumes. In general, the transport and storage costs are often estimated at 10 €/tonne of CO_2, but in reality, these costs can vary from 4 to 45 €/tonne of CO_2 for onshore pipeline transport and storage (Smith et al., 2021). To compensate for the costs of capture, transport and storage, additional funding mechanisms are needed. Since 2015, CO_2 capture and storage installations have also been included in the EU ETS, meaning that captured and safely stored CO_2 is considered as not emitted under the EU ETS (European Commission, 2023a). In other words, no emission allowances need to be surrendered anymore for CO_2 emissions that are captured and stored, creating an incentive for CCS within the EU ETS. However, the price of emission allowances in the EU ETS – i.e. the cost per tonne of CO_2 produced –remained at a low level, fluctuating between 5 and 25 €/tonne of CO_2 from 2015 to 2020 (Sandbag, 2023). Hence, the incentive to invest in emission reduction technologies failed to materialise in the EU ETS. In 2023, the CO_2 price surpassed the symbolic threshold of 100 € per tonne of CO_2. Despite the increasing CO_2 prices, investments for CCS projects are still lagging. The absence of an attractive business case for CCS has raised attention to Carbon Capture and Utilization (CCU) (Bruhn et al., 2016).

1.1.2 Carbon Capture and Utilization

CCU covers a broad range of technologies that capture and use CO_2 in a production process to create valuable products or services. While CCS focuses on trapping the CO_2 for permanent storage, CCU aims to utilize the CO_2 as an input to other products or services. CCU is generally classified into two categories: (1) the direct use of CO_2, where the CO_2 molecule is not chemically altered (non-conversion) and (2) the transformation of CO_2 through chemical or biological processes (conversion) (IEA, 2021a). This classification of CCU technologies is presented in Figure 1.1. An example of the first category – the direct use of CO_2 – is CO_2-enhanced oil recovery (CO_2-EOR), where the captured CO_2 is injected into oil reservoirs to increase the production of oil. Other examples are the direct use of CO_2 in the soft drink industry or for refrigerant fluids (C.-H. Huang & Tan, 2014). The conversion of CO_2 – the second category – can be further divided into three main routes: mineralization, chemical-based and bio-based conversion routes (Chauvy, Meunier, Thomas, & De Weireld, 2019).

CO_2 mineralization is an approach that allows to capture CO_2 and store it in the form of carbonate minerals, e.g. calcite ($CaCO_3$) or magnesite ($MgCO_3$) (National Academics of Sciences, 2019). Carbon8 has developed a CCU technology based on the concept of mineralization, called Accelerated Carbonation Technology (Carbon8, 2023). With their technology, the CO_2 can be captured and used to create carbonated products for the construction industry, in which the CO_2 is then stored. Chemical CO_2 conversion routes cover a wide range of routes, from e.g. catalytic hydrogenation of CO_2 to electrochemical conversion of CO_2. Carbon Recycling International (CRI) was the first to build a CCU plant that transforms CO_2 from flue gases and hydrogen (H_2) into renewable methanol (MeOH) on an industrial scale, already in 2012 (CRI, 2023). Finally, CO_2 can be converted using biological processes. One example of a bio-based CCU route is the use of microalgae to convert CO_2 into biofuels. This brief overview highlights the variety of technologies that are all labelled today as 'CCU'.

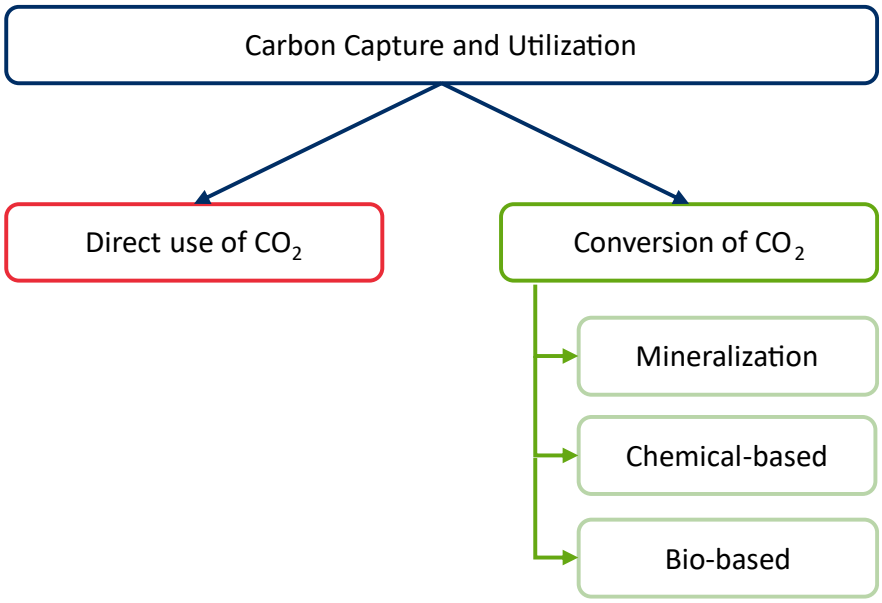


Figure 1.1: Classification of CCU technologies.

While the umbrella term 'CCU' is quite new[1], the idea of using CO_2 – either directly or in a conversion route – is not new. The direct use of CO_2 can be traced back to the 1970s, when CO_2 was captured from natural gas production to be used for CO_2-EOR. The history of CO_2 conversion also started in the 1970s, when chemical researchers started exploring the idea of using CO_2 as an alternative source of carbon (Michele Aresta, 2010). Since there were no legal obligations yet to reduce CO_2 emissions in the 1970s, the industry did not recognize the benefits of using CO_2 at that time. Due to this lack of support from industry, the research efforts for CO_2 conversion decreased again in the following decades. In 2008, as oil prices increased and environmental concerns slipped into the public debate, the interest in an unconventional source of carbon, as an alternative to oil, began to grow (Bruhn et al., 2016). As a result, the interest in CO_2 conversion was sparked again.

1.1.3 The role of CCU in the transition to net-zero

As CCU is starting to gain momentum now, the role of CCU in climate change mitigation pathways is being acknowledged more and more. The IEA recognizes CCU as an important technology, particularly to reduce the hard-to-abate emissions from heavy industry (steel, cement and chemicals production) (IEA, 2020b). As mentioned before, heavy industry is responsible for about 20% of global CO_2 emissions, emphasizing the importance of realizing emission reductions in these sectors. However, heavy industry is known for its hard-to-abate emissions, which are emissions that cannot be reduced with existing abatement technologies at a reasonable cost. While many industrial processes can reduce the majority of their emissions by switching to renewable energy and increasing energy efficiency, this is much harder to achieve in heavy industry. The reason is that in these sectors – steel, cement and chemical – fossil fuels are often still the cheapest option for many of their critical production processes. For example, most processes in the chemical industry have high-temperature requirements. Fossil fuels are still predominantly used to provide the necessary high-temperature heat, as it would be impractical and costly to generate the same heat from electricity. Moreover, fossil fuels are not only used as energy input in heavy industry. The chemical industry relies heavily on fossil fuels, oil in particular, for their production processes. The production of plastics is the best-known example of this. Another example of hard-to-abate emissions can be found in the cement industry. Clinker, one of the main raw materials, is produced by heating limestone ($CaCO_3$). This process releases the carbon (C) that was trapped in the limestone again into the atmosphere, which can then recombine with oxygen (O_2) to form CO_2, resulting in substantial process emissions that cannot be abated by e.g. switching to renewables.

CCU technologies can provide an answer to this challenge, by using CO_2 as an alternative source of carbon, hence reducing the dependency on fossil fuels. In their Sustainable Development Scenario, the IEA forecasts that about one-third to one-quarter of the emissions reduction in heavy industry will be delivered by the combination of CCU and CCS (IEA, 2021a). For the cement industry in particular, the IEA estimates that CCUS will contribute about 60% of the emission reductions by 2050. Consistent with the outlook for CCU presented by the IEA, a role is also reserved for CCU in EU policy to become the first climate-neutral continent. In the EU's long-term vision to achieve net-zero emissions by 2050, CCU is mentioned as one of the strategies to reduce industrial emissions, particularly in the cement, steel and chemicals sectors (European Commission, 2018a; Thielges et al., 2022).

Today, the utilization of CO_2 amounts to about 230 Mt of CO_2 annually (IEA, 2021a). Commercial CCU applications mostly involve the direct use of CO_2, with the largest amounts of CO_2 used observed for the production of fertilisers (125 Mt) and CO_2-EOR (70-80 Mt). Relative to the global CO_2 emissions in

[1] The first publication in Web of Knowledge that uses the term 'Carbon Capture and Utilization' was published in 2008.

2021 (37 Gt), the amount of CO_2 used in CCU pathways seems negligible, as it only accounts for about 0.6% of today's annual emissions. However, new CCU pathways are emerging, with renewed attention to the conversion of CO_2.

The expected innovation in CCU, together with the increasingly stringent environmental regulations, results in elevated forecasts for the mitigation potential of CCU in the future. The European Commission estimated the global long-term mitigation potential of CCU at 1 to 2 Gt of CO_2 per year (European Commission, 2018b). Varying estimates are found in the literature; a range from 1 to 4.2 Gt CO_2 per year is estimated for fuels production through CCU (Hepburn et al., 2019), while a potential up to 3.5 Gt CO_2 per year is estimated for chemical production processes, conditional on the use of clean electricity (Kätelhön, Meys, Deutz, Suh, & Bardow, 2019).

While CCU can play an important role in meeting global climate goals, particularly in the reduction of hard-to-abate emissions, several barriers – or rather questions – remain to be addressed before CCU can be deployed on a large scale as emission reduction technology.

One of the first challenges is that most CCU technologies do not provide long-term storage of CO_2 (Bruhn et al., 2016): the CO_2 is released again once the products are used. The CO_2 will only be stored for days or weeks in fuels until the fuel is burnt again, whereas the CO_2 can be stored for decades or even centuries in building materials. How long the CO_2 is stored, could influence the effective mitigation potential of the CCU route. Second, concerns have been raised about the risk of extending the use of fossil fuels due to CCU (Olfe-Kräutlein, 2020). Because CCU can use and valorise the captured CO_2 from e.g. fossil power plants, the concern has risen that CCU might lengthen the lifetime of fossil power plants and consequently, delay the uptake of renewable energy. Such negative lock-in effects need to be avoided. The role of CO_2-EOR as a CCU technology has been under debate in particular, as this technology is specifically used to increase the production of oil. Third, the amount of CO_2 that can be utilized in CCU routes is limited by the market of CCU-based products (Mac Dowell, Fennell, Shah, & Maitland, 2017). As mentioned before, 230 Mt of CO_2 is currently used annually, mostly in pathways for direct use of CO_2. The conversion of CO_2 is, however, gaining importance as well. Based on the projects that are currently in the pipeline, the IEA estimates that 10 Mt of CO_2 will be used annually for the conversion of CO_2 into fuels, chemicals and building materials by 2030 (IEA, 2022c). Compared to the CO_2 emissions of around 37 Gt in 2021 (Ritchie et al., 2020b), this amount of CO_2 that can be used in CCU still seems very small. Fourth, CO_2 is a very stable molecule that requires a lot of energy to be transformed into other products, because of its low thermodynamic energy value (Ampelli, Perathoner, & Centi, 2015; M. Aresta & Tommasi, 1997). While this does not pose any problem for the direct use of CO_2, it does create an additional challenge for the conversion of CO_2. The stability of the CO_2 increases the energy needs of CO_2 conversion routes. The high energy consumption is often the main contributor to the high operational costs of these CCU technologies. Moreover, if the energy is not produced from renewable energy sources, the energy consumption also contributes heavily to global warming and other environmental impacts of the CCU process.

While the direct use of CO_2 is already applied in commercial applications today, e.g. for the production of fertilizer or the improved production of oil in CO_2-EOR, the conversion of CO_2 is just gaining momentum. Because the CO_2 conversion routes are still subject to more challenges, and have more potential to reduce those hard-to-abate emissions in heavy industries, this thesis will focus on CO_2 conversion routes.

The high stability of the CO_2 molecule is perhaps the greatest challenge to overcome to make the conversion of CO_2 feasible. The quest for CCU technologies that can transform CO_2 with a minimum of energy has already been going on for decades. In this thesis, one potential CCU technology is

investigated, that may have the right properties to conquer the high stability of the CO_2 molecule. Although it has been used in other applications before, it is rather new to the CCU research field. Plasma catalysis has several unique characteristics that make it a promising candidate for the conversion of CO_2 into other products.

1.2 Plasma catalysis: a CCU technology in the making

The first plasma-catalytic experiments already happened in the early 1920s, although the researchers didn't label their study as plasma catalysis at that time (Ray & Anderegg, 1921). The term plasma was only introduced a couple of years later, in 1928, by Langmuir (1928). More than a hundred years of plasma research have resulted in a broad range of applications, including plasma televisions, ozone production through plasma and even cancer treatments (Carreon, 2019). In recent years, the interest in plasma technologies for the conversion of CO_2 has been stirred. Plasma can bring some unique features to the CO_2 conversion playing field, but its complexity requires a brief introduction first.

99.9% of our visible universe is plasma: the stars, including the sun, and the Aurora Borealis are examples of plasma that appeal to everyone's imagination. Plasma is an ionized gas, and it contains both charged and neutral species, including atoms, ions, electrons, radicals and neutrals. All these different species can interact with each other in the plasma, creating a highly reactive chemical mixture. Besides the three well-known states of matter – solid, liquid, and gas – plasma is often called 'the fourth state of matter'. (Carreon, 2019; Snoeckx & Bogaerts, 2017a)

Two main types of plasma can be identified: thermal and non-thermal plasma (Carreon, 2019). Thermal plasmas need to be created either at high temperatures, between 4,000 K and 20,000 K (equivalent to 3,726 and 19,726 °C), or at a high gas pressure (Snoeckx & Bogaerts, 2017a). Thermal plasmas are in thermodynamic equilibrium, which means that the temperature of all species in the plasma is the same. The high temperatures that can be reached in thermal – also known as 'hot' – plasmas, allow reactions to take place even with a stable molecule such as CO_2. However, these high temperatures also come with a downside: the energy efficiency of these conversion processes is typically very low. This is why the focus for CO_2 conversion applications has been on non-thermal plasmas. Non-thermal plasmas operate at atmospheric pressures and the bulk of the gas in the plasma is close to room temperature. However, the electrons in the plasma are at much higher temperatures, reaching temperatures in the order of 10,000 K (Carreon, 2019). Because of this disparity between the temperatures of different species in the plasma, non-thermal plasma is not in thermodynamic equilibrium. The absence of an equilibrium between the gas molecules (close to room temperature) and the electrons (temperatures in the order of 10,000 K) creates a very reactive environment, that allows reactions to happen which are energy-intensive. Non-thermal plasma can be created by supplying electrical energy to the gas and thus, it can make use of renewable energy (Bogaerts & Neyts, 2018). On the border between thermal and non-thermal plasma, a third type of plasma is identified that shares properties with both (Snoeckx & Bogaerts, 2017a). This type of plasma is called warm plasma.

The most commonly reported types of plasma for CO_2 conversion applications are microwave (MW), gliding arc (GA) plasmas and dielectric barrier discharge (DBD) plasmas (Snoeckx & Bogaerts, 2017a). The MW and GA plasmas are warm plasmas and require complex designs to generate the plasma. A DBD is a non-thermal plasma, where the bulk of the gas is roughly at room temperature, while the electrons are at a much higher temperature due to the electric field in the plasma. A DBD consists of two electrodes, of which one is connected to a high-voltage power supply, and the other is grounded.

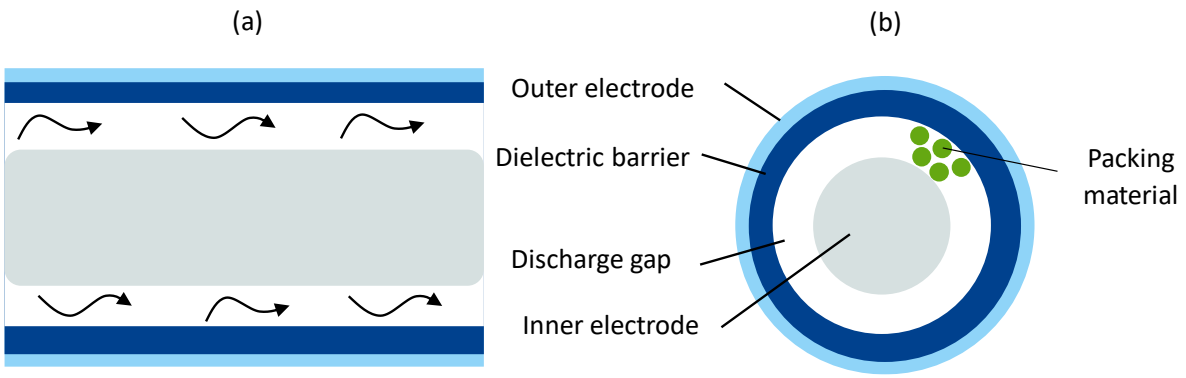


Figure 1.2: The DBD reactor set-up, (a) frontal view and (b) top view.

As the name suggests, these electrodes are separated by a dielectric[2] barrier, which acts as an insulating layer between both electrodes. In the gap between both electrodes (and the barrier), a space is created where gas can flow through the DBD reactor, i.e. the discharge gap. When gas flows through this discharge gap and an electric field is induced between both electrodes, by supplying a high-voltage current to one of the electrodes, the electrical discharge[3] is created. In the DBD reactor, the plasma is now generated. The gas can flow and interact with the plasma in the discharge gap. As the gas flows through the DBD reactor, it is gradually converted into other components. The different components of the DBD reactor are illustrated in **Figure 1.2**, in a cylindrical DBD reactor set-up.

DBD is known as one of the most versatile plasma technologies (Carreon, 2019): numerous variations in the chosen materials for the electrode or the size of the discharge gap are possible. The DBD can operate at atmospheric pressure, making it an attractive technology for various applications in industry. The first successful industrial application is the use of DBD reactors for ozone generation, and it still is the benchmark technology for ozone synthesis today. Another, more familiar, example of a DBD application today is plasma televisions. This illustrates the variety of applications for which the DBD reactor can be used. The potential application of the DBD reactor for the conversion of CO_2, as a CCU route, will be investigated in-depth in this thesis.

The use of the DBD as plasma technology for the conversion of CO_2 can indeed offer several advantages (Bogaerts & Neyts, 2018). First, the simplicity of the DBD's design makes it suitable for implementation on an industrial scale. The upscaling of the DBD reactor can be done linearly, by placing the required number of DBD reactors in parallel, in a honeycomb structure. This has been illustrated by the commercialization of DBD reactors for ozone synthesis (Kogelschatz, 2003). Second, the versatility of the DBD reactor is also an important advantage (Bogaerts & Neyts, 2018). Variations in the size of the discharge gap and the materials for the electrode are possible. Moreover, different types of reactions can be carried out in the DBD reactor. The DBD reactor can accommodate the conversion of pure CO_2, as well as the conversion of CO_2 in the presence of e.g. CH_4, known as Dry Reforming of Methane (DRM). Third, the plasma can be turned on and off quickly (Bogaerts & Neyts, 2018). The DBD reactor operates on electrical energy (not thermal energy). Once the electricity is supplied to the gas, the plasma is created and the gas conversion in the DBD reactor starts. Hence, the DBD reactor does not need long preheating or stabilization times. This provides a unique opportunity to combine the DBD reactor with renewable energy sources, being able to tap into the renewable

[2] A dielectric is an insulator in which practically no electric current can flow, and that can be polarized by placing it in an electric field (Britannica, 2023).
[3] An electric discharge is created by passing an electric current through a (gaseous) medium, resulting in the excitation of the atomic states in that medium (Magnusson, 2017).

energy production peaks. Finally, the most interesting feature of the DBD reactor is perhaps the possibility of introducing packing beads in the gap between both electrodes. These packing beads can have particular properties, which can help to steer the conversion towards the desired products. These are catalysts: materials that can accelerate the pace of a chemical reaction by providing an alternative route that requires less energy, without participating in the chemical reaction itself. The potential effect of the catalyst depends on the type of the reaction (Snoeckx & Bogaerts, 2017a). For CO_2 splitting reactions, when mainly CO and O_2 are formed, the main effect of the catalyst is to improve the energy efficiency, and perhaps also the conversion rate, of the reaction. When CH_4 (or another co-reactant) is added to the reaction, many more products can be formed. In this case, the catalyst can also improve the selectivity towards the targeted product.

The combined effect of plasma (DBD) and catalysts (packing beads) results in a new process, called plasma catalysis. Plasma catalysis brings together the reactivity of the plasma, to enable reactions that are normally unfavourable, and the selectivity of the catalysts, to steer the conversion of the gas towards the desired products (Carreon, 2019). This process is illustrated in **Figure 1.3**. The combination of a plasma with a catalyst can result in improved conversion, selectivity and energy efficiency of the CO_2 conversion reactions. This synergistic effect of plasma catalysis has been to date investigated most often in DBD plasmas, because of the ease with which catalysts can be introduced in a DBD reactor (Snoeckx & Bogaerts, 2017a).

Inserting catalysts in the discharge gap of a DBD reactor is indeed very convenient, due to the simple design and the operation of the reactor close to room temperature (Snoeckx & Bogaerts, 2017a). Catalysts could theoretically also be introduced to MW and GA plasma, however, this is less convenient. Because of the high temperatures that are reached in MW plasma, and the complex geometry of the GA plasma, the catalysts cannot be placed inside the discharge zone itself. Instead, the catalyst needs to be added downstream of the plasma.

The most interesting set-up is, however, the one where the catalysts can be inserted into the discharge zone, because the catalyst can interact with all of the species that are activated by the plasma, and the catalyst can be influenced by the plasma itself (and vice versa). Therefore, the ease of adding a catalyst into the discharge gap of the DBD reactor is probably the main asset of this type of plasma technology, compared to MW and GA plasmas. Previous research observed that the CO_2 conversion in DBD reactors packed with catalyst is always higher than the CO_2 conversion in the unpacked DBD reactor, illustrating the advantage of the ability to insert a catalyst in the discharge zone.

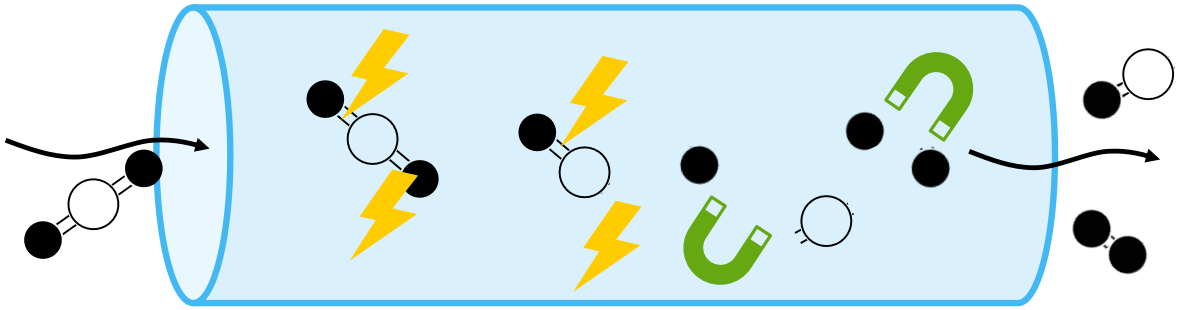


Figure 1.3: Graphical illustration of the plasma-catalytic conversion of CO_2 in the DBD reactor. The plasma (lightning) allows the breaking of the bonds of the CO_2 molecule and the catalysts (magnets) enable the combination of the elements again into the desired products.

While the DBD plasma offers a simple, versatile design where catalysts can easily be added, the advantage of the GA and MW plasma over the DBD plasma should be recognized as well. In comparison to MW and GA plasmas, DBD plasma struggles with much lower energy efficiency levels. This means that more energy is needed in a DBD to convert the same amount of CO_2 in a MW or GA plasma. The review of Snoeckx and Bogaerts (2017a) identified the low energy efficiency level of the DBD reactor as its main barrier.

As CCU is still a relatively new field of research, many other types of novel CO_2 conversion technologies are emerging as well. The plasma-catalytic approach is benchmarked against other emerging CO_2 conversion technologies in **Table 1.1** for the following features: the use of rare earth materials, reliance on renewable energy, turnkey process (on/off quickly), need for separation steps and the overall flexibility of the process. This comparison is based on the benchmarking between plasma catalysis and other CO_2 conversion technologies presented by Snoeckx and Bogaerts (2017a). One of the main obstacles for other CO_2 conversion technologies is their use of rare earth materials, which is a critical issue for their future development. This is not a concern for plasma catalysis in the DBD reactor. All of the technologies in **Table 1.1** can operate on renewable energy, with a difference in being able to use it directly (e.g. solar radiation) or indirectly (electricity). The intermittent character of renewable energy creates a need for grid stabilization. Technologies that can be switched on and off quickly, i.e. turnkey processes, can play an important role in the energy transition. Being able to switch the technology on and off quickly, in response to peaks or lows in the energy supply, would indeed be an important asset. The photochemical and plasma-catalytic technologies are both turnkey processes and can respond instantly to peaks or lows in the supply of renewable energy. This makes plasma catalysis an extremely attractive solution for grid stabilization: at moments of peak renewable energy, the plasma catalysis can be turned on and the excess renewable energy can be used to produce e.g. hydrogen as a temporary energy carrier. Except for solar thermochemical technologies, all of these technologies need post-reaction separation steps, to produce individual product streams. Since the products leave the plasma reactor all in one feed, there is also a need for a separation step after the conversion of CO_2 in plasma catalysis. Finally, the flexibility of the CO_2 conversion technology is discussed. Plasma catalysis in a DBD reactor has a great advantage here, thanks to its flexibility in the feed to the reactor (e.g. pure CO_2 or CO_2 and CH_4), its versatility in the design of the reactor, its scalability and its quality of being a turnkey process. This comparison highlights the advantages of plasma catalysis over other CO_2 conversion technologies, with its main remaining challenge being the need for post-reaction separation steps.

Table 1.1: A comparison of plasma catalysis to other emerging CO_2 conversion technologies. Based on the overview presented in Table 2 by Snoeckx and Bogaerts (2017a).

	Use of rare earth materials	**Renewable energy**	**Turnkey process**	**Need for separation**	**Overall flexibility**
Electro-chemical	Yes	Indirect	No	Yes	Medium
Solar thermochemical	Yes	Direct	/	No	Low
Photochemical	Yes	Direct	Yes	Yes	Low
Biochemical	No	Direct	No	Yes	Low
Plasma catalysis	No	Indirect	Yes	Yes	High

Despite all of these advantages of plasma catalysis, plasma catalysis technologies are not taking over the CCU market and converting CO_2 on a commercial scale yet. Although the DBD reactor in itself is a mature technology and is already applied on an industrial scale for the generation of ozone (Kogelschatz, 2003), the installation of a DBD reactor packed with catalysts for CO_2 conversion processes is still at an early stage. Before plasma catalysis in the DBD reactor can be deployed as a commercial CCU technology, several aspects will need to be addressed.

First, plasma catalysis will require newly developed, tailor-made catalysts, due to the complexity of interactions between plasma and catalyst (Snoeckx & Bogaerts, 2017a). Various types of interactions can be identified: the catalyst can affect the plasma and vice versa, and both physical and chemical effects can be present. While a variety of traditional catalysts for thermal catalysis already exists, the use of these catalysts in plasma catalysis will likely not be the most optimal choice, due to these interactions between plasma and catalysts.

Second, in the case of DRM reactions in the DBD reactor, when CO_2 is co-fed with CH_4, many products could be targeted. While this creates the possibility to convert CO_2 and CH_4 in one step into oxygenated products, such as ethanol or methanol, it opens the question of which products should be targeted. The selectivity of the DRM reaction in the DBD reactor can be steered by the catalyst, again underlining the importance of the choice of catalyst.

Third and finally, the versatility of the DBD reactor, while offering many opportunities for its implementation as CO_2 conversion technology, also raises many questions. Numerous variations in the design of the DBD reactor are possible, including e.g. the size of the discharge gap or the material for the electrodes. Hence, the question can be raised how the design of the DBD reactor can be altered, to improve the conversion rate and the energy efficiency of the CO_2 splitting or DRM reactions.

The search for the optimal catalyst for plasma catalysis, together with the numerous variations that are possible in the design of the DBD reactor, will give rise to plenty of combinations of catalyst and DBD reactor. To be able to identify the effect of the catalyst and the effect of the different variations in the design of the DBD reactor, systematic assessments of different experimental set-ups are needed, in which variations in the chosen catalyst and DBD reactor set-up are analysed one-by-one.

1.3 Towards the design of an economically and environmentally desirable CCU technology in an uncertain future

It is clear that the plasma-catalytic conversion of CO_2 (and CH_4) in a DBD reactor still faces several challenges on its path to becoming a commercial CCU technology. The search for the catalyst is ongoing and it is unclear when – or if – the 'right' catalyst will be found. The versatility in the design of the DBD reactor adds to the possibility of improving the conversion rate, energy efficiency and selectivity of the plasma-catalytic conversion of CO_2 (and CH_4) in a DBD reactor.

While the pursuit of the most optimal catalyst and design of the DBD reactor is a unique challenge for this type of CCU technology, other obstacles that are shared by all novel CCU technologies need to be overcome as well.

For CCU technologies, the current regulatory framework still leaves many questions unanswered. The EU ETS is one of Europe's main climate policy instruments. The EU ETS directives are revised frequently to mirror the new climate targets of the EU. Since 2015, installations that are covered by the EU ETS no longer have to surrender emission allowances for CO_2 emissions that are captured and transported for permanent storage (Article 12(3a). Since the revision of the EU ETS in May 2023, the obligation to

surrender emission allowances has also been lifted for CO_2 emissions that have been utilised in such a way that they are permanently chemically bound (Article 12(3b)) (European Commission, 2023c). While this opens the door a little bit for some specific CCU technologies, i.e. mineralization, this new regulation does not yet cover all CCU technologies. For most chemical-based and bio-based CCU routes, the EU ETS does not (yet) provide any incentive.

The current lack of policy support makes the question of economic feasibility of crucial importance for the viability of novel CCU technologies. If the technology proves to be economically feasible, investments will follow, otherwise not. In addition to the questions about the business case of a novel CCU technology, questions can (and should) also be raised about the environmental impacts of the novel CCU route. CCU technologies aim to play a role in meeting global climate goals. Hence, investing in CCU routes does not make sense if the CCU technology cannot generate any reduction in emissions or other climate benefit, e.g. a reduction in the industry's dependency on fossil fuels. Therefore, the environmental impacts of novel CCU technologies should be analysed in detail as well. If the environmental assessment reveals that CCU technologies are not able to create any environmental benefit, this can have implications for policy support as well. In that case, the inclusion of CCU in the EU ETS cannot be justified.

Despite these questions that remain about the policy support, economic feasibility and environmental desirability of novel CCU technologies, emerging technologies also bring opportunities to the table. As long as the technology is in development, adjustments can be made to its design. The early assessment of a novel technology provides the perfect opportunity to change the design upfront, to make it (more) economically attractive and environmentally sound.

Plasma catalysis is this novel CCU technology, that is still in the development phase where changes can and need to be made before it can become a viable solution for CO_2 conversion. In 2019, a new FWO project started with the aim of defining the design rules for the catalyst to make the conversion of CO_2 in plasma more selective and energy-efficient. The PlasMaCatDESIGN project, as it was called, brings together researchers from different universities and disciplines and also includes partners from industry to meet their interests.

Researchers at VITO, UGent and UHasselt developed the supports, coating and catalytic nanoparticles for the packing beads to be inserted in the gap in the DBD reactor. These newly designed and developed packing beads were then tested in the laboratory at the University of Antwerp. Simultaneously, chemical scientists at the University of Antwerp tried to model the plasma chemistry and interactions, to suggest new pathways to be explored.

Within this project, multiple rounds of experiments were performed in the laboratory to investigate systematically how variations in the design of the DBD reactor and the chosen catalyst affect the plasma-catalytic conversion of CO_2 (and CH_4). These experiments deliver data on how effectively the CO_2 is converted (CO_2 conversion), how much energy is consumed (energy efficiency) and which end-products are produced (product mix) for variations in the design of the DBD reactor and the chosen catalyst.

While these experiments provide information about how these systematic variations affect the technical performance of this novel CCU technology, it does not inform us about the economic and environmental impacts that are associated with these technological variations. Moreover, the experimental work only describes the technical performance of plasma catalysis in a DBD reactor in isolation and does not discuss the other processes that would be needed to build a full CCU value chain around the plasma-catalytic conversion of CO_2 in the DBD reactor.

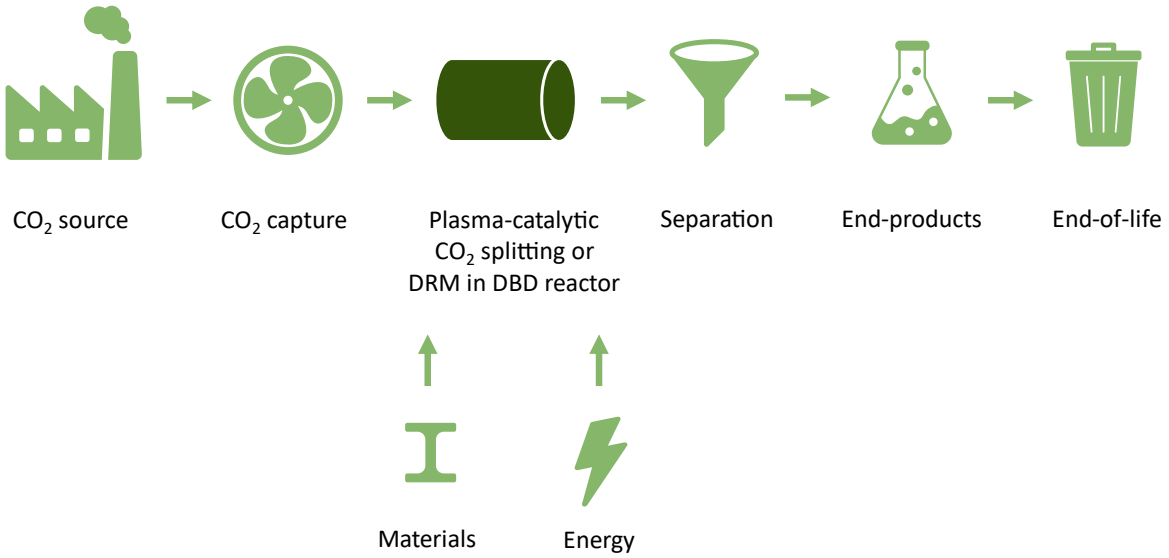


Figure 1.4: A simplified representation of the CCU value chain, with plasma-catalytic reactions in a DBD reactor as CO_2 conversion technology. In this value chain, it is assumed that the CO_2 is used on-site, eliminating the need for transport.

The positioning of plasma catalysis in a DBD reactor in the CCU value chain is shown in **Figure 1.4**. Other processes in the CCU value chain include the capture of CO_2, the supply of materials and energy for the plasma process in the DBD reactor, and the end-products.

This gives rise to the following overall research question that will be addressed in this dissertation:

How do variations in the design of a novel CO_2 conversion technology, i.e. plasma catalysis in a DBD reactor, affect the economic feasibility and environmental desirability for a CCU value chain, given an uncertain future?

Before going further, some arrangements need to be made about the terminology that will be used in the remainder of this thesis. Until now, we referred to variations in the design of the DBD reactor and the chosen catalyst. From here on, the terms *reactor configuration* and *process parameters* are introduced to describe the variations that were analysed in the experiments for the plasma-catalytic conversion of CO_2 in the DBD reactor. The term *reactor configuration* refers to the geometry of the DBD reactor, i.e. the discharge gap, discharge length, reaction volume, electrode morphology and packing material. Henceforth, the packing material, or catalyst, is part of the chosen *reactor configuration*. In the experiments, not only variations in the *reactor configuration* were analyzed, but also variations in certain *process parameters*. The relevant *process parameters* in this work are the flow rate, feed ratio, input power and specific energy input (SEI) (Khoja, Tahir, & Amin, 2019). Their meaning will be explained in more detail in Chapter 3. To refer to the chosen *reactor configuration* and *process parameters* jointly, the terms *combination* or *set-up* will be used in this thesis.

The experimental dataset, in which these variations in *reactor configuration* and *process parameters* have been tested, provides a unique starting point to address the overall research question and to develop the technology further. The overall research question will now be divided further into four research questions, that will help us to address several research gaps within the CCU literature.

While the interest in CCU as a key technology in the path towards net-zero emissions has risen considerably in recent years, the question remains how the business case of CCU can and should be developed. Together with the sparked interest in CCU, we have observed a growing number of economic feasibility studies for novel CCU technologies. However, the majority of these economic studies assess the feasibility of one set-up of the CCU technology and do not investigate variations in the technological design of the CCU route. Instead, these economic feasibility studies often focus on the influence of market parameters, such as the electricity price or the product price, on the economic feasibility of a CCU project. While market parameters are generally uncontrollable by the potential investor, technological parameters can still be improved by adjusting the design of the technology. Because the majority of CCU technologies are still in the development phase, it can be particularly interesting to evaluate how variations in the design of the CCU technology would affect its economic performance.

As discussed earlier, plasma catalysis is one of these novel CCU technologies. The PlasMaCatDESIGN project delivers data on different combinations of the DBD *reactor configuration* and *process parameters*, and their technical performance. Thanks to the interdisciplinary collaboration within the project, the experimental data describing the plasma catalysis' technical performance can be translated into economic numbers. The first research question of this dissertation reads as follows:

1. *How do variations in the design of the DBD plasma technology, for the plasma-catalytic conversion of CO_2, translate into economic impacts for the CCU value chain as a whole?*

In this question, the design of the DBD plasma technology refers to the combination of the chosen *reactor configuration* and *process parameters*, as mentioned earlier. This research question focuses on the economic aspect of the development of plasma catalysis in the DBD reactor. In Chapter 2, a review is presented of economic feasibility studies that were done in the past for CCU technologies. This review helps to identify the methodological pitfalls of assessing the economic performance of a novel CCU technology. In Chapter 3, a Techno-Economic Assessment (TEA) is performed to assess the economic feasibility of different DBD plasma set-ups. A TEA integrates the technical and economic evaluation into one study and explicitly links the technical performance to the economic metrics. This is a very informative methodology to compare the economic feasibility of different designs of one technology. In this thesis, a TEA is performed for all combinations of *reactor configurations* and *process parameters* that were tested in the laboratory. To automate the repetition of the TEA for each tested combination, an Excel tool is developed with an integrated Visual Basic for Applications (VBA) script. Hence, with this tool, a TEA can be performed for all tested combinations of *reactor* configuration and *process parameters* with one click. In this interactive tool, assumptions about costs, e.g. the electricity price, can easily be changed and their effect on the results can be quickly analysed. As a result, the TEA enables the comparison of the different variations in the plasma catalysis technology that were tested in the laboratory. Based on the results from the TEA, recommendations are formulated about which *reactor configuration* and *process parameters* to focus on in the future development of the technology, from the economic perspective.

In addition to the evaluation of the business case, the environmental performance of the CCU technology needs to be assessed as well, if CCU technologies are to play a role in the transition to net-zero emissions. Despite the increasing number of studies that assess the environmental impact of CCU technologies over their life cycle in recent years, a lack of environmental assessments for the chemical CCU routes is observed (Cuéllar-Franca & Azapagic, 2015). Moreover, the results of previous studies may be outdated quickly, because CCU technologies are evolving rapidly (Garcia-Garcia, Fernandez, Armstrong, Woolass, & Styring, 2021). Similar to the economic assessment, here too it is recommended to perform an environmental assessment at an early stage when there is still an

opportunity to influence the design of the technology. The experimental data from the PlasMaCatDESIGN can now be used to translate the technical performance of plasma catalysis into environmental impacts, giving rise to the second research question:

2. *How do variations in the design of the DBD plasma technology, for the plasma-catalytic conversion of CO_2, translate into environmental impacts for the CCU value chain as a whole*?

This research question addresses the concerns about the environmental impacts of plasma catalysis technology. A Life Cycle Assessment (LCA) is implemented in Chapter 4, to evaluate the environmental impacts that occur over the full value chain of the plasma-catalytic conversion of CO_2 in the DBD reactor. Similar to the TEA, a tool is developed that allows performing the LCA easily for the different DBD *reactor configurations* and *process parameters*. Hence, the LCA results enable the identification of the set-up with the lowest environmental impact.

The third research question aims to compare the economic and environmental assessment.

3. *What are the potential trade-offs between the economic and environmental impacts that could result in diverging design choices?*

In Chapter 4, the results of the TEA and LCA are compared with each other. Both the economic and environmental indicators are combined, for all tested reactor configurations in the laboratory. This integration provides valuable information for the future development of the technology. It reveals whether diverging design choices would be made based on either the economic or environmental perspective, or whether the same set of *reactor configuration* and *process parameters* is preferred from both perspectives. Evaluating the economic and environmental performance of each tested DBD reactor configuration allows for excluding some of the tested catalysts for future research. This integrated perspective is crucial to steer the future research and development of this technology in the laboratory.

While Chapter 3 focuses on the implementation of a TEA for the novel CCU route, Chapter 4 concentrates on the application of an LCA for this novel CCU route. However, in Chapters 3 and 4, different sets of *reactor configuration* and *process parameters* are evaluated. In Chapter 3, a *reactor configuration* with a gap size of 0.455 mm is analysed. The discharge gap is filled with either no packing or a SiO_2 packing material. For the *process parameters*, a feed of pure CO_2 or a mix of CO_2 and CH_4 is tested, and the flow rate is decreased stepwise to vary the space time between 2.91 and 72.71 s. In Chapter 4, the *reactor configuration* has a gap size of 4.44 mm, and this gap is filled with γ-Al_2O_3, iron oxide (Fe_2O_3)-based or copper oxide (CuO)-based packing materials. For the *process parameters*, the feed ratio (CO_2:CH_4 1:1) is kept constant during the experiments, while the flow rate is decreased stepwise to vary the space time of the gas between 5 and 80 seconds. The materials for the electrodes are the same in both Chapters, as is the input power (30 W) during the experiments. The tested *process parameters* and *reactor configurations* in Chapters 3 and 4 are summarized in **Table 1.2** and **Table 1.3**.

Table 1.2: The set of *process parameters* evaluated in Chapter 3 and Chapter 4.

	Chapter 3	**Chapter 4**
Flow rate	2 mL/min – 50 mL/min (empty); 1.03 mL/min – 28.79 mL/min (SiO_2)	6.9 mL/min – 110.36 mL/min
Feed ratio	Pure CO_2, CO_2:CH_4 1:1	CO_2:CH_4 1:1
Plasma power	30 W	30 W
SEI	35.54 kJ/L – 903.42 kJ/L (empty); 62.37 kJ/L – 1742.14 kJ/L	16.33 kJ/L – 262.23 kJ/L

Table 1.3: The analyzed *reactor configuration* in Chapter 3 and Chapter 4.

	Chapter 3	**Chapter 4**
Discharge gap	0.455 mm	4.44 mm
Discharge length	100 mm	100 mm
Discharge volume	2.42 mL	9.19 mL
Electrodes		
Inner electrode	Stainless-steel rod	Stainless-steel rod
Dielectric barrier	α-alumina dielectric tube	α-alumina dielectric tube
Outer electrode	Stainless-steel mesh	Stainless-steel mesh
Packing material	SiO_2	γ-Al_2O_3, 2%Fe_2O_3@γ-Al_2O_3, 10%Fe_2O_3@γ-Al_2O_3, 2%CuO@γ-Al_2O_3, 10% CuO@γ-Al_2O_3

Based on the economic and environmental assessments that were performed to answer the first three research questions, one could easily be convinced that a potential investor has the necessary information to decide whether or not to invest in CCU. However, other factors will influence the decision to invest in a novel CCU technology and hence, need to be taken into account as well.

First, CCU is not the only technology that can support firms in the reduction of their hard-to-abate CO_2 emissions. CCS can capture and store the CO_2 permanently in the deep underground. As CCS technologies are already more advanced than most CCU technologies, this might be an attractive alternative for firms to invest in. Besides the choice to invest in CCS or CCU separately, the possibility of integrating CCS and CCU in a CCUS value chain should be considered as well.

Second, investment decisions in emerging technologies are typically characterised by a high level of uncertainty. Two main sources of uncertainty affect the decision to invest in a novel CCU technology: the technological uncertainty, i.e. the innovation pace of the CCU technology, and the market uncertainty, i.e. the unknown future evolution of the CO_2 price in the EU ETS.

This leads to the final research question:

4. *How is the investment decision in CCUS technologies affected by technological uncertainty, i.e. the innovation pace in CCU, and market uncertainty, i.e. the CO_2 price in the EU ETS?*

While the first three research questions focused on the development of plasma catalysis as a novel CCU technology, the final research question of this thesis aims to analyse the investment decision into emerging CCU technologies in a more general framework. We aim to identify the optimal timing to invest in CCS, CCU or CCUS, implying that firms have the flexibility to choose the timing of investment.

The investment decision in CCS, CCU and CCUS projects has been analysed in multiple ways before. Typically, a TEA is performed to assess the profitability of the CCS, CCU or CCUS projects and make the investment decision. However, a TEA only considers the investment decision in a deterministic setting and hence, can only advise to either adopt the technology now (if it is profitable) or never (if it is too costly). The dynamics, uncertainties and risks of the real-world setting are typically neglected in this type of assessment. Real options analysis, on the contrary, allows for valuing flexibility in investment decisions, acknowledging the fact that decision-makers can delay investment decisions in practice (Dixit & Pindyck, 1994). Real options theory provides the right framework to find the CO_2 price threshold that defines the optimal timing to invest, taking into account the multitude of investment strategies and the present sources of uncertainty. Chapter 5 presents a literature review of studies that implemented a real options analysis for investment decisions in CCU projects. Finally, Chapter 6 develops different real options models to find the optimal timing to invest in CCS, CCU or CCUS, in

terms of the CO_2 price threshold for investment. The real options analysis provides unique insights into how uncertainty and flexibility affect the investment decisions in CCS, CCU and CCUS value chains. The presence of market uncertainty, i.e. the unknown CO_2 price, and technological uncertainty, i.e. the unknown time for the market entrance of the CCU technology, are investigated in particular in Chapter 6.

In sum, this thesis provides valuable insights into the economic and environmental performance of the DBD reactor for CO_2 conversion applications and can help to make design choices in the laboratory, supporting its evolution from the early stage to a pilot plant, and perhaps even to the commercial use of plasma catalysis for the conversion of CO_2 someday. Besides the design-oriented recommendations for the development of plasma catalysis as an emerging CCU technology, this thesis also generates insights into the possible interaction between CCS and CCU and the effect it has on investment decisions.

2

Economic Feasibility Studies for Carbon Capture and Utilization Technologies: A Tutorial Review

Carbon Capture and Utilization (CCU) involves the capture and use of CO_2 as a resource to create valuable products. The competitiveness of various CCU technologies has been investigated frequently resulting in a variety of economic feasibility studies and economic indicators. This study performs a tutorial review, in which practical guidance is given on the implementation of Techno-Economic Assessments (TEAs) for chemical CCU technologies. The tutorial review maps the differences in the methods and assumptions of economic feasibility studies for CCU technologies and advises how these studies can be improved in the future. A TEA framework, drafted by the CCU research community, is used as a benchmark in this review, to allow for objective comparisons between various economic feasibility studies. The four phases of an exhaustive TEA are (I) goal and scope, (II) data inventory, (III) calculation of indicators and (IV) interpretation. The tutorial review reveals that economic feasibility studies for chemical CCU technologies can and should be improved in various manners. Phases I and II are often skipped or incomplete. In Phase III, a very diverse indicator set is observed, which hampers comparability across CCU technologies. Phase IV, the interpretation of results, is often missing in the literature set or lacks thorough uncertainty and sensitivity analyses. The comparison with the TEA framework revealed the diversity in assumptions and methodological choices in the literature set. These findings suggest that future economic feasibility studies should be made in a more standardized way to improve both the quality and comparability of economic feasibility studies. Four improvements to the TEA framework are suggested: (i) focussing more on the impact of technical parameters in sensitivity analyses, (ii) adapting the assessment to the Technology Readiness Level (TRL) of the technology, (iii) implementing real options analysis (ROA) in the TEA and (iv) integrating an environmental assessment or LCA with the TEA. Further research is needed to investigate how ROA can be integrated into conventional TEA frameworks to analyse the investment decision in CCU technologies in a dynamic setting.

Parts of this chapter have been published in:

Lamberts-Van Assche, H., & Compernolle, T. (2021). Economic feasibility studies for Carbon Capture and Utilization technologies: a tutorial review. *Clean Technologies and Environmental Policy*. doi:10.1007/s10098-021-02128-6

Takeaway messages

- The existing literature on economic feasibility assessments of CCU technologies is diverse, both in the type of technologies that is assessed and in methodological choices. This hampers comparability of the results.
- The most common economic assessment indicator calculated in the investigated literature set is the Net Present Value (NPV).
- The parameters that are included in sensitivity analyses of these economic studies are mostly economic (e.g. electricity price or product price) or policy-oriented (e.g. the carbon tax) parameters.
- The technical parameters in the economic assessments are often the result of chemical modelling or simulations, and assuming a change in these parameters would require changes in the design of the modelled CCU plant itself. Hence, the effect of variations in these technical parameters, such as the CO_2 conversion rate or the plant scale, are analysed in just a handful of papers.
- While economic and policy parameters are external to the technology developer, the technical parameters could still be adjusted to some extent. Hence, it could be interesting to reflect on how these technical parameters would need to improve before the investigated CCU plant is economically attractive.
- We observe a trade-off between the need to develop a TEA framework that allows a certain level of flexibility, to adapt the assessment to its specific goal and scope, and the need for a more standardize dframework that allows comparing the results of different TEAs with the same goal and scope.

2.1 Introduction

In 2018, annual global anthropogenic CO_2 emissions exceeded 36 billion tons (Ritchie et al., 2020b). Although the share of renewable energy has increased drastically in the last decade, our reliance on fossil fuels will continue to exist in the short and medium term. To stay below the '+ 2 °C' target, it will not suffice to reduce energy consumption, impose carbon taxes and increase energy efficiency. CO_2 emissions from power plants and heavy industry must be reduced significantly to achieve the climate objectives (European Commission, 2018a). Moreover, the depletion of resources by consuming resources faster than they can be replenished is becoming an increasingly important issue for the present and future generations (Vijay Kumar, Shastri, & Hoadley, 2020). Hence, Carbon Capture and Utilization (CCU) technologies are acknowledged as a crucial component of the decarbonization strategy. CCU can lower the concentration of CO_2 in the atmosphere in two ways: (i) by decreasing CO_2 emissions at the source itself and (ii) by increasing the efficiency of industrial processes and replacing the conventional fossil-based raw materials (Michele Aresta & Dibenedetto, 2007; Baena-Moreno et al., 2019). CCU technologies can provide substitutes for fossil resources, hence slowing down the depletion of fossil resources.

Although the terms are often confounded, Carbon Capture and Storage (CCS) and CCU are two distinct concepts. CCS technologies capture CO_2 emissions from large point sources and inject the captured CO_2 into geological formations for long-term storage underground (Leonzio, Foscolo, & Zondervan, 2019). Contrary to CCS, CCU does not store CO_2 permanently underground but utilizes it as a raw material to produce other goods or services. Thus, CCU can add additional revenue streams to the reduction of CO_2 emissions.

The International Energy Agency (IEA) distinguishes two main CCU pathways: (i) the direct use or non-conversion of CO_2, in which the CO_2-molecule is not chemically altered, and (ii) the indirect use or conversion of CO_2 into fuels, chemicals or building materials. **Table 2.1** provides the breakdown of CCU into the two pathways (indirect and direct use) and their major applications. Examples of products are given for each application. Commercial CCU applications today mostly involve the direct use of CO_2, e.g. the use of CO_2 for the production of food and beverages, in greenhouses, or CO_2-enhanced oil recovery (EOR). In 2015, the largest user of CO_2 was the fertilizer industry, where around 130 Mt CO_2 per year was directly used to produce urea (IEA, 2019c). The second largest user was the oil industry, with an annual consumption of 70–80 Mt of CO_2 for EOR. The use of CO_2 for the production of fuels, chemicals or building materials was in 2015 still negligible (around 4% of global CO_2 consumption). However, in recent years, the conversion route has attracted more and more interest, driven by national and international climate mitigation objectives, the rise of (cheap) renewable energy and the quest for energy security.

Table 2.1: Classification of CCU pathways, based on Figure 2 from the report '*Putting CO_2 to use*' from IEA (2019c).

Pathways	Applications	Examples
Direct use	Yield boosting	Greenhouses, algae, fertilizer/urea
	Solvent	EOR
	Heat transfer fluid	Refrigeration
	Other	Food and beverages, medical uses, welding
Indirect use	Fuels	Methane, methanol, gasoline/diesel
	Chemicals	Chemical intermediates, polymers
	Building materials	Cement, concrete

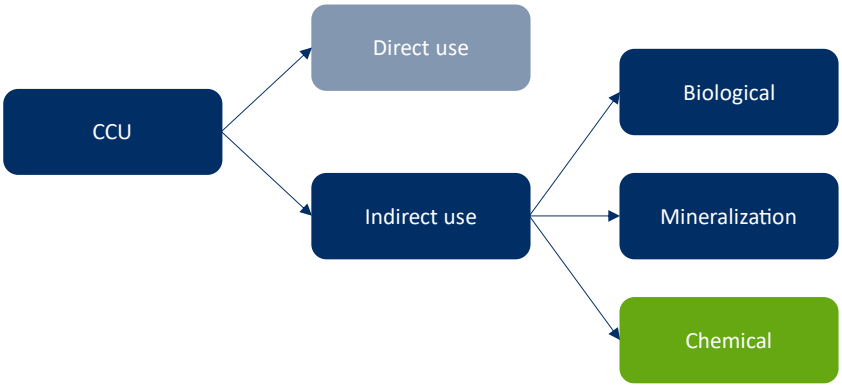


Figure 2.1: Overview of CCU technology routes.

For the indirect use of CO_2, three main technology routes can be identified: the biological, mineralization or chemical route (Chauvy et al., 2019). **Figure 2.1** presents a schematic overview of the different CCU routes. Biological routes employ the natural ability of micro-organisms to capture and convert CO_2 into chemicals or fuels (National Academies of Sciences & Medicine, 2019). One example is the use of green algae to convert CO_2 into other organic compounds. Mineralization, or carbonation, is a natural process where CO_2 reacts with calcium- or magnesium-containing minerals to produce valuable construction materials. In chemical routes, the CO_2 is used as a reactant or feedstock for the synthesis of commodity chemicals and fuels.

The sparked interest in CCU technologies also generated a large body of research in recent years. A crucial aspect of its implementation on a commercial scale is the techno-economic feasibility of the technology. A Techno-Economic Assessment (TEA) is one type of assessment method that can be used to assess the economic performance of novel technologies. For this study, we define a TEA as a method that integrates the technological and economic feasibility evaluation into one systematic study. Despite the importance of the TEA, no generally accepted methodologies are practised yet and thus, the comparability and readability of TEAs of novel CCU technologies remain low (Zimmermann et al., 2020). To introduce more transparent and comparable TEAs, Zimmermann et al. (2020) developed guidelines for TEAs, in particular for CCU technologies. Guidance is given on the formal structure that the TEA should follow, starting with the definition of the goal and scope of the TEA, followed by the inventory, the calculation of indicators and the interpretation of the results. We will evaluate if these four phases are carried out in economic feasibility studies for CCU technologies.

According to Sick et al. (2020), TEA is a very useful methodology to assess the feasibility of CCU technologies. However, a TEA is also very flexible in its application; results may vary significantly, depending on the defined system boundaries and assumptions. The variety of indicators makes it also difficult to compare results. Therefore, Sick et al. (2020) expressed the need for a harmonized framework for TEAs for CCU technologies. Naims (2020) also expressed the need for TEAs of novel CO_2-based products. In sum, TEAs are an important instrument in the development of novel CCU technologies. However, because of its flexibility, the quality of the TEAs may differ significantly between different studies. Several researchers have expressed their concerns about the comparability of the results of different TEAs before (Sick et al., 2020; Zimmermann & Schomäcker, 2017). Therefore, it is important to be able to assess the quality of a TEA or an economic feasibility study in general, before concluding whether or not the CCU technology is economically viable based on that particular study. This paper will attempt to evaluate the quality of the performed assessments in a literature set of economic feasibility studies.

Centi, Perathoner, Salladini, and Iaquaniello (2020) also observed the need for a critical reflection on the evaluation of CO_2 economics. Their critical analysis reveals a large variability in the estimated cost of methanol and methane production, beyond the commonly assumed 30% variation in costs in preliminary TEAs. Stemming from the variety in methodologies, parameters and boundary limits, different conclusions can be drawn on the techno-economic feasibility of a CCU technology, even if the assessment is based on the same data. The need for a proper contextualization of results is acknowledged, in terms of the context of the study (time, location, method and data) and the context of the proper CO_2 value chain. The lack of homogeneity in terms of costs for raw materials, methodologies and system boundaries is recognized; however, these different aspects of the economic evaluations are not analysed in more detail. In other words, Centi et al. (2020) observed large variations in the results but did not further analyse what differences in economic assessments produced that variability. The current paper fills this gap by analysing the methodological choices made in economic evaluations for CCU technologies in detail.

This study performs a tutorial[4] review, in which practical guidance is given on the implementation of TEAs for chemical CCU technologies. This tutorial review critically examines the economic feasibility studies that have been performed in this field and advises on how these studies can be improved in the future. A detailed and critical analysis of these studies concerning the implemented methods has not been done before. Two main objectives are set. Firstly, we aim to compare all economic feasibility studies, by using the TEA guidelines of Zimmermann et al. (2020) as a benchmark. This will help us to map the differences in the methodological choices and assumptions that may produce variation in results. Secondly, we explore how the quality and comparability of current economic feasibility studies can be improved further. Additions to existing TEA frameworks that may further increase the quality, comparability and practical impact of the economic feasibility studies for CCU technologies are proposed at the end of this tutorial review. The findings of this study can contribute to the discussion on the structure of a high-quality TEA for CCU technologies.

This tutorial review aims to contribute to the growing area of research on CCU by exploring to what extent economic feasibility studies differ, in what aspects they differ and how these studies can be improved further. Hence, this tutorial review can help CCU researchers to rethink and critically reflect on their economic feasibility studies. The tutorial review provides a basis to evaluate the quality of a TEA, which can be helpful to assess whether or not the results of the TEA are credible or not. For inexperienced CCU researchers, this tutorial review can provide a good starting point to understand how to perform economic assessments.

The scope of this paper is limited to the indirect use of CO_2, and more specifically to the chemical CO_2 utilization route. The direct use of CO_2 is excluded because these technologies are already available on a commercial scale today. Economic assessments for technologies in the market are more clear-cut, and thus, an extensive review of these methods is not needed. Moreover, the IEA (2019c) observed an increased interest in the indirect use pathway in recent years, resulting in a growing body of the literature. Within the conversion route, we choose to focus on chemical CO_2 utilization technologies. A literature set arranging the relevant economic assessments for chemical CO_2 utilization technologies is established. This literature set will serve as the starting point for our analysis.

The paper is organized as follows. The next section is devoted to the Method of this tutorial review. The selection of the literature set and the TEA guidelines from (Zimmermann et al., 2020) are

[4] The definition of tutorial according to Merriam-Webster (2020) is: 'a paper, book, film, or computer program that provides practical information about a specific subject'.

explained in more detail. Four important methodological choices—system boundaries, the cost of CO_2, assessment indicators and uncertainty and sensitivity analyses—are also clarified further here. This is then followed by the Results. The attributes of the literature set are discussed, including the type of CCU products that are investigated and the type of methods that are used to evaluate the economic feasibility. Afterwards, we contrast the studies in the literature set to the TEA framework. This is followed by a more detailed revision of four important methodological choices, one per phase: the chosen system boundaries (I—Goal and Scope), the assumed cost of CO_2 (II—Data Inventory), the selected assessment indicators (III—Calculation of Indicators) and the presence or absence of uncertainty and sensitivity analysis (IV—Interpretation). Afterwards, the economic assessment methods for methanol synthesis CCU technologies are revised in more detail. Next, it is examined whether the studies in the literature set focus on economic (cf. market-based), policy or technical parameters in their analysis. Finally, the Results end with four possible additions to the TEA guidelines from Zimmermann et al. (2020). In the Discussion, explanations for the findings are given, together with the implications for future research. The paper ends with concluding remarks on TEAs for CCU technologies and some recommendations on how to move forward in this research area.

2.2 Method

A systematic literature search was conducted to establish a comprehensive literature set. Three consecutive search queries were performed in the online databases Web of Science (2021) and Scopus (2021), in January 2021. The first search included variations on 'techno-economic' and 'analysis', combined with different synonyms and spelling methods of 'Carbon Capture and Utilisation'. A secondary search focussed on the chemical transformation CCU technologies, by including terms related to 'chemical transformation'. The third search included the term 'raw material', because of the use of CO_2 as raw material or input.[5] The searches in Web of Science and Scopus resulted in a total of 69 unique results. This was further reduced to 24 papers, by excluding the papers that did not fit the scope of this review. Finally, 3 relevant articles, which were already known to the authors, were added manually to the literature set, bringing the total up to 27 papers. The full literature set is shown in **Table A.2.2** in Appendix 2.A. This literature set is the starting point for this in-depth tutorial review: the literature set will be analysed thoroughly (i) to appraise the quality of the techno-economic feasibility studies, (ii) to map the differences in the methodological choices and assumptions that may produce variation in results and (iii) to propose further additions or improvements that can be made to the TEA guidelines from (Zimmermann et al., 2020).

2.2.1 Techno-Economic Assessment (TEA)

TEA is a methodology framework with different understandings and different applications circulating in literature. Kuppens et al. (2015) describe the TEA as an iterative process, in which the integration of the technical analysis with the economic analysis is crucial and proper risk analyses are needed to identify potential barriers. Van Dael, Kuppens, Lizin, and Van Passel (2015) highlight that the TEA should help to make choices during the development of a new technology or process. Four fundamental steps are identified: (i) a market study, (ii) the technological backbone, including Process Flow Diagram (PFD) and mass and energy balances (M&EB), (iii) the economic evaluation and (iv) the sensitivity assessment. Thomassen, Van Dael, Van Passel, and You (2019) advocated the implementation of a prospective techno-economic and environmental assessment framework that integrates both the techno-economic feasibility and the environmental impacts into one assessment. Recent TEA guidelines for CCU technologies in particular were published by Zimmermann et al. (2020).

[5] The exact search queries can be found in **Table A.2.1** in Appendix 2.A.

Four major phases are proposed: (i) setting the goal and scope, (ii) building the data inventory, (iii) calculating the indicators and (iv) interpreting results. According to these guidelines, the TEA is finalized by writing a formal report on the TEA's findings.

Although the guidelines developed by Zimmermann et al. (2020) were the result of a comprehensive literature review and multiple workshops with leading CCU researchers, several authors have expressed their criticism on different aspects of the TEA guidelines. Roh et al. (2020) criticize that these TEA guidelines did not consider the maturity level of the investigated technology. Therefore, the evaluation of emerging CCU technologies at an early stage of development remains challenging. Following Centi et al. (2020), the TEA guidelines help to increase the transparency and readability of the results, but several other critical issues that arise with the economic evaluation of CCU technologies remain unsolved. Firstly, the TEA should be capable of dealing with the dynamics of emerging technologies. The evolutions in costs and the relevant market(s) should be taken into account, together with possible learning effects. Moreover, the guidelines should reflect that traditional economic concepts, such as economies of scale, are not always valid for CCU technologies. Traditional cost scaling methods cannot be used for cost estimation in this case. Novel indicators that reflect these concerns should be developed and integrated into both TEAs and LCAs.

Despite the valid critiques on the TEA framework from Zimmermann et al. (2020), their guidelines remain one of the most complete attempts to formalize and standardize TEAs for CCU technologies specifically. For this reason, these guidelines are used in this study as a benchmark, to which the techno-economic feasibility studies for chemical CCU technologies are compared. **Figure 2.2** presents the four basic phases of their TEA framework.

A complete TEA should start with defining the *goal and scope* of the study. This includes describing the reasons for carrying out the TEA, which questions it should address, defining the system boundaries and choosing the assessment indicators. Setting the scope also includes the definition of the benchmark system, to which the product's performance can be compared. The chosen benchmark system is often the best-in-class or the market leader.

This is followed by the creation of a *data inventory* for the TEA. The Block Flow Diagram (BFD) or PFD depicts how the process design looks like, from an engineering perspective. The M&EB describe the flows in the system and are used as input to calculate the selected assessment indicators. Besides the technical data, economic data must be gathered as well. A market study is performed to examine the competitive environment for the novel CCU technology. Data on product prices, utility prices and the price of CO_2 are collected in the data inventory.

The third phase is *the calculation of the assessment indicators*. These can be technical, economic and/or environmental indicators, depending on the scope of the TEA.

Finally, the *interpretation* phase is a crucial step for high-quality TEAs. In this phase, both the uncertainty and sensitivity of the results of the TEA can be assessed. With uncertainty analysis, the uncertainty about the results, which can arise e.g. due to measurement errors, is analysed and quantified. Sensitivity analysis aims to assess how variations in the input variables change the model output. Although they are often confounded, uncertainty analysis and sensitivity analysis serve different goals. While uncertainty analysis aims to evaluate the level of uncertainty in the output of the model, sensitivity analysis aims to assess which of the input variables affects the output the most (Zimmermann et al., 2018). The interpretation of the results is thus very important, as it helps to understand the impact of your results and helps to reveal what should be improved to the technology, process or product to become competitive.

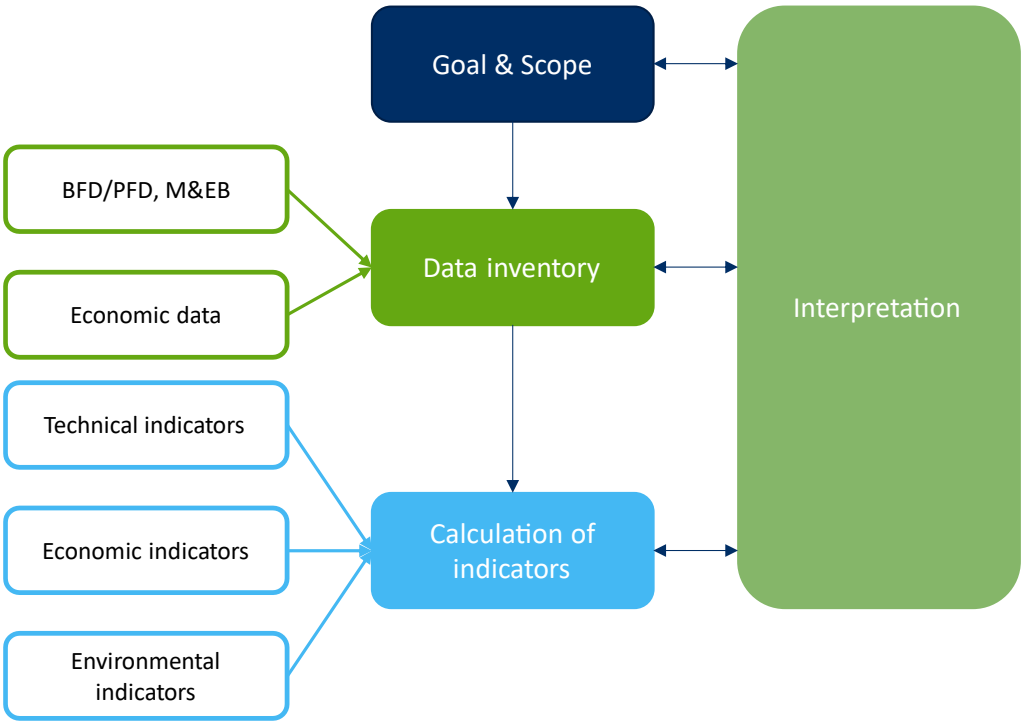


Figure 2.2: Four phases of an exemplary TEA for CCU technologies, based on and adapted from Zimmermann et al. (2020).

Importantly, it should be stressed that this TEA framework is merely used as a benchmark in this study, to allow for objective comparisons between various economic feasibility studies. The chosen benchmark should not be seen as the established norm that should be followed strictly. The TEA framework is not rigid and can still be adapted to new insights from the CCU research field. Moreover, TEAs are not exclusively performed in the CCU research field. The structure as described above can be applied to other research fields, where the techno-economic feasibility of technologies needs to be assessed. Some parts of the TEA methodology that will be described in this tutorial review are, however, specific to CCU technologies. The chosen system boundaries are specific for the CO_2 value chain. The cost of CO_2 is an important element in the data inventory that must be considered for the CCU technologies. In general, the majority of CCU technologies are still at an early stage of development (IEA, 2019c), which also needs to be taken into account in the TEA. This is discussed further in the tutorial review.

In this tutorial review, we will assess whether these phases are present in the techno-economic feasibility studies in the literature set. Of course, not all studies in the literature set perform a TEA. Other economic assessment methods are practised as well to assess the economic feasibility. Economic assessment methods can show a large variety of quality, ranging from 'back-of-the-envelope' calculations to well-structured and detailed assessment methods. Life Cycle Costing (LCC) is a well-structured method that assembles all costs that the producer of a product will incur over the entire lifetime of a product (Accounting Tools, 2020). The TEA differs from the LCC in its integration of the economic assessment, where both costs and revenues are estimated, and the technical assessment (Zimmermann et al., 2018). Readers who are interested in a more detailed discussion on the differences and similarities between LCC and TEA are referred to Giacomella (2020). Other types of economic assessment methods are, for example, business models and cost–benefit analyses (CBA).

In a CBA, other societal costs and benefits can be added to the analysis, while technical parameters are less important compared to a TEA.

Since the TEA framework offers the most complete methodology to assess the techno-economic feasibility, by integrating costs, revenues and technical parameters, all economic feasibility studies in the literature are contrasted with the four major phases of a TEA, as identified above.

Four methodological choices are analysed in more detail. Firstly, the chosen system boundaries will be critically reviewed. Secondly, the various costs or prices of CO_2 that are assumed in the literature set will be summarized and evaluated. Thirdly, the calculated assessment indicators, with a focus on the economic indicators, in the literature set will be listed and compared. Finally, the implementation of the interpretation phase in the literature set will be evaluated.

2.2.2 System boundaries

System boundaries are defined by the researchers and determine which stages of the CO_2 value chain are included or excluded from the economic analysis. To this end, a simplified CO_2 value chain and its possible system boundaries are presented in **Figure 2.3**. The value chain of the conversion of CO_2 into fuels or chemicals involves the following stages: the capture of CO_2, the actual conversion of CO_2 into the final product, the production of low-carbon energy to drive the (energy-intensive) transformation process, the transport of energy and materials for the conversion process and the delivery of the final product to the customer (Jarvis & Samsatli, 2018). When system boundaries are drawn around the CCU plant itself, a gate-to-gate approach is applied. As indicated in **Figure 2.3**, this includes the conversion of CO_2 into a valuable product but excludes the CO_2 capture and the transport of the final product. In other words, the economic assessment covers the processes between the front and the end gate of the CCU plant. Adding the CO_2 capture process gives the cradle-to-gate system from a manufacturer's perspective. When transport and distribution of the final product are included as well, a retailer's perspective is adopted. The cradle-to-grave approach includes the entire value chain, from resource extraction to end-of-life treatment (Zimmermann et al., 2018). Hence, the choice of system boundaries defines which economic impacts are included or excluded from the analysis. Besides, the chosen boundaries also affect how the price of CO_2 is incorporated into the economic assessment.

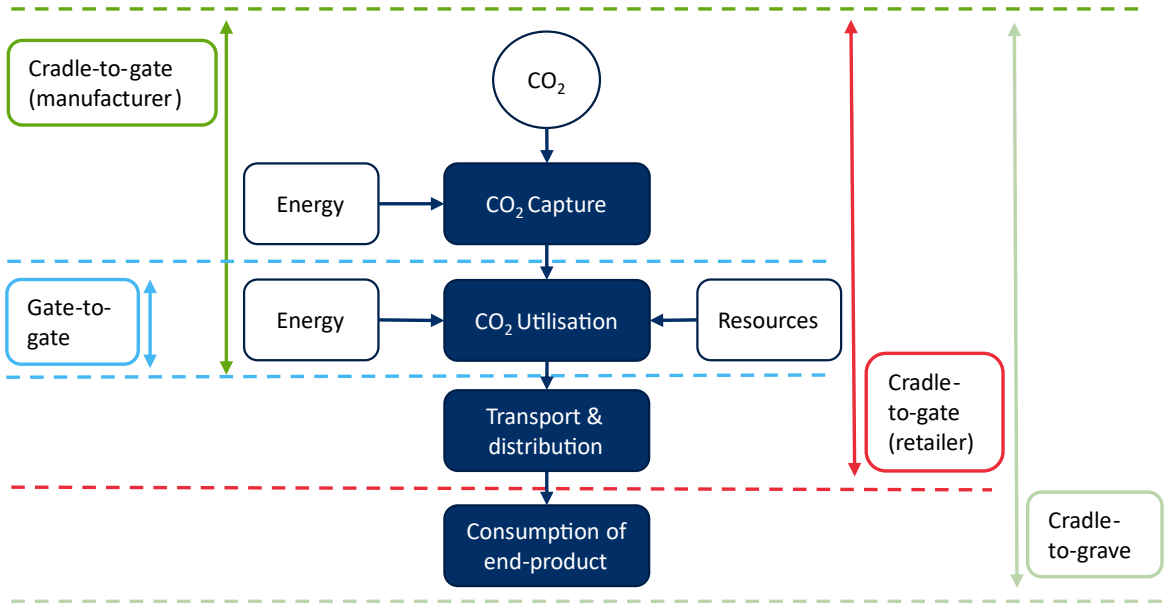


Figure 2.3: Possible system boundaries in a TEA for a CCU value chain.

2.2.3 The cost of CO_2

In a CCU plant, the CO_2 is a feedstock that is converted into a commercial end-product. However, the cost of CO_2 can be included in the economic assessment of a CCU plant in various manners. The main distinction is whether the CO_2 is treated as a resource for which a price has to be paid, or as 'waste' from another plant for which a price is received. The presumed CO_2 price level is often related to the chosen system boundaries and affects the outcomes of the economic indicators. This also relates to the discussion of whether or not CCU is included in the Emission Trading System (ETS), if one is present. Various assumptions for the cost (or price) of CO_2 are possible. The observed approaches in the literature set are discussed in more detail in the Results section.

2.2.4 Assessment indicators

Zimmermann et al. (2020) already observed a lack of a common indicator basis in TEAs for CCU technologies, which hampers comparison between different TEAs and technologies. We will list the observed indicators per category, analyse which indicators are the most common and evaluate the chosen assessment indicators. Three main categories of indicators are distinguished: technical, economic and environmental indicators.

Technical indicators are criteria to assess the technical performance of the process or technology. Energy efficiency or energy demand and the conversion rate of CO_2 are common technical indicators for CCU technologies.

Economic indicators are metrics or evaluation criteria used by researchers to assess the economic feasibility of the CCU technology under investigation. A distinction can be made between cost-oriented indicators and profit-oriented indicators. Cost-oriented indicators solely comprise relevant costs of the CCU technology. Capital Expenditures (CAPEX) and Operational Expenditures (OPEX) are typical examples of cost-oriented indicators. Another cost-oriented indicator is the Levelized Cost of Product (LCOP), which is a measure of the unit selling price that is required for the CCU technology to earn a certain return on investment (ROI) (Fernández-Dacosta et al., 2017). The LCOP is often practised as an economic indicator in an LCC analysis. Profit-oriented indicators, on the other hand, integrate both costs and revenues of the CCU plant. The Net Present Value (NPV) is a well-known example of a profit-oriented indicator. NPV is the present value of the difference between all revenues and costs over a certain period (Investopedia, 2020). In other words, the NPV gives today's value of a future stream of cash flows. The NPV is commonly used as an indicator in the economic evaluation of a TEA.

Environmental indicators are indicators to evaluate the environmental impact of the process or technology. Examples are the net amount of CO_2 used, CO_2 emissions or depletion of fossil fuels. The calculated values of all assessment indicators are highly dependent on the assumptions that are made during the economic assessment.

2.2.5 Uncertainty and sensitivity analyses

Uncertainty and sensitivity analyses are the key instruments in the interpretation phase to review the reliability of data and to put the results in perspective. Uncertainty and sensitivity analysis are, although related, two distinct types of analyses to explore the uncertainty in a model. While uncertainty analysis (UA) aims to quantify the amount of uncertainty in the model output, sensitivity analysis (SA) aims quantify which of the input variables is responsible for the most variation in the model output (Saltelli et al., 2019). In other words, SA studies how the uncertainty in the model output can be attributed to the sources of uncertainty in the model inputs (Saltelli, 2002). Ideally, the UA precedes the SA: first, you estimate the amount of uncertainty in the output (= UA), then you attribute

this uncertainty to the input variables (= SA) (Saltelli et al., 2019). Both UA and SA have their role in the interpretation phase of the TEA. Saltelli et al. (2019) listed several best practices for UA and SA. First, they recommend preferring a global analysis of the input variables over local or one-at-a-time (OAT) analysis, both for SA and UA. Global analyses investigate the variation of multiple variables simultaneously, whereas local analyses look at the variation in input variables one-at-a-time. Monte Carlo is the most common technique for global analyses, wherein thousands of simulations are performed to get a probability distribution for the output. Second, Saltelli et al. (2019) advocate to perform UA and SA together. Third, to guarantee the relevance of the UA and SA, the analyses should focus on a question that needs to be addressed in the study. While these 'best practices' create a clear framework to adhere to, it will not always be possible or desirable to comply with all three best practices. For example, performing a global SA requires much more time and effort than a local SA. Hence, depending on the goal and scope of the economic assessment, a local SA may be sufficient. How researchers deal with UA and SA in economic assessments for CCU projects is discussed in detail in the following section.

2.3 Results

Two important attributes of the literature set are surveyed first: the product categories that were analysed and the type of economic assessment methods that were used in the literature set. The tutorial review contrasts the studies in the literature set with the TEA structure from Zimmermann et al. (2020), followed by a detailed analysis of four methodological choices. The synthesis of methanol via chemical CCU technologies is reviewed to identify barriers preventing the commercialization of this technology. Finally, enhancements to the TEA structure from Zimmermann et al. (2020) are proposed.

2.3.1 Attributes of the literature set

Literature was sought within the scope of this paper, which is the indirect use of CO_2, and more specifically the chemical CO_2 utilization route. The literature set consists of 27 papers, covering various types of chemical CO_2 utilization routes. The indirect use of CO_2 results in higher-value products, that can be divided into three main product categories: CO_2-derived chemicals, CO_2-derived fuels and CO_2-derived building materials (IEA, 2019c). CO_2-derived chemicals include a wide variety of chemicals or intermediates, such as urea, syngas or formic acid. CO_2-derived fuels can be liquid hydrocarbon fuels, syngas, methanol or methane. CO_2-derived building materials are typically produced through mineralization processes, and hence, this product category was not observed in our literature set. **Figure 2.4** presents the breakdown of the literature set according to the product category. Methanol, methane and hydrogen can serve both as a chemical and a fuel. Therefore, separate categories were created for these products. As shown in **Figure 2.4**, methanol (16 studies) is the most prevalent product in the literature set, followed by CO_2-based chemicals (11) and fuels (5). **Table 2.2** presents the full list of CO_2-based chemicals and fuels in the literature set: a diverse range of products is observed. **Table 2.3** summarizes the labelled economic assessment methods that were observed in the literature set. Naturally, techno-economic analysis or assessment is the most common label used by researchers in the literature set: 12 papers claim to perform a techno-economic analysis or assessment. Six studies combine the TEA with an evaluation of the environmental impacts. Two studies design a business model, one study limits the assessment to LCC, and the remaining six papers use a variety of methods. In the next section, we will analyse how the studies in the literature set accord with the TEA structure proposed by Zimmermann et al. (2020).

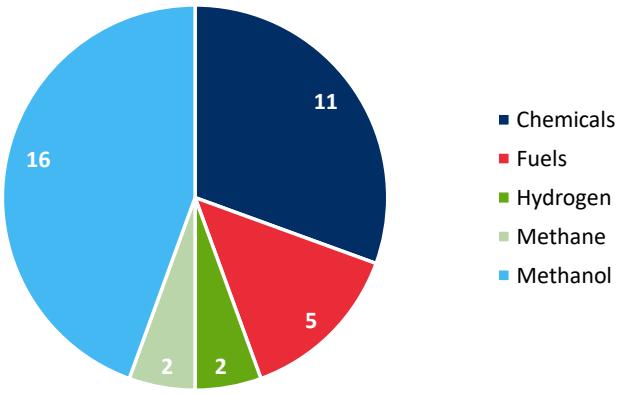


Figure 2.4: CO_2-derived product categories addressed in the literature set. Several papers investigate multiple product categories, which explains why the sum in the pie chart is larger than 27.

Table 2.2: List of the CO_2-based chemicals and CO_2-based fuels.

CO_2-based chemicals	**# of studies**	**CO_2-based fuels**	**# of studies**
Baking soda	1	Bio-LNG	1
Dimethyl carbonate (DMC)	1	Formic acid	1
Ethylene	1	Light olefins	1
Formic acid	1	Liquid hydrocarbon fuels	2
High value waxes	1	SNG	1
Methyl formate	1		
Polyol	1		
Polyoxymethylene (POM)	1		
Soda ash	1		
Syngas	1		
Urea	1		

Table 2.3: Labelled economic assessment methods in the literature set

Labelled method	**# of studies**
Business model	2
LCC	1
Market simulation model	1
Multi-objective Mixed Integer Linear Programming (mo-MILP)	1
Multi-scale analysis	1
Process and economic analysis	1
Technical and economic feasibility	1
Technical and economical evaluation	1
Techno-economic analysis/assessment	12
Techno-economic and climate impact analysis	1
Techno-economic and environmental assessment/evaluation	4
Techno-economic and life cycle assessment	1
Total	27

2.3.2 TEA framework

The studies in the literature set were read thoroughly and compared to the guidelines from Zimmermann et al. (2020). For the first phase, we assessed whether the system boundaries were explicitly defined or not and whether a benchmark system or product was selected. The creation of the data inventory was assessed by checking whether a technical inventory (PFD and M&EB) and market study were present or not. For the third phase, we observed which type of indicators was selected: technical (TECH), economic (ECON) or environmental (ENV). Finally, the implementation of the interpretation phase was evaluated by examining if a sensitivity analysis (one-at-a-time (OAT) or combined) or a Monte Carlo simulation was performed, or not.

Table 2.4 indicates which phases of the TEA structure are present or not, per study. Thus, **Table 2.4** allows a transparent comparison between the applied methods in the economic feasibility studies. A colour code—green, orange and red— is used to indicate whether or not these steps were implemented in the study. A green block indicates that this step is fully present, an orange block indicates that it is only partially completed and a red one implies that the step is missing in the study.

More specifically, the orange colour for the system boundaries indicates that the system boundaries were not defined explicitly in the paper. For the technical inventory, an orange block implies that either the PFD or M&EB was absent in the study. An 'orange' market study means that the market study is rather limited (e.g. only one forecast for future market). For the indicators, the green block implies that at least one of this type of indicator is present; it does not say anything about the quality of the selected indicator. In the interpretation phase, either a OAT sensitivity analysis, a combined sensitivity analysis or a Monte Carlo simulation is performed in the literature set.

It can be seen from the colour codes in **Table 2.4** that the majority of the studies in the literature set lacked several important phases. A market study was missing in 15 papers and only partially completed in 9 papers of the literature set, the system boundaries were not explicitly defined in 16 papers, and the technical backbone was also missing or incomplete in 9 papers. The interpretation phase was skipped in 10 studies, although this step is crucial to interpret the results of the assessment correctly. Pérez-Fortes, Schöneberger, Boulamanti, Harrison, and Tzimas (2016) and Pérez-Fortes, Schöneberger, Boulamanti, and Tzimas (2016) incorporated all phases in their studies for methanol and formic acid synthesis, resulting in thorough economic feasibility studies. The quality of their assessment could only have been improved by performing a more detailed interpretation phase, to account more for the uncertainty in the data.

The TEA framework from Zimmermann et al. (2020) aimed to harmonize TEA methodologies in the CCU research area. However, as shown in this tutorial review, this framework is far from being implemented in practice. Most studies in the literature lack multiple phases of the proposed TEA structure. This demonstrates that significant efforts will be needed to harmonize TEAs in CCU research. It is also apparent from **Table 2.4** that the economic feasibility studies differ significantly in their applied methodologies to assess the economic feasibility of a CCU technology. Except for four studies (Godini et al., 2020; Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al., 2016; Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016; Y. Yang, Zhang, Yu, & Feng, 2021), all studies differ in the implementation of one or multiple phases. The methodological differences in the literature set, highlighted in **Table 2.4**, can give rise to diverging quality of the economic feasibility studies.

Table 2.4: Presence of the four fundamental phases of a TEA, indicated by colour codes. Red = absent, orange = present, but limited, green = present.

I - Goal and Scope		II - Data Inventory		III - Calculation of Indicators			IV - Interpretation			References
System boundaries	Benchmark system	Technical inventory	Market study	TECH	ECON	ENV	SA OAT	SA combined	MC simulation	
										(Horschig et al. 2019)
										(Hoppe et al. 2018)
										(González-Aparicio et al. 2017)
										(Putra et al. 2017)
										(Deng and Adams II 2020)
										(Jens et al. 2019a)
										(Kuenen et al. 2016)
										(Lainez-Aguirre et al. 2017)
										(John et al. 2021)
										(Pérez-Fortes et al. 2014)
										(Zhang et al. 2017)
										(Godini et al. 2020b; Yang et al. 2021)
										(Kim et al. 2018a)
										(Gonzalez-Aparicio et al. 2018)
										(Zhang et al. 2019)
										(Zhang et al. 2015b)
										(Dimitriou et al. 2015)
										(Yusuf et al. 2019)
										(Kim and Han 2020b)
										(Bellotti et al. 2019)
										(Chiuta et al. 2016)
										(Lee et al. 2020)
										(Fernandez-Dacosta et al. 2017)
										(Szima and Cormos 2018)
										(Pérez-Fortes et al. 2016b, a)

It is important to note, however, that most of the studies included in the literature set were published before the guidelines from Zimmermann et al. (2020). Hence, it is more appropriate to state that the existing economic assessments for CCU technologies, published between 2015 and 2021, lack harmonization. Future studies can still demonstrate more efforts to comply with the guidelines from Zimmermann et al. (2020).

2.3.3 Goal and Scope: system boundaries

By defining the system boundaries of the economic assessment, the researcher determines which phases of the CCU process are included or excluded from the economic evaluation. In the literature set, two types of system boundaries are observed: gate-to-gate or cradle-to-gate. The majority of the studies (18 papers) analysed economic feasibility from gate-to-gate. Thus, the great majority of papers draws the boundaries around the CCU plant itself. The carbon capture process is not analysed or simulated in detail. The remaining nine papers set the boundaries from cradle-to-gate, from a manufacturer's perspective (Bellotti, Sorce, Rivarolo, & Magistri, 2019; Dimitriou et al., 2015; Fernández-Dacosta et al., 2017; Hoppe, Bringezu, & Wachter, 2018; Jens, Müller, Leonhard, & Bardow, 2019; John, Wan Alwi, & Omoregbe, 2021; Lainez-Aguirre, Pérez-Fortes, & Puigjaner, 2017; Putra, Sutikno, & Handogo, 2017; Y. Yang et al., 2021). These papers included the capture of CO_2 within their system boundaries but did not specify the costs related to the transport and distribution of the end-product and the end-of-life treatment of the product.

2.3.4 Data inventory: the cost of CO_2

The cost of CO_2 is an important parameter in economic assessments for CCU projects. The main distinction is whether the CCU operator needs to pay for the CO_2, or whether the CCU operator receives a price for the CO_2 to be utilized. The treatment of the cost of CO_2 can be subdivided further. In the literature set, five different approaches were observed on how the cost of CO_2 was included in the economic assessment. **Table 2.5** summarizes these five different approaches.

In the first approach, zero costs are assumed for CO_2: the price of CO_2 as a raw material is zero, there are no costs of capture, or no price received for the CO_2 that will be utilized. Hence, CO_2 is assumed to be available for free.

In the second approach, the price of CO_2 as a raw material is again zero. However, the second approach now considers the presence of an emissions trading system (ETS). This implies that a CO_2-emitting plant needs to buy emission allowances for its CO_2 emissions. As a result, the ETS imposes a penalty on the conventional CO_2-emitting plant, relative to the CCU plant. Four papers follow the second approach 2 and include an ETS that is equal or very similar to the EU ETS. One of these four studies considers the scenario where the CCU operator is even eligible for a 'carbon credit', thanks to the presented emission savings (Chiuta, Engelbrecht, Human, & Bessarabov, 2016). Since 2023, provisions are included for CCU in the EU ETS. Under the current EU ETS directive, the obligation to surrender emission allowances is lifted for CO_2 emissions that have been captured and utilised in such a way that they are permanently chemically bound (Article 12(3b)) (European Commission, 2023c). However, not all utilized CO_2 is indeed permanently chemically bound.

In the third approach, the CO_2 is considered to be a raw material for the CCU plant, that is supplied to the plant, for which a price is paid. However, the price of CO_2 can vary from negative to positive, where negative prices mean that the CCU plant receives revenue for using the CO_2. These references all perform a sensitivity analysis, to investigate the effect of the CO_2 price fluctuations on the economic feasibility. These references estimate the CO_2 price level based on the existence of a carbon market; thus, a carbon tax/credit scheme is present once again.

The fourth approach includes a fixed cost for the capture of CO_2 in the price. A surplus is added to the price of CO_2 because it needs to be captured first. The process of capturing CO_2 is not modelled in these references. Instead, the price of captured CO_2 is based on average or generic data that are available in the literature.

Finally, the fifth approach includes the cost of carbon capture by including the capture unit in its analysis. While other references draw their boundaries around the CCU plant and exclude the capture unit from the modelling, these references model the capture unit carefully and calculate all costs associated with it (investment costs, operating costs, etc.). In other words, a cradle-to-gate approach is adopted by these papers. Although these papers all include the costs associated with the capture unit in their economic analysis, the price of CO_2 as a raw material is assumed to be zero in these papers. CO_2 is considered to be a flue gas from an emitting plant which is also part of their system; thus, the CO_2 source is within the boundaries of the analysis. In other words, the CO_2 itself is free of charge, but it is the capturing of the CO_2 which is costly. Four of these papers do not consider the presence of a carbon tax or credit, while the two remaining papers do include a carbon tax/credit scheme in their analysis. One paper is excluded from **Table 2.5** because it does not fit one of these five approaches. Fernández-Dacosta et al. (2017) perform a break-even analysis, which results in the minimum price of CO_2 that would make the CCU plant more profitable than the conventional plant. In this paper, the price of CO_2 is a result of the economic analysis, not an input.

Table 2.5 highlights the qualitative differences between the five approaches. However, the values that are then assumed for the cost (or price) of CO_2, and included in the economic assessment, vary greatly within one approach as well.

Table 2.5: Five different approaches for incorporating the cost of CO_2 in the economic assessment were observed.

Approach	**Pricing schemes**			**References**
	RM price	Cost of capture	Carbon tax/credit	
1. Zero costs	-	-	-	(Pérez-Fortes et al. 2014; Kuenen et al. 2016; Horschig et al. 2019; Godini et al. 2020a; Yang et al. 2021)
2. CO_2 as GHG	-	-	✓	(Zhang et al. 2015a, 2017; Chiuta et al. 2016; Szima and Cormos 2018; Kim and Han 2020a)
3. CO_2 as RM	✓	-	✓	(Pérez-Fortes et al. 2016b; Kim et al. 2018b; Gonzalez-Aparicio et al. 2018; Zhang et al. 2019)
4. Fixed capture costs	✓	✓	-	(Pérez-Fortes et al. 2016a; González-Aparicio et al. 2017; Lee et al. 2020; Deng and Adams II 2020)
5. Cradle-to-gate	-	✓	-	(Dimitriou et al. 2015; Putra et al. 2017; Jens et al. 2019b; Yusuf et al. 2019)
			✓	(Lainez-Aguirre et al. 2017; Hoppe et al. 2018; John et al. 2021)

RM, Raw Material; GHG, Greenhouse Gas

Figure 2.5 (a) presents the ranges of assumed carbon taxes and credits in Approach 2. Chiuta et al. (2016) presume that a carbon credit can be granted to a CCU plant as well, as shown by the negative number in **Figure 2.5** (a). **Figure 2.5** (b) presents the prices of CO_2 that were observed in Approach 3. Once again, large differences between these papers can be observed. A very high negative price of 400 €/ton CO_2 is assumed in Pérez-Fortes, Schöneberger, Boulamanti, and Tzimas (2016), implying a significant carbon revenue for the CCU plant. Other papers make more modest estimates, up to 100 €/ton CO_2. For comparison, the carbon prices on the European Emission Allowances market fluctuated around 25 €/ton CO_2 at the beginning of 2020 (Ember, 2021). At the beginning of 2018, the carbon price was only about 8 euros per tonne of CO_2. Assuming that the carbon price would rise from 25 euros to 100 or even 400 euros per tonne CO_2 soon seems overly optimistic. In reality, carbon prices remain to date relatively low and their evolution will be prone to policy changes. Two preliminary conclusions can be drawn from **Figure 2.5**. Firstly, a large range of assumed prices of CO_2 is observed in the literature set. Secondly, researchers tend to be overly optimistic about the future levels of the carbon price, while CO_2 emissions treated in CCU processes are not yet considered as emission savings in the current EU ETS framework.

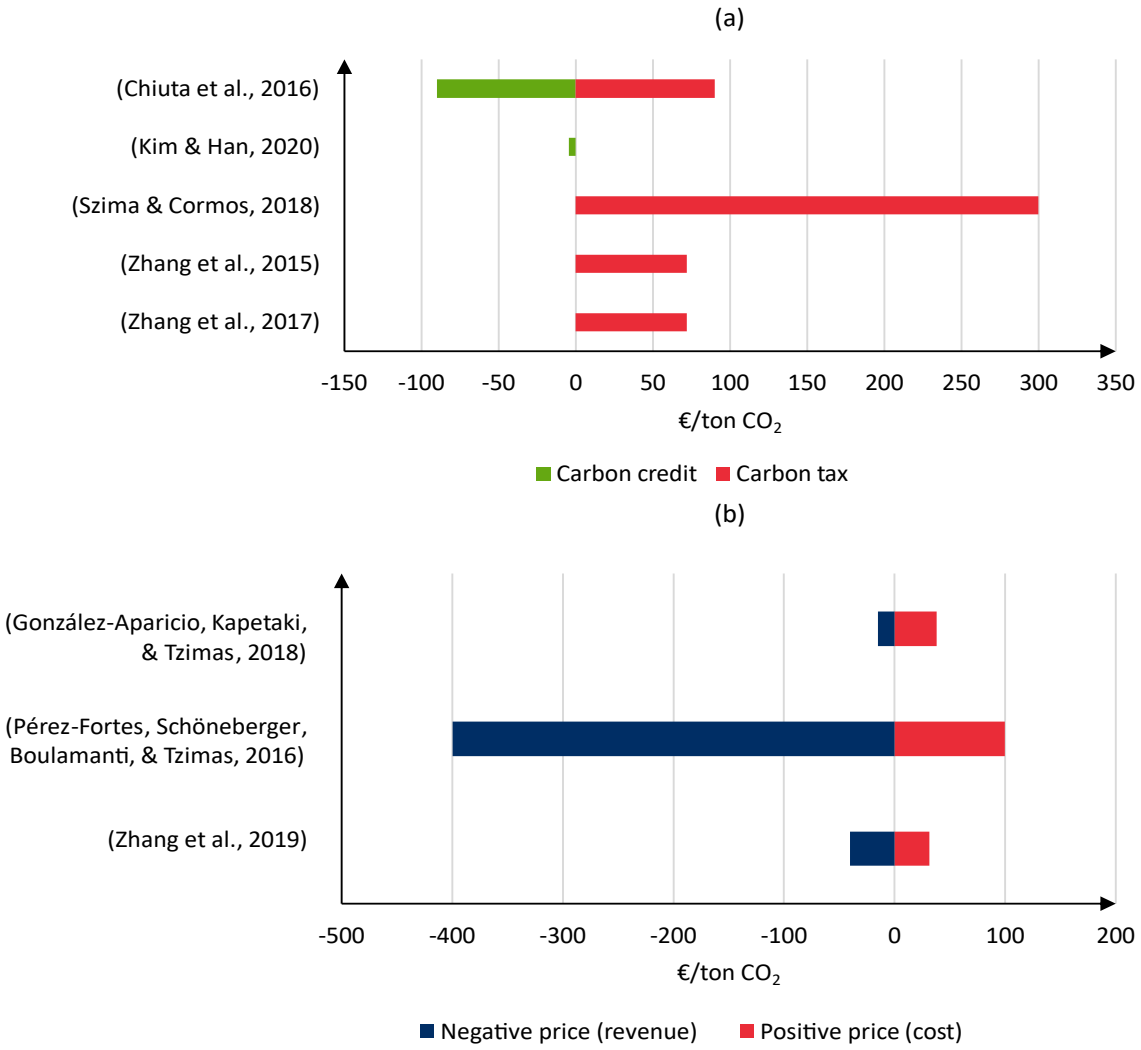


Figure 2.5: (a) the assumed ranges for carbon taxes and/or credits observed in Approach 2, in euro per ton CO_2, (b) the assumed prices for CO_2 as raw material observed in Approach 3, in euro per ton CO_2.

2.3.5 Calculation of indicators: the selection of assessment indicators

Table 2.6 lists all economic indicators used in the literature set, split up into cost-oriented and profit-oriented indicators. In total, 18 different economic indicators were found in 27 papers. First, some general reflections on the use of economic indicators are expressed. This is then followed by a closer look at the cost-oriented and the profit-oriented indicators, respectively.

Firstly, a diverse set of indicators is observed in the literature set. Interestingly, the majority of the indicators only appear once or twice in the literature set. The NPV (9), (Total) Product(ion) Cost ((T)PC—8) and (Discounted) Payback Period ((D)PBP—7) are the only indicators used repeatedly in more than five different papers. This variety of indicators makes it difficult to compare the economic feasibility of various CCU technologies. Sick et al. (2020) already raised this issue and reported the need for a harmonized TEA toolkit. A second observation from **Table 2.6** is the prevalence of cost-oriented indicators. Cost-oriented indicators are used if the revenues of the CCU plant are not known yet or are very uncertain. The market prices of the endproducts, produced in the CCU plant, are very uncertain in many cases (Dimitriou et al. 2015). However, cost-based indicators can never be used on a stand-alone basis to assess economic feasibility. Cost-based indicators can compare the cost efficiency of the CCU-based process to the conventional production process. However, the revenues of the CCU process are equally important to assess the economic feasibility. Finally, the majority of papers in the literature set combine several economic indicators to assess the economic feasibility of the CCU plant. For example, NPV, Internal Rate of Return (IRR) and (D)PBP are often used jointly (Zhang et al. 2015, 2017).

Cost-oriented indicators are used in 15 studies in the literature set and used on a stand-alone basis (without profit-oriented indicators) in 6 studies. The (T)PC, CAPEX and Total (Fixed) Capital Investment T(F)CI are the most frequent cost-oriented indicators. OPEX, LCOP and Cost of Electricity (CoE) are all practised twice. CAPEX and OPEX are usually computed in an intermediate stage to calculate the final indicator, such as the NPV. In this literature set, several papers selected CAPEX and/or OPEX as final indicators to assess economic performance. As explained before, the use of cost-oriented indicators alone does not allow to establish whether the CCU process generates sufficient revenues to be economically feasible or not. Nevertheless, the level of CAPEX can have an impact on the economic feasibility of the CCU technology, e.g. in C. Zhang, Jun, Gao, Kwak, and Park (2017) and Hoppe et al. (2018), the CAPEX is mentioned as a decisive factor for the economic feasibility. Hence, the CAPEX should be estimated as correctly as possible. Due to the complex composition of the CAPEX, measuring it accurately is a challenging task. Various computation methods exist, making it difficult for readers to interpret the results.

Therefore, researchers should always be transparent on how the CAPEX was estimated and what was included or excluded from their calculations. The cost estimation methodology described in Towler and Sinnott (2013b) provides clear procedures to estimate the CAPEX and OPEX. The CAPEX is split into the Fixed Capital Investment (FCI) and Working Capital. The FCI is further split into the inside battery limits (ISBL) investment, the outside battery limits (OSBL) investment, the engineering and construction costs and the contingency charges. Peters, Timmerhaus, and West (2003) provide an alternative approach, where the capital investment is split into direct and indirect costs and the different cost components can be calculated as a percentage of the purchased equipment costs. To date, no consensus has been reached in the academic literature on the preferred cost estimation method. The LCOP can be calculated in various ways as well. The term ‘LCOP’ is used twice in the literature set, and it is computed differently in the two papers. Chiuta et al. (2016) define LCOP as the total annual costs of a system divided by the throughput of the product. In Fernández-Dacosta et al.

(2017), the LCOP incorporates all positive and negative cash flows of the project levelized over the project lifetime and divided by the levelized amount of the product that is generated in that period. This adds proof to the statement that standardization in economic evaluations for CCU technologies is still lacking, as different formulas are used, even for the same indicator.

Profit-oriented indicators integrate both costs and revenues in one indicator, providing a more complete picture of the economic feasibility of a CCU technology than the cost-oriented indicators. The NPV and (D)PBP are the most frequently used profit-oriented indicators, with mentions in 9 and 7 papers, respectively. The NPV is used in one-third of the literature set, which makes it a very popular economic indicator. Although the use of NPV is very common in economic assessments, the use of NPV also has some drawbacks. Assumptions need to be made about the discount rate, the projected returns and the investment costs (Investopedia, 2020). Moreover, under the presence of uncertainty, the use of NPV can lead to suboptimal decisions when the investment is irreversible and/or possible to delay, according to Real Options theory (Dixit & Pindyck, 1994). The PBP indicates how long it takes before the investment is repaid, but fails to account for the time value of money (Investopedia, 2020). The DPBP discounts future cash flows and thus recognizes the time value of money. The (D)PBP gives a clear indication of how long it will take to earn back the initial investment. However, the (D)PBP remains limited to the amount of time needed to repay the initial investments. It does not consider the cost or revenue streams thereafter.

Table 2.6: List of economic indicators, subdivided into cost-oriented and profit-oriented indicators.

Economic indicators	**# uses**	**References**
Cost-oriented indicators		
CAPEX	3	(Pérez-Fortes et al. 2014; Fernandez-Dacosta et al. 2017; Yusuf et al. 2019)
CoE	2	(Bellotti et al. 2019; Yusuf et al. 2019)
LCOP	2	(Chiuta et al. 2016; Fernandez-Dacosta et al. 2017)
OPEX	2	(Fernandez-Dacosta et al. 2017; Yusuf et al. 2019)
TAC	1	(Putra et al. 2017)
T(F)CI	4	(Dimitriou et al. 2015; Zhang et al. 2015a, 2019; Deng and Adams II 2020)
Total cost	1	(John et al. 2021)
(T)PC	8	(Dimitriou et al. 2015; Zhang et al. 2015a, 2019; Kuenen et al. 2016; Kim et al. 2018a; Hoppe et al. 2018; Lee et al. 2020; Deng and Adams II 2020)
Utility costs	1	(Jens et al. 2019c)
Profit-oriented indicators		
(D)PBP	7	(Zhang et al. 2015a, 2017; González-Aparicio et al. 2017; Fernandez-Dacosta et al. 2017; Kim et al. 2018a; Godini et al. 2020b; Deng and Adams II 2020)
IRR	3	(Zhang et al. 2017; González-Aparicio et al. 2017; Bellotti et al. 2019)
Market uptake (# plants)	1	(Horschig et al. 2019)
MSP	2	(Jens et al. 2019a; Kim and Han 2020b)
NPV	9	(Zhang et al. 2015a, 2017; Pérez-Fortes et al. 2016c, a; Lainez-Aguirre et al. 2017; Kim et al. 2018a; Szima and Cormos 2018; Deng and Adams II 2020; Yang et al. 2021)
Profit	2	(González-Aparicio et al. 2017; Gonzalez-Aparicio et al. 2018)
PVR	1	(Kim et al. 2018a)
Sales	2	(Kuenen et al. 2016; Putra et al. 2017)
TPR	1	(Zhang et al. 2019)

In sum, the economic assessment indicators currently lack standardization, both in the choice of indicators and the formulas used to calculate them. In the literature set, the NPV is the most popular and complete indicator to assess economic feasibility. However, the use of this indicator also has its limitations, which should be recognized by the researchers who use it as a criterion. To include more flexibility in the investment decisions and to account for the uncertainties in the assessment, additional analyses should be performed.

2.3.6 Interpretation: uncertainty and sensitivity analysis

Following the guidelines from Zimmermann et al. (2020), the fourth phase of a TEA should be the correct interpretation of the results. Interpretation should be done to check the consistency, reliability and quality of the data inventory and the related results. Uncertainty and sensitivity analyses are the key instruments to review the reliability of data and to put the results in perspective. Uncertainty and sensitivity analysis are, although related, two distinct types of analyses to explore the uncertainty in a model. **Figure 2.6** shows how the interpretation phase was fulfilled in the literature set. Fourteen papers performed a local (or OAT) SA, where the value of one input variable at a time is varied to investigate the impact on the results.

Chiuta et al. (2016) implemented a local sensitivity analysis to investigate the impact of various input variables separately, but they also analysed the combined effect in a future outlook. Lee et al. (2020) performed a Monte Carlo simulation to identify the cumulative probability of the H_2 production cost. Here, the Monte Carlo technique is used as UA: the level of uncertainty is quantified by estimating the cumulative probability of the production cost. Eight studies did not implement any type of uncertainty or sensitivity analysis. Fernández-Dacosta et al. (2017) performed a pedigree analysis to qualitatively identify the uncertainties and executed a SA to identify the uncertainties quantitatively. Two studies performed scenario analysis to investigate how results change under different scenarios (Hoppe et al., 2018; Horschig, Welfle, Billig, & Thrän, 2019). **Figure 2.6** shows the absence of UA in the literature set. In the literature set, local SA is the preferred instrument in the interpretation phase. A local SA is indeed a quick and easy method to identify the input variables that contribute the most to the variation in the output. Local SA is sufficient for a quick screen on the most important input variables, however, it does not allow for input variables to fluctuate together. Hence, if one aims to fully explore the entire input variable space, global SA should be preferred.

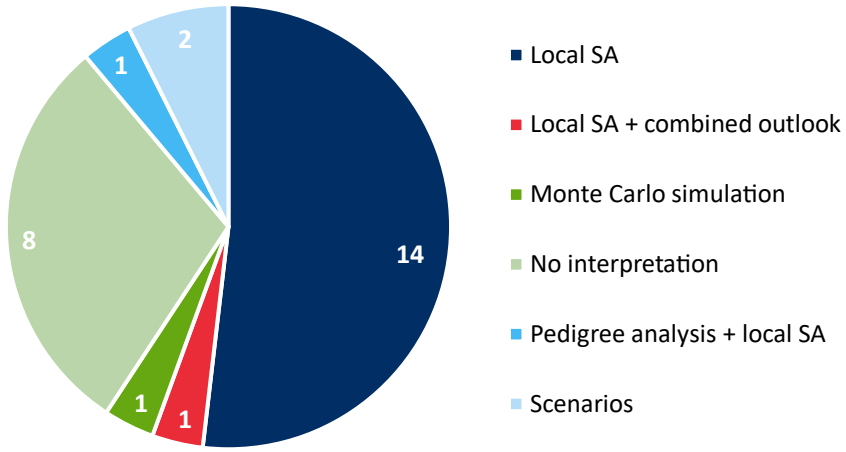


Figure 2.6: Realization of the interpretation phase in the literature set.

2.3.7 Methanol synthesis via CCU technologies

Based on the studies in the literature set, methanol is the most prevalent chemical CCU-based product. Olah (2013) identified methanol as a 'feasible and economic substitute for oil', thus launching the so-called methanol economy. Methanol is commonly used as a raw material in the production process of chemical products, to substitute the use of oil in manufacturing. Methanol can also be used as an energy carrier, both as a transportation fuel and as an intermediate energy storage medium. Global methanol production surpassed 80 million tonnes in 2018 (Carbon Recycling International, 2021). Thus, the potential market volumes for methanol are larger than those for products that only serve as chemicals. Consequently, the potential CO_2 emissions reduction of CCU-based methanol production can be significant. However, the economic feasibility of the various methanol synthesis CCU technologies still shows divergent patterns. Six studies calculated the NPV for the methanol synthesis process, ranging from negative to highly positive. To analyse this observed disparity in estimated NPVs, the (economic) assumptions made in each study are listed together with the estimated NPVs in **Table 2.8**.

The methanol synthesis route, the plant's location, the chosen system boundaries, the source of CO_2, the capture of CO_2, the plant's lifetime, the operational time per year, the methanol price and the production capacity are summarized in **Table 2.8**. From the investigated methanol synthesis route to the assumed price of methanol: the context in which the NPV is calculated is different for each study Hence, it is difficult to compare the estimated NPVs between these studies. Based on the NPV alone, an investor would choose the methanol synthesis route with the highest NPV, that is the CO_2/steam-mixed reforming and CO_2 hydrogenation presented by C. Zhang et al. (2017). However, this study did not include the cost for CO_2 capture, which would increase the costs of the CCU plant. Moreover, this study assumed the largest production capacity and the longest annual operational time. In other words, if other assumptions would be made in the economic assessment, the NPV may not be so high anymore and a different methanol synthesis route could yield the highest NPV.

Table 2.7 compares the different costs of CO_2 that were assumed in the studies in more detail. As in the rest of the literature set, the assumed values for the cost of CO_2 vary greatly, from negative (representing revenue for the utilized CO_2) to positive values (representing a cost).

Table 2.7 and **Table 2.8** highlight the different backgrounds against which the economic assessments for methanol synthesis routes have been performed. **Table 2.8** also reveals that half of these methanol synthesis processes are not yet economically feasible at the moment.

Table 2.7: The costs of CO_2 adopted in the six economic feasibility studies for methanol synthesis CCU technologies with NPV estimation.

Approach to the cost of CO_2	Cost of CO_2 (€/t)	Reference
1 – zero costs	0	(Y. Yang et al., 2021)
2 – CO_2 as GHG	0; 65	(C. Zhang et al., 2017)
2 – CO_2 as GHG	10	(Szima & Cormos, 2018)
3 – CO_2 as RM	-221.7; 0	(Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016)
4 – Fixed capture costs	61	(Deng & Adams Ii, 2020)
5b – Cradle-to-Gate + carbon tax	5.5	(Lainez-Aguirre et al., 2017)

Table 2.8: The estimated NPVs for methanol synthesis and the economic assumptions that were made in the studies, ranked from low to high NPV. NPV estimates in US $ are converted to euro with 1 US $ = € 0.85.

MeOH synthesis route	Location CCU plant	System boundaries	CO_2 source	CO_2 capture included?	Plant lifetime (yrs)	Operation time (h/yr)	MeOH price (€/t)	Production capacity (t/yr)	NPV (min; max) (M €)	Reference
MeOH synthesis based on hydrolysis	Spain	Cradle-to-Gate	Biomass power plant	Yes (chemical absorption using MEA)	10	7800	350	440,000	-€ 1,148.60	(Lainez-Aguirre et al. 2017)
Direct CO_2 catalytic hydrogenation	Western Europe	Gate-to-Gate	Pulverised coal power plant	No	20	8000	400	440,000	-€ 1,036.20	(Pérez-Fortes et al. 2016c)
Catalytic process with $Cu/ZnO/Al_2O_3$ catalyst	Romania	Gate-to-Gate	An 'energy-intensive plant'	No	25	8000	400	97,500	-€ 295.75	(Szima and Cormos 2018)
COG desulphurization and COG + BFG to methanol process	Ontario, USA, Finland, Mexico, China	Gate-to-Gate	Steel refineries	Yes (chemical absorption using MEA)	30	-	421.2	200,000	€ 45.90; € 195.05	(Deng and Adams II 2020)
SMR to produce syngas, for MeOH synthesis*	China	Cradle-to-Gate	Industrial plant	Yes (chemical absorption using MDEA)	30	-	332	51,740; 121,720	€ 49.90; € 93.08	(Yang et al. 2021)
CO_2/steam-mixed reforming and CO_2 hydrogenation	US Gulf	Gate-to-Gate	Unknown	No	20	8400	340	1,750,000	€ 410.90; € 729.98	(C. Zhang et al., 2017)

* In this study, the CO_2 is captured after the methanol synthesis and then used for the production of urea.

BFG, blast furnace gas; COG, coke oven gas; MDEA, monodiethanolamine; MEA, monoethanolamine; MeOH, methanol

Sixteen studies in the literature set analysed the economic feasibility of methanol synthesis CCU technologies, of which ten studies explicitly identified some of the barriers that need to be removed to make the CCU process economically competitive with its benchmark. The market-based and technical barriers that were identified by the studies as the most important aspects preventing commercialization are summarized here. The price of methanol should increase to make the CCU processes economically feasible (González-Aparicio, Kapetaki, & Tzimas, 2018; Lainez-Aguirre et al., 2017; Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016; C. Zhang et al., 2017). Following C. Zhang et al. (2017) and D. Kim and Han (2020), carbon taxes should go up to improve the economic feasibility. The price of CO_2 and the cost of CO_2 capture, on the other hand, should go down (Bellotti et al., 2019; Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016). The current level of the carbon tax remains too low to make CO_2 utilization profitable. Prices of raw materials (H_2, O_2 and natural gas) should decrease to make the CCU technologies competitive. The cost of electricity should also be reduced (Bellotti et al., 2019; Hoppe et al., 2018; Szima & Cormos, 2018). Technical barriers are identified less often in the studies. Energy efficiency and electricity consumption are mentioned as important barriers to profitability in three studies (D. Kim & Han, 2020; Lainez-Aguirre et al., 2017; Szima & Cormos, 2018). Finally, the plant scale should be increased according to C. Zhang et al. (2017) to improve profitability. The market-based and technical barriers are summarized in **Table A.2.3** and **Table A.2.4** in Appendix 2.B.

2.3.8 Key parameters in the sensitivity analysis

The previous paragraph already revealed that most studies for methanol synthesis focus on market-related or economic barriers, while technical barriers are mentioned less frequently. In this paragraph, we explore whether the studies in the whole literature set focus on economic (cf. market-based), policy or technical parameters in their analysis. It is valuable to understand whether CCU researchers focus their analysis on factors that can be manipulated, i.e. technology-related parameters, or on factors that are out of their hands, i.e. market-based or policy parameters. To learn the focus of the studies, all parameters whose impact is investigated in a local or global sensitivity analysis in the literature set are listed in **Table 2.9**. The majority of the investigated parameters are economic or market-based, for example, the product price, the electricity price, the capital investment or the cost of raw materials. These parameters are all determined by the market and cannot be influenced by the researchers. The carbon tax, or price for CO_2 in an ETS, is the only policy-related parameter that was investigated in the literature set. Technical parameters, related to the design of the CO_2 conversion technology or plant, were included in sensitivity analysis in only seven studies from the current literature set. Technical parameters such as the CO_2 conversion or energy efficiency are in several studies the result of optimization or modelling in e.g. CHEMCAD or Aspen Plus. Hence, it is not always possible or meaningful, from the engineering point of view, to include these parameters in a sensitivity analysis.

Table 2.9 reveals the focus of the literature on economic parameters, which are often largely determined by the market (or by policymakers, in the case of the carbon tax). In contrast, the technical parameters are included less frequently in sensitivity analysis. As discussed above, the technical parameters are often the result of chemical modelling or simulations, and assuming a change in these parameters would require changes in the design of the modelled CCU plant itself. Nevertheless, it could be interesting to reflect on how these technical parameters would need to improve before the investigated CCU plant is economically attractive. For example, Dimitriou et al. (2015) investigate how technology should be altered to improve economic performance. Their analysis reveals that the production costs are most sensitive to CO_2 conversion efficiency. Thus, improving the technical performance is prioritized, to increase the economic feasibility of the process.

Table 2.9: Economic, policy and technical parameters that were investigated in sensitivity analyses in the literature set.

Category	Parameter	References
Economic	Capital investment [a]	(Bellotti et al., 2019; Chiuta et al., 2016; Dimitriou et al., 2015; Fernández-Dacosta et al., 2017; Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016; C. Zhang et al., 2019; C. Zhang, Jun, Gao, Lee, & Kang, 2015)
	CO_2 price	(González-Aparicio et al., 2018; Lee et al., 2020; Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016; C. Zhang et al., 2019)
	Consumables price [b]	(Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al., 2016)
	Discount rate	(Fernández-Dacosta et al., 2017; D. Kim & Han, 2020)
	Electricity price	(Bellotti et al., 2019; Chiuta et al., 2016; Dimitriou et al., 2015; D. Kim & Han, 2020; S. Kim, Ryi, & Lim, 2018; Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al., 2016; Szima & Cormos, 2018)
	Hydrogen price [c]	(Dimitriou et al., 2015; D. Kim & Han, 2020; Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016; C. Zhang et al., 2019)
	Interest rate	(Dimitriou et al., 2015)
	Labour cost	(S. Kim et al., 2018)
	Natural gas price	(C. Zhang et al., 2017; C. Zhang et al., 2015)
	Operating & Maintenance (O&M) cost	(Chiuta et al., 2016)
	Product price [d]	(Bellotti et al., 2019; Dimitriou et al., 2015; Fernández-Dacosta et al., 2017; Lee et al., 2020; Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al., 2016; Szima & Cormos, 2018; Y. Yang et al., 2021; Yusuf et al., 2019; C. Zhang et al., 2017; C. Zhang et al., 2015)
	Reactant price	(S. Kim et al., 2018)
	Shale gas price	(Y. Yang et al., 2021)
	Steam price	(Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al., 2016)
	Tax rate	(D. Kim & Han, 2020)
	Utilities cost [e]	(C. Zhang et al., 2019)
Policy	Carbon tax	(Chiuta et al., 2016; D. Kim & Han, 2020; Szima & Cormos, 2018; C. Zhang et al., 2017; C. Zhang et al., 2015)
Technical	CO_2 conversion	(Dimitriou et al., 2015)
	Operation hours	(Dimitriou et al., 2015)
	Plant lifetime	(Dimitriou et al., 2015; D. Kim & Han, 2020)
	Plant scale	(Dimitriou et al., 2015; C. Zhang et al., 2019; C. Zhang et al., 2017; C. Zhang et al., 2015)
	Reaction heat	(Fernández-Dacosta et al., 2017)
	Reactor design	(S. Kim et al., 2018)
	Selectivity	(Fernández-Dacosta et al., 2017)

[a] CAPEX or ISBL; [b] catalysts, solvents; [c] hydrogen as a raw material; [d] the market price of the product (hydrogen, methanol, soda ash, sodium hydroxide, synthetic oil, olefin, formic acid, oxygen, urea, sulfur); [e] cooling water, electricity, natural gas

This raises a follow-up question: are trade-offs or relationships between different parameters, e.g. between energy efficiency and conversion efficiency, explored in the current literature set? In this literature set of 27 economic feasibility studies for CCU technologies, no trade-offs between different parameters were identified. Despite the early stage of development of most CCU technologies, little consideration is given to the technical aspects that could affect the economic feasibility. At low TRL, it is still possible to alter the design of the technology. Therefore, it can be valuable to evaluate how the economic performance would change if one of the technical parameters would improve, even hypothetically. This could be explored in a local sensitivity analysis, by calculating how much e.g. the NPV would change in response to a 10% increase in the CO_2 conversion rate, keeping all other parameters the same. This type of hypothetical exercise could provide a lot of information to potential investors and technology developers. It indicates when it might be profitable to invest in the CCU plant, given current market conditions, and it sets a target for the developers to work towards. Moreover, it can help to judge whether the investigated CCU plant could ever become profitable, or not.

2.3.9 Extending the TEA methodology

The guidelines written by Zimmermann et al. (2020) were used as a valuable benchmark, to objectively compare all studies in the literature set. Their framework can potentially lead to more harmonization in future CCU research. To date, the diversity in methods, indicators and assumptions remains considerable. The guidelines written by Zimmermann et al. (2020) can also be extended further to improve the economic assessment of novel CCU technologies.

As discussed in the previous section, the majority of studies in the literature set focussed on the impact of market-based parameters in their sensitivity analysis. Depending on the goal of the study, it can indeed be justifiable to focus more on either market-based, policy or technical parameters. For example, if the study aims to assess the influence of the product price on economic feasibility, market-based parameters will be prioritized. If, however, the study plans to investigate the economic viability of a novel type of CO_2 conversion technology that is being tested in the laboratory, it can be advisable to include technical parameters as well. In sum, it is not per se recommended to prefer one type of parameter over the other. Instead, the advice should be: it depends, on the goal of the economic assessment, on the context, on the investigated technology. Nevertheless, it remains remarkable that so few studies in the current literature set investigated the impact of technical parameters. Particularly for low-maturity technologies, it can be very valuable to understand how technical parameters affect economic performance.

Roh et al. (2020) remarked that the current TEA framework does not consider the technology's maturity level. However, the evaluation of novel CCU technologies in early development phases can differ significantly from the assessment of a mature technology. Therefore, the TEA methodology can be improved further by integrating the Technology Readiness Level (TRL) into the TEA framework. Buchner, Zimmermann, Hohgräve, and Schomäcker (2018) developed a novel TEA framework for the chemical industry that emphasizes the need to tailor the TEA to the TRL of the studied technology. This framework can also be very useful for CCU technologies, as these are often still low-mature technologies, that require particular assessment indicators. The use of 'static' indicators, which do not account for time dependence, is proposed for technologies with TRL 1–4, with TRL 1 the observation of basic principles and TRL 4 the validation of the technology in a laboratory. In a more recent paper, Buchner, Stepputat, Zimmermann, and Schomäcker (2019) developed a TRL scale specifically for the chemical industry. This scale should help to identify the correct TRL for the investigated technology. Surprisingly, only two studies in the literature set explicitly stated the TRL of the technology under

investigation (Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al., 2016; Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016). The lack of integration of the TRL in economic feasibility studies is worrying, as the level of maturity can have an impact on the assessment. Future research should address how assessment indicators for CCU technologies should be adapted for low TRL technologies.

The TEA methodology can also be extended by including flexibility in the investment decision. In classic economic analysis, an investment decision is a now-or-never decision. However, the decision to invest or not can be much more flexible in practice. The investor can choose to invest now or to wait for more information in the future. Because of the uncertainties that are present, it can indeed be valuable for a potential investor to wait. For example, if there is uncertainty about the introduction of a carbon tax, the investor could postpone the decision until the carbon tax is effectively imposed. Moreover, the investor generally does not have one, but multiple technologies to choose from. **Figure 2.7** presents this continuum of possible decision paths for the investor. The investor can invest immediately in Year 1 or wait year after year for more information. The investor can adopt a chosen technology after 1 or 2 years of waiting or start with one technology and scale up later with the help of another technology. In the presence of uncertainties, this flexibility to delay the investment decision creates a 'value of waiting'. However, once the investment is made, the value of waiting is lost: an opportunity cost is incurred. The value of this lost option, or the value of waiting, should be calculated and incorporated into the economic assessment (Dixit & Pindyck, 1994).

The NPV is the difference between the estimated positive and negative cash flows over the plant's lifetime, converted to the present value by a discount rate that reflects the risk profile and conditions in the capital market. This methodology, which is used frequently in economic assessments, completely neglects the value of waiting for more information. The level of the discount rate that is used in NPV calculations must also be chosen and it should reflect the risk profile of the investment at a particular point in time. However, the risk profile of the investment can change over time, while the discount rate is kept constant. Over time, the technology is developed further and technical or market uncertainties can be reduced. To integrate this evolution, one could work with a dynamic discount rate that is adapted to the adjusted risk profile. However, this does not soften the 'now-or-never' decision that is imposed by the NPV methodology. The NPV criterion simply states that one should invest whenever the NPV is positive and this decision must be made at one particular moment.

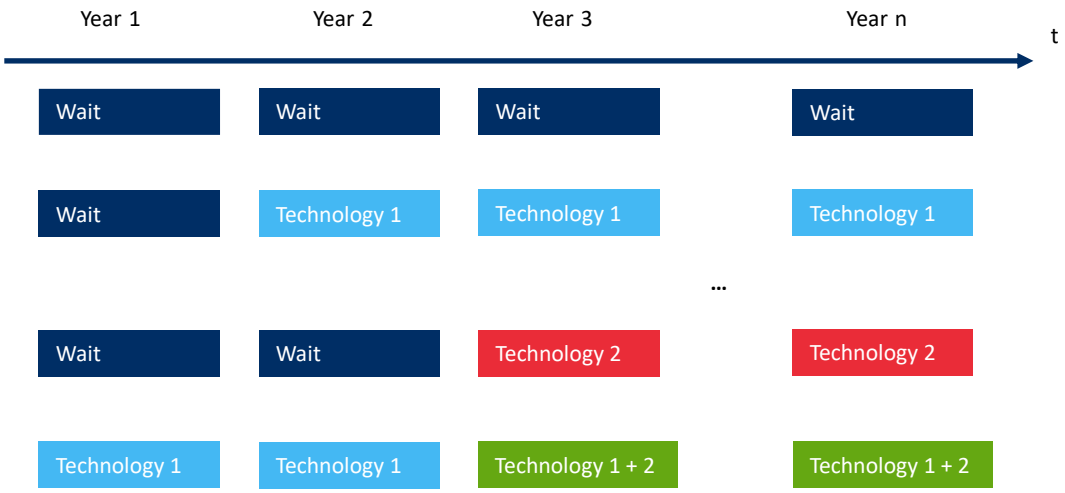


Figure 2.7: A continuum of possible decision paths. Including the possibility for the investor to wait for more information introduces flexibility in the investment decision. The investor can wait for more information to be available next year or invest now in Technology 1 or 2.

However, in a real-life market, the estimated cash flows will change due to uncertainties, competition and changed market conditions. Therefore, flexibility can be very valuable for management to alter its strategy, as new information becomes available and uncertainty about future cash flows and market conditions is resolved (Trigeorgis, 1993). To incorporate more managerial flexibility in the economic analysis, the TEA could be extended with a Real Options Analysis (ROA). ROA is a financial valuation technique, used to estimate the opportunity cost of the option that is lost. According to the Real Options Theory, one should only invest when the NPV of the project or technology is greater than the value of the lost option (Dixit & Pindyck, 1994). This theory also allows us to build a decision tree for a project, which allows for different investment decisions at different points in time, depending on the evolution of the investigated technology or project. The Real Options Theory has already been applied to CO_2-EOR projects, to account for this value of information. Compernolle, Welkenhuysen, Huisman, Piessens, and Kort (2017), for instance, investigated the impact of oil and CO_2 price uncertainties on the investment decisions for a CO_2-EOR value chain and show that market price uncertainty typically postpones investment at both the CO_2 capture unit and the EOR plant. W. Zhang, Dai, Luo, and Ou (2021) also raised the issue that traditional methods are no longer capable of dealing with the technological, market and policy uncertainties of low-TRL CCU technologies. They propose a Real Options model that includes different types of uncertainties and aim to investigate the impact of policy incentives on CCUS technologies in China. Applying this model to the European context would be very valuable for the development of CCU in the EU. Moreover, not only the effect of policy incentives, but also the effect of technological or market uncertainties should be analysed in more detail.

Efforts should be made to extend the application of ROA to novel CCU technologies. Not only can this help to introduce flexibility in the investment decision, but also account for the various technological and/or price uncertainties which can have an impact on the optimal timing of the investment in CCU technologies. Various types of technical uncertainty can prevail, for example, uncertainty on the energy and conversion efficiencies. Low-maturity technologies, in particular, can have a high level of technical uncertainty. Market or price uncertainties concern the market variations which can be difficult to predict, e.g. the CO_2 price, product prices, etc. The carbon tax can be an important driver for the profitability of the CCU technology, while raw material and product prices can be serious barriers, as discussed before. ROA can be a convenient tool to incorporate these types of uncertainty in the assessment fittingly. For example, the evolution of the CO_2 price can be modelled by a Geometric Brownian Motion (GBM), which is a stochastic process that can be used to model the evolution of uncertain variables.

The interpretation phase alone, as described by Zimmermann et al. (2020), is not sufficient to analyse the investment decision in CCU technologies in a realistic marketplace. Because of the generally low TRL of CCU technologies, better methods to deal with the high level of uncertainty in economic assessments should be recommended. The guidelines from Zimmermann et al. (2020) should be adapted to include more managerial flexibility in their economic assessment. ROA offers a method that is already implemented in other research fields to account properly for more flexibility.

Finally, the TEA could also be enhanced by including an environmental assessment. Thomassen et al. (2019) propose a new integrated Environmental and Techno-Economic Assessment (ETEA) framework. Wunderlich, Armstrong, Buchner, Styring, and Schomäcker (2021) more recently also recommended the integration of the TEA with the Life Cycle Analysis (LCA) to assess the potential of sustainable chemical technologies. Reporting results of TEA and LCA separately may result in conflicting conclusions, which complicates decision-making. The integration of both techno-economic and environmental assessments is highly relevant to society today. Novel technologies need to have

lower environmental impacts than their conventional counterparts to have a positive impact. However, unless these technologies can compete with the conventional equivalent, green technologies will never be adopted. Therefore, both the environmental and economic performance should be examined from the start to optimize the novel technology.

2.4 Discussion

The findings of this tutorial review paper have several implications for the future development of a TEA framework.

First, it is important to understand the goal of the TEA and consider the informative role that it has to play. Different questions can be answered with a TEA. A TEA that serves to assess the influence of a new policy measure to support CCU technologies or a TEA that aims to analyse the economic feasibility of a novel CCU technology that has only been tested in the laboratory, will focus on different parameters in their analysis. In the current literature set of 27 studies, we observed predominantly TEAs that focused on market parameters and how changing market conditions affect the economic feasibility. However, a TEA can also support the further development of the technology under study. Since the majority of CCU technologies are still in an early development phase, a TEA that reveals the relationship between technical and economic parameters is a powerful tool to identify the technical hurdles to be tackled and to optimize the technology's design and operation.

In addition to this, the TRL of the investigated CCU technology, and the level of uncertainty that is related to this, should be considered at the start of the TEA. Technologies with a low TRL are generally characterized by low availability of data and a high level of uncertainty. However, differences can be observed between the methods to deal with the low data availability, on the one hand, and the high level of uncertainty, on the other hand. For low-TRL technologies with limited data availability, the use of 'static' indicators is proposed. These indicators do not account for time dependencies, are less complex and usually require less information than dynamic indicators, which are used for mature technologies. However, low-TRL technologies are also characterized by high levels of uncertainty. As a result, potential investors generally wait for more information and delay the investment decision. Real Options Analysis can be an informative tool to calculate the value of waiting and determine the optimal moment of investment in novel CCU technologies, taking into account these uncertainties. However, Real Options Analysis is a complex method that can require intensive computational efforts. This is in stark contrast with the suggestions of Buchner et al. (2018) to use less complex indicators for low-TRL technologies. Thus, we observe a precarious balance between adapting the indicators to the limited data availability by simplifying the assessment indicators, on the one hand, and incorporating the uncertainties and flexibility in the analysis by modelling the uncertainties in the model through complex processes, on the other hand.

These observations again underline that it is important to understand the goal of the TEA. In this tutorial review, many variations in the choice of e.g. the system boundaries, cost of CO_2 or the assessment indicators was observed. Part of this diversity can be attributed to the different goals that are served by the different studies in the investigated literature set.

When the TEA must contribute to a better understanding of the technology and its aspects that need to change to move forward, the importance of the technical backbone cannot be underestimated. A simple local sensitivity analysis to investigate how changes in a technical parameter, e.g. the CO_2 conversion, would affect the economic criterium can be a very informative exercise in these studies. If, however, one needs to understand the conditions under which it will be favourable to invest in the

technology, considering the impact of various uncertainties, local sensitivity analysis will not be sufficient. In this case, Real Options Analysis may offer a more sophisticated method to include uncertainties and flexibilities in the assessment.

Thus, it should be clear that TEAs can inform policymakers or firms in many different ways. These observations introduce a trade-off that should be considered carefully in the future development of the TEA framework. On the one hand, a flexible TEA framework should be envisaged, which can be adapted to the type of information needed and the level of detail that is required. On the other hand, a more standardized framework was advocated, to allow for comparison between different TEAs. To balance this trade-off between flexibility and comparability, we suggest that future TEA frameworks should include a certain level of flexibility, to adjust the TEA to the level of information needed. Once decided on what type of information the TEA should provide, the TEA framework should give clear guidance on the type of appropriate indicators. If the same type of indicators is used for TEAs with the same goal and scope, the results of these TEAs can be compared.

2.5 Conclusions

The main purpose of this tutorial review was to map the differences in the methods and assumptions of economic feasibility studies for CCU technologies by comparing their methods to the TEA framework of (Zimmermann et al., 2020) and to explore how the quality and comparability of these studies could be improved in the future. The comparison between the TEA guidelines from Zimmermann et al. (2020) and the economic feasibility studies in the literature set revealed a great deal of variation in the applied methods and assumptions in the literature set. The economic feasibility studies for methanol synthesis CCU technologies were revised in more detail. This revealed divergent methods, assumptions and economic outcomes for methanol synthesis CCU technologies. Because of the many different assumptions that are involved, it remained hard to establish a causal relationship between the assumptions and the results. Further, the key parameters investigated in sensitivity analyses in the literature set were listed as well. The majority of economic feasibility studies only investigated the impact of market-based parameters in their sensitivity analysis. In contrast, the technical parameters, such as the CO_2 conversion efficiency or the plant's design, were analysed less frequently in the literature set. To improve the quality and comparability of (techno-)economic feasibility studies in the future, four improvements to the TEA framework were suggested: (i) focusing more on the impact of technical parameters in sensitivity analyses, (ii) adapting the assessment to the TRL of the technology, (iii) implementing ROA in the TEA and (iv) integrating an environmental assessment or LCA with the TEA. For low-TRL CCU technologies, the use of static indicators was proposed, which require less information to be calculated. However, low-TRL CCU technologies are also characterized by high levels of uncertainty. To treat this uncertainty correctly and to introduce more flexibility in the investment decision, the implementation of Real Options Theory (Dixit & Pindyck, 1994) was proposed. Further work is needed to investigate how ROA can be integrated into conventional TEA frameworks to account for uncertainty and managerial flexibility. This trade-off between using either simple, static indicators (to reflect limited data availability) or complex models with ROA (to introduce flexibility) should be considered carefully in future research. The goal of the TEA should decide whether a rough estimation suffices or a more complex analysis is required. Further research is needed to develop a TEA framework that allows both a certain level of flexibility, to adapt the TEA to its specific goal and scope, and that allows a comparison between the results of different TEAs with the same goal and scope.

Appendix – Chapter 2

2.A Literature set

Table A.2.1: Search queries in Web of Science and Scopus.

Search query 1 – Web of Science	TITLE: ((("techno-economic"* OR ("techn* NEAR economic") OR "economic*") AND (analysis OR assessment OR evaluation OR study OR feasibility)) OR ((cost OR revenue OR market OR finance* OR business OR economic*) AND (evaluat* OR assess* OR analysis OR model OR study))) AND TITLE: (("CCU" OR "CDU" OR "CCUS" OR "Carbon capture utili?ation" OR "Carbon dioxide utili?ation") OR (("carbon dioxide" OR CO2 OR carbon) AND (utili?ation OR conversion)))
Search query 1 – Scopus	(TITLE (((techno-economic* OR (techn* AND near AND economic) OR economic*) AND (analysis OR assessment OR evaluation OR study OR feasibility)) OR ((cost OR revenue OR market OR finance* OR business OR economic*) AND (evaluat* OR assess* OR analysis OR model OR study))) AND TITLE (("CCU" OR "CDU" OR "CCUS" OR "Carbon capture utili?ation" OR "Carbon dioxide utili?ation") OR (("carbon dioxide" OR co2 OR carbon) AND (utili?ation OR conversion))))
Search query 2 – Web of Science	TITLE: ((("techno-economic"* OR ("techn* NEAR economic") OR "economic*") AND (analysis OR assessment OR evaluation OR study OR feasibility)) OR ((cost OR revenue OR market OR finance* OR business OR economic* OR feasibility) AND (evaluat* OR assess* OR analysis OR model OR study))) AND TITLE: (("CCU" OR "CDU" OR "CCUS" OR "Carbon capture utili?ation" OR "Carbon dioxide utili?ation") OR (("carbon dioxide" OR CO2 OR carbon) AND (utili?ation OR conversion))) AND TOPIC: (("chemical "OR "chem*") AND ("transformation" OR "conversion"))
Search query 2 – Scopus	(TITLE (((techno-economic* OR (techn* AND near AND economic) OR economic*) AND (analysis OR assessment OR evaluation OR study OR feasibility)) OR ((cost OR revenue OR market OR finance* OR business OR economic*) AND (evaluat* OR assess* OR analysis OR model OR study))) AND TITLE (("CCU" OR "CDU" OR "CCUS" OR "Carbon capture utili?ation" OR "Carbon dioxide utili?ation") OR (("carbon dioxide" OR co2 OR carbon) AND (utili?ation OR conversion))) AND TITLE-ABS-KEY (("chemical" OR "chem*") AND ("transformation" OR "conversion")))
Search query 3 – Web of Science	TITLE: (("techno-economic"* OR ("techn* NEAR economic") OR "economic*") AND (analysis OR assessment OR evaluation OR study OR feasibility)) AND TITLE: (("carbon dioxide" OR "CO2" OR carbon) AND ("raw material" OR conversion OR utili?ation))
Search query 3 – Scopus	(TITLE (("techno-economic" * OR ("techn* NEAR economic") OR "economic*") AND (analysis OR assessment OR evaluation OR study OR feasibility)) AND TITLE (("carbon dioxide" OR "CO2" OR carbon) AND ("raw material" OR conversion OR utili?ation)))

Table A.2.2: Literature set.

N°	Title	Reference
1	Carbon dioxide utilisation for production of transport fuels: process and economic analysis	(Dimitriou et al., 2015)
2	Carbon dioxide utilization in a gas-to-methanol process combined with CO2/Steam-mixed reforming: Techno-economic analysis	(C. Zhang et al., 2017)
3	CO2 utilization from power plant: A comparative techno-economic assessment of soda ash production and scrubbing by monoethanolamine	(Yusuf et al., 2019)
4	Direct conversion of carbon dioxide to liquid fuels and synthetic natural gas using renewable power: Techno-economic analysis	(C. Zhang et al., 2019)
5	Economic assessment of CO2-based methane, methanol and polyoxymethylene production	(Hoppe et al., 2018) *
6	Economic evaluation of bio-based supply chains with CO2 capture and utilisation	(Lainez-Aguirre et al., 2017)
7	Efficient utilization of carbon dioxide in gas-to-liquids process: Process simulation and techno-economic analysis	(C. Zhang et al., 2015)
8	Formic acid synthesis using CO2 as raw material: Techno-economic and environmental evaluation and market potential	(Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al., 2016)
9	From Paris agreement to business cases for upgraded biogas: Analysis of potential market uptake for biomethane plants in Germany using biogenic carbon capture and utilization technologies	(Horschig et al., 2019)
10	Improving methanol synthesis from carbon-free H2 and captured CO2: A techno-economic and environmental evaluation	(Szima & Cormos, 2018) *
11	Methanol synthesis using captured CO2 as raw material: Techno-economic and environmental assessment	(Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016)
12	Multi-scale analysis of integrated C1 (C44 and CO2) utilization catalytic processes: Impacts of catalysts characteristics up to industrial-scale process flowsheeting, part II: Techno-economic analysis of integrated C1 utilization process scenarios	(Godini et al., 2020)
13	Opportunities of Integrating CO2 Utilization with RES-E: a Power-to-Methanol Business Model with Wind Power Generation	(González-Aparicio, Pérez-Fortes, Zucker, & Tzimas, 2017)
14	Prospective techno-economic and environmental assessment of carbon capture at a refinery and CO2 utilisation in polyol synthesis	(Fernández-Dacosta et al., 2017)

15	Tech-economic and environmental analysis of energy-efficient shale gas and flue gas coupling system for chemicals manufacture and carbon capture storage and utilization	(Y. Yang et al., 2021)
16	Technical and economic feasibility under uncertainty for methane dry reforming of coke oven gas as simultaneous H2 production and CO2 utilization	(Lee et al., 2020)
17	Technical and Economical Evaluation of Carbon Dioxide Capture and Conversion to Methanol Process	(Putra et al., 2017)
18	Techno-economic analysis (TEA) for CO2 reforming of methane in a membrane reactor for simultaneous CO2 utilization and ultra-pure H-2 production	(S. Kim et al., 2018)
19	Techno-economic analysis for the integration of a power to fuel system with a CCS coal power plant	(Bellotti et al., 2019) *
20	Techno-economic analysis of carbon dioxide capture and utilisation analysis for an industrial site with fuel cell integration	(John et al., 2021)
21	Techno-economic analysis of coke oven gas and blast furnace gas to methanol process with carbon dioxide capture and utilization	(Deng & Adams Ii, 2020)
22	Techno-economic and climate impact analysis of carbon utilization process for methanol production from blast furnace gas over Cu/ZnO/Al2O3 catalyst	(D. Kim & Han, 2020)
23	Techno-Economic Assessment of Carbon Utilisation Potential in Europe	(Perez-Fortes, Bocin-Dumitriu, & Tzimas, 2014)
24	Techno-economic assessment of power-to-methane and power-to-syngas business models for sustainable carbon dioxide utilization in coal-to-liquid facilities	(Chiuta et al., 2016)
25	Techno-economic evaluation of the direct conversion of CO2 to dimethyl carbonate using catalytic membrane reactors	(Kuenen, Mengers, Nijmeijer, van der Ham, & Kiss, 2016)
26	To Integrate or Not to Integrate-Techno-Economic and Life Cycle Assessment of CO2 Capture and Conversion to Methyl Formate Using Methanol	(Jens et al., 2019)
27	Wind energy and carbon dioxide utilisation as an alternative business model for energy producers: A case study in Spain	(González-Aparicio et al., 2018)

** indicates papers added manually to the literature set*

2.B Market-based and technical barriers

Table A.2.3: Market-based barriers that should be improved (i.e. lowered in the case of costs, increased in the case of prices of products) to become economically feasible. Direction of improvement indicates whether this factor should increase or reduce to become economically feasible.

Market-based barrier	Direction of improvement	Reference
MeOH price	Increase	(González-Aparicio et al., 2018; Lainez-Aguirre et al., 2017; Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016; C. Zhang et al., 2017)
CAPEX	Reduce	(Bellotti et al., 2019; Hoppe et al., 2018; C. Zhang et al., 2017)
NG price	Reduce	(C. Zhang et al., 2017)
Carbon tax	Increase	(D. Kim & Han, 2020; C. Zhang et al., 2017)
Electricity cost	Reduce	(Bellotti et al., 2019; Hoppe et al., 2018; Szima & Cormos, 2018)
CO_2 price	Reduce (negative)	(Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016)
H_2 price	Reduce	(John et al., 2021; Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016)
O_2 price	Increase	(Bellotti et al., 2019)
Cost of CO_2 capture	Reduce	(Bellotti et al., 2019)
Discount rate	Reduce	(D. Kim & Han, 2020)
Carbon tax	Increase	(D. Kim & Han, 2020)

Table A.2.4: Technical barriers that should be improved to become economically feasible. Direction of improvement indicates whether this factor should increase or reduce to become economically feasible.

Technical barrier	Direction of improvement	Reference
Plant scale	Increase	(C. Zhang et al., 2017)
Energy efficiency	Increase	(Lainez-Aguirre et al., 2017)
Electricity consumption	Reduce	(D. Kim & Han, 2020; Szima & Cormos, 2018)
Local electricity grid carbon intensity	Reduce	(Deng & Adams Ii, 2020)

3

A Prospective Techno-Economic Assessment of Plasma Catalysis for the Conversion of CO_2 into Chemicals

The persistent increase in CO_2 emissions and the continued depletion of fossil resources are two major challenges of the 21st century. These challenges can be tackled with Carbon Capture and Utilization (CCU), by capturing and using CO_2 as a valuable feedstock. Plasma presents a reactive environment to convert the CO_2 molecule efficiently into higher-value chemicals and is a promising CCU technology in an early development stage. This study analyses the economic feasibility of plasma as a novel CCU route to convert CO_2 into other chemicals, based on the results from experimental work with a Dielectric Barrier Discharge (DBD) reactor as plasma technology. The variations in three features of the plasma are analysed: the type of packing material (SiO_2 packing or empty), the type of feed (CO_2 or CO_2 and CH_4) and the space time (2.91 – 72.71 s). The goal of this study is to analyze these combinations of the chosen *reactor configuration* and *process parameters* for the plasma technology and evaluate how the variations in technical parameters of these combinations translate into economic parameters in a Techno-Economic Assessment (TEA). The economic feasibility is assessed by calculating the Net Present Value (NPV). The results from the TEA will help us to identify the major cost items of this CCU technology and identify which technological improvements would be needed to make the technology economically feasible. The results of the economic analysis revealed that none of the 35 analyzed DBD set-ups could create a positive NPV. The major cost categories are the high expenses for electricity and the investment for the high-voltage power supply. The highest (i.e. least negative) NPV is calculated for the unpacked DBD reactor, with a feed of pure CO_2 and a short space time of 2.91s, because this set-up has the lowest costs. However, the highest revenues are found for the SiO_2-packed reactor, with a feed of CO_2 and CH_4 and a longer space time of 55 s. Hence, the future challenge is to find a DBD set-up that can boost the revenues, while minimizing the energy demand and the associated costs for the DBD reactor.

Parts of this chapter have been published in:

Lamberts-Van Assche, H., Thomassen, G., & Compernolle, T. (2022). The early-stage design of plasma for the conversion of CO_2 to chemicals: A prospective techno-economic assessment. *Journal of CO_2 Utilization, 64*, 102156. doi:https://doi.org/10.1016/j.jcou.2022.102156

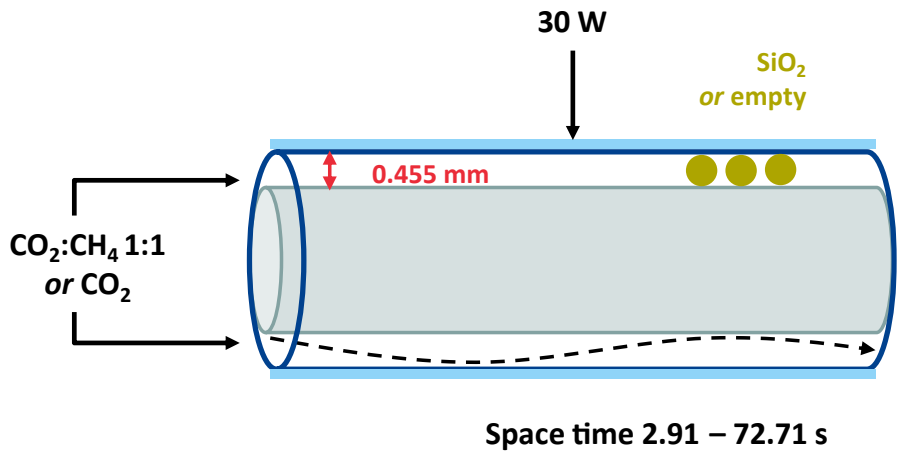
Takeaway messages

- The main objective of this TEA is to evaluate how the chosen *reactor configuration* and *process parameters* affect the economic feasibility of CO_2 splitting and DRM reactions in the DBD reactor.
- The translation of the technical parameters, observed in the laboratory for 35 combinations of *reactor configuration* and *process parameters*, results in a negative NPV for all 35 combinations.
- The high energy demand of the DBD reactor, to generate the plasma, is the main reason for this negative NPV.
- The highest (i.e. least negative) NPV is calculated for the unpacked DBD reactor, with a feed of pure CO_2 and a short space time of 2.91 s, because this set-up has the lowest costs.
- The highest revenues, however, are found for the SiO_2-packed reactor, with a feed of CO_2 and CH_4 and a longer space time of 55 s.
- The future challenge is to find a combination of *reactor configuration* and *process parameters* that allows the combination of a high conversion rate and selectivity towards chemicals with high market prices (to boost the revenues), with low energy needs (to minimize the costs). Other packing materials should be analyzed to explore whether this trade-off can be solved or not.

The experimental background

In Chapter 3 and Chapter 4, the terms *reactor configuration* and *process parameters* will be used frequently. The term *reactor configuration* refers to the geometry of the DBD reactor, i.e. the discharge gap, discharge length, reaction volume, electrode morphology and packing material. The relevant *process parameters* in this work are the flow rate, feed ratio, input power and specific energy input (SEI) (Khoja et al., 2019). The flow rate is reflected in the space time: a higher flow rate translates into a shorter space time, and vice versa. The terms *combination* or *set-up* will be used to refer to the chosen *reactor configuration* and *process parameters* jointly.

In this Chapter, the TEA is performed to assess the economic feasibility of various set-ups of the DBD reactor that were tested and analysed by Uytdenhouwen et al. (2021). In their experimental work, the *reactor configuration* has a gap size of 0.455 mm, and this gap is either filled with SiO_2 packing or no packing. The DBD reactor is supplied with pure CO_2 or a mix of CO_2 and CH_4, and the flow rate is decreased stepwise to vary the space time between 2.91 and 72.71 s. The input power (30 W) is kept constant during the experiments. In Chapter 4, a new DBD reactor set-up will be evaluated, with a different *reactor configuration* and a different set of *process parameters*.



3.1 Introduction

In 2020, a new record high was measured for the global average CO_2 concentration in the atmosphere, with an unprecedented level of 412.5 ppm (Lindsey, 2020). Carbon Capture and Storage (CCS) is often put forward as a key technology to reduce CO_2 emissions substantially. CCS technologies capture the CO_2 from an industrial plant or even directly from the air, transport the captured CO_2 by ship or via pipelines and store it permanently underground, on- or offshore. Despite the high Technology Readiness Level (TRL) of CCS (TRL 9) and the urgent call for action to reduce CO_2 emissions, the uptake of CCS on a larger scale remains slow. The high capture costs and the low CO_2 prices in the EU Emission Trading System (ETS) make it undesirable to incur large sunk costs from a firm's perspective today.

The absence of an attractive business case for CCS has redirected the attention to Carbon Capture and Utilization (CCU). CCU involves the capture and use of CO_2 to produce valuable products, such as chemicals, fuels or building materials (IEA, 2022a). Instead of storing the CO_2 underground, the CO_2 is now used as an input to other products or services.

CCU is generally classified into two categories: (1) the direct use of CO_2, where the CO_2 molecule is not chemically altered (non-conversion) and (2) the transformation of CO_2 through chemical or biological processes (conversion) (IEA, 2021a). An example of the first category is CO_2-enhanced oil recovery (CO_2-EOR), where the captured CO_2 is injected into oil reservoirs to increase the production of oil. An example of the second category is the conversion of CO_2 into methanol by using geothermal energy, in Iceland (CRI, 2022). Three main routes for the conversion of CO_2 can be distinguished further: mineralization, chemical-based conversion and bio-based conversion routes. The maturity of CCU technologies varies for each application. For example, the production of urea is a commercial and mature CCU process, while methanol synthesis is being demonstrated in a pilot plant and the production of formic acid production is still a lab-scale prototype (Chauvy et al., 2019). The bulk of CCU technologies is classified at a TRL of 5 to 6, being in the demonstration phase at the lab or pilot plant level. In sum, CCU is a diverse class of low-carbon technologies in various phases of technology maturity.

In sum, CCU utilizes CO_2 to transform it into other, and as such acknowledges CO_2 as an inexpensive and abundant source of carbon. A wide variety of industrial processes currently use fossil fuels as the source of carbon, and hence, CO_2 could replace fossil fuels as a feedstock and reduce the consumption of fossil fuels in these production processes. Despite the potential to replace fossil fuels as a source of carbon, the actual size of CO_2 utilization remains limited: in 2016, only 200 Mt of CO_2 was used, a trivial amount compared to the total anthropogenic emissions of 32,000 Mt in this year (Michele Aresta, Dibenedetto, & Angelini, 2013). While the current level of CO_2 utilization remains below expectation, CCU technologies still present a promising business case, as additional revenues are generated by utilizing the captured CO_2 (compared to storing the CO_2 underground).

As a result, CCU keeps attracting attention, in particular from hard-to-abate industries, such as the steel or cement industry. This increased interest has emphasized the need for economic feasibility studies of these novel technologies. As a result, many recent studies analysed the viability of a variety of CCU technologies. Pérez-Fortes, Schöneberger, Boulamanti, and Tzimas (2016) evaluated the economic and environmental impacts of a methanol (MeOH) plant using H_2 and captured CO_2 as raw materials. The total cost of production was dominated by the cost of H_2 and the MeOH plant was found to be not economically feasible under current conditions. In a similar study, Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al. (2016) analysed the feasibility of formic acid (FA) synthesis from captured CO_2 and H_2, where the high costs of catalysts and electricity were identified as the main

barriers. Nyári, Magdeldin, Larmi, Järvinen, and Santasalo-Aarnio (2020) investigated the feasibility of a MeOH CCU plant at an industrial scale, using CO_2 and H_2. The high cost of H_2 resulted in high production costs of MeOH, causing the CCU plant to be infeasible. Wiesberg, De Medeiros, Alves, Coutinho, and Araújo (2016) analysed direct and indirect chemical conversion routes of CO_2 to MeOH. For both routes, the costs of electricity and labour were observed to be the most important factors. C. Zhang et al. (2019) assessed the techno-economic feasibility of a power-to-liquid process and a hybrid power-to-liquid/power-to-gas process, converting CO_2 to liquid fuels and syngas. Both processes can become economically feasible when the H_2 prices decrease or the CO_2 prices become negative. The price of H_2 and the capital expenditures (CAPEX) were shown to be the most important cost factors. Fernández-Dacosta et al. (2017) performed a prospective economic and environmental assessment to evaluate the utilization of CO_2 for the synthesis of polyol. Their results demonstrate how a combination of storage and utilization can result in both environmental and economic benefits.

This brief literature overview demonstrates that most CCU technologies still struggle to become economically viable. The high costs for electricity, CAPEX and costs of H_2 were often mentioned as barriers to the economic feasibility of the CCU route. Alternatively, it could be concluded that the targeted end-products are not valuable enough to compensate for the costs. As discussed in Chapter 2, previous economic feasibility studies for CCU technologies tend to focus more on the impact of market-based parameters, in particular in the sensitivity analysis of the study. The importance of varying market-parameters, such as the price of electricity, is very often analyzed, whereas the importance of changing technological parameters, such as the CO_2 conversion rate of the CCU technology, is much less investigated. While economic parameters are mostly external and uncontrollable, the design of the plant and its technical parameters can often still be steered, in particular at lower TRLs. As an exception to this rule, Fernández-Dacosta et al. (2017) included technical parameters in the sensitivity analysis. However, two separate sensitivity analyses were conducted: one to investigate the effect of the technical parameters on the energy requirements of the system and one to analyse the effect of market parameters on the cost of production. This illustrates the lack of integration between the technical and economic assessments of novel technologies. Although the majority of CCU technologies are still at an earlier stage of development, where their design can still be altered and optimized, the existing economic feasibility studies fail to reflect on how modifications in the technology's design could affect its economic feasibility at maturity.

One promising CO_2 conversion technology, at this early stage of development, is plasma technology (Snoeckx & Bogaerts, 2017a). Plasma is often called the "fourth state of matter" and is a highly reactive chemical mixture, containing both charged and neutral particles such as atoms, ions or excited electrons (Carreon, 2019). It is an ionized gas, which can be created by supplying thermal or electric energy to a gas. Two types of plasma are generally distinguished: thermal plasmas and non-thermal plasmas (NTPs). Thermal plasmas are generated at high temperatures or high gas pressures, whereas NTPs can be realized at low temperatures. Various types of plasma set-ups exist, of which Dielectric Barrier Discharge (DBD), Gliding Arc (GA) and Microwave (MW) plasma are the most commonly reported in the literature (Snoeckx & Bogaerts, 2017a). **Table 3.1** summarizes the highest reported CO_2 conversion (%) and energy efficiency (%) levels per type of plasma in the literature. Snoeckx and Bogaerts (2017a) reported a maximum conversion rate of 42% that was reached so far in the DBD reactor, while the highest energy efficiency observed at that time was 23%. In the GA plasma, the maximum CO_2 conversion reaches only 20%, while higher energy efficiency levels can be reached of 40 to 50%, with a maximum of 65%. For the MW plasma, energy efficiencies in the range of 10 to 50% are typically observed, with CO_2 conversions as high as 95%.

Table 3.1: The highest reported CO_2 conversion and energy efficiency levels in the literature per type of plasma, based on Snoeckx and Bogaerts (2017a).

	DBD	**MW**	**GA**
CO_2 conversion (%)	42% (Snoeckx & Bogaerts, 2017a); 71% (Uytdenhouwen et al., 2021)	95%	20%
Energy efficiency (%)	23%	50%	65%

Despite the higher conversion rates (MW) and higher energy efficiency levels (MW and GA) reported in other plasma types, the DBD reactor is most commonly used for today's plasma research. This is due to the DBD reactor's simple design and the possibility of adding packing material to the reactor. The DBD reactor is a mature technology, well-known for its application in ozone generation on an industrial scale (Kogelschatz, 2003). The scalability of the DBD reactor has been proven with its application as an ozone generator (Kogelschatz, 2003) and for the removal of Volatile Organic Compounds (VOCs) (S. Li et al., 2020). Schönekerl et al. (2020) and Assadi, Bouzaza, and Wolbert (2016) demonstrated that scaling up from laboratory-scale to pilot plant level is possible for DBD reactors.

A DBD is a discharge between two planar or cylindric electrodes, separated by at least one dielectric barrier (e.g. glass) which creates one or more insulating layers. In the gap between the two electrodes, which can range from 1 mm to several cm, gas can flow and interact with the plasma. **Figure 3.1** shows a cylindrical configuration of a DBD reactor. To improve the performance of the DBD reactor, packing materials can be introduced in the discharge gap. These packing beads can have catalytic properties or can be wrapped with a catalytic material, which can steer the process towards more selective production of targeted elements. When plasma is produced in a DBD reactor filled with catalytic packing beads, the high reactivity of the plasma is combined with the selectivity of the catalyst in a process that is called plasma catalysis (Bogaerts & Neyts, 2018).

The use of the DBD reactor for plasma has several advantages: (1) the ambient operating conditions, (2) the flexible reactor design, allowing different types of reaction to occur, (3) the modularity and linearity in upscaling, allowing for local or on-demand production schemes, (4) the lack of use of rare earth materials, (5) the possibility to turn the reactor on and off quickly, as it requires no preheating or cooling-down, (6) the ability to use renewable energy as an energy source, creating the opportunity for energy storage and (7) the possibility to insert catalysts in the reactor (Bogaerts & Neyts, 2018; Snoeckx & Bogaerts, 2017a).

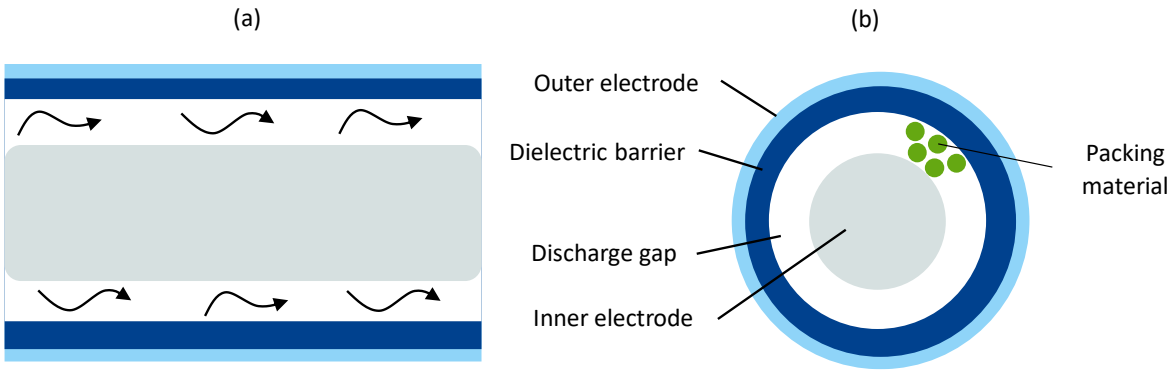


Figure 3.1: (a) Frontal view and (b) top view of the cylindrical configuration of a DBD reactor.

The use of catalysts in a DBD reactor is not only studied for the splitting of CO_2, but also for plasma-catalytic dry reforming of methane (DRM). DRM is a widely studied chemical process that enables the conversion of CO_2 and methane (CH_4) into other chemical components, primarily syngas. Plasma-catalytic DRM reactions in a DBD reactor allow the conversion of two important greenhouse gases (GHG) at ambient operating conditions in an easy and flexible reactor design, making it an attractive technology.

Besides the previously listed advantages of a DBD reactor for the conversion of CO_2, two main barriers can be identified: the low energy and conversion efficiency of the DBD reactor. While the low energy efficiency results in high energy costs, the low conversion rate can result in higher required investment costs and separation costs (Bogaerts & Neyts, 2018). However, it remains unsettled whether the low conversion or energy efficiency is the most important barrier. van Rooij, Akse, Bongers, and van de Sanden (2017) demonstrated that separation costs were the dominant cost factor for the production of CO in a plasma reactor using renewable energy. Consequently, they argued that the low conversion rate was largely responsible for the high production costs (van Rooij et al., 2017). Martini et al. (2019), on the other hand, claim that the high energy consumption of the plasma reactor is the main barrier preventing commercialization. Both conversion and energy efficiency can be altered by tuning the design of the DBD reactor: the space time of the gas, the packing material, the feed and the gap size influence both efficiencies in various manners (Snoeckx & Bogaerts, 2017a).

The present paper investigates the economic viability of the plasma-catalytic CO_2 splitting and DRM reactions in a DBD reactor, into higher-value chemicals, as potential CCU technology. Contrary to other CCU routes, no H_2 is consumed as raw material, no thermal energy is needed and higher-value chemicals can be targeted. To the author's knowledge, no economic assessment for the conversion of CO_2 into chemicals in a plasma reactor has been performed before. Rouwenhorst and Lefferts (2020) assessed the feasibility of plasma catalysis for ammonia synthesis and Chaudhary (2019) investigated the production of hydrogen in a plasma reactor. However, the investigated plasma technologies in these studies aimed at renewable energy storage, by producing ammonia or H_2 as a (temporary) energy carrier. Hence, the targeted end-product is not a chemical product, but energy. In this Chapter, we aim to assess the economic feasibility of the plasma-catalytic reactions in a DBD reactor as an alternative production route for chemicals. This paper also extends previous research by analyzing various combinations of the chosen *reactor configuration* and *process parameters* for the plasma-catalytic reactions in the DBD reactor, and evaluating how the different technical parameters of these combinations translate into economic parameters in a Techno-Economic Assessment (TEA). Changes in the plasma reactor's design on a lab scale affect the technical performance of the reactor. These changes are now translated directly into economic costs and benefits in the TEA. The results of the TEA will help us to identify those design features that may lead to improvements in the technical performance and consequently, to higher economic benefits at an early stage. Tschulkow et al. (2020) highlighted the need for such an integrated TEA, that links the technical and economic parameters, for low-TRL projects to identify the crucial R&D steps.

In sum, this study explicitly investigates the influence of the design of the DBD reactor on its economic viability. The results of an experimental study, where both the *reactor configuration* and *process parameters* were varied, are translated into economic cashflows on a pilot plant level. This allows the identification of the major cost items and the prioritization of future R&D steps.

3.2 Materials and Methods

To translate the results from the experimental study for the lab-scale DBD reactor into economic metrics and to assess the economic feasibility of the conversion of CO_2 and CH_4 in a plasma DBD reactor, a TEA is performed in this study. A TEA is a methodological framework that integrates both technological and economic evaluation into one study (Van Dael et al., 2015).

One advantage of the TEA is that changes in technical performance are immediately translated into changes in the economic parameters as well. Van Dael et al. (2015) developed a methodology that consists of four main steps: (1) the market study, (2) the calculation of the Process Flow Diagram (PFD) and mass and energy balances, (3) the economic analysis, and (4) the risk analysis. As presented earlier in Chapter 2, Zimmermann et al. (2020) developed TEA guidelines for CCU technologies in particular. Four phases are distinguished: (1) the definition of the goal and scope of the TEA, (2) the inventory phase, including the collection of economic and technical data, (3) the calculation of indicators, i.e. the economic analysis, and (4) the interpretation phase. Although slightly different from the four steps presented by Van Dael et al. (2015), the same activities are covered by both frameworks. For example, while Van Dael et al. (2015) begin the TEA with the market study, Zimmermann et al. (2020) include the market study in the creation of the inventory. In this Chapter, the guidelines of Zimmermann et al. (2020) are followed, to be consistent with Chapter 2.

The splitting of CO_2 and the DRM reactions in the plasma DBD reactor are currently only tested and demonstrated at the lab scale, which corresponds to a TRL of 3 to 4 (proof of concept – lab prototype). Performing a TEA at this low TRL can be particularly valuable because the technology can still be altered in response to the findings. First, the goal and scope of the TEA are defined. Second, the data inventory is created. The technical data is collected from the experimental work of Uytdenhouwen et al. (2021), which investigated the performance of various DBD reactor setups in the laboratory. Based on their measurements of the technical parameters, the mass and energy balances can be established. Third, the economic analysis is performed. The Net Present Value (NPV) is selected as the main indicator to assess the economic viability of the technology. Finally, the interpretation phase concludes the TEA. In this study, a one-at-a-time sensitivity analysis is performed to identify the parameters that contribute the most to the variation in the NPV. Moreover, a scenario analysis is performed, to analyze the technological improvements that would have to occur or market conditions that would have to change to make the technology economically feasible.

3.2.1 Goal and Scope

As stated before, the goal of the TEA is to assess how the chosen *reactor configuration* and *process parameters* affect the economic viability of the technology and to select the most promising combination in economic terms. The combinations that were tested in the laboratory are translated into economic parameters in this TEA. In addition, the results from the TEA will help us to identify the major cost items of this CCU technology and identify which technological improvements would be needed to make the technology economically feasible.

Figure 3.2 visualizes the CCU value chain from the source of CO_2 to the end-product. First, the CO_2 needs to be captured from a CO_2 source, e.g. a power plant, a chemical plant or a cement plant. This study assumes that the CO_2 source and the CO_2 use are located on the same site. The captured CO_2 is then supplied directly to the DBD reactor, together with CH_4. Stainless steel and alumina are needed to construct the DBD reactor. The SiO_2 packing material also needs to be assembled and inserted in the DBD reactor. To generate the plasma, electricity needs to be supplied. Once the plasma is generated, the plasma-catalytic CO_2 splitting or DRM reactions can take place in the DBD reactor.

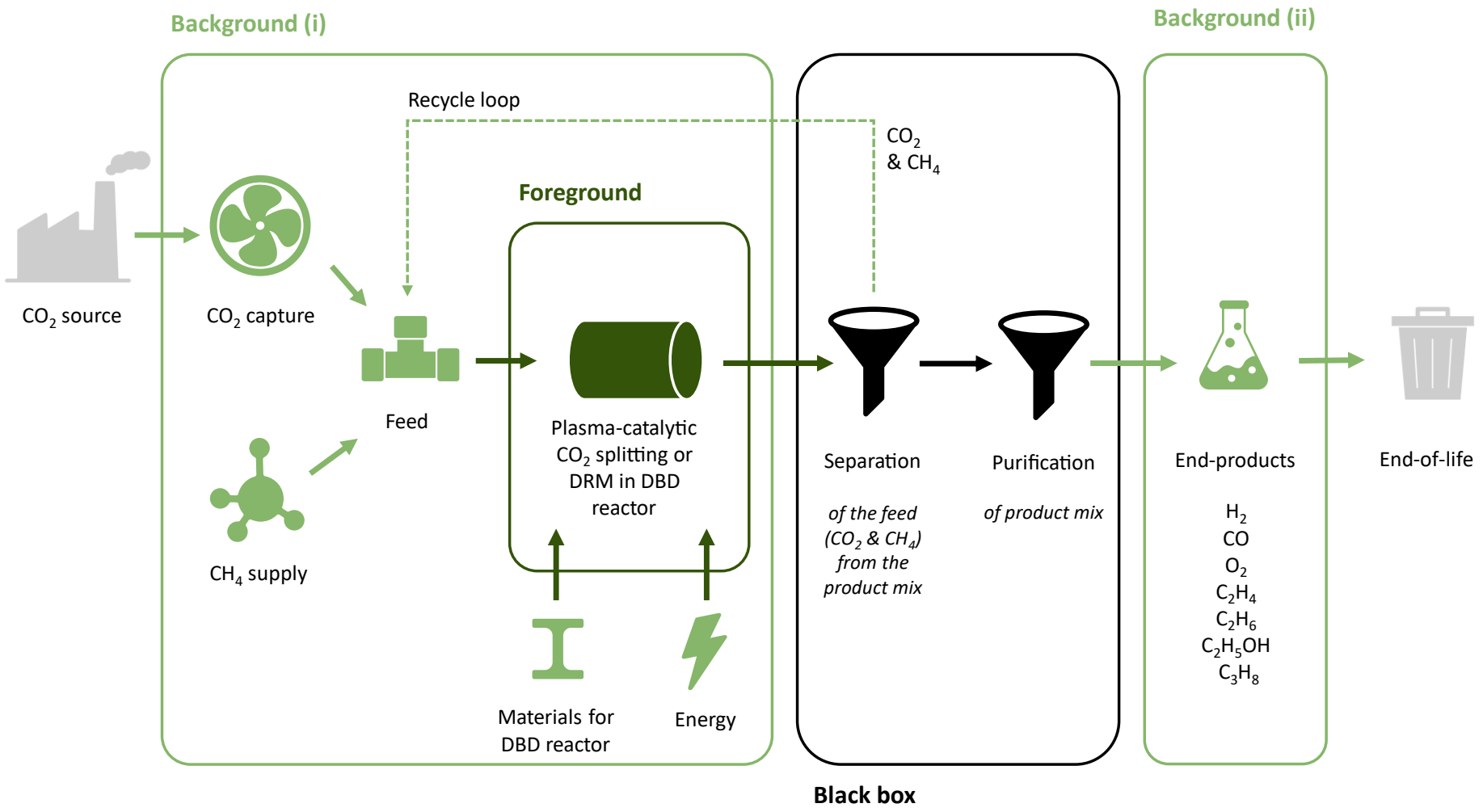


Figure 3.2: The system boundaries of the plasma-catalytic CCU value chain for the TEA. Four boxes are indicated in the value chain: background (i), foreground, black box (with the separation unit) and background (ii).

The CO_2 and CH_4 are converted into other components, resulting in a product mix that leaves the DBD reactor. This product mix contains CO_2, CH_4, H_2, CO, O_2, C_2H_4,C_2H_6, C_2H_5OH, and C_3H_8 (Table 3.4). The feed components CO_2 and CH_4 are separated from the end-products, to be recycled and looped back to the DBD reactor. Next, the product mix is purified to get the end-products that can be sold for consumption. The final step is the end-of-life treatment of these end-products.

The system boundaries of the TEA include all stages from the capture of CO_2 and supply of CH_4 until the separated end-products. The CO_2 source and the end-of-life treatment lie outside the scope of this TEA. As illustrated in **Figure 3.2**, the value chain is further divided into a foreground system, a background system, and a black box. The foreground system typically only includes those processes that can be manipulated by the decision-maker for whom the study is performed, whereas the background system covers the remaining processes that can not or only indirectly be influenced by the decision-maker (Frischknecht, 1998). In **Figure 3.2**, the foreground system is drawn such that it only includes the plasma-catalytic CO_2 splitting and DRM reaction in the DBD reactor, for which technical data is directly available from the experiments. The background system includes the capture of CO_2, the supply of CH_4, the materials for the DBD reactor, the energy supply and the end-products.

As can be seen in **Figure 3.2**, the separation and purification of the product mix are treated as a black box. New, innovative separation technologies need to be developed to separate the CO_2 and CH_4 from the rest of the product mix and to further purify the end-products as desired. Hence, it is yet unknown which technology will be used for the separation and purification, and consequently, estimating the costs for the separation and purification would come with high levels of uncertainty. To deal with this unknown step in the CCU value chain, the separation is treated as a black box: we make an abstraction of how these processes will occur and make assumptions about the separation rate to calculate the ins and outflows of the black box. The black box procedure allows us to calculate the costs of all other processes in the value chain and enables us to calculate what the maximum acceptable cost for separation and purification would be within this CCU value chain.

3.2.2 Inventory

The second step of the TEA is the creation of the data inventory, including both the technical and economic data.

Technical data

The CCU value chain with the plasma-catalytic CO_2 splitting or DRM reaction was already presented in **Figure 3.2**, and was divided into a foreground system, a background system and a black box.

The foreground system included the plasma-catalytic conversion of CO_2 and CH_4 in the DBD reactor. For the plasma-catalytic reactions in the DBD reactor, data is gathered directly from the experimental work done at the LADCA and PLASMANT research groups of the University of Antwerp. Three different series of experiments were performed to explore the conversion of CO_2 and CH_4 in a micro DBD reactor. The first group of experiments studied the effect of the discharge gap size on the performance of the micro DBD reactor (Uytdenhouwen et al., 2018). Afterwards, the influence of process parameters and different types of packing material was studied (Uytdenhouwen et al., 2019). Lastly, the third round of experiments was performed to unravel the kinetics and equilibria of plasma-based reactions, and in particular of DRM reactions (Uytdenhouwen et al., 2021). In this paper, the data from the last round of experiments with the micro-gap reactor is analysed in more detail.

Figure 3.3 shows the cylindrical configuration of the DBD reactor in the experimental setup from (Uytdenhouwen et al., 2021), in the laboratory (a) and frontal view (b).

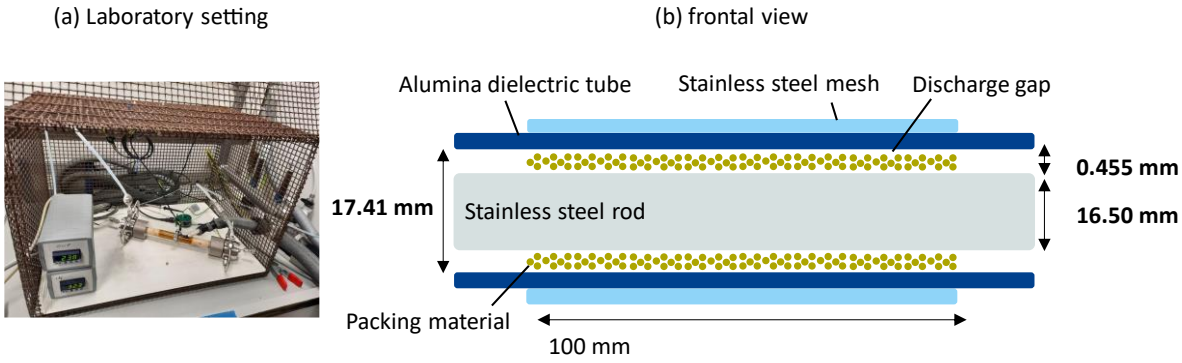


Figure 3.3: Cylindrical configuration of the DBD reactor in the experimental setup, (a) in the laboratory, and (b) frontal view.

The DBD reactor is made of an alumina dielectric tube, with an inner diameter of 17.41 mm. In the center of the alumina tube, a stainless-steel rod is placed to act as the inner (grounded) electrode, with an outer diameter of 16.50 mm. This results in a discharge gap between the stainless-steel rod and the dielectric barrier of 0.455 mm. Because of this small gap size, this DBD reactor is also referred to as a 'micro DBD reactor'. The alumina tube is wrapped with a stainless-steel mesh, to act as the outer (high-voltage) electrode, over a length of 100 mm. The empty volume – this is the volume in the reactor where the gas can flow when no packing material is introduced yet – is 2.42 cm^3. When the packing material is inserted in the discharge gap of the DBD reactor, the volume in which the gas can flow and interact with the plasma is reduced. This is called the discharge or reaction volume. A packing efficiency of 49.51% was estimated (Uytdenhouwen et al., 2019), resulting in a packed volume of 1.20 cm^3 and an unpacked reaction volume of 1.22 cm^3.

In this *reactor configuration*, either no packing material or a silicon dioxide (SiO_2) packing material was tested. For the unpacked *reactor configuration*, the reaction volume still equals 2.42 cm^3. For the SiO_2-packed reactor configuration, the reaction volume is reduced to 1.22 cm^3. By testing both the empty and packed *reactor configuration*, the effect of the SiO_2 packing on the reaction can be evaluated as well. The SiO_2 packing was chosen for the experiments by Uytdenhouwen et al. (2021) because of its inert nature. SiO_2 is a substance that is not chemically reactive, which allowed the researchers to minimize any additional effects, such as catalytic effects, that the packing could have on the performance of the DBD reactor itself. In other words, the experimental work of Uytdenhouwen et al. (2021) did not intend to focus on plasma-catalytic reactions, but rather on the pure kinetics of the DRM reaction in the DBD reactor, and how the kinetics change when the *reactor configuration* (e.g. packing or no packing) or *process parameters* (e.g. the space time) change. Nevertheless, their experimental work was chosen as dataset for this TEA, because of its completeness. The experimental dataset included data on the reaction conditions, the CO_2 and CH_4 conversion efficiencies, the energy consumption and concentrations of the different components at the outlet of the DBD reactor.

The set of *process parameters* are the feed ratio, the flow rate, and the plasma power. Two different types of feed are analyzed in this TEA: pure CO_2 and the mixture of CO_2 and CH_4, in a molar ratio of one-to-one (CO_2:CH_4 1:1). The flow rate is adjusted to manipulate the space time: lower flow rates mean longer space times, and vice versa, higher flow rates translate into shorter space times. The space time, i.e. the amount of time the gas spends in the reactor, varies between 2.50 and 72.71 s. The plasma power is the same for all tested combinations (30 W).

These combinations of *reactor configuration* and *process parameters* result in a dataset of 35 data points, as presented in **Table 3.2**.

Table 3.2: The tested combinations from the experimental work of Uytdenhouwen et al. (2021) that are analysed in this TEA.

Packing material	Feed	Space time (s)	FR (mL/min)	Plasma power (W)	CO_2 conv. (%)	CH_4 conv. (%)	SEI (kJ/L)
Empty	CO_2	2.91	50.00	29.61	13.41		35.54
Empty	CO_2	3.64	40.00	29.06	16.43		43.59
Empty	CO_2	4.85	30.00	29.35	21.54		58.70
Empty	CO_2	7.50	19.35	29.06	29.84		90.11
Empty	CO_2	14.54	10.00	28.71	39.34		172.26
Empty	CO_2	19.39	7.50	29.98	47.84		239.81
Empty	CO_2	28.90	5.03	29.76	50.72		354.94
Empty	CO_2	41.55	3.50	30.53	53.14		523.37
Empty	CO_2	48.47	3.00	30.15	54.52		602.95
Empty	CO_2	58.17	2.50	30.31	54.36		727.37
Empty	CO_2	72.71	2.00	30.11	53.50		903.42
Empty	CO_2:CH_4 1:1	2.91	50.00	30.00	17.30	17.30	62.37
Empty	CO_2:CH_4 1:1	10.00	14.54	30.00	40.25	40.25	249.05
Empty	CO_2:CH_4 1:1	17.50	8.31	30.00	54.24	54.24	435.50
Empty	CO_2:CH_4 1:1	25.00	5.82	30.00	60.72	60.72	623.83
Empty	CO_2:CH_4 1:1	32.50	4.47	30.00	66.66	66.66	807.03
Empty	CO_2:CH_4 1:1	40.00	3.64	30.00	66.88	66.88	998.39
Empty	CO_2:CH_4 1:1	55.00	2.64	30.00	71.16	71.16	1178.96
Empty	CO_2:CH_4 1:1	70.00	2.08	30.00	72.15	72.15	1374.33
SiO_2	CO_2	2.55	28.79	29.93	15.16		1742.14
SiO_2	CO_2	10.20	7.20	29.88	42.42		36.00
SiO_2	CO_2	17.85	4.11	29.85	57.39		123.78
SiO_2	CO_2	25.50	2.88	29.93	64.18		216.63
SiO_2	CO_2	33.15	2.22	29.79	67.09		309.44
SiO_2	CO_2	40.79	1.80	29.95	68.95		402.32
SiO_2	CO_2	48.46	1.52	29.77	70.46		495.19
SiO_2	CO_2	56.09	1.31	29.98	74.01		680.79
SiO_2	CO_2	71.42	1.03	29.85	72.57		36.00
SiO_2	CO_2:CH_4 1:1	2.50	29.37	30.00	19.90	23.37	123.78
SiO_2	CO_2:CH_4 1:1	10.00	7.34	30.00	59.46	64.87	216.63
SiO_2	CO_2:CH_4 1:1	17.50	4.20	30.00	73.21	76.78	309.44
SiO_2	CO_2:CH_4 1:1	25.00	2.94	30.00	79.21	81.47	402.32
SiO_2	CO_2:CH_4 1:1	32.49	2.26	30.00	81.92	83.52	495.19
SiO_2	CO_2:CH_4 1:1	39.99	1.84	30.00	83.40	84.71	680.79
SiO_2	CO_2:CH_4 1:1	55.00	1.34	30.00	85.35	84.78	866.63

CO_2 conv., CO_2 conversion; CH_4 conv., CH_4 conversion; FR, flow rate. Note that no data points are available for the SiO_2-packed reactor with CO_2 & CH_4 after a space time of 55 s. The packing material reduces the available volume, which implies that lower flow rates are needed to reach the same space time as in the unpacked reactor. The technical lower limit of the measurement equipment (i.e. 0.65 mL/min) prevented measurements at 70 s for the SiO_2-packed reactor with CO_2 and CH_4.

The experiments were performed at the lab scale, in a DBD reactor with low flow rates from 1 to 50 mL/min (i.e. 0.002 – 0.05 m³/h) to show how each reactor configuration translates into different CO_2 conversion rates, energy efficiency levels and product concentrations (Uytdenhouwen et al., 2021). However, these small flow rates are not relevant at an industrial scale. To assess the techno-economic feasibility, higher production capacities must be analysed. One of the main advantages of the DBD reactor is that it can easily be scaled by numbering up multiple tubes in parallel, in a honeycomb structure (S. Li et al., 2020). Assadi et al. (2016) tested lab- and pilot reactor scales for NTP and demonstrated the continuity in terms of removal capacity, by-product formation and ozone production. Hence, the use of experimental data at the lab scale for the design of the reactor at an industrial scale is justified.

Industrial applications of DBD reactors can be found today in ozone generators, featuring several hundred tubes of 1 to 3 meters to reach a production capacity of 100 kg/h (Kogelschatz, 2003). DBD reactors are also increasingly being applied for air pollution control (S. Li et al., 2020). Pilot experiments for the removal of VOCs with DBD reactors have been performed, with flow rates ranging from 5 m³/h (Schmidt, Jõgi, Holub, & Brandenburg, 2015) to 100 m³/h (Liang et al., 2015) or even 50,000 m³/h (Martini et al., 2019). In this Chapter, the total flow rate in the CCU pilot plant is set at 100 m³/h, which is reached by (1) increasing the length of one DBD tube from 10 cm to 1 m and (2) arranging several DBD tubes in parallel. The required number of DBD tubes to reach 100 m³/h depends on the space time of the gas: the longer the gas is in the DBD reactor, the lower the flow rate in one tube is, and hence, the more tubes are needed to reach a total flow rate (Q_{pilot}) of 100 m³/h.

The performance of the plasma DBD reactor is characterized by two important technical parameters: (1) the CO_2 conversion and (2) the energy consumption of the DBD reactor. The conversion rates should in theory be as high as possible, while the energy consumption should be kept as low as possible. The CO_2 conversion measures how much of the CO_2 is converted in the reactor, relative to the original feed of CO_2†:

$$X_{CO_2}(\%) = \frac{CO_{2,in} - CO_{2,out}}{CO_{2,in}}, \tag{3.1}$$

The energy consumption measures how much kJ of energy is needed to produce one mole of product mix (kJ/mol converted):

$$Energy\ consumption\ \left(\frac{kJ}{mole}\right) = \frac{SEI\ \left(\frac{kJ}{L}\right) * V_m\left(24.45\frac{L}{mol}\right)}{X_{total}\ (\%)}, \tag{3.2}$$

with SEI the Specific Energy Input based on the ratio of the source power and the flow rate, X_{total} the total conversion rate of CO_2 and CH_4 and V_m the molar volume (24.45 L/mol) (Snoeckx & Bogaerts, 2017a). SEI is the total energy input per litre of gas that enters the DBD reactor and is a determining factor for the conversion rate and energy efficiency.

While scaling the data from the laboratory scale to a pilot scale with a flow rate of 100 m³/h, we want to maintain the performance of the plasma in the DBD reactor. In other words, the conversion rate (3.1) and energy consumption (3.2) that were measured for the DBD reactor in the laboratory are also adopted for the pilot-sized DBD reactor. To be able to assume this, two conditions need to be met: the space time of the gas in one DBD tube and the SEI need to be on the same level in the pilot-size DBD reactor as the lab-scale DBD reactor. These parameters are defined by equations (3.3) and (3.4):

$$space\ time\ (s) = \frac{reaction\ volume\ 1\ tube\ (mL)}{Q_{1\ tube}\ (\frac{mL}{min})} * 60\ (\frac{s}{min}), \tag{3.3}$$

$$SEI\ \left(\frac{kJ}{L}\right) = \frac{plasma\ power\ (W)}{Q\ (m\,L/m\,in)} * 60\ (s/min). \tag{3.4}$$

The space time is defined by the ratio of the reaction volume and the flow rate in one tube ($Q_{1\ tube}$). The reaction volume increases linearly with the length of the tube, which is increased from 10 cm (lab scale) to 100 cm (pilot plant). Hence, to keep the space time of the gas in one tube constant, the flow rate in one tube should be increased tenfold as well. The flow rates can be calculated by transforming equation (3.3), which reveals that the flow rate is directly proportional to the reaction volume.

Equation (3.4) defines the SEI as the plasma power divided by the total flow rate in the DBD reactor (Q), i.e. the accumulated flow rate over all tubes, which is 100 m³/h. To preserve the original SEI level while scaling up, the power supplied to the reactor needs to be adjusted similarly. Due to losses in the reactor, only part of the power that is supplied to the reactor will effectively run through the plasma, causing a discrepancy between the so-called source power and plasma power. The SEI is generally based on the plasma power, i.e. the power absorbed by the plasma electrons, while the source power is the actual power applied to the reactor. The power source efficiency was approximately 50% for the experiments in the micro-gap DBD reactor, meaning that only 50% of the source power is effectively absorbed by the plasma (Uytdenhouwen et al., 2021). In (3.2), the SEI needed for the energy consumption was calculated based on the source power. From the SEI (3.4), the plasma power can be derived that is needed to maintain the same level of SEI at the higher overall flow rate of 100 m³/h.

Finally, the number of tubes required in the pilot plant is calculated by dividing the overall flow rate (100 m³/h) in the pilot plant by the flow rate in one tube:

$$Number\ of\ tubes = \frac{Q(\frac{m^3}{h})}{Q_{1\ tube}\ (\frac{m^3}{h})}. \tag{3.5}$$

In this study, two types of pilot plant arrangements A and B will be compared. The scale-up from lab to pilot A was explained above. In sum, pilot A assembles thousands of tubes in one plasma reactor to reach the incoming capacity of 100 m³/h. The number of tubes needed to reach the capacity of 100 m³/h is calculated in (3.5). Depending on the reactor configuration, the required number of tubes and the power supply requirements for pilot A will differ. Based on expert insights from the industry, an alternative pilot installation B with a fixed power supply of 144 kW (12x12 kW) is investigated as well. Pilot installation B consists of 12 individual DBD reactors, each supplied with a power supply of 12 kW. To maintain the same level of SEI in one tube, the number of tubes in one DBD reactor should be equal to 20 (12 000 W/600 W). Multiplying the number of tubes in one plasma reactor (i.e. 20) by the number of reactors (i.e. 12) gives a total of 240 tubes.

Table 3.3 summarizes the scale-up from 1 tube at lab scale to pilot B with 12 reactors. In sum, pilot plant A has a fixed flow rate of 100 m³/h and a varying number of tubes and power supply needs, while pilot plant B has a variable flow rate and a fixed number of tubes equal to 240 and a power supply of 144 kW. Based on these scale-up procedures and the experimental data, the mass and energy balances for pilot plants A and B are established. The CO_2 conversion (3.1) and energy consumption (3.2) are calculated for each configuration of pilot plants A and B.

Table 3.3: From 1 lab-scale tube to 12 x 20 tubes in pilot installation B.

	Power supply	Length	Number of tubes
1 lab-scale tube	60 W	10 cm	1
1 pilot-scale tube	600 W	100 cm	1
20 pilot-scale tubes in 1 pilot plasma reactor	12 kW	100 cm	20
12 pilot plasma reactors	144 kW	100 cm	12 x 20 = 240

The described scaling procedures are used to scale-up the data presented in **Table 3.2**, to provide the technical data for the foreground system (**Figure 3.2**).

The background system includes the capture of CO_2, supply of CH_4, the materials for the DBD reactor, the energy supply and the end-products (after separation and purification). For the CO_2 capture, we assume that the most mature CO_2 capture technology to date is deployed. Chemical absorption, with amine-based solvents such as monoethanolamine (MEA), is the most advanced capture technology and is already used in commercial capture facilities today (Chai, Ngu, & How, 2022; IEA, 2020a). For some of the tested combinations in **Table 3.2**, CH_4 needs to be supplied as well. CH_4 is also an important greenhouse gas that can be present in the flue gases from a specific point source. For reasons of simplification, the CH_4 supplied to the DBD reactor is assumed to be natural gas. The materials that are needed for the construction of the DBD reactor include alumina (for the dielectric tube) and stainless steel (for the inner and outer electrode). Electrical energy needs to be supplied to create the plasma inside the DBD reactor. The energy need of the plasma-catalytic DRM reaction in the DBD reactor is calculated based on the power that was supplied to the DBD reactor in the experiments in the laboratory. The energy consumption for the lab-scale DBD reactor is then scaled to the size of a pilot DBD reactor. Finally, the background system includes the end-products, that could be sold on the market. These are the products that are observed at the outlet of the DBD reactor, after the separation and purification (black box).

The mass and energy flows for the background system, i.e. the CO_2 capture, supply of CH_4, the construction of the DBD reactor, the energy supply and the end-products, are calculated for the 35 combinations, the material and energy flows in these processes are based on the performance of the DBD reactor in the foreground system. The mass and energy balances are presented in the Results.

The black box in **Figure 3.2** included the separation of the CO_2 & CH_4 feed from the product mix and the purification of the product mix. Due to the complexity of the product mix at the outlet of the DBD reactor, and the variety in the product mix between the tested combinations from **Table 3.2**, the type of separation technology that could be used is yet undetermined. Hence, the separation of the product mix is treated as a black box. Within this black box, we assume a separation rate of 90%, implying that 90% of the unconverted CO_2 and CH_4 can be separated from the product mix and that 90% of each product in the product mix can successfully be purified and sold.

Economic data

The price assumptions for several steps in the CCU value chain are discussed here. The cost estimation methodology is discussed in more detail in the next section.

For the capture of CO_2, cost estimates for chemical absorption using MEA solvents range from € 46 per tonne of CO_2 captured (Hassan, Douglas, & Croiset, 2007), to € 78.6 per tonne of CO_2 avoided (K. Li, Leigh, Feron, Yu, & Tade, 2016). In this TEA, we assume a cost of € 50 per tonne of CO_2 captured.

The CO_2 source is undefined in this TEA, but this type of CO_2 capture technology can be retrofitted to e.g. power plants or cement plants. For the supply of CH_4, the price of natural gas is included in the TEA, i.e. € 300 per tonne of CH_4 (Pasini et al., 2019). For the SiO_2 packing, a cost of € 90 per kg of SiO_2 is assumed (Deng & Adams Ii, 2020). The electricity needs of the DBD reactor are met by the Belgian electricity mix. An electricity price of 0.10 €/kWh is assumed in this study. This is based on discussions with experts from the energy industry in Belgium (Engie) and supported by the observed electricity prices for non-household consumers in Belgium, between 2018 and 2022, presented in **Figure 3.4**. The electricity price depends on the consumption band, where higher consumption band results in a lower electricity price. Based on the current energy consumption of the DBD reactor, the plant would be categorized in the highest consumption band (>150 000 MWh). However, energy consumption should (and is expected to) decrease before commercialization. Hence, the electricity prices for the consumption band 2,000 MWh and 19,999 MWh are shown here.

The end-products are listed in **Table 3.4**. The CO_2 splitting reactions in the DBD reactor result in a mix of CO_2, CO and O_2 that is produced. In the DRM reactions, when both CO_2 and CH_4 are fed to the reactor, more complex chemicals can be produced as well, such as hydrogen, ethene, ethane, propane and ethanol. The prices for these products are presented in **Table 3.4**, together with the annual production volumes (if data is available). The price data is corrected for inflation using the Harmonised Index of Consumer Prices (HICP) for the European Union (Eurostat, 2023c). To convert prices in US $ to €, an exchange rate of 0.91 €/$ was adopted.

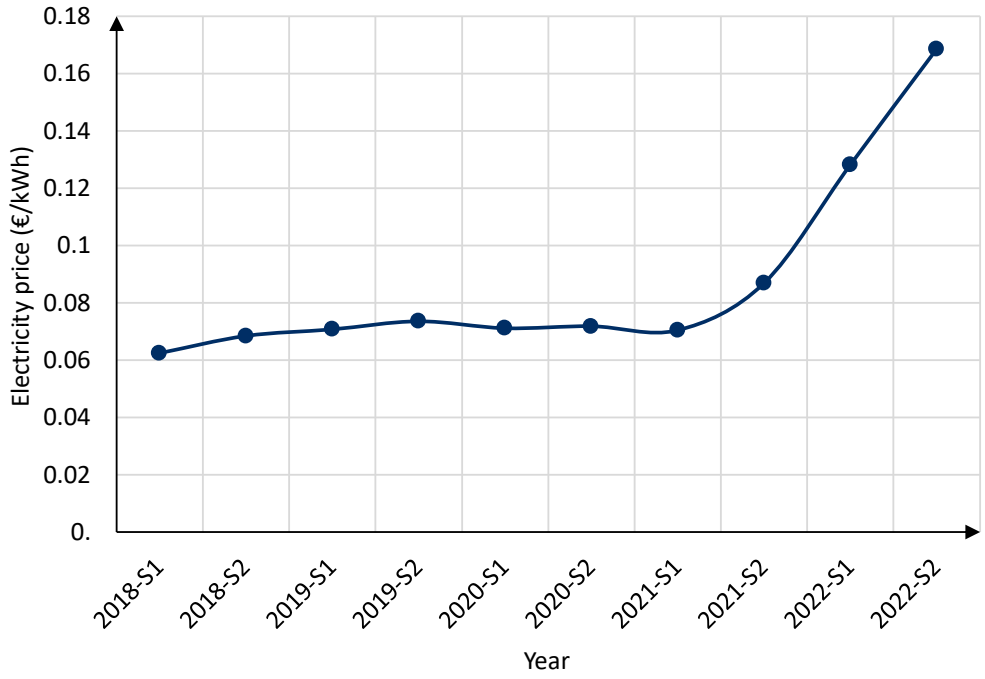


Figure 3.4: Electricity prices for non-household consumers in Belgium in the consumption band from 2,000 to 19,999 MWh, between 2018 and 2022. Data retrieved from (Eurostat, 2023b).

Table 3.4: Prices and production volumes of end-products.

Product	Price (€$_{2022}$/t)	Reference	Production (Mt/y)	Reference
Carbon monoxide (CO)	400	(Bushuyev et al., 2018; Lu & Jiao, 2016; van Rooij et al., 2017)[a]		
Oxygen (O_2)	65	(Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al., 2016)		
Hydrogen (H_2)	3960	(IEA, 2019a)		
Ethene (C_2H_4)	850	(CarbonNext, 2017; Pacheco, Bresciani, & Alves, 2021)[a]	24.5[b]	(CarbonNext, 2017)
Ethane (C_2H_6)	160[c]	(EIA, 2023b)		
Propane (C_3H_8)	150[d]	(EIA, 2023a)		
Ethanol (C_2H_5OH)	680	(CarbonNext, 2017; Pacheco et al., 2021)[a]	80.00[e]	(Chauvy et al., 2019)

[a] The average price was calculated from these references.

[b] Production and imports in EU 28.

[c] 64 $ cents per gallon.

[d] 6.9. $ per million BTU.

[e] Global production.

3.2.3 Economic analysis

The economic analysis evaluates the economic viability of the conversion of CO_2 and CH_4 in 35 different configurations of a pilot DBD reactor and helps to identify the main cost drivers. The technology's low maturity level implies high levels of uncertainty. Buchner et al. (2018) proposed in their work that the chosen profitability indicators should depend on the TRL. However, using different indicators at different TRLs hampers comparability and understandability across different studies and TRLs (Lamberts-Van Assche & Compernolle, 2021). Therefore, we choose to calculate the Net Present Value (NPV), despite the low TRL of the plasma catalysis. The NPV integrates both costs and revenues in one metric and evaluates the economic performance over the entire plant lifetime. Moreover, NPV is the most common indicator in CCU literature and is easy to interpret (Lamberts-Van Assche & Compernolle, 2021).

The NPV is the present value of the difference between the incoming and outgoing cash flows over the lifetime of the project:

$$NPV = \sum_{n=0}^{t} \frac{CF_n}{(1+i)^n} = \sum_{n=0}^{t} \frac{Revenues_n - OPEX_n - CAPEX_n}{(1+i)^n}. \quad (3.6)$$

To calculate the NPV, yearly cash flows are calculated. The Operational Expenditures (OPEX) and CAPEX constitute the negative cashflows, while the revenues create positive cashflows.

The CAPEX represent the investments that are needed to operate the DBD reactor. Two major installations are needed: the DBD reactor itself, and the high-voltage power supply.

The cost for the lab-scale DBD tube, which was custom-made, amounted to € 1,500 for one tube. Under the assumption that this cost will be lower once the technology is more mature and the tubes are made in batches, we adopted a cost of € 1,000 per tube. The six-tenth rule is then applied to

calculate the cost for the whole DBD reactor. This rule has been used before in cost estimations for plasma reactors (Delikonstantis, Scapinello, & Stefanidis, 2017; Martini et al., 2019).

The cost for the high-voltage generator is based on price estimations from a company specialising in plasma reactors. The price estimations depend on the power requirements. A curve is fitted to these price estimations, resulting in a cost function for the high-voltage generator as a function of the required kW, presented in **Table A.3.1** and **Figure A.3.1** in Appendix 3.A. The cost for the high-voltage power supply for different set-ups of pilot plant A is calculated using this function. For pilot plant B, the price estimation for a 12x12 kW installation was obtained. **Table 3.5** summarizes the estimation of the CAPEX, as the sum of the capital costs for the power supply and the plasma reactor. For pilot plant A, the CAPEX is different for each tested combination in **Table 3.2**, depending on the flow rate and SEI.

The OPEX are the yearly costs incurred for the operation of the plant. The OPEX can be split into Fixed Costs of Production (FCOP), which are costs incurred independent of the plant's output, and Variable Costs of Production (VCOP), which depend on the production rate. To estimate the OPEX, the cost estimation methodology of Towler and Sinnott (2013a) is largely followed. In this methodology, several components of the OPEX are calculated as a fraction of the Inside Battery Limits (ISBL) and Outside Battery Limits (OSBL), which are components of the CAPEX. The assumptions made for the calculation of ISBL and OSBL are presented in **Table A.3.2**, in Appendix 3.A. The FCOP include the costs for labour, maintenance, land, property taxes, insurance and corporate overhead charges. The VCOP comprise the costs for raw materials (CO_2 and CH_4), consumables (SiO_2 packing) and electricity. The cost estimation methodology for the OPEX is shown in **Table 3.6**, with a brief clarification of the assumptions that are made.

Finally, the revenues are obtained by selling all products that are produced at the outlet of the DBD reactor. The products and their prices were previously listed in **Table 3.4**.

The NPV can now be calculated using equation (3.6). The plant is assumed to operate for 20 years, with a running time of 8000 hours annually. The discount rate i is assumed to be 12%. Other economic assessments for CCU technologies generally assumed slightly lower discount rates, e.g. 8% (Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al., 2016; Pérez-Fortes, Schöneberger, Boulamanti, & Tzimas, 2016), 8.1% (Montiel-Bohórquez, Saldarriaga-Loaiza, & Pérez, 2021) and 7.5% (Fernández-Dacosta, Stojcheva, & Ramirez, 2018). However, Van Dael et al. (2015) advised to adopt a discount rate of 15 – 20% for R&D projects. Because of the R&D nature of the investigated technology in this TEA, a discount rate was chosen between the values of 8 and 15%. The construction of the DBD reactor is assumed to take place in the first 3 years, with 35% of the CAPEX incurred in year 0, 50% in year 1 and the remaining 15% in year 2. The annual depreciation was calculated using a linear depreciation method, assuming a depreciation rate of 10%, and starting in year 2. The tax rate in Belgium was assumed to be 25% (Loyens & Loeff, 2018). Finally, the prices were all estimated for the reference year 2022, and assumed to be constant for the next 20 years.

Table 3.5: CAPEX breakdown and assumed parameters. (A) refers to the pilot reactor with Q = 100 m^3/h and (B) refers to the pilot reactor with a fixed power supply of 144 kW.

	(A)	**(B)**	**Reference**
DBD reactor (1)	€ 1,000/tube [# tubes] * $1000^{0.6}$	€ 1,000/tube 240 * $1000^{0.6}$	Cost on lab scale (Delikonstantis et al., 2017; Martini et al., 2019)
Power supply (2)	1500 * [#kW] + 900	€ 173,000	Industry
CAPEX	(1) + (2)	€ 188,142.98	

Table 3.6: Cost estimation methodology for the OPEX, based on Towler and Sinnott (2013a).

OPEX	Cost components	Assumptions	Note
FCOP	Labour costs		
	Operating labor	2 shift positions, 3 operators per shift position	The rule of thumb is to have 3 shift positions in one plant, with 4.8 operators per shift position (to allow for weekends and holidays) (Towler & Sinnott, 2013a). Lower values were assumed here, because of the pilot scale of the DBD reactor.
		€101,900 €/yr 1 FTE	The labour cost for 1 FTE in the manufacturing of chemicals and chemical products, in Belgium, in 2018. Data provided by (Eurostat, 2023a)
	Supervision	10% of operating labour	Supervision is usually taken as 25% of operating labour (Towler & Sinnott, 2013a). However, the required level of supervision depends on the size of the plant. Because of the limited scale of the investigated DBD reactor, a lower value was chosen.
	Direct salary overhead costs	45% of operating labour and supervision	Typically 40 to 60% of operating labor plus supervision (Towler & Sinnott, 2013a). Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al. (2016) assumed a value of 45%.
	Maintenance	3% of ISBL	Typically 3 to 5% of ISBL (Towler & Sinnott, 2013a). Maintenance was calculated as 3% of ISBL by Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al. (2016).
	Land	1% of ISBL + OSBL	Typically 1 to 2% of ISBL and OSBL (Towler & Sinnott, 2013a).
	Property taxes	1% of ISBL	Typically 1 to 2% of ISBL (Towler & Sinnott, 2013a).
	Insurance	1% of ISBL	Typically 1 to 2% of ISBL (Towler & Sinnott, 2013a).
	Corporate overhead charges	General costs are 30% of labour; R&D is 5% of revenues	Nyári et al. (2020) estimate the general overhead cost as 30% of the labour cost. R&D can be less than 1% of revenues e.g. in petrochemical sector, to more than 15% of revenues for pharmaceutical companies (Towler & Sinnott, 2013a).
VCOP	Raw materials	50 €/t CO_2	Based on the cost of 46 €/t CO_2 captured that was estimated by Hasan, Baliban, Elia, and Floudas (2012) for CO_2 capture using chemical absorption.
		300 €/t CH_4	Pasini et al. (2019) adopt a natural gas of 0.29 $/kg, which is converted from US $ to € using an exchange rate of 0.91 €/$ and corrected for inflation using the HICP.
	Consumables	Packing material SiO_2: 100 €/kg	The price for industrial-grade SiO_2 is in the range of 1 – 100 $ per kg (Deng & Adams Ii, 2020). The upper value was selected as a conservative estimate, converted to € and corrected for inflation.
		Lifetime packing material: 8000 hours	Wiesberg et al. (2016) assume that the catalyst in their process is replaced after one year of operation, equivalent to 8000 hours of operation in this study.
	Utilities	Electricity: 0.10 €/kWh	Price for non-household consumers, in consumption band between 2,000 MWh and 19,999 MWh (Eurostat, 2023b).

Table 3.7 summarizes these assumptions for the calculation of the NPV.

Table 3.7: Economic assumptions for the calculation of the NPV in (3.6).

	Assumption	**Reference**
Plant location	Belgium	
Plant lifetime	20 years	
Load factor	8000 h/yr	(Wiesberg et al., 2016)
Discount rate	12%	
Construction period	Year 0, 1 and 2	
Depreciation	10% (linear depreciation, starting from year 2)	(Wiesberg et al., 2016)
Tax rate	25%	(Loyens & Loeff, 2018)
Prices	Time-invariant; constant currency	

3.2.4 Interpretation

The interpretation is the fourth and final phase of a TEA, following the guidelines of Zimmermann et al. (2020). In Chapter 2, the tutorial review of economic assessments on CCU technologies, it was highlighted that the analysis performed should be in line with the goal of the TEA.

The main goal of the TEA is to assess how the chosen *reactor configuration* and *process parameters* affect the economic viability of the technology and to select the most promising combination in economic terms. This is achieved by translating the technical performance from the laboratory in this TEA.

In addition, the TEA should identify which processes in the CCU value chain contribute the most to the costs. To this end, a local or one-at-a-time (OAT) sensitivity analysis is performed. In Chapter 2, the lack of the inclusion of the technical parameters in the sensitivity analysis was hackled. In this TEA, the variation in technical parameters is already present in the extensive dataset of experiments, for which economic parameters are calculated now. In addition, two technical parameters are included in the sensitivity analysis. The effect of a 20% increase and a 20% reduction in the SEI and the power source efficiency are investigated. The SEI describes the energy need of the reactor and should be as low as possible. The power source efficiency describes how much of the source power is effectively absorbed by the plasma, that is how much of the source power is translated into plasma power. The plasma power is always kept at 30 W, so a higher power source efficiency would mean that less source power needs to be supplied to the reactor to effectively reach a plasma power of 30 W. With the current equipment, the power source efficiency varied around 50% in the experiment.

Four other market-based parameters are varied as well: the electricity price, the product prices, the capital cost for the high-voltage power supply (per kW) and the cost for CO_2 capture. This will allow us to identify which of these variables currently affect the NPV the most. The values of the market parameters for the sensitivity analysis are listed in **Table 3.8**. These variations to these technical and market parameters are investigated for the combinations of the DBD reactor configuration with SiO_2 as packing material and the CO_2 and CH_4 feed. The sensitivity analysis is performed for the 7 combinations with the SiO_2-packed *reactor configuration* and the CO_2 & CH_4 feed (**Table 3.2**).

Finally, another objective of the TEA was to identify which technological improvements would be needed to make the technology economically feasible in the future. For this purpose, a scenario analysis is performed. These scenarios include step-wise improvements in the technology and changes in the market conditions, that would be needed to achieve an economically feasible set-up.

Linked to this, the TEA should also help identify the type of chemicals that should be targeted in the DBD reactor. The Minimum Selling Price (MSP) is calculated to this end. The MSP is the price that should be received on average for the product mix to reach an NPV that equals zero.

Table 3.8: Parameter values in the sensitivity analysis.

	-20%	**Base case**	**+20%**
Electricity price (€/kWh)	0.08	0.10	1.2
Capital cost (€/kW)	1200	1500	1800
CO_2 capture cost (€/t CO_2)	40	50	60

3.3 Results

The results of the TEA are now presented. First, the technical performance of the tested combinations from **Table 3.2** is discussed. The results of the economic analysis are then presented. Finally, the results are interpreted, through a local sensitivity analysis and a scenario analysis.

3.3.1 Inventory (technical data)

Figure 3.5 presents the CO_2 conversion (a) and energy consumption in MJ per mole converted (b), for the 35 tested combinations presented in **Table 3.2**. As shown in **Figure 3.5** (a), the CO_2 conversion increases at first when the space time increases, but once the space time exceeds 20 s, the CO_2 conversion curve starts to flatten. **Figure 3.5** (a) also shows that the CO_2 conversion is higher for the SiO_2-packed reactor (triangular marks) than for the empty reactor (square marks). The conversion rate also increases by adding CH_4 to the feed (dashed lines). The highest conversion rate is reached for the SiO_2-packed reactor supplied with CO_2 and CH_4.

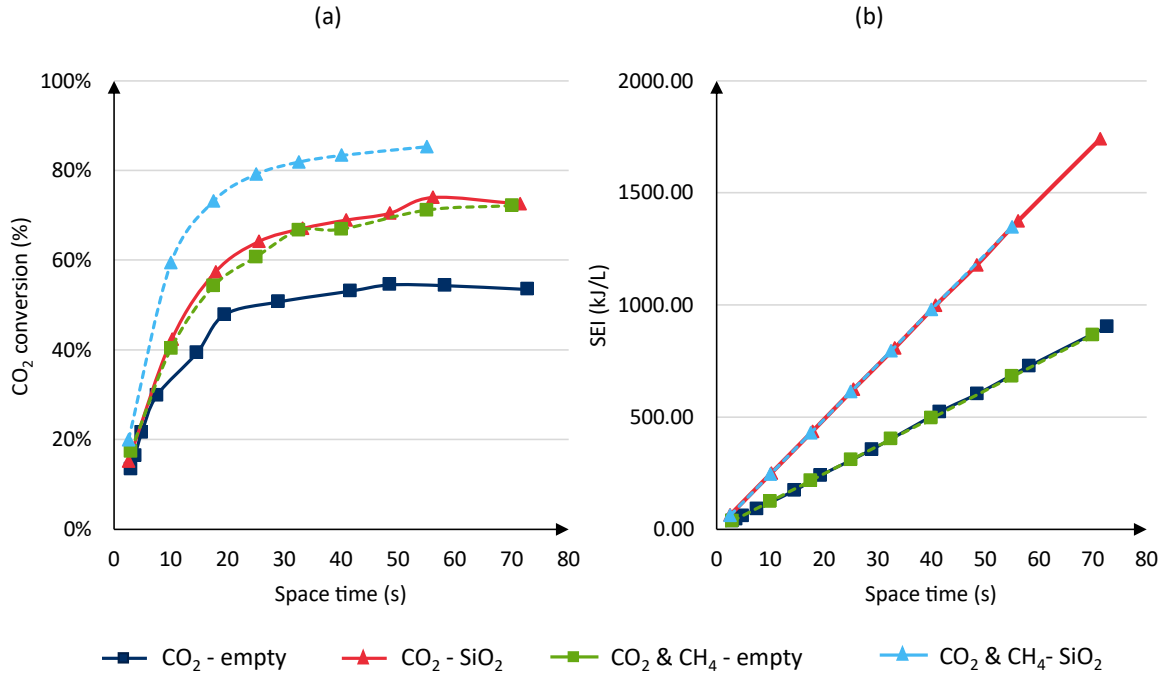


Figure 3.5: (a) CO_2 conversion (%) and (b) SEI (kJ/L) plotted as a function of space time, for the tested combinations with pure CO_2 and no packing (square), pure CO_2 and SiO_2-packing (triangle), CO_2 and CH_4 and no packing (square, dashed line) and CO_2 and CH_4 and SiO_2-packing (triangle, dashed line). Data from Uytdenhouwen et al. (2021).

Figure 3.5 (b) shows that the energy consumption increases linearly with longer space times. Here, the packing material has a detrimental effect: the highest energy consumption is observed for the packed reactor. Adding CH_4 to the feed (dashed lines) lowers the energy consumption, compared to the pure CO_2 feed (solid line). Hence, the lowest energy consumption is observed for the unpacked reactor that is supplied with a mix of CO_2 and CH_4. **Figure 3.5** is the same for pilot plants A and B.

The detrimental effect of the packing material on the SEI can be attributed to the reduction in the available reaction volume where the gas can flow when the packing material is introduced. Adding packing material to the reactor, with a packing efficiency of 49.51%, reduces the reaction volume in the DBD reactor by half. Hence, the flow rate in the packed reactor will only be half of the flow rate in the unpacked reactor at the same space time (3.3). These lower flow rates increase the SEI (3.4), at the same plasma power. From **Figure 3.5**, it can indeed be seen that the SEI in the SiO_2-packed reactor is almost double the SEI in the unpacked reactor at the same space time.

Table 3.9 presents the mass and energy balances for 4 combinations from **Table 3.2**: the unpacked reactor fed with pure CO_2 (CO_2-empty), the unpacked reactor fed with the mix of CO_2 and CH_4 (CO_2 & CH_4-empty), the SiO_2-packed reactor fed with pure CO_2 (CO_2-SiO_2) and the SiO_2-packed reactor fed with CO_2 and CH_4 (CO_2 & CH_4-SiO_2).

Table 3.9 only shows the specific mass and energy balances for four rows of **Table 3.2**. In total, however, 35 different combinations were analyzed in this TEA, resulting in 35 different balances. The total flow rate at the inlet of the DBD reactor, however, is fixed at 100 m^3/h for all combinations (in the pilot plant A setup). Hence, the feed to the DBD reactor in tonnes per year is the same for all combinations: 1,440 t CO_2 (CO_2 splitting) or 720 t CO_2 and 262.41 t CH_4 (DRM).

Table 3.9: Mass and energy balances for 4 tested combinations of *reactor configuration* and *process parameters*, in pilot plant A arrangement.

Feed	**CO_2**	**CO_2**	**CO_2 & CH_4**	**CO_2 & CH_4**
Packing material	-	SiO_2	-	SiO_2
Space time	19.39 s	17.85 s	17.50 s	17.50 s
Feed (t/yr)				
CO_2	1,440.00	1,440.00	720.00	720.00
CH_4			262.41	262.41
Products (t/yr)				
CO	394.60	473.44	244.15	321.69
O_2	225.40	270.44	0.07	0.16
H_2			16.68	20.12
C_2H_4			0.80	0.91
C_2H_6			16.82	10.80
C_3H_8			5.32	2.47
C_2H_5OH			0.41	0.25
Recycle loop (t/yr)				
CO_2	676.00	552.07	300.67	172.37
CH_4			86.91	53.85
Energy				
Electricity (GWh)	106.58	193.56	98.59	196.83

To put these numbers into perspective, these amounts can be compared to the amount of CO_2 emissions that are emitted globally, regionally, or from a particular industry. In 2021, global CO_2 emissions from energy combustion and industrial processes amounted to 37.12 Gt. The EU-27 countries were responsible for 2.79 Gt of these emissions in 2021. These quantities are of course a multiple of the CO_2 emissions that are fed to the DBD reactor. For the capture of CO_2, the study of Hassan et al. (2007) was consulted to estimate the capture costs. In this study, the CO_2 is captured from a cement plant using chemical absorption with MEA. This cement plant emits almost 100,000 tonnes of CO_2 per year, which is still about a hundred times more than the feed of CO_2 to the DBD reactor. Moreover, the feed of CO_2 is not equal to the amount of CO_2 that is utilized. Part of the supplied CO_2 is not converted and recycled to run through the DBD reactor again. Hence, the amount of CO_2 that is effectively utilized in this process is the CO_2 feed reduced by the amount of CO_2 recycled, e.g. 764 tonnes of CO_2 are utilized in the first combination of **Table 3.9**.[6]

While the DBD reactor in this TEA is still on a pilot scale and would probably be scaled to a larger size for commercialization, it is not likely to be sized up at such a scale that all CO_2 emissions of this cement plant could be used. The amount of CO_2 that can be utilized is limited – either due to market constraints or to the limited availability of raw materials. Hence, CCU technologies are not expected to take up the lion's share of global CO_2 emissions. Estimates for the amount of CO_2 that could be utilized in CCU routes for chemicals vary from 180 Mt (Bruhn et al., 2016) to 700 Mt (Mac Dowell et al., 2017), representing 0.5% to 1.9% of total CO_2 emissions in 2021.

The other flows that are presented in **Table 3.9**, such as the amount of the products and the energy consumption, are different for each combination, depending on the CO_2 conversion rate and energy efficiency that was measured during the experiments. The outgoing flow, i.e. the production rate, varied for the different reactor configurations, depending on the conversion rate and selectivity of the process. The production rate varied from +/- 100 tonnes per year for lower conversion rates to +/- 700 tonnes per year at higher conversion rates.

3.3.2 Economic analysis

The NPV is calculated from the OPEX, CAPEX and revenues over the plant's lifetime. To understand how the NPV is built up, the CAPEX, OPEX and revenues are presented separately first.

Figure 3.6 presents the OPEX and CAPEX for the 35 combinations of the DBD *reactor configuration* and *process parameters*, in the pilot A arrangement, plotted as a function of space time. As can be seen from **Figure 3.6** (a), the OPEX increases linearly with space time. This increasing trend in OPEX can be attributed to the increasing energy consumption with longer space times, as shown in **Figure 3.5** (b). **Figure 3.6** (a) also reveals an upward shift from the OPEX curve shifts when introducing the SiO_2 packing material to the reactor. This increase in OPEX can be attributed to the higher SEI of the packed reactor, compared to the unpacked reactor (**Figure 3.5** (b)). The breakdown of the OPEX in the different components from **Table 3.6** is shown in **Figure A.3.2** in Appendix 3.B. The cost for the utilities, i.e. the cost for electricity, dominate the OPEX.

Similar to the OPEX, the CAPEX increase with longer space times and with the addition of packing material to the reactor, as shown in **Figure 3.6** (b). The longer the space time of the gas in one tube, the lower the flow rate of the gas in that tube. Hence, the required number of tubes to reach the total flow rate of 100 m^3/h increases. Longer space times also involve higher SEI (**Figure 3.5**), resulting in

[6] Note that this amount does not yet consider the additional CO_2 emissions that are created through the CCU process, e.g. due to the energy consumption. Hence, the amount of CO_2 that can be considered avoided is even lower.

increased power supply requirements. The addition of the SiO_2 packing reduces the available reaction volume in the reactor, which reduces the flow rate that can be reached in the tube (see equation (3.3)) and consequently increases the needed number of tubes.

The breakdown of the CAPEX into the investment cost for the high-voltage power supply and the DBD reactor is shown in **Figure A.3.3** in Appendix 3.B. The investment cost for the high-voltage power supply is much larger than the investment cost for the DBD reactor. Hence, the rising CAPEX at longer space times can be attributed to the increased power supply requirements. In sum, both OPEX and CAPEX increase with longer space times and the addition of the packing material, due to the higher SEI.

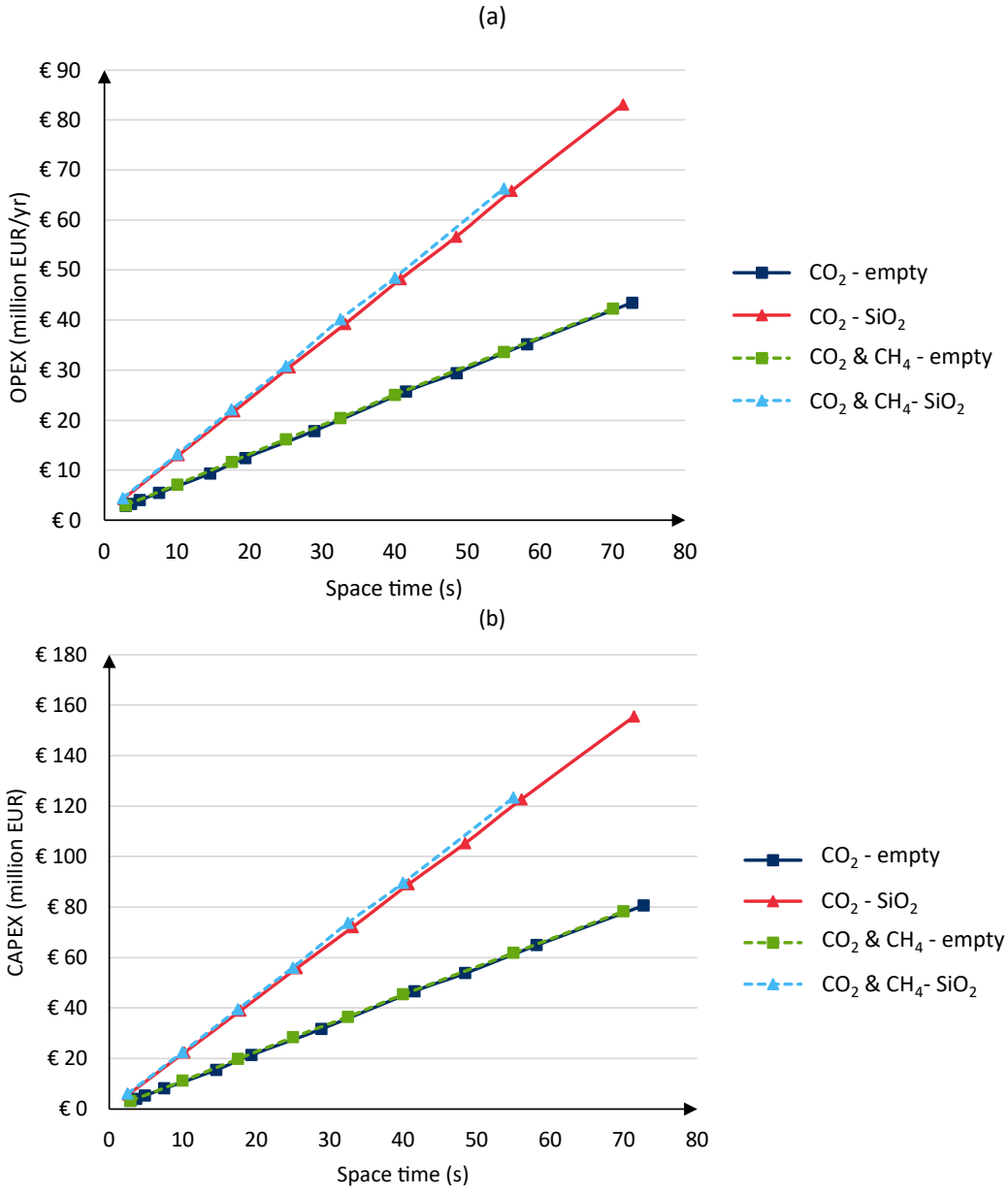


Figure 3.6: (a) OPEX (million EUR/year) and (b) CAPEX (million EUR) plotted as a function of space time, for the set-ups with pure CO_2 and no packing (square), pure CO_2 and SiO_2-packing (triangle), CO_2 and CH_4 and no packing (square, dashed line) and CO_2 and CH_4 and SiO_2-packing (triangle, dashed line), in the pilot plant A arrangement.

Figure 3.7 shows how the revenues evolve in function of the space time. Contrary to the costs, the revenues do not increase linearly with the space time. Instead, the revenues follow the evolution of the CO_2 conversion: first, the revenues increase when the gas spends more time in the reactor, but once the space time exceeds 20 s, the curve starts to flatten. The set-ups with SiO_2 packing and the mix of CO_2 and CH_4 reach the highest revenues. This can be explained by two reasons: (1) the CO_2 conversion is higher for packed reactors and with the additional feed of CH_4 and (2) the mix of CO_2 and CH_4 allows the production of higher-value chemicals.

Figure 3.8 shows the breakdown of the revenues for 4 tested combinations, illustrating how much each product contributes to the yearly revenues. For the pure CO_2 feed, carbon monoxide (CO) dominates the revenues. With a feed of CO_2 and CH_4, CO and hydrogen (H_2) constitute the larger part of the revenues. Note that this breakdown depends both on the observed product concentrations at the outlet of the DBD reactor in the experiments and on the assumed product prices (**Table 3.4**).

The NPV is now calculated from the OPEX, CAPEX and revenues over the plant's lifetime and presented in **Figure 3.9**. The further increasing OPEX at longer space times, and the upward shift in the OPEX with the SiO_2 packing in **Figure 3.6** are mirrored in the evolution of the NPV in **Figure 3.9**.

The NPV is negative for all cases under current market conditions and decreases further for longer space times, despite the higher CO_2 conversion rates that are reached. The rise in the OPEX and CAPEX, caused by the increasing electricity needs, outweighs the revenues and causes the NPV to decrease with longer space times. Reflecting the higher level of OPEX and CAPEX for the SiO_2-packed reactor, the NPVs for the SiO_2-packed reactors (triangular marks) are significantly lower than the unpacked reactors (square marks), in particular at longer space times. While the SiO_2-packed DBD reactor configurations have higher revenues than their unpacked counterparts, the OPEX and CAPEX are also higher because of the increased electricity needs. **Figure 3.9** also illustrates that the presence of CH_4 does not affect the NPV strongly. Based on the NPVs presented in **Figure 3.9**, the conclusion can be drawn that the pure CO_2 splitting or DRM reactions in the DBD reactor, with a gap size of 0.455 mm, are economically infeasible at present.

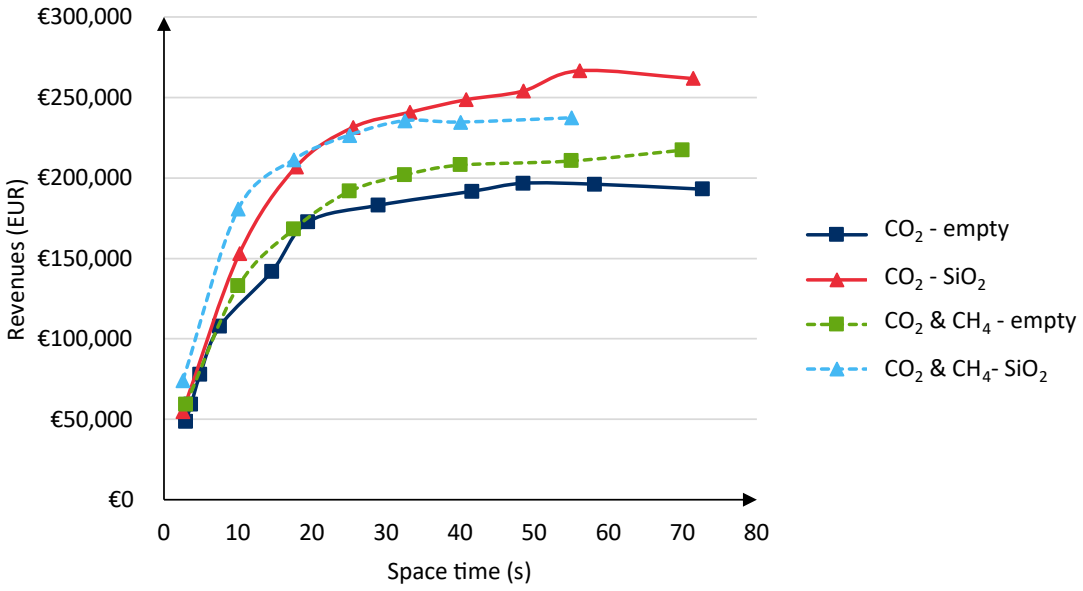


Figure 3.7: Revenues (EUR) plotted as a function of space time, for the set-ups with pure CO_2 and no packing (square), pure CO_2 and SiO_2-packing (triangle), CO_2 and CH_4 and no packing (square, dashed line) and CO_2 and CH_4 and SiO_2-packing (triangle, dashed line), in the pilot plant A arrangement.

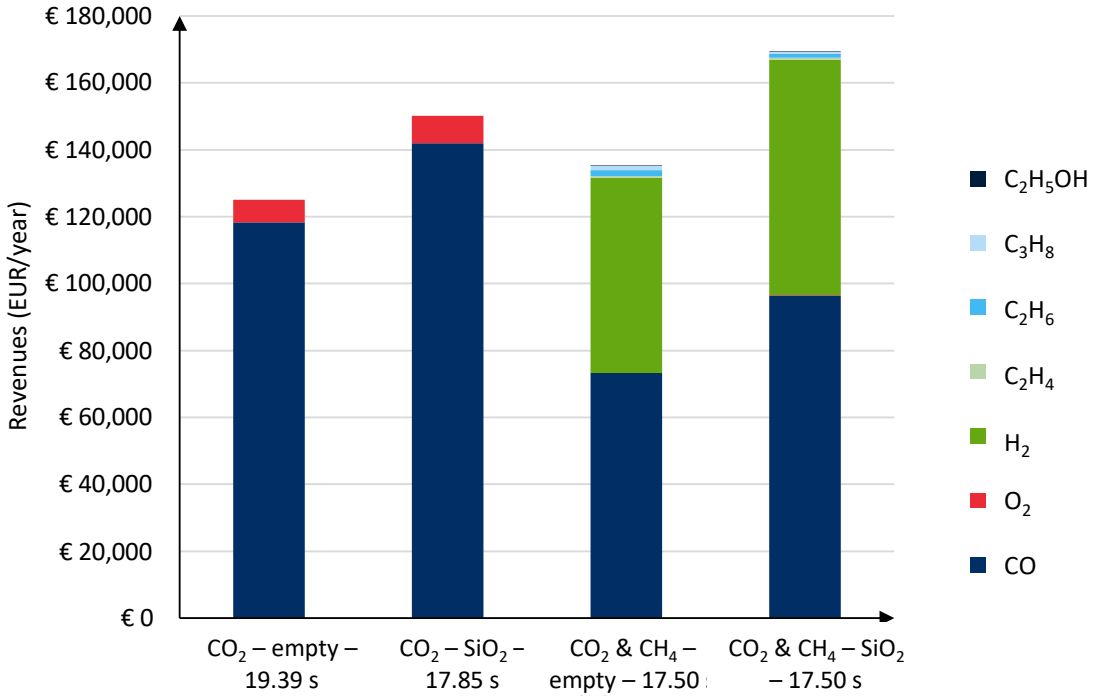


Figure 3.8: The breakdown of the revenues (EUR/year) for 4 tested combinations (**Table 3.9**).

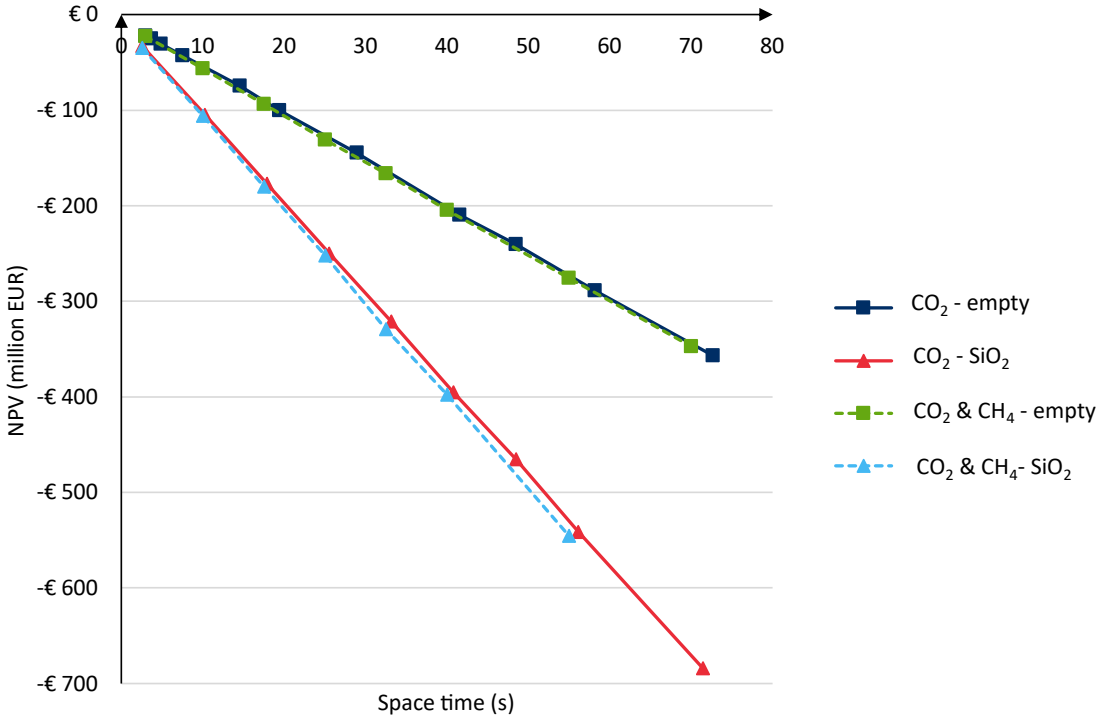


Figure 3.9: NPV (million EUR) plotted as a function of space time for the set-ups with pure CO_2 and no packing (square), pure CO_2 and SiO_2-packing (triangle), CO_2 and CH_4 and no packing (square, dashed line) and CO_2 and CH_4 and SiO_2-packing (triangle, dashed line) in the pilot plant A arrangement.

Figure 3.6 - **Figure 3.9** presented the results of the economic analysis for pilot plant arrangement A (with the fixed total flow rate of 100 m^3/h). **Figure 3.10** shows the NPV and yearly revenues for pilot plant arrangement B. Instead of fixing the the total flow rate, the source power is now fixed at 144 kW for all tested combinations. **Figure 3.10** (a) presents the NPV for this type of arrangement, which appears to be at the same level for all tested combinations from **Table 3.2**. Because of the fixed source power at 144 kW, the utility expenses are the same for all reactor configurations. The CAPEX for the high-voltage power supply is the same for all combinations as well. Hence, both the OPEX and CAPEX remain almost constant over all reactor configurations (**Figure A.3.4** and **Figure A.3.5**).

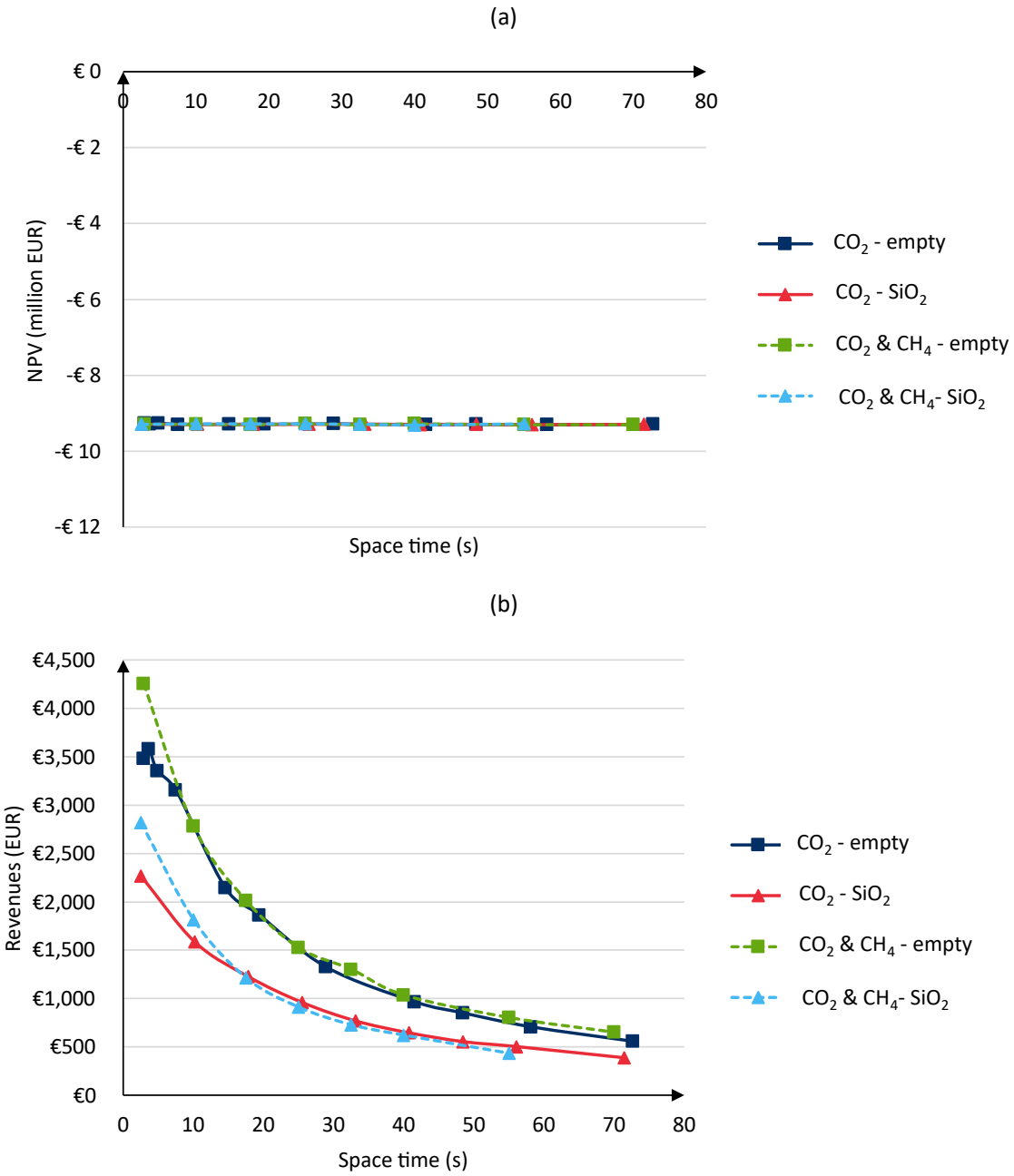


Figure 3.10: (a) NPV (million EUR) and (b) revenues (EUR/year) plotted as a function of space time, for the set-ups with pure CO_2 and no packing (square), pure CO_2 and SiO_2-packing (triangle), CO_2 and CH_4 and no packing (square, dashed line) and CO_2 and CH_4 and SiO_2-packing (triangle, dashed line), in the pilot plant B arrangement.

Figure 3.10 (b) plots the revenues for pilot plant B for the various configurations. Contrary to the findings for pilot plant A, the revenues now decrease as a function of space time. While the total flow rate was fixed for pilot plant arrangement A for all combinations (100 m^3/h), this is no longer the case in pilot plant B arrangement. As a result, varying total flow rates are now observed for different combinations in pilot plant B arrangement. At longer space times, lower total flow rates can be reached, and this results in decreasing revenues. This decreasing trend is not apparent in the evolution of the NPV in **Figure 3.10** (a), because of the low share of revenues. Analogue to the results for pilot plant arrangement A, the NPV is still negative for all cases.

3.3.3 Interpretation

First, the results of the local or OAT sensitivity analysis are presented, to investigate which of the variables affect the NPV the most. For the sensitivity analysis, the combinations with the SiO_2-packed *reactor configuration* and a feed of CO_2 and CH_4 from **Table 3.2** are investigated in more detail. Six factors are varied one-at-a-time: (1) the power source efficiency (PSE), (2) the SEI, (3) the electricity price, (4) the product prices, (5)the investment cost per kW for the high-voltage power supply, and (6) the CO_2 capture cost. For each of these factors, the effect of a 20% increase and a 20% decrease is analyzed. **Figure 3.11** presents the results of the OAT sensitivity analysis for the first three factors, and **Figure 3.12** for the latter three factors.

In **Figure 3.11**, at the space time of 55 s, it can be seen that the 20% reduction in power source efficiency reduced the NPV the most, while the 20% reduction in SEI increased the NPV the most. Hence, surprisingly, the 20% increase and reduction do not have symmetrical effects on the NPV. Compared to the other two factors, the electricity price has a smaller effect on the NPV.

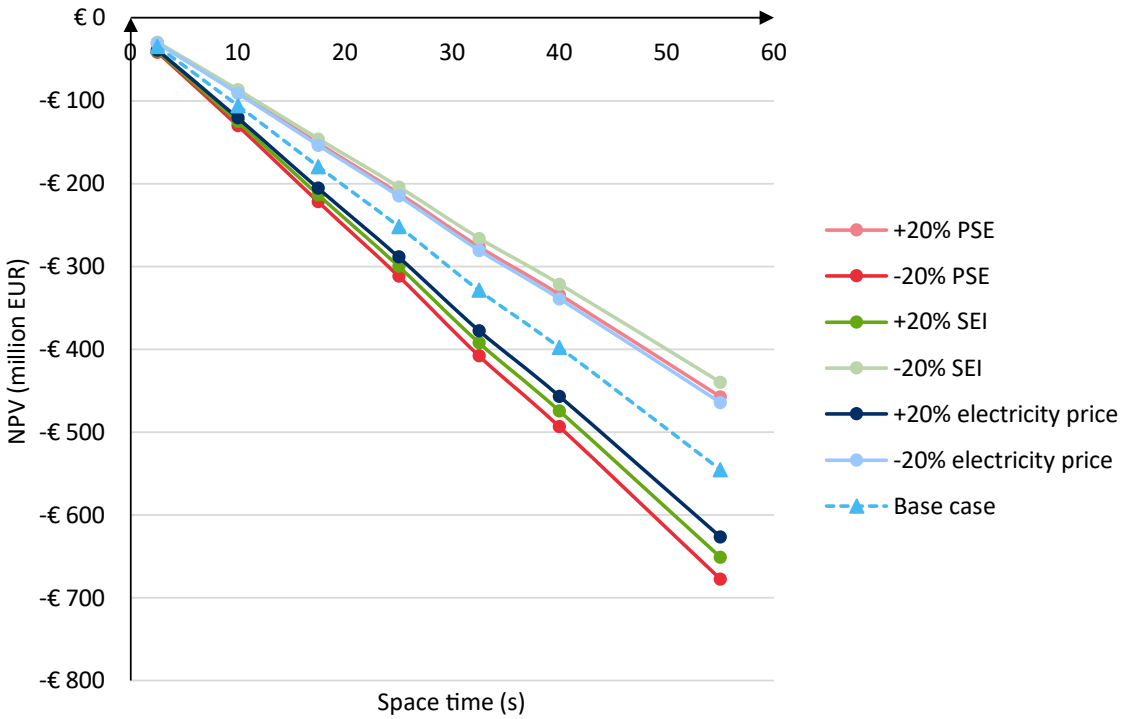


Figure 3.11: The OAT sensitivity analysis for the SiO_2-packed reactor with CO_2 and CH_4. The light blue dashed line with triangular marks represents the base case values. The values of PSE, SEI and electricity prices are increased and decreased by 20%.

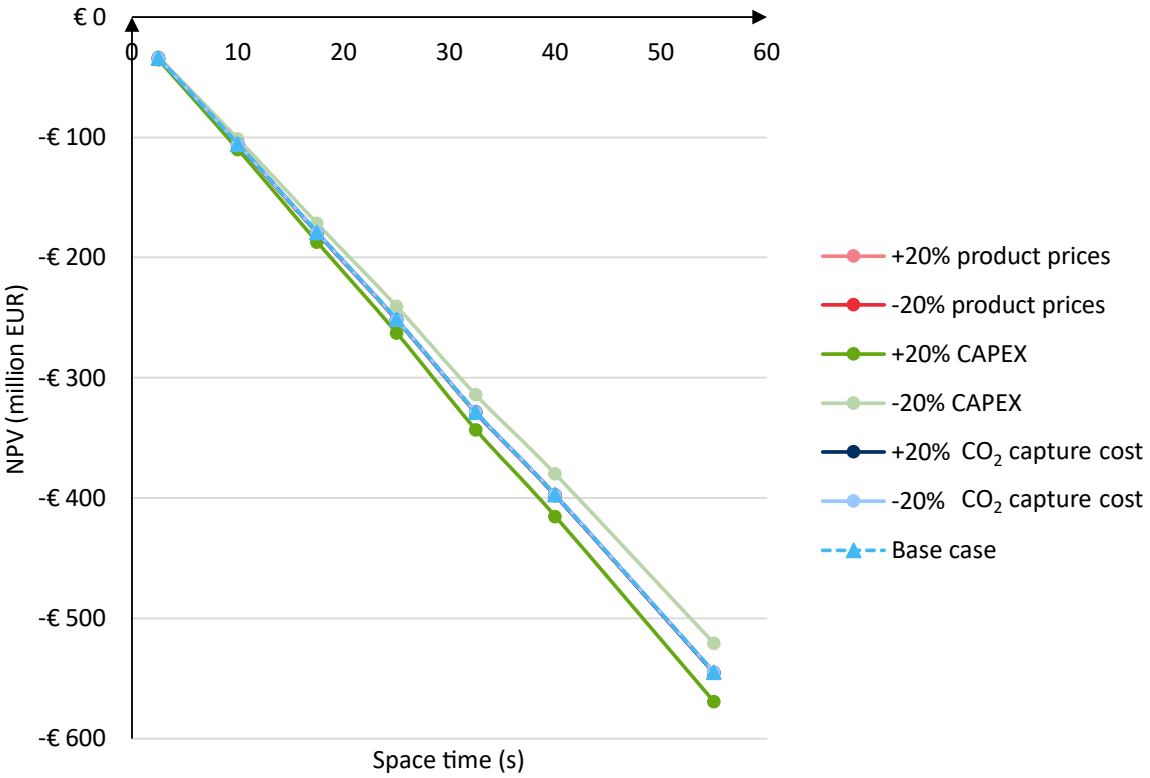


Figure 3.12: The OAT sensitivity analysis for the SiO_2-packed reactor with CO_2 and CH_4. The light blue dashed line with triangular marks represents the base case values. The values of product prices, the capital cost for the high-voltage power supply and the CO_2 capture cost are increased and decreased by 20%.

Figure 3.12 presents the results of the OAT sensitivity analysis for the changes in product prices, the CAPEX and the cost for CO_2 capture. In comparison to **Figure 3.11**, it is clear that changes in these factors have much smaller effects on the NPV. The changes in the product prices and the CO_2 capture cost have no visible effect on the NPV. The change in the assumed investment cost per kW for the high-voltage power supply has a more outspoken effect on the NPV, however, the effect of this factor on the NPV is still more limited than those in **Figure 3.11**.

In addition to the OAT sensitivity analysis, the Minimum Selling Price (MSP) is calculated. The MSP is the price that should be received on average for the product mix to reach an NPV that equals zero. This will help us to identify the type of products that should be targeted, based on the current performance of the DBD reactor. The MSP provides insights into the required product prices if no cost reductions can be realized.

Figure 3.13 presents the MSP for all 35 combinations from **Table 3.2**. The lowest MSP is found for the unpacked reactor with a feed of pure CO_2 and equals almost 19,000 € t-1. The highest MSP reaches almost 120,000 € t-1, in the SiO_2-packed reactor with CO_2 and CH_4. In comparison, the highest product price in the current product mix is 3,960 € t-1 (H_2). Hence, the product price should increase five to thirtyfold, or completely different products should be targeted, to reach an NPV equal to zero.

Figure 3.13 presents the results of pilot plant arrangement A. The MSP for pilot installation B shows the same trends and is presented in **Figure A.3.6**. For pilot plant B, the lowest MSP is also observed for the unpacked reactor with pure CO_2. However, the lowest MSP already equals almost 108,000 € t-1. The highest MSP exceeds 1,000,000 € t-1, in the SiO_2-packed reactor with CO_2 and CH_4.

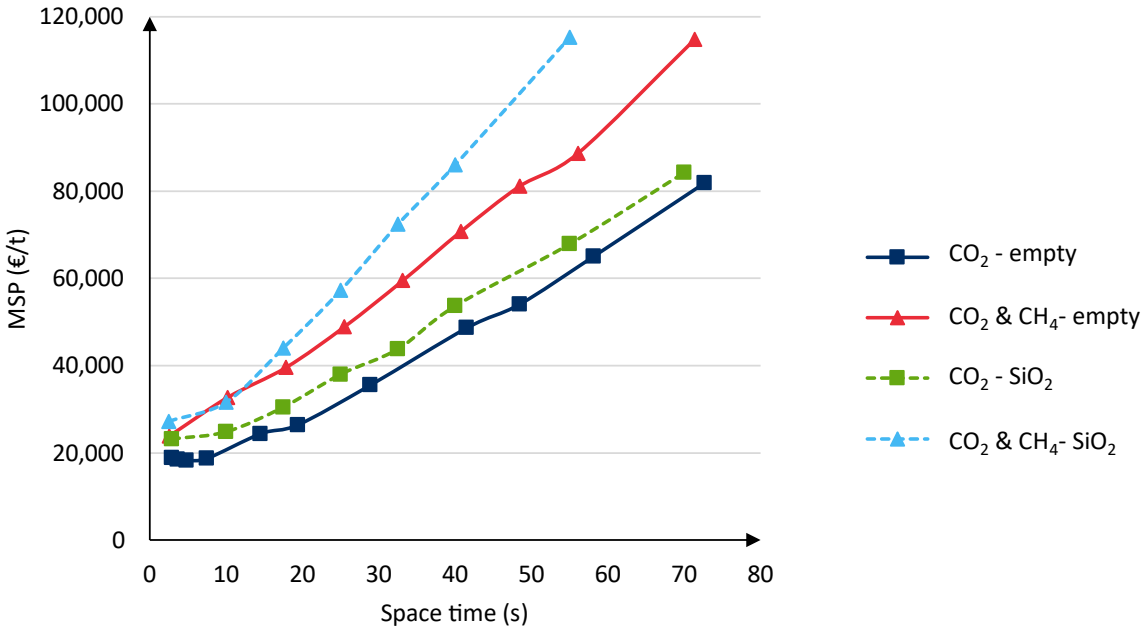


Figure 3.13: Minimum Selling Price (MSP) (EUR/t) for the set-ups with pure CO_2 and no packing (square), pure CO_2 and SiO_2-packing (triangle), CO_2 and CH_4 and no packing (square, dashed line) and CO_2 and CH_4 and SiO_2-packing (triangle, dashed line), in the pilot plant A arrangement.

While the NPVs for pilot plant B were higher (i.e. less negative) than for pilot plant A, the MSPs for pilot plant B are an order of 10 higher than those for pilot plant A. These high MSPs for pilot plant B are caused by the low flow rates, ranging from 0.28 m^3/h to 7.2 m^3/h at most. Compared to the flow rate of 100 m^3/h in pilot plant A, the lower flow rates in pilot plant B result in lower output levels and consequently require higher prices per tonne to compensate for the lower production rates.

Finally, a scenario analysis is performed to asses which technological improvements would be needed to make the technology economically feasible in the future. At this low TRL, it is useful to assess whether a potential design exists that is economically feasible and realistic under the assumption of future improvements (Thomassen et al., 2019). To identify a scenario with a positive NPV, step-wise improvements are made to the SiO_2-packed *reactor configuration*, with a feed of CO_2 and CH_4 and a space time of 55 s. This reactor configuration demonstrated the highest CO_2 and CH_4 conversion rates of 85.35% and 84.48% respectively. First, the space time is reduced to 2.50 s, accompanied by a lower SEI of 36 kJ/L. Shorter space times result in higher flow rates in one tube and lower energy requirements. Second, the dimensions of the tube are increased to a length of 3 m and a gap size of 15 mm, to further increase the flow rate in one tube. Third, the selectivity of the DRM reaction is improved, such that only the chemical with the highest price of 3,9600 €/t (i.e. H_2) is now produced. This improved selectivity could be reached by inserting the right type of packing material. Finally, the number of operators is reduced to 1, to lower the labour costs. These iterative improvements are summarized in **Table 3.10**. In these future scenarios, the dimensions of one tube are enlarged to investigate the effect of a lower required number of tubes. However, it is not yet clear what the effect of larger tubes would be on the plasma's performance. Uytdenhouwen et al. (2018) compared DBD reactors with different gap sizes and concluded that conversion rates increased and energy efficiency decreased for smaller gap sizes. In this study, it is assumed that conversion rate and energy efficiency remain constant.

Table 3.10: Iterative technological improvements in the performance of the DRM reactions in the SiO_2-packed reactor. The starting point is the the performance observed during the experiments for the SiO_2-packed reactor configuration with a feed of CO_2 & CH_4 and a space time (ST) of 55 s. The CO_2 and CH_4 conversion and the flow rate in the reactor are kept constant.

	Experimental set-up CO_2 & CH_4 – SiO_2 ST 55 s	**Shorter ST**	**Shorter ST Larger tube**	**Shorter ST Larger tube Selectivity**	**Shorter ST Larger tube Selectivity Reduced labour costs**
Space time (s)	55.00	2.50	2.50	2.50	2.50
Length (m)	1	1	3	3	3
Outer & inner diameter (mm)	17.41 - 16.50	17.41 - 16.50	40.00 - 10.00	40.00 - 10.00	40.00 - 10.00
Product price (€/t)	494.31	494.31	494.31	3,960	3,960
# Operators	6	6	6	6	1
Gap (mm)	0.455	0.455	15.00	15.00	15.00
Flow rate 1 tube (m^3/h)	0.001	0.018	2.57	2.57	2.57
Number of tubes	124,844	5,675	39	39	39
Flow rate reactor (m^3/h)	100	100	100	100	100
SEI (kJ/L)	1,348.31	36.00	36.00	36.00	36.00
Plasma power (kW)	37,453.18	1,000.00	1,000.00	1,000.00	1,000.00
Source power (kW)	76,936.58	2,054.21	2,054.21	2,054.21	2,054.21
CO_2 conversion (%)	85.35	85.35	85.35	85.35	85.35
CH_4 conversion (%)	84.48	84.48	84.48	84.48	84.48

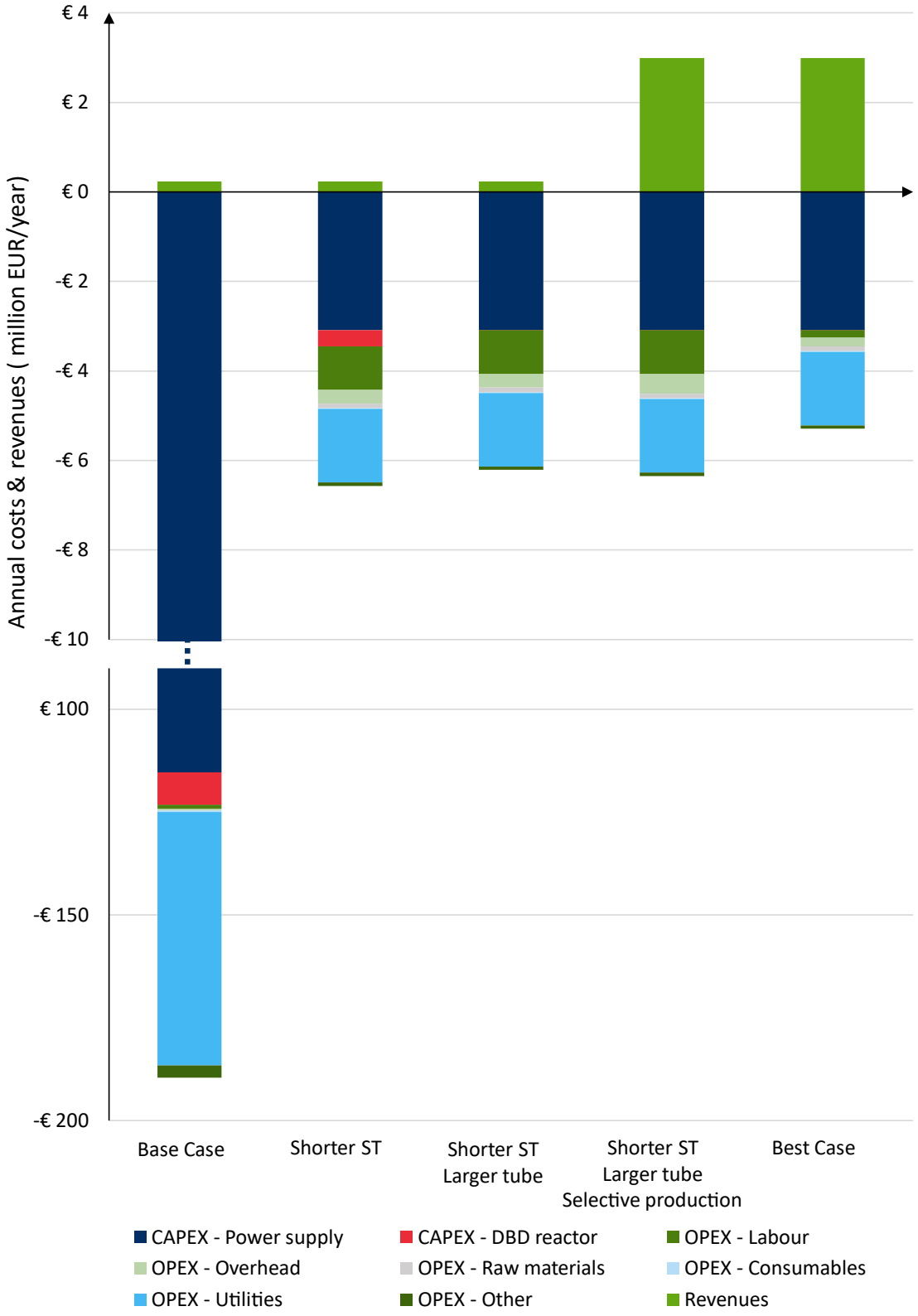


Figure 3.14: Step-wise improvements towards a future design, which results in a positive NPV. From left to right: (1) reactor performance based on the experimental results, with space time (ST) = 55 s, (2) shorter ST (2.5 s) and the associated lower SEI (36 kJ/L), (3) dimensions of one tube are increased from 1 m to 3 m length and from 0.455 mm to 15 mm gap size, (4) improved selectivity towards a product with a price of 2,000 €/t and (5) improved selectivity towards a product with a price of 3,000 €/t and reduced labour costs.

Figure 3.14 shows the annual OPEX, CAPEX and revenues for each investigated scenario from **Table 3.10**. The CAPEX is annualized by multiplying the annual capital charge ratio (ACCR) with the total capital investment. The ACCR is the fraction of the total investment that must be paid each year to pay off the total CAPEX and the interest over the lifetime of the plant.

As can be seen from **Figure 3.14**, in the base case, the annual costs greatly surpass the revenues for the experimental reactor performance, resulting in a negative NPV of 545 million euros. The first iteration includes the shorter space time of 2.50 s, together with the lower SEI. The reduction of the energy needs results in large cost reductions. The CAPEX for the power supply (dark blue) and the OPEX for the utilities (light blue) are both reduced almost 30 times. The second step included the increase in the length and gap size of one DBD tube, which has a negligible effect on the costs. It only reduces the CAPEX of the DBD reactor, thanks to the lower amount of tubes needed to reach 100 m^3 h-1. Third, the selectivity of the reaction is improved such that only hydrogen, with a price of 3,960 € t-1, is produced. This increases the revenues almost eightfold. Finally, the labour requirements are reduced, from 6 operators to 1 operator. With this iteration of technological improvements, a positive NPV of 2.5 million euros is achieved. The price of 3,960 € t-1 can be achieved for some of the chemicals that could potentially be produced in the DBD reactor. For example, the prices of H_2 (3,960 €/t), dimethyl ether (1,290 (Fernández-Dacosta et al., 2018) – 5,465 (Pacheco et al., 2021) €/t) and dimethyl carbonate (5,542 €/t (Pacheco et al., 2021)) exceed this price and would result in a positive NPV for this final scenario.

3.4 Discussion

The main goal of the TEA was to assess how the chosen *reactor configuration* and *process parameters* affect the economic viability of the technology and to select the most promising combination from the economic perspective. In this work, the experimental results for 35 different combinations of *reactor configuration* and *process parameters* were analyzed and translated into economic parameters. The NPV, which represents the present value of all cashflows of the CCU project over its lifetime, was negative for all 35 combinations.

Based on the NPV as the economic metric, the empty (unpacked) *reactor configuration*, with the following set of *process parameters* should be investigated further: a feed of pure CO_2 and a space time of 2.91 s. This combination results in the highest, i.e. least negative, NPV. Based on the CO_2 conversion as a technical parameter, however, a *reactor configuration* with SiO_2 packing material, a feed of CO_2 and CH_4 and a space time of 55 s of should be pursued, as this yields the highest CO_2 conversion rate (see **Figure 3.5** (a)). This controversy is caused by the opposite evolutions of the SEI and the conversion rate: while the CO_2 conversion rate increases (i.e. improves) when the space time of the gas increases, the SEI for the reaction also increases (i.e. deteriorates) when the space time is prolonged (**Figure 3.5**).

The unpacked reactor fed with pure CO_2 and a space time of 2.91 s faces the lowest expenses, due to its low level of SEI, whereas the SiO_2-packed reactor fed with CO_2 and CH_4 and a space time of 55 s creates the highest revenues, because of its high conversion rate.

The future challenge is to find a combination of *reactor configuration* and *process parameters* that allows the combination of a high conversion rate and selectivity towards chemicals with high market prices (to boost the revenues), with low energy needs (to minimize the costs). Other packing materials should be analyzed to explore whether this trade-off can be solved or not. The SiO_2 packing material that was tested in the experiments of Uytdenhouwen et al. (2021), was selected by the researchers

specifically because of its inert nature. Therefore, it is not surprising that the packing does not yet create many positive effects on the performance of the DBD reactor. Hence, future research should also test other packing materials, with catalytic properties to analyze the synergetic effects of plasma catalysis. In Chapter 4, other packing materials will be tested and analyzed.

To become economically viable, the trade-off between cost and revenues should be resolved: revenues should be increased and costs should be lowered simultaneously, by targeting higher-value products and reducing energy requirements. Because of the high energy expenses, one could argue that the low energy efficiency, and not the low conversion rate, is the main barrier preventing the commercialization of the DBD reactor as CCU technology. However, the remarkably low sales revenues are as challenging as the high expenditures.

The revenues could be improved in three ways. First, the conversion rates of CO_2 and CH_4 in the DBD reactor could be increased. However, there is not much leeway for further improvements in the conversion rates. In the SiO_2-packed reactor, conversion rates higher than 80% are already reached (see **Figure 3.5** (a)). Second, chemicals with considerably higher market prices could be targeted. **Figure 3.8** shows that the major part of the revenues was attributable to the sales of carbon monoxide (CO). However, CO is a chemical with a relatively low price, i.e. 400 €/t (**Table 3.4**). The reason for its important share in the revenues is the high concentration of CO in the product mix, up to 53.3 % (figure appendix). For the combinations with a feed of CO_2 and CH_4, an important share of the revenues was attributed to the sales of hydrogen (H_2). Contrary to CO, the concentration of H_2 in the product mix was smaller, with a maximum of 40.2%, but its price is almost tenfold, i.e. 3,960 €/t. If the DRM reactions in the DBD reactor could be targeted more towards H_2, instead of chemicals with a lower price such as CO, the revenues would increase significantly. Moreover, other chemicals could be produced by changing the feed to the reactor or by introducing different types of packing material in the DBD reactor. For example, dimethyl ether (CH_3OCH_3) could be targeted, for which price estimates up to 5,465 €/t have been found in the literature (Pacheco et al., 2021). Hence, it is not so much the conversion rate, but the selectivity towards products with a higher market price that should be improved through future research. Third and finally, the production capacity of the DBD reactor could be increased. The DBD reactor that was investigated in this study had a gap size of 0.455 mm, which limited the amount of gas that could run through one tube for a certain space time (i.e. the flow rate). When scaling the DBD reactor from the laboratory to a pilot-scale installation, this translated into a high number of tubes that would be needed to reach the total flow rate of 100 m^3/h in the pilot reactor. A DBD reactor with a larger gap size could be more interesting. However, changing the gap size of the reactor will also affect the conversion rate and the SEI of the reactions. In Chapter 4, a DBD reactor with a larger gap size is investigated.

The effect of some technological improvements, such as lower SEI and improved selectivity, were investigated in the scenario analysis. Although the goal of this scenario analysis was to investigate which improvements would be necessary to reach a positive NPV, the question could be raised about how realistic these improvements, listed in **Table 3.10**, are. The iterative improvements were applied to the SiO_2-packed reactor with a feed of CO_2 and CH_4 and a space time of 55 s, which yielded the highest CO_2 conversion rate of 85.35%. In the first iteration, a lower space time was adopted, which was accompanied by a lower SEI (i.e. 36 kJ/L). While this low level of SEI has been observed in experiments at shorter space times, it is always accompanied by lower conversion rates (**Figure 3.5**). Finding a combination that gives both a high conversion rate and a low SEI is indeed one of the main technological changes that are hard to overcome. The second iteration involved an increase in the gap size of the DBD tubes, up to a gap size of 15 mm. This is considerably larger than the current gap size

(0.455 mm), and would likely affect the technical performance of the DBD reactor as well. In the third step, the assumption was made that the converted CO_2 and CH_4 were transformed solely into H_2, with a price of 3,960 €/t. A selectivity of 100% towards one chemical has not been observed yet. Finally, the labour requirements were reduced, from 6 operators to 1 operator. The required number of operators will only be known when the DBD reactor is put into operation. The assumption of 6 operators may be on the conservative side for the size of the investigated DBD reactor, whereas only 1 operator is more optimistic. In sum, the scenario analysis should be read as a hypothetical exercise to illustrate what it takes for the DBD reactor to yield an NPV that is greater than zero.

A final point of discussion is the cost of separation in the CCU value chain. As explained earlier, the cost of separation is not yet included in this TEA. The separation and purification processes were instead treated as a black box, due to the uncertainty about the type of separation technology that could be implemented. Moreover, we expect that innovation will have to take place in terms of separation as well, to be consistent with the needs of the CCU technology.[7] For example, one of the advantages of the DBD reactor is that it can switched on and off very quickly. To be able to capitalize on this advantage, the downstream process, including separation, should also be able to be switched on or off instantly. To deal with this black box for separation, the Maximum Acceptable Cost (MAC) for separation was proposed, which represents the maximum cost the separation process could produce, to reach a NPV equal to zero. Because the NPV was negative for all combinations that were analyzed in this Chapter, the MAC for separation could not be calculated. Including the costs for separation in a future TEA study would further increase the costs of the CCU value chain and reduce the NPV further.

3.5 Conclusions

The objective of the TEA was threefold: (1) to evaluate how the chosen *reactor configuration* and *process parameters* affect the economic feasibility of CO_2 splitting and DRM reactions in a DBD reactor, (2) to identify which steps in the CCU value chain contributed the most to the costs, and (3) to identify which technological improvements would be needed to make the plasma technology an attractive CCU solution.

The observations from an experimental study, in which the *reactor configuration* and *process parameters* were altered systematically, resulting in a dataset of 35 different set-ups of the DBD reactor, were translated into economic cashflows on the scale of a pilot-sized DBD reactor. This allowed us to evaluate how variations in technical parameters, i.e. CO_2 conversion and SEI, translated into economic parameters. The results of the economic analysis revealed that none of the 35 analyzed DBD set-ups could create a positive NPV. The major cost categories are the high expenses for electricity (in the OPEX) and the investment for the high-voltage power supply (in the CAPEX). The costs soar when the space time of the gas in the DBD reactor increases, due to the increased energy needs. The generated revenues by selling the produced chemicals can only cover a fraction of these costs. The high OPEX and CAPEX, together with the lack of high revenues result in strongly negative NPVs. The highest (i.e. least negative) NPV is calculated for the unpacked DBD reactor, with a feed of pure CO_2 and a short space time of 2.91s, because this set-up has the lowest costs. However, the highest revenues are found for the SiO_2-packed reactor, with a feed of CO_2 and CH_4 and a longer space time of 55 s. Hence, the future challenge is to find a DBD set-up that can boost the revenues, without blowing up the costs.

[7] This is discussed in more detail in Chapter 4 , p. 104 – 106 and p. 124 – 125.

The sensitivity analysis revealed that the technical parameters, related to the energy requirements of the CO_2 splitting and DRM reactions in the DBD reactor, affect the NPV substantially. Exploring methods to improve the power source efficiency of the high-voltage power supply, or to reduce the SEI of the reaction is an effective way to improve the NPV. The electricity price, as a market parameter, also affected the NPV strongly. Although the technology developer cannot control the market conditions, it is important to consider the importance of the electricity price and to take this into account in future developments of the CCU value chain. For example, the electricity price could be an important element in choosing the optimal location of the CCU plant or choosing the electricity source.

Future research could explore how the use of different packing materials changes the composition of the product mix, how higher conversion rates could be reached already at short space times and how the gap size can be increased to increase the production capacity, without deteriorating the conversion rate.

Appendix – Chapter 3

3.A Materials and methods

Table A.3.1: CAPEX for the high voltage generator for a DBD reactor, based on data from an expert in the industry.

kW	€
2	12,000
8	21,000
12	27,000

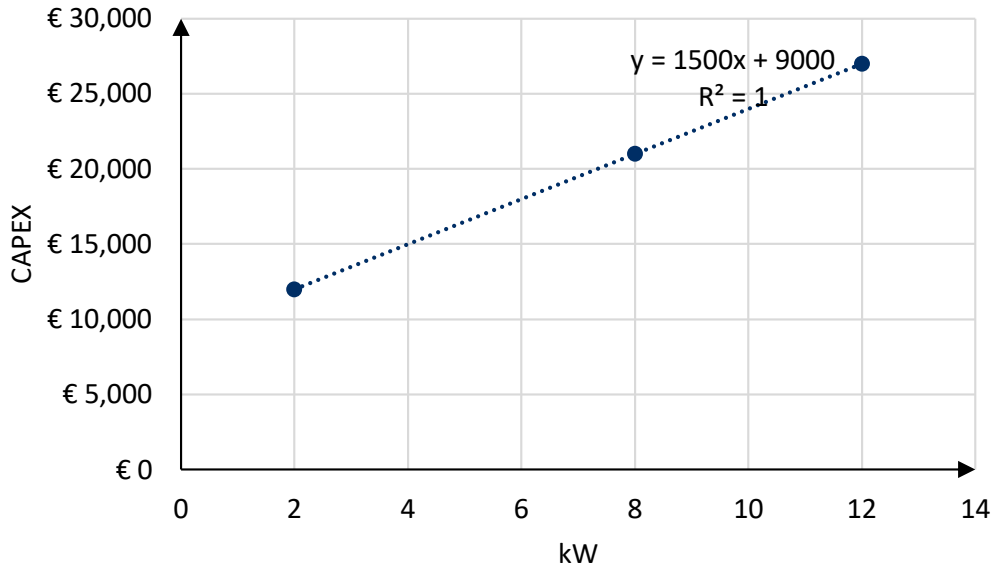


Figure A.3.1: Fitted curve through price estimates for the high-voltage generator.

Table A.3.2: Cost breakdown of CAPEX into ISBL and OSBL. Methodology based on (Towler & Sinnott, 2013a), factors taken from (Pérez-Fortes, Schöneberger, Boulamanti, Harrison, et al., 2016).

	Factors
ISBL	
OSBL	35% of ISBL
Engineering costs (EC)	30% of ISBL + OSBL
Contingency charges (CC)	30% of ISBL + OSBL
FCI	= ISBL + OSBL+EC +CC
Working capital (WC)	20% of ISBL + OSBL
CAPEX	= FCI + WC

3.B Results

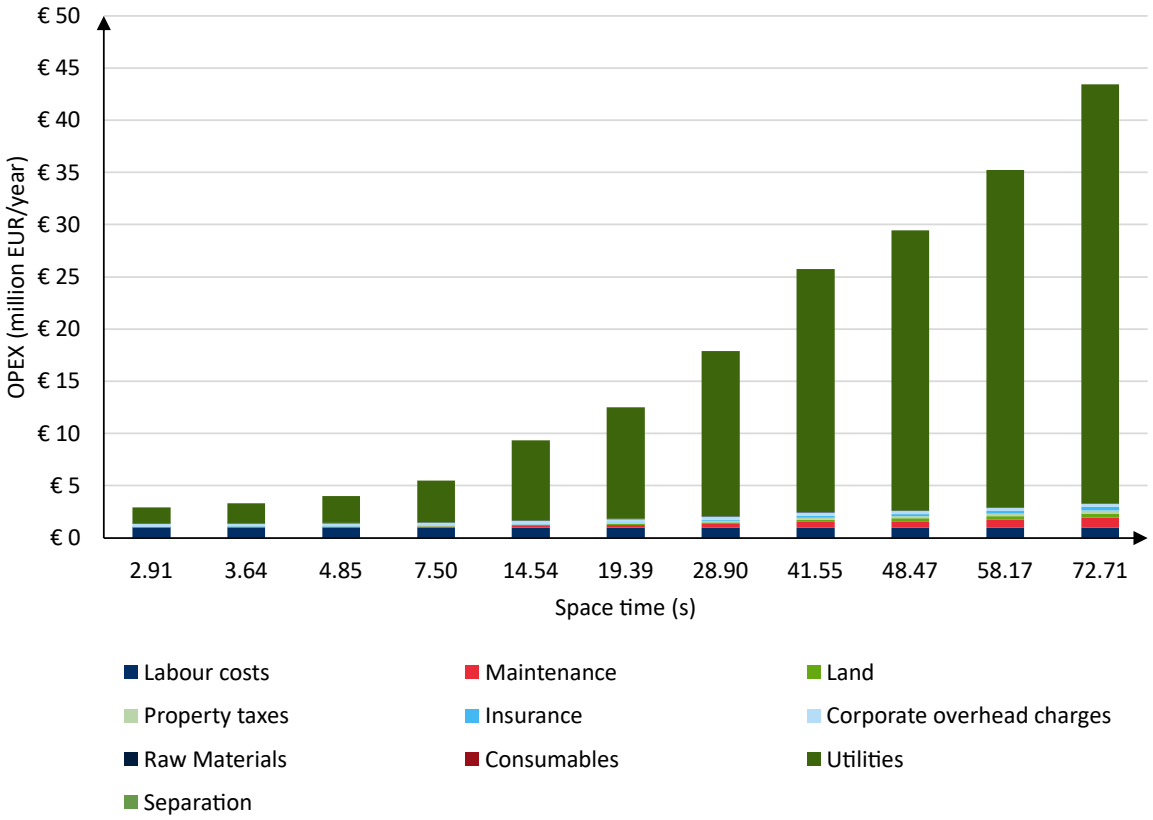


Figure A.3.2: OPEX breakdown for the tested combinations with no packing material and a pure CO_2 feed.

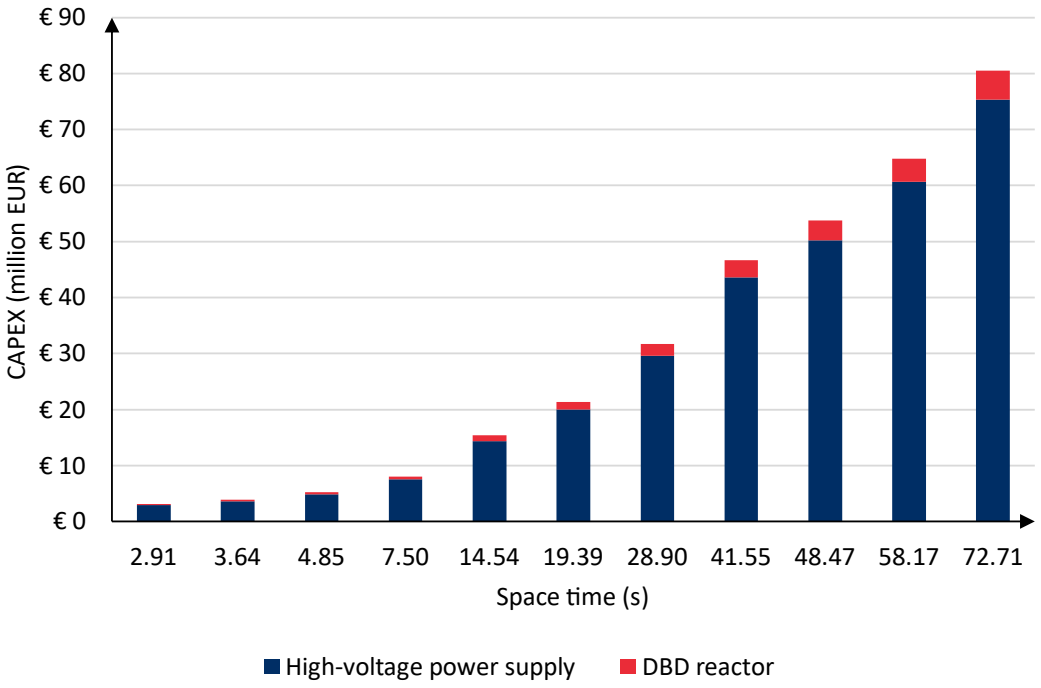


Figure A.3.3: CAPEX breakdown into the investment cost for the high-voltage power supply and the DBD reactor, for the tested combinations with no packing material and a pure CO_2 feed.

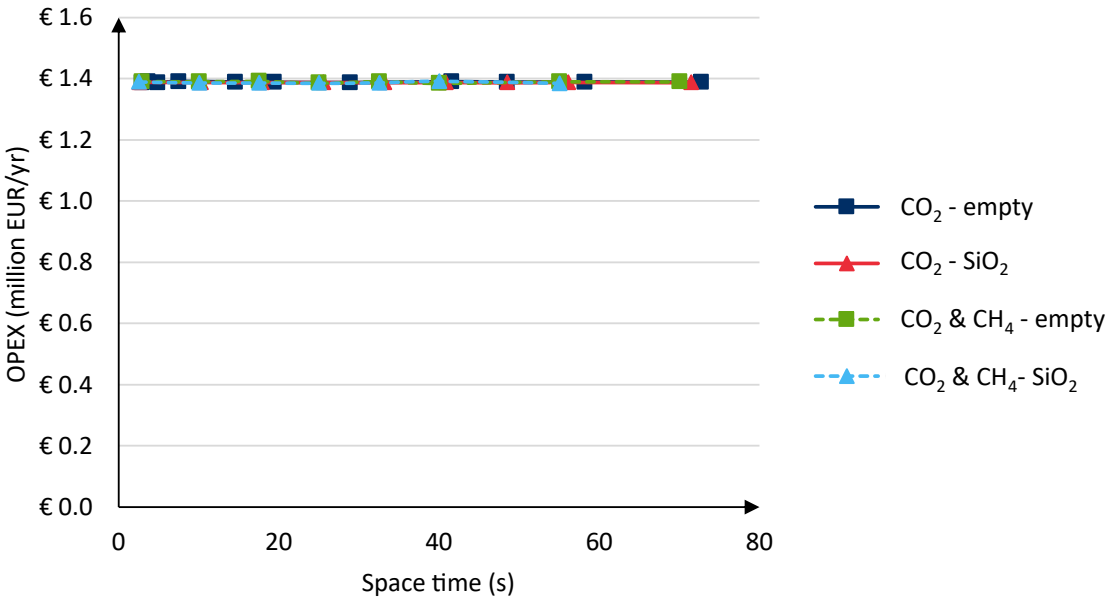


Figure A.3.4: OPEX (million EUR/year) plotted as a function of space time, for the set-ups with pure CO_2 and no packing (square), pure CO_2 and SiO_2-packing (triangle), CO_2 and CH_4 and no packing (square, dashed line) and CO_2 and CH_4 and SiO_2-packing (triangle, dashed line), in the pilot plant B arrangement.

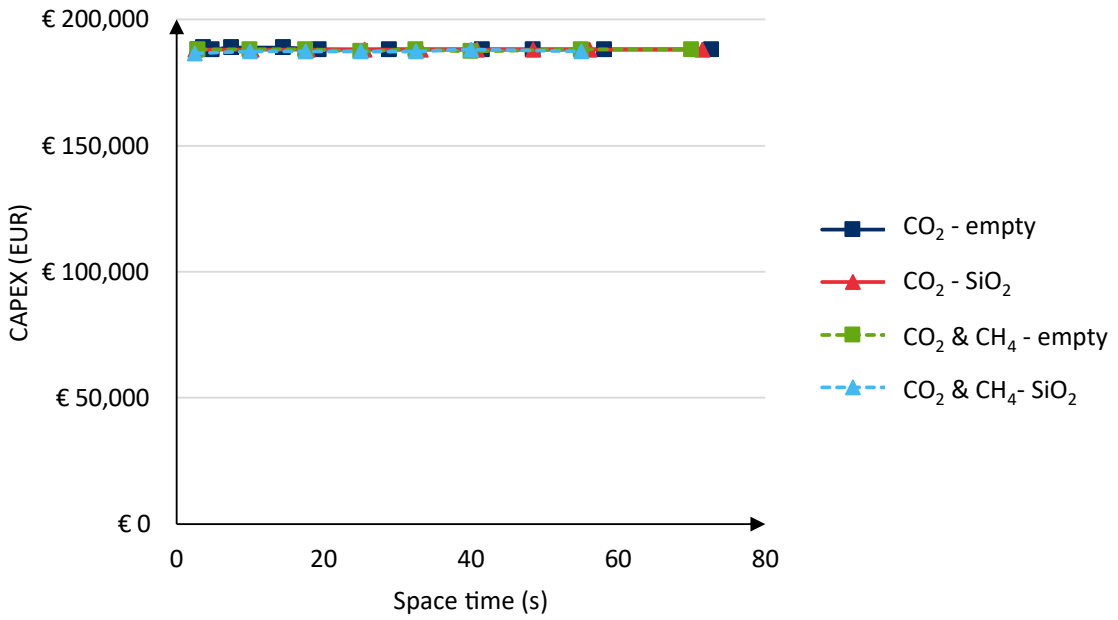


Figure A.3.5: CAPEX (million EUR) plotted as a function of space time, for the set-ups with pure CO_2 and no packing (square), pure CO_2 and SiO_2-packing (triangle), CO_2 and CH_4 and no packing (square, dashed line) and CO_2 and CH_4 and SiO_2-packing (triangle, dashed line), in the pilot plant B arrangement.

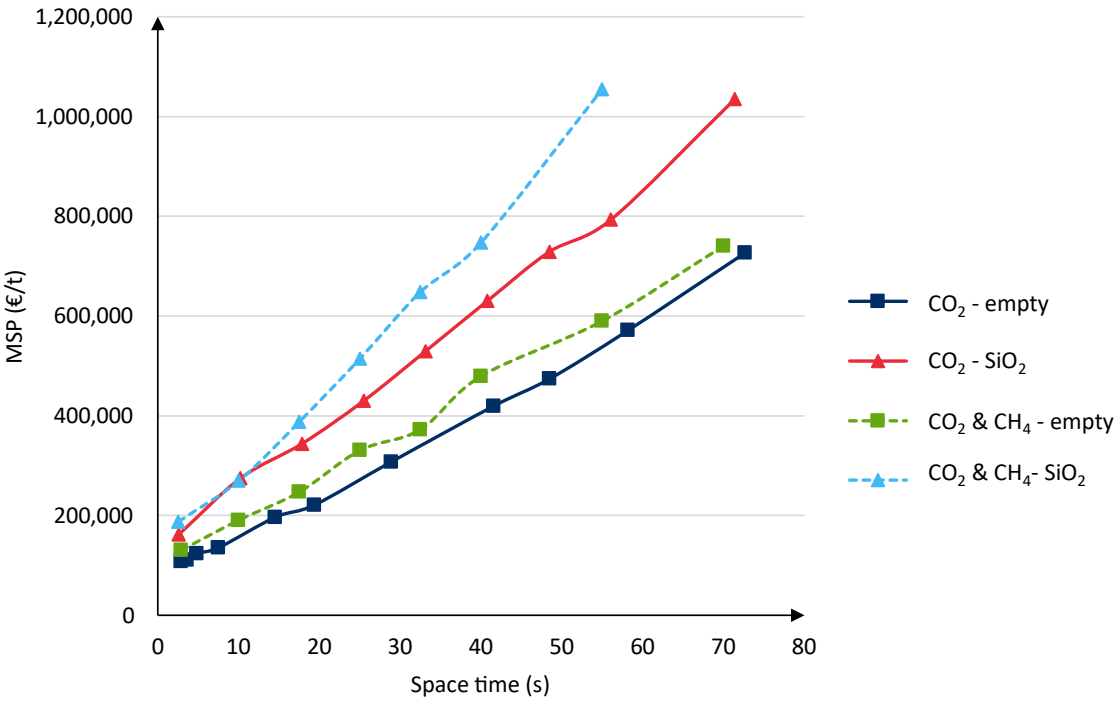


Figure A.3.6: Minimum Selling Price (MSP) (EUR/t) for the set-ups with pure CO_2 and no packing (square), pure CO_2 and SiO_2-packing (triangle), CO_2 and CH_4 and no packing (square, dashed line) and CO_2 and CH_4 and SiO_2-packing (triangle, dashed line), in the pilot plant B arrangement.

4

A Prospective Life Cycle Assessment of Plasma Catalysis for the Conversion of CO_2 into Chemicals

Carbon Capture and Utilisation (CCU) is the capture, transport and use of CO_2 to produce valuable products, such as fuels, chemicals or building materials. One of the main challenges for CCU is the high stability of the CO_2 molecule, resulting in energy-intensive processes to allow the conversion of CO_2. To overcome this barrier, novel CCU technologies are being researched intensively. One of these novel technologies, that enables the conversion of CO_2 at room temperature, is plasma catalysis. This technology is currently being tested and optimised in the laboratory, where different packing materials are investigated to increase the selectivity and energy efficiency of the process. Therefore, a prospective Life Cycle Assessment (LCA) is performed to assess whether the conversion of CO_2 in plasma catalysis can indeed reduce environmental impacts and to evaluate which plasma set-up offers the greatest environmental benefit. To reflect the possible phases in the technology's development, three scenarios are evaluated: (1) the Laboratory scenario, in which the technical performance is based on the observations from the laboratory, (2) the Energy-Efficient scenario, which assumes an improvement in the energy efficiency level and (3) the Selective scenario, which includes an improvement in the energy efficiency, the conversion rate and the selectivity towards high-value chemicals. While plasma catalysis is not able to present a net reduction in global warming impact, it can deliver net negative fossil resource scarcity impacts in the Selective scenario. This result confirms that the greatest environmental benefit of CCU technologies lies in reducing the dependency on fossil fuels. To identify possible trade-offs between both the environmental and economic dimensions, the results from the LCA are integrated with the results from a Techno-Economic Assessment (TEA). Plasma set-ups with the γ-Al_2O_3 or copper oxide-based packing materials and at intermediate space times can reduce our fossil resource scarcity and generate economic benefits. The focus of future research activities should be on the γ-Al_2O_3 and copper oxide-based packing materials and on the development of new packing materials that will enable us to reach the targeted CO_2 conversion and energy efficiency levels.

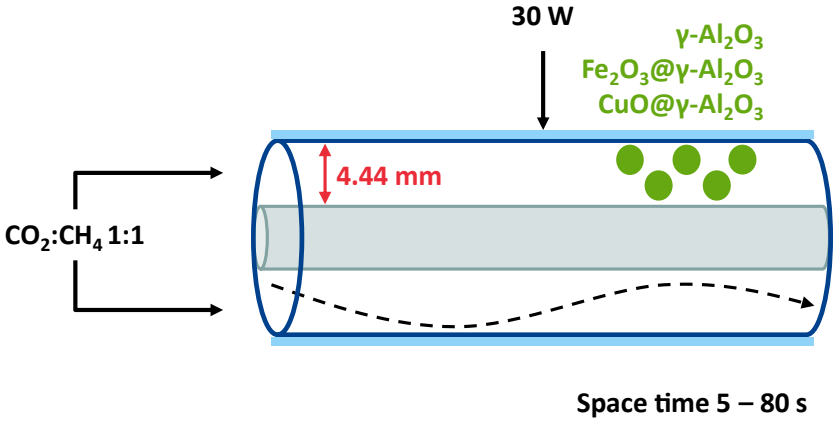
Takeaway messages

- The main objective of this LCA is to evaluate how the chosen *reactor configuration* and *process parameters* affect the environmental desirability of the conversion of CO_2 in the DBD reactor.
- The technical parameters, observed in the laboratory for 48 combinations of *reactor configuration* and *process parameters*, are translated into environmental impacts for the CCU value chain in which plasma catalysis is embedded as CO_2 conversion technology.
- No reductions are observed in the global warming and fossil resource scarcity impact categories for the CCU value chain, due to the DBD reactor's high energy demand.
- The assessment of future technology development scenarios shows that the CCU value chain has the potential to reduce fossil resource scarcity.
- Based on the results of the LCA, the most promising combinations include a *reactor configuration* with a γ-Al_2O_3 or CuO-based packing, and a short to intermediate space time.
- The integration with the TEA reveals that increasing energy efficiency alone is not sufficient. Improvements in the CO_2 conversion rate and selectivity are indispensable to establish a DBD plasma set-up that is both environmentally desirable and economically feasible.
- The 'Maximum Acceptable Impact' (MAI) for separation illustrates the magnitude of the environmental impacts the separation steps in the CCU value chain can have.

The experimental background

As in Chapter 3, the terms *reactor configuration* and *process parameters* will be used frequently. The term *reactor configuration* refers to the geometry of the DBD reactor, i.e. the discharge gap, discharge length, reaction volume, electrode morphology and packing material. The relevant *process parameters* in this work are the flow rate, feed ratio, input power and specific energy input (SEI) (Khoja et al., 2019). The flow rate is reflected into the space time: a higher flow rate translates into a shorter space time, and vice versa. The terms *combination* or *set-up* will be used to refer to the chosen *reactor configuration* and *process parameters* jointly.

In Chapter 4, the LCA is performed to assess the environmental impact of multiple variations in *reactor configuration* and *process parameters* that were tested and analysed in Seynnaeve et al. (n.d.). In their experimental work, the *reactor configuration* has a gap size of 4.44 mm, and this gap is filled with γ-Al_2O_3, iron oxide (Fe_2O_3)-based or copper oxide (CuO)-based packing materials. The *process parameters* of feed ratio (CO_2:CH_4 1:1) and input power (30 W) are kept constant during the experiments. The flow rate is decreased stepwise to vary the space time of the gas between 5 and 80 seconds. Note that the *reactor configuration* has a larger gap size and is filled with different types of packing materials than the one in Chapter 3 and that the space time is varied in a different range.



4.1 Introduction

While CO_2 emission levels continue to rise worldwide, the need for low-carbon or even carbon-negative technologies becomes more and more urgent. Although renewable energy technologies can help to reduce the emission levels from energy-intensive industries, not all emissions can be avoided through renewable energy technologies. For example, the chemical industry and cement industry, responsible for respectively 2.2% and 3%[8] of global greenhouse gas (GHG) emissions (Ritchie, Roser, & Rosado, 2020a), both have a substantial share of CO_2 emissions that cannot be avoided due to the nature of their activities. In the cement industry, for example, the calcination reaction to produce clinker, the active ingredient of cement, is responsible for about two-thirds of the industry's emissions (IEA, 2020b). This reaction includes the decomposition of calcium carbonate ($CaCO_3$) into calcium oxide (CaO) and CO_2. Carbon Capture Utilization and Storage (CCUS) presents a solution to reduce CO_2 emissions from those hard-to-abate industries, where CO_2 emissions are (almost) inevitable.

Carbon Capture and Storage (CCS) is the capture and transport of CO_2 to storage sites, both on- and offshore, where the CO_2 can be trapped for permanent storage. Although CCS offers permanent storage of CO_2, it struggles with high capture costs and a lack of revenues (Bruhn et al., 2016). Hence, attention has been drawn towards Carbon Capture and Utilization (CCU). CCU is the capture, transport – if necessary – and use of CO_2 to produce valuable products, such as fuels, chemicals or building materials. Instead of storing the CO_2 permanently underground, the CO_2 is now utilised to produce other materials. CCU refers to a suite of technologies that use CO_2 as an input to other products or services. CCU covers both the direct use of CO_2, where the CO_2 molecule is not chemically altered (non-conversion) and the transformation of CO_2 through chemical or biological processes (conversion) (IEA, 2021a). Three main conversion routes are distinguished: mineralization, chemical-based conversion and bio-based conversion routes.

However, CO_2 is a very stable molecule, resulting in high energy requirements to convert CO_2 into other products. To overcome this barrier, plasma is put forward as a promising technology for the chemical conversion of CO_2 (Snoeckx & Bogaerts, 2017a). Plasma is called the "fourth state of matter" and is a highly reactive chemical mixture (Carreon, 2019). Various types of plasma set-ups exist, of which the Dielectric Barrier Discharge (DBD) reactor is the most commonly used type in today's plasma research. The DBD reactor offers many advantages, including the simple and modular design of the reactor, the ability to operate on renewable energy, and the possibility of inserting packing material into the reactor. These packing materials can have catalytic properties, to increase the selectivity of the process towards the targeted products. When plasma is produced in a DBD reactor filled with catalytic packing beads, the high reactivity of the plasma is combined with the selectivity of the catalyst in a process that is called plasma catalysis (Bogaerts & Neyts, 2018). The use of catalysts in a DBD reactor is not only studied for the splitting of CO_2 but also for plasma-catalytic dry reforming of methane (DRM). DRM is a widely studied chemical process that enables the conversion of CO_2 and methane (CH_4) into other chemical components, primarily syngas. Plasma-catalytic DRM reactions in a DBD reactor allow the conversion of two important greenhouse gases (GHG) at ambient operating conditions in an easy and flexible reactor design, making it an attractive technology. A review of the state-of-the-art of plasma-catalytic DRM reactions in DBD reactor illustrates the wide variety of packing materials, reactor designs and reaction conditions that have been analysed in previous studies (Khoja et al., 2019). The review reveals one common bottleneck for plasma-catalytic DRM in a DBD reactor: the energy efficiency remains currently too low to make the process viable.

[8] Excluding the produced emissions from energy inputs in these sectors.

In spite of plasma catalysis' promising features and the considerable amount of research on plasma-catalytic reactions in DBD reactors, it is not clear yet whether the plasma-catalytic conversion of CO_2 (and CH_4) in a DBD reactor can actually offer environmental benefits. The DBD reactor's low energy efficiency could significantly hamper the environmental performance of the process. Moreover, other steps in the CCU value chain can introduce new environmental impacts as well. For example, the capture of CO_2 is energy-intensive, hence this process creates additional CO_2. Additionally, the required material for the capture and conversion of CO_2 will also have an environmental impact. Therefore, the use of CO_2 in CCU processes in general, and in plasma-catalytic DRM reactions in particular, does not automatically lead to a lower environmental impact. The actual emission reduction will depend on the source of CO_2, the energy used for the conversion of CO_2, the product that is made and how long the CO_2 will be stored in that product (IEA, 2022b).

To assess whether CCU can offer a reduced environmental impact, a holistic environmental assessment is needed (Müller et al., 2020). Life Cycle Assessment (LCA) is a broadly accepted method to analyse the environmental impacts of a product, process or service over the full life cycle. Following the ISO 14040 standard, an LCA typically consists of four steps: (i) the definition of goal and scope, (ii) the Life Cycle Inventory (LCI), (iii) the Life Cycle Impact Assessment (LCIA) and (iv) the interpretation. Although the four-step framework for LCA is well-established, it still leaves much room for methodological choices such as the selection of system boundaries, functional unit or impact assessment methods. Hence, LCA guidelines for CCU technologies have been established by Müller et al. (2020), in an attempt to harmonise LCA studies for CCU technologies and increase the comparability of the results.

The number of LCA studies for CCU technologies has been growing in recent years. Cuéllar-Franca and Azapagic (2015) reviewed and compared the life cycle environmental impacts of both CCS and CCU technologies. Their comparison revealed that the average environmental impact is lower for CCS than for CCU. In their analysis, the conversion of CO_2 to chemicals was identified as the worst CCU route due to the large amount of reactant needed, the high energy intensity of the CO_2 conversion and the relatively short lifespan of the produced chemical. However, this conclusion was based on merely one study for the production of chemicals in CCU, indicating a lack of LCA studies for the chemical CCU routes. Although the number of studies that assess CCU is rapidly increasing, some CCU processes and products have indeed not been assessed yet. Moreover, CCU technologies are rapidly evolving, making previous studies quickly outdated (Garcia-Garcia et al., 2021). To assess the current status of CCU technologies, Garcia-Garcia et al. (2021) provide an overview of the environmental impacts of the most promising CCU products, i.e. methanol, methane, dimethyl ether (DME), dimethyl carbonate (DMC), propane and propene. They show how CCU technologies generally can reduce the global warming potential and the depletion of fossil fuels, compared to their conventional counterparts. However, this may come at the cost of increases in other environmental impact categories, such as ecotoxicity. Their review also highlights how methodological choices influence the results of the LCA. Whether or not CO_2 capture is included in the LCA, the allocation method that is chosen and the selected impact categories all affect the results of the LCA. Moreover, the use of renewable energy sources is crucial to achieve a reduction in environmental impact. Garcia-Garcia et al. (2021) also recommend to perform these assessments for early technologies that are still in development, as this provides the greatest opportunity to still influence their design.

Plasma catalysis is such an emerging technology in the field of CCU. However, to the author's knowledge, no LCA has been done before to assess the environmental impact of plasma catalysis to convert CO_2 into chemicals. Currently, LCA studies can be found on plasma-based technologies for the removal of NOx, SOx and VOCs from flue gases (Stasiulaitiene et al., 2016) and for the integration of

plasma with a steam methane reforming (SMR) reactor to produce hydrogen (H_2) (King et al., 2021). Stasiulaitiene et al. (2016) have performed an LCA to compare the environmental impact of plasma-based and conventional technologies to remove NOx, SOx and VOCs from flue gases. King et al. (2021) also used the LCA technique to compare the environmental impact of a conventional steam methane reforming (SMR) reactor and a dielectric barrier discharge (DBD) plasma reactor to produce hydrogen. The existing LCA studies for plasma evaluate mature applications of plasma, while plasma catalysis for the conversion of CO_2 is still at an early stage of design.

This study aims to fill this gap by performing a prospective LCA to evaluate the environmental impact of plasma catalysis at this early stage of design. The overall goal of the LCA is to give guidance for the development of a future CCU value chain with plasma catalysis as the CO_2 conversion technology. In this paper, we contribute to the development of this future CCU value chain in four ways.

First, we evaluate how the selected *reactor configuration* and *process parameters* of the plasma catalytic-DRM reaction in the DBD reactor affect the environmental impacts of the CCU value chain. Two features of the plasma catalytic-DRM reaction in the DBD reactor are altered: (1) the type of packing material in the DBD reactor (*reactor configuration*), and (2) the space time of the gas in the reactor (*process parameter*). In total, 48 combinations are evaluated, which enables a comparison of the chosen *reactor configurations* and *process parameters* in terms of environmental impacts.

Second, the need for product separation is discussed, and the maximum acceptable environmental impact for separation is calculated. One of the main remaining challenges for plasma catalysis is the need for post-separation processes, as the products leave the DBD reactor in one feed (Snoeckx & Bogaerts, 2017a). Pure CO_2 splitting results in a mix of CO_2 and O_2, whereas DRM can result in a mixture of CO, H_2 and other by-products, e.g. hydrocarbons or oxygenates. This mixture of products that remains after the plasma-catalytic reaction needs to be separated, however, current superation techniques are still energy-intensive. van Rooij et al. (2017) evaluated the economic potential of a novel plasma technology to convert CO_2 into CO and found that product separation is the dominant cost factor. The separation needs can also be substantial for other types of chemical CO_2 conversion technologies. Garcia-Herrero et al. (2016) investigated the environmental impact of the electrochemical synthesis of dimethyl carbonate (DMC) from CO_2 and observed that more than 80% of the total energy needs originated from the separation step. The need for post-reaction separation steps can result in substantial economic and environmental impacts. However, the selection of a separation technique is not straightforward. It depends on the composition of the product mix and the envisaged downstream processes. Moreover, innovative separation techniques will likely be needed to deal with the complexity of the product mix at the outlet of the DBD reactor. Because the separation technique is currently unknown, the separation step is treated as a black box. The maximum acceptable environmental impact for separation will be calculated in the LCA.

Third, the influence of technological developments in the DBD reactor on its environmental impacts is evaluated. This paper will make additional projections about the development of plasma catalysis from lab-scale to commercialisation and analyse how different projections on the CO_2 conversion rate and energy efficiency affect the environmental performance. Besides the technology's development itself, the context in which the technology operates will also change in the future. To anticipate these evolving circumstances, future electricity mixes are considered as well.

Finally, the LCA is integrated with a Techno-Economic Assessment (TEA), to evaluate the plasma-catalytic CCU value chain both from the economic and environmental perspectives. The TEA framework developed by Lamberts-Van Assche, Thomassen, and Compernolle (2022) is now applied to the 48 combinations analysed in this Chapter. The TEA and LCA results are then compared, to

explore potential trade-offs between the economic feasibility and environmental desirability of this new CCU value chain.

This chapter is structured as follows. The following section describes the Materials and Methods, elaborating on how the four-step framework of LCA will be applied to our study. Afterwards, the Results of the LCA will be presented. This chapter ends with the Discussion and Conclusions.

4.2 Materials and Methods

4.2.1 Goal and Scope

This LCA aims to develop and evaluate a future plasma-catalytic CCU value chain, located in Belgium. The presence of large chemical clusters, e.g. in the Port of Antwerp-Bruges, creates an opportunity to develop this CCU value chain in Belgium. Four subgoals are distinguished for this LCA:

(1) Select the most promising plasma catalysis' reactor configuration and process parameters, in terms of environmental impacts (later referred to as 'Design').
(2) Identify the Maximum Acceptable Impact (MAI) the separation and purification processes can have in this plasma-catalytic CCU value chain (later referred to as 'MAI for separation').
(3) Analyse how projected technological improvements from lab-scale to commercialisation would affect the environmental impacts (later referred to as 'Outlook').
(4) Integrate the economic and environmental evaluation of the plasma-catalytic CCU value chain, to identify potential trade-offs (later referred to as 'Integration').

Figure 4.1 presents the plasma-catalytic CCU value chain and the adopted system boundaries. The value chain starts at a CO_2 source from which the CO_2 in its flue gas is captured. The CO_2 source could be e.g. a power plant, chemical plant or cement plant. The captured CO_2 is supplied to the DBD reactor, together with CH_4. Stainless steel, alumina and the packing material are needed to build the DBD reactor. To generate the plasma in the DBD reactor, electricity needs to be supplied. Once the plasma is generated, the plasma-catalytic DRM reactions can take place in the DBD reactor. The CO_2 and CH_4 are converted into other components, resulting in a product mix that leaves the DBD reactor. This product mix contains CO_2, CH_4, H_2, CO, C_2H_2,C_2H_4,C_2H_6, C_2H_5OH, CH_3OH, C_3H_8, and CH_3OCH_3 (**Table 4.1**: List of end products.**Table 4.1**). The feed components CO_2 and CH_4 are separated from the end-products, to be recycled and looped back to the DBD reactor. How much CO_2 and CH_4 can be recycled, depends on how much of the CO_2 and CH_4 are converted in the DBD reactor: a higher conversion rate results in a lower amount of unconverted CO_2 and CH_4 and hence a lower fraction of CO_2 and CH_4 to be recycled. Next, the product mix is purified to get the end-products, listed in **Table 4.1**, that can be sold for consumption. The final step is the end-of-life treatment of these end-products.

Table 4.1: List of end products.

Chemical formula	Name
CO	Carbon monoxide
H_2	Hydrogen
C_2H_2	Ethyne
C_2H_4	Ethene
C_2H_6	Ethane
C_3H_8	Propane
C_2H_5OH	Ethanol
CH_3OH	Methanol
CH_3OCH_3	Dimethyl ether

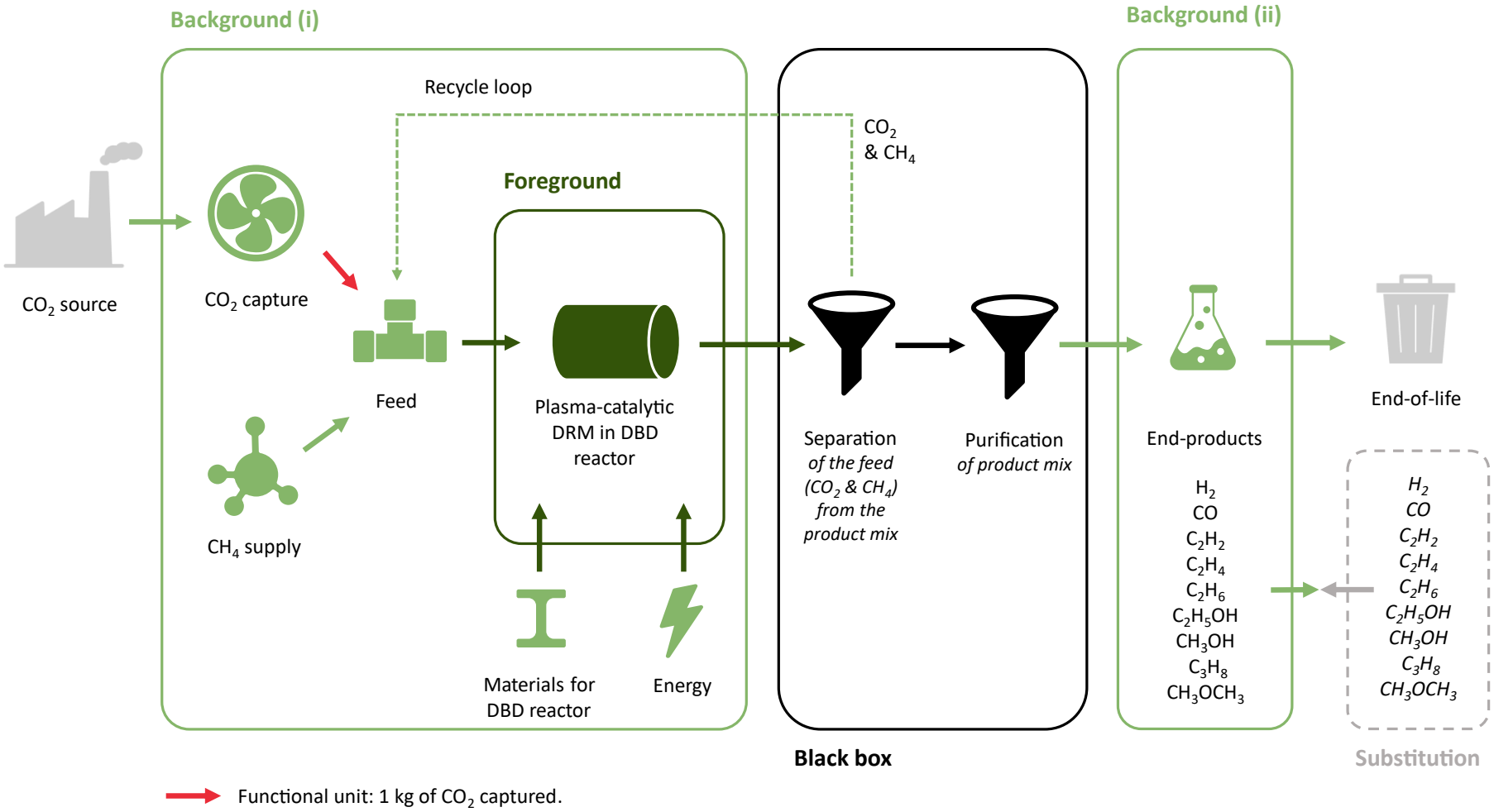


Figure 4.1: Flowsheet and system boundaries of the plasma-catalytic CCU value chain. Five boxes are indicated in the value chain: background (i), foreground, separation black box, background (ii) and substitution. The dark-green coloured arrow indicates the total feed of CO_2 and CH_4 to the DBD reactor, which consists of the CH_4, the captured CO_2 and the recycled CO_2. The red arrow represents the functional unit, defined as the utilisation of 1 kg of CO_2 captured.

This study adopts a cradle-to-gate perspective: the system boundaries of the LCA cover all stages from the feed (CO_2 and CH_4) until the separated end-products. The CO_2 source and the end-of-life treatment lie outside the scope of this LCA. The value chain is further divided into the foreground system, the background system, the separation black box and the substituted products. The foreground system typically only includes those processes that can be manipulated by the decision-maker for whom the LCA is performed, whereas the background system covers the remaining processes that cannot or only indirectly be influenced by the decision-maker (Frischknecht, 1998). In **Figure 4.1**, the foreground system is drawn such that it only includes the plasma-catalytic DRM reaction in the DBD reactor. This choice is made because the main goal of this LCA is to find the optimal set-up of plasma catalysis in terms of environmental impact and because plasma catalysis is still in the phase of technological development where choices can be made. The background system includes the capture of CO_2, the supply of CH_4, the materials for the DBD reactor, the energy supply and the end-products.

As can be seen in **Figure 4.1**, the separation and purification of the product mix are treated as a black box. New, innovative separation technologies need to be developed to separate the CO_2 and CH_4 from the rest of the product mix and to further purify the end-products as desired. Hence, it is yet unknown how the separation and purification will take place exactly. Therefore, we make an abstraction of how these processes will occur and make assumptions about the separation and purification rate to calculate the in and outflows of the black box. The black box procedure allows us to analyse the impacts of all other processes in the value chain and to calculate the maximum impact that separation and purification can have within this CCU value chain.

The next step in the CCU value chain represents the purified end-products that are produced in the CCU route (**Table 4.1**). This step is also part of the background system in this LCA. Finally, the conventional production routes of these chemicals are also included in the value chain, as they are (partially) substituted by the novel CCU route.

The functional unit is the relative basis on which the impacts are compared. In this study, the functional unit is defined as the treatment of 1 kg of captured CO_2, that is 1 kg of CO_2 that is captured from the CO_2 source (red arrow in **Figure 4.1**). The feed to the DBD reactor consists of the captured CO_2, together with the supply of CH_4 and the recycled CO_2 and CH_4. The molar ratio of CO_2 and CH_4 in the feed is always one-to-one.[9] The amount of CO_2 (and CH_4) that can be recycled is different for each reactor configuration because it depends on the conversion rate. The higher the conversion rate, the more CO_2 is already converted into other products, and hence, the less CO_2 can be recycled.

Although the functional unit is more commonly chosen in terms of an end product, we chose to define the functional unit from the perspective of the amount of utilised CO_2. The main rationale behind CCU is to use CO_2 as a substitute for fossil fuels as a source of carbon in production processes. By setting the functional unit as the utilisation of 1 kg of captured CO_2, we can evaluate which of the 48 value chains succeeds in using 1 kg of CO_2 captured most effectively, in environmental and economic terms.

Two other, more pragmatic, reasons also justify this methodological choice. First, 48 different plasma set-ups are compared in this LCA, each resulting in a different product mix with different shares of

[9] During the experiments, the total feed of CO_2 and CH_4 is kept constant for all tested combinations, i.e. 50 m^3/h CO_2 and 50 m^3/h CH_4. As the amount of CO_2 that can be recycled depends on the conversion rate, the amount of CO_2 captured needs to be adjusted accordingly, to keep the total feed of constant. The required amount of CO_2 captured is calculated for each plasma configuration and shown in **Figure A.4.1Figure A.4.1** in 4.A Functional unit. Since the functional unit here is defined as 1 kg of CO_2 captured, all the processes are rescaled to 1 kg of captured CO_2.

each end product. Hence, defining the functional unit on the end product would be complex and reduce interpretability.[10] Second, the choice of a functional unit is important for the comparability of the results (Müller et al., 2020). Cuéllar-Franca and Azapagic (2015) converted the results from different studies to the functional unit of 1 kg of CO_2 removed, to be able to compare the studies even when different end-products were initially targeted.

4.2.2 Life Cycle Inventory

The LCI describes the collection of data needed to perform the LCIA. The creation of the LCI is discussed for each box in the plasma-catalytic CCU value chain (**Figure 4.1**) separately: the foreground system, the background system, the black box (separation), and the substituted end-products.

Foreground system

The foreground system included the plasma-catalytic conversion of CO_2 and CH_4 in the DBD reactor. For the plasma-catalytic DRM reactions in the DBD reactor, data is gathered directly from the experimental work done at the LADCA and PLASMANT research groups of the University of Antwerp (Seynnaeve et al.). Their experimental work aimed to systematically analyse the effect of catalytically activated packing materials on DRM in a DBD reactor.

Figure 4.2 illustrates the reactor configuration that was used for all experiments. The DBD reactor is made of an alumina dielectric tube, with an inner diameter of 16.85 mm. In the centre of the alumina tube, a stainless-steel rod is placed to act as the inner (grounded) electrode, with an outer diameter of 7.99 mm. This results in a discharge gap between the stainless-steel rod and the dielectric barrier of 4.44 mm. The alumina tube is wrapped with a stainless-steel mesh, to act as the outer (high-voltage) electrode, over a length of 100 mm. The resulting reactor volume – without packing material – is 17.30 cm^3. The packing material is now inserted in the discharge gap of the DBD reactor, which reduces the available reaction volume. A packing efficiency of 46.87% was estimated, resulting in a packed volume of 8.11 cm^3 and an unpacked reaction volume of 9.19 cm^3.

Five different packing materials are tested in this *reactor configuration*, to analyse their effect on the DRM reaction: γ-Al_2O_3, 2% Fe_2O_3@γ-Al_2O_3, 10% Fe_2O_3@γ-Al_2O_3, 2% CuO@γ-Al_2O_3 and 10% CuO@γ-Al_2O_3. The γ-Al_2O_3 support is not catalytically activated and is tested as a benchmark. Previous studies have established the beneficial effect of the γ-Al_2O_3 support on the conversion rate and selectivity (Khoja et al., 2019). The γ-Al_2O_3 support is then impregnated with two different metal oxides for further catalytic activation of the packing and to observe how this affects the plasma catalysis' performance (Seynnaeve et al.).

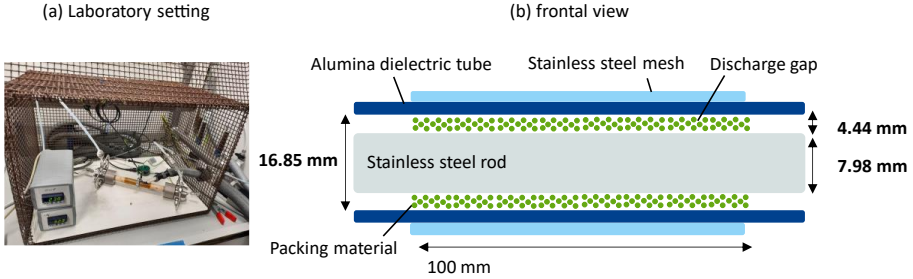


Figure 4.2: The cylindrical configuration of the DBD reactor in the experimental setup, (a) frontal view, and (b) in the laboratory.

[10] Either one particular product could be chosen as functional unit, treating all other products as waste, or a particular product mix with fixed ratios of each product, treating the remaining fractions as waste.

Iron and copper are selected as two promising and non-toxic metals that have previously shown satisfactory CO_2 conversion rates in catalysis (Kondratenko, Mul, Baltrusaitis, Larrazábal, & Pérez-Ramírez, 2013). For example, L. Wang, Yi, Guo, and Tu (2018) found that the combination of plasma with a Cu/γ-Al_2O_3 catalyst resulted in higher CO_2 conversion rate and higher methanol yield, compared to the plasma process without catalyst. Kondratenko et al. (2013) even stated that the most selective catalysts contain Cu as main active component.

The set of *process parameters* are the feed ratio, the flow rate, the plasma power and the Specific Energy Input (SEI). The feed ratio (CO_2:CH_4 1:1) and plasma power (30 W) are kept constant during the experiments. The flow rate is adjusted to manipulate the space time: lower flow rates mean longer space times, and vice versa, higher flow rates translate into shorter space times. The space time, i.e. the amount of time the gas spends in the reactor, varies between 5 and 80 s.

The SEI is based on the ratio of the plasma power and the flow rate:

$$SEI\left(\frac{kJ}{L}\right) = \frac{plasma\ power\ (W)}{Q\ (m\,L/m\,in)} * 60\ (s/min). \tag{4.1}$$

While the plasma power is the same for all experiments (30 W), the flow rate varies over the different experimental set-ups. Consequently, the SEI will also change, when the flow rate of the gas in the reactor is altered.

Table 4.2 summarises the 48 combinations for which the LCA is performed, resulting from the different alterations of packing material (*reactor configuration*) and space time (*process parameter*). The experiments deliver data for the CO_2 conversion (%), CH_4 conversion (%), energy consumption (kJ/L), and product mix composition (%) for each tested combination, presented in Appendix 4.B. in **Figure A.4.2** - **Figure A.4.5**. The experiments in the laboratory are performed with a lab-scale DBD reactor, with flow rates ranging from 6.9 to 110.4 mL/min. However, these low flow rates are not relevant at an industrial scale. Therefore, the LCA is performed for a pilot-scale DBD reactor. The DBD reactor can easily be scaled by numbering up multiple tubes in parallel, in a honeycomb structure (S. Li et al., 2020). The same methodology from the Techno-Economic Assessment (TEA) in Chapter 3 is used to scale the DBD reactor up to a pilot size with a flow rate of 100 m^3/h while adopting the same levels of CO_2 conversion (%), CH_4 conversion (%), energy consumption (kJ/L), and product mix composition (%) from the laboratory (Lamberts-Van Assche et al., 2022).

Background system

The background system includes the capture of CO_2, supply of CH_4, the materials for the DBD reactor, the energy supply and the end-products (after separation and purification).

The capture of CO_2 can be performed at the level of post-combustion, pre-combustion or oxyfuel combustion (Chai et al., 2022). Post-combustion capture involves the installation of a capture unit after the combustion, to separate the CO_2 from the flue gases. Post-combustion capture has received the most interest because it can easily be retrofitted to existing plants. Four main CO_2 capture techniques are identified: chemical absorption, adsorption, membrane separation and cryogenic distillation. Chemical absorption, with amine-based solvents such as monoethanolamine (MEA), is the most advanced capture technology and is already used in commercial capture facilities today (Chai et al., 2022; IEA, 2020a).

Table 4.2: The tested combinations from the experimental work of Seynnaeve et al. (n.d.). that are analyzed in this LCA.

Packing material	Space time (s)	Flow rate (mL/min)	Plasma power (W)	CO_2 conv. (%)	CH_4 conv. (%)	SEI (kJ/L)
γ-Al_2O_3	5	110.36	30.36	7.61	9.77	16.50
	10	55.18	29.75	11.98	16.72	32.34
	15	36.79	29.76	16.94	23.76	48.54
	20	27.59	30.02	18.95	26.96	65.28
	30	18.39	29.98	27.58	37.72	97.79
	40	13.80	29.77	30.57	42.43	129.50
	50	11.04	29.84	35.39	47.19	162.24
	60	9.20	30.19	38.73	52.08	196.94
	70	7.88	29.78	42.00	54.67	226.69
	80	6.90	30.18	44.26	57.48	262.57
2% Fe_2O_3@γ-Al_2O_3	5	110.36	30.11	3.68%	5.28%	16.37
	10	55.18	30.09	8.60%	12.86%	32.72
	15	36.79	29.88	12.26%	17.56%	48.74
	20	27.59	29.97	14.53%	21.41%	65.17
	30	18.39	30.03	15.72%	24.71%	97.96
	40	13.80	30.02	18.94%	29.45%	130.56
	50	11.04	29.96	19.28%	32.59%	162.90
	60	9.20	29.95	25.00%	37.98%	195.42
	70	7.88	29.95	27.26%	42.03%	227.98
	80	6.90	30.01	29.62%	45.22%	261.03
10% Fe_2O_3@γ-Al_2O_3	5	110.36	29.97	3.65%	5.34%	16.29
	10	55.18	30.01	3.58%	9.41%	32.63
	15	36.79	30.00	7.38%	12.65%	48.92
	20	27.59	30.04	8.97%	16.96%	65.33
	30	18.39	30.01	9.83%	18.57%	97.88
	40	13.80	30.00	15.09%	24.37%	130.50
	50	11.04	29.96	18.38%	29.84%	162.91
	60	9.20	30.02	16.88%	31.58%	195.85
	70	7.88	29.99	21.19%	35.86%	228.23
	80	6.90	29.99	20.11%	35.57%	260.91
2% CuO@γ-Al_2O_3	10	55.18	30.34	11.16%	15.73%	32.99
	15	36.79	29.60	15.98%	22.79%	48.28
	20	27.59	29.96	19.48%	27.06%	65.15
	30	18.39	29.64	24.79%	35.37%	96.70
	40	13.80	29.74	31.49%	43.45%	129.33
	50	11.04	30.27	32.90%	46.67%	164.55
	60	9.20	29.93	38.88%	52.26%	195.24
	70	7.88	30.05	40.41%	54.97%	228.68
	80	6.90	30.05	27.43%	50.49%	261.44
10% CuO@γ-Al_2O_3	10	55.18	29.94	12.35%	17.30%	32.56
	15	36.79	30.21	11.68%	19.29%	49.27
	20	27.59	30.13	15.99%	26.44%	65.51
	30	18.39	30.07	25.17%	37.03%	98.08
	40	13.80	30.17	27.84%	42.74%	131.24
	50	11.04	29.95	33.91%	49.88%	162.81
	60	9.20	30.05	33.75%	50.75%	196.02
	70	7.88	30.16	35.56%	59.23%	229.57
	80	6.90	30.08	37.58%	62.02%	261.68

Giordano, Roizard, and Favre (2018) performed an LCA of post-combustion CO_2 capture technologies, including chemical absorption with MEA. In this study, the CO_2 is captured from the flue gases of a pulverized coal-fired power plant, with a capture ratio of 90%. Giordano et al. (2018) provide the material and energy requirements and emissions to air, per tonne of CO_2 separated, presented in Appendix 4.B (**Table A.4.1**). These material and energy flows are translated into environmental impacts in the LCIA, to account for the impact of the CO_2 capture process. This results in a GWP of 0.403 kg CO_2-eq and a FFP of 0.079 kg oil-eq for 1 kg of CO_2 captured, which is added to the LCIA.[11] This is in the same order of magnitude as the GWP calculated in other studies for MEA-based CO_2 capture. For example, Grant, Anderson, and Hooper (2014) found a GWP of 0.232 kg CO_2-eq and Giordano et al. (2018) themselves found a GWP of 0.453 kg CO_2-eq per kg of CO_2 captured.

The materials that are needed for the construction of the DBD reactor include alumina (for the dielectric tube) and stainless steel (for the inner and outer electrode). The DBD reactor is also packed with various packing materials, that are composed of aluminium oxide (γ-Al_2O_3), aluminium oxide and iron oxide (Fe_2O_3@γ-Al_2O_3), or aluminium oxide and copper oxide (CuO@γ-Al_2O_3). The environmental impacts for using these materials in the construction of the DBD reactor and the assembly of the packing materials are retrieved from the ecoinvent 3.8 database. The used materials and quantities for one DBD tube and one kg of packing material are summarised in **Table A.4.2** and **Table A.4.3.** in Appendix 4.B.

Electrical energy needs to be supplied to create the plasma inside the DBD reactor. The energy need of the plasma-catalytic DRM reaction in the DBD reactor is calculated based on the power that was supplied to the DBD reactor in the experiments in the laboratory. The energy consumption for the lab-scale DBD reactor is then scaled to the size of a pilot DBD reactor. The electricity consumption of the DBD reactor is met by the Belgian electricity mix in 2018, which is included in the ecoinvent database. Since the plasma technology will only start operating in the future, the impact of changing from the current (2018) to a future electricity mix (2030) is investigated as well. The electricity mix for Belgium in 2030 is based on the Reference scenario 2020, which gives projections on the energy system for the EU as a whole and for the individual member states (European Commission et al., 2021). The electricity mixes for 2018 and 2030 are presented in **Figure A.4.6** in Appendix 4.B. The data for the modelling of the electricity mixes in 2030 in SimaPro is shown in **Table A.4.4**.

Finally, the background system includes the end-products, that could be sold on the market. These are the products that are observed at the outlet of the DBD reactor, after the separation and purification (black box).

The mass and energy flows for this background system, i.e. the CO_2 capture, supply of CH_4, the construction of the DBD reactor, the energy supply and the end-products, are calculated for the 48 combinations of the pilot-size DBD reactor, based on the performance of the lab-scale DBD reactor.

Separation (black box)

The black box in **Figure 4.1** includes the separation of the CO_2 & CH_4 feed from the product mix and the purification of the product mix. Snoeckx and Bogaerts (2017a) identified this need for post-separation, because all the products are in one feed, as one of the main disadvantages of the plasma technology, compared to other CO_2 conversion technologies. Due to the complexity of the product mix at the outlet of the DBD reactor and the generally high energy needs of separation technologies, innovation will be needed in separation technologies for the CCU value chain.

[11] Note that the same impact will be added to all 48 configurations, as the functional unit is 1 kg of CO_2 captured.

Figure 4.3 presents the composition of the product mix for five different combinations at a space time of 40 s and for the five types of packing. The main components in the product mix are the unconverted CO_2 and CH_4, H_2 and CO. The other components are observed in much lower fractions. However, it could still be valuable to separate these products from the mix because of high product prices or high environmental impacts in their conventional production routes. The presence of these high-value chemicals at low concentrations, e.g. dimethyl ether (CH_3OCH_3), can make the separation and purification process challenging.

This is further supported by **Figure 4.4**, which compares the boiling points, i.e. the temperature at which the liquid changes into a vapour, of each component in the product mix. While some boiling points are far apart, others are much closer to each other, which makes it much harder to separate these components. For example, the alcohols C_2H_5OH and CH_3OH have much higher boiling points than the rest of the product mix. This makes it more convenient to separate these from the rest of the product mix. In contrast, the boiling points of CO_2, C_2H_2, C_2H_4 and C_2H_6 are very close to each other, which can make it complicated to separate and recycle the unconverted CO_2 from the product mix.

Figure 4.3 and **Figure 4.4**illustrate why the separation and purification of the product mix at the outlet of the DBD reactor could require innovative separation techniques. However, two other caveats need to be made regarding the need for (innovative) separation technologies in the CCU value chain.

First, it is not per se necessary to reach 100% pure products. This depends on the downstream processes in which the end products are used. For example, the methanol (CH_3OH) in the product mix could be used in a methanol-to-olefin (MTO) process, which is one of the most important reactions in chemistry with one-carbon molecules and produces low-carbon olefins (Tian, Wei, Ye, & Liu, 2015). Using the same reaction mechanism, ethanol (C_2H_5OH) or dimethyl ether (CH_3OCH_3) could also be converted into olefins. Hence, these components do not necessarily have to be separated from each other but could be supplied in one mixture to an MTO plant. This example illustrates that the downstream processes in which the end products will be used are decisive for the separation needs.

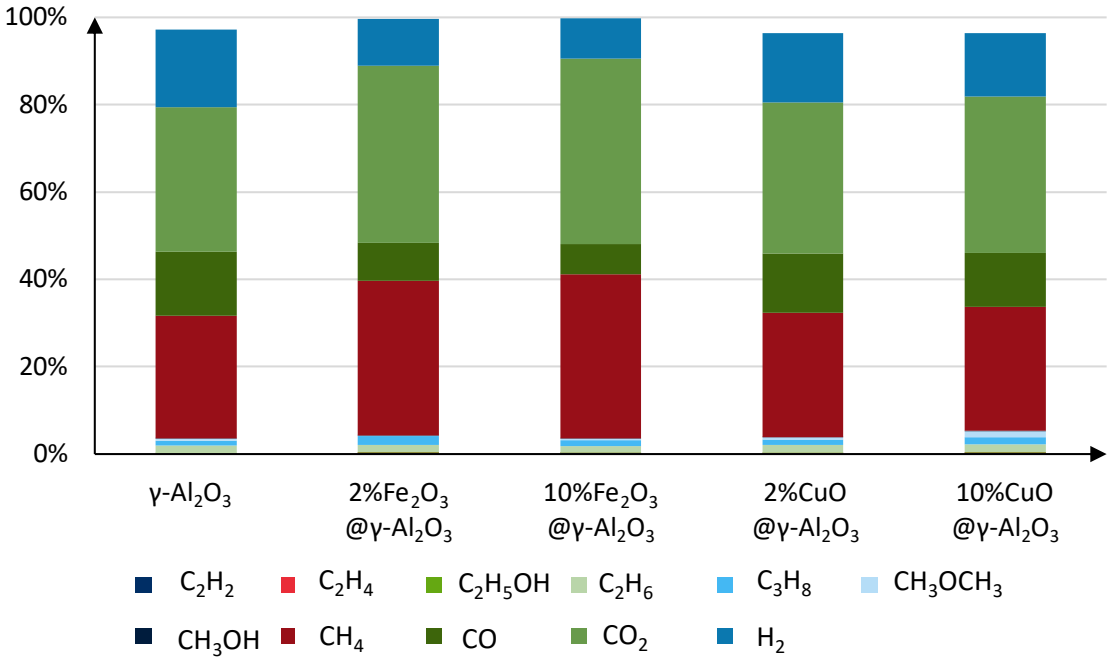


Figure 4.3: The composition of the product mix at the outlet of the DBD reactor at space time 40 s.

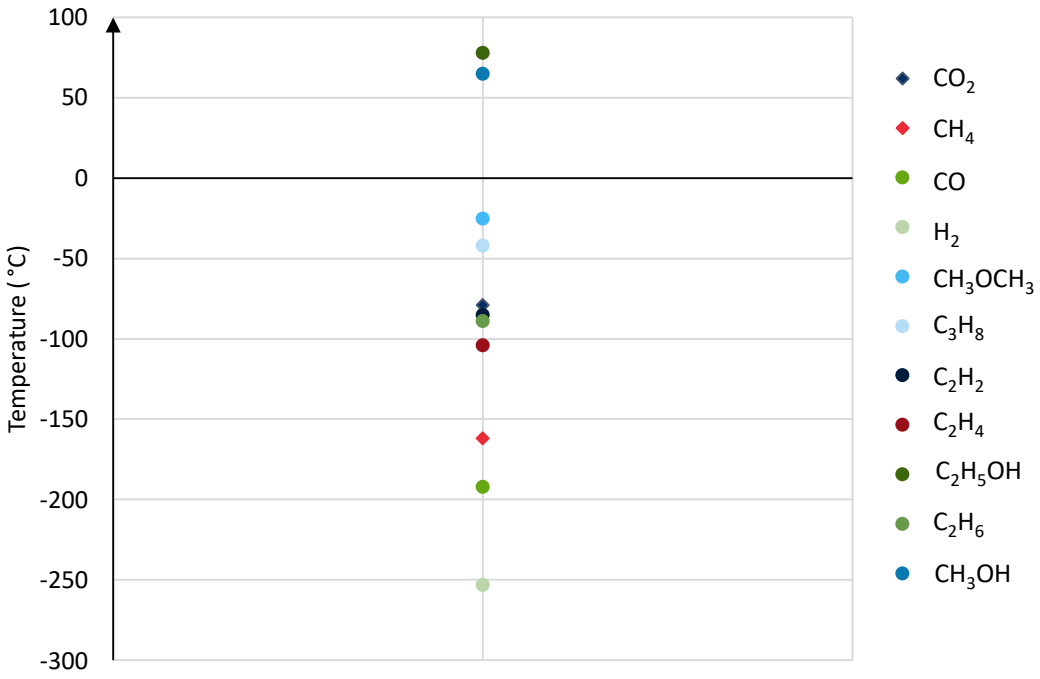


Figure 4.4: Boiling points of each component in the product mix at the outlet of the DBD reactor.

Second, the window of opportunity to improve separation technologies exists. **Figure 4.5** compares the relative energy use of different types of separation technologies. This figure demonstrates that it is possible to drastically reduce the energy consumption of separation, by choosing a different separation technique. For example, adopting membrane separation, instead of the more common distillation technique, could reduce energy use by more than 80% (none, 2005).

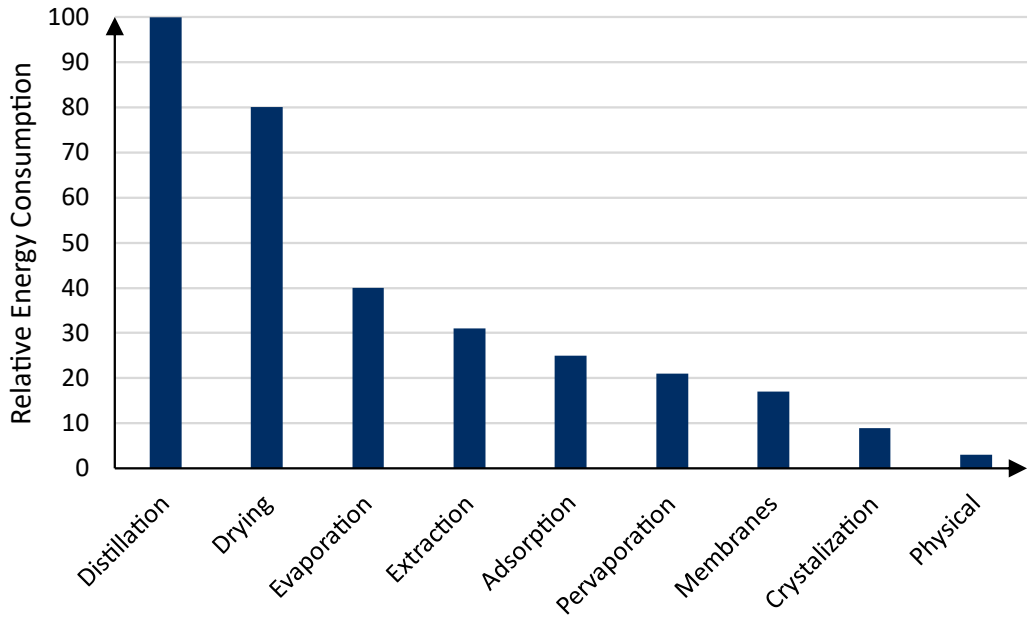


Figure 4.5: The relative energy consumption of various separation technologies. Adapted from "Materials for Separation Technologies. Energy and Emission Reduction Opportunities" (none, 2005).

For these reasons, the separation of the product mix is treated as a black box. Within this black box, we assume a separation rate of 90%, implying that 90% of the unconverted CO_2 and CH_4 can be separated from the product mix and that 90% of each product in the product mix can successfully be purified. The 10% unconverted CO_2 and CH_4 that cannot be recycled is assumed to be released as emission to air. These assumptions allow us to analyse the environmental impacts of the rest of the CCU value chain, without specifying the separation technique that would be used. Moreover, it enables us to calculate what the maximum impact of these separation steps can be to achieve a net-zero environmental impact over the full CCU value chain.

Substitution

Once the necessary separation and purification steps have been completed, the end-products are, in theory, ready to be sold on the market. As a result, the CCU-products can replace chemicals from conventional production processes. Hence, a credit is given, to represent the environmental burdens that are avoided by replacing the conventional production route. Ideally, this avoided impact is larger than the impact from the CCU route. This principle is called substitution (Zimmermann et al., 2018) and is represented by the grey box in **Figure 4.1**. The impacts from the conventional routes are retrieved from the ecoinvent 3.8 database. The selected processes are summarized in **Table A.4.5**.

4.2.3 Life Cycle Impact Assessment

The life cycle of a product or process is associated with the emissions of substances and the extraction of resources. In the LCIA, these emissions and the extraction of resources are translated into environmental impact score. In other words, the flows that were described in the LCI are now translated into the environmental impacts they can cause.

The translation from emissions and resources extraction to environmental score is done by using characterization factors, which indicate what the environmental impact is per unit of emission or per unit of resource used (Huijbregts et al., 2016). This characterization can happen at the midpoint or at the endpoint level. Midpoint indicators represent a single environmental impact category, e.g. climate change or land use, while endpoint indicators are the aggregation of multiple environmental indicators. Endpoint indicators present a measure of the damage to three higher levels: human health, biodiversity or resource scarcity. While endpoint categories better reflect the environmental relevance of the flows, midpoint categories have a lower level of uncertainty and are closer to the actual environmental flow. Following the ILCD Handbook, midpoint indicators are preferred because endpoint indicators are associated with subjective value choices that have to be made in the aggregation steps, and hence, with a higher level of uncertainty (Joint Research Centre Institute for Environment Sustainability, 2011).

The SimaPro 9.4 software is used to perform the LCIA. The characterization factors are retrieved using SimaPro. The calculations are performed using Microsoft Excel and Visual Basic for Applications (VBA). The ReCiPe 2016 Midpoint (H) method is selected to calculate the indicators (Huijbregts et al., 2016). The ReCiPe method offers 18 midpoint indicators. Two midpoint indicators are selected for more detailed analysis: global warming and fossil resource scarcity. These two are the most commonly investigated midpoint impact categories for CCU technologies (Müller et al., 2020).

The characterization factor of global warming (or climate change) at the midpoint level is the Global Warming Potential (GWP), expressed in kg CO_2-eq. The GWP expresses how much radiative forcing[12]

[12] Radiative forcing measures the difference between how much energy is entering the Earth's atmosphere and the amount of energy leaving the atmosphere (MIT Climate Portal, 2023). When more energy is entering the atsmophere than leaving, the atmosphere will warm up.

is caused by 1 kg of a GHG that is emitted into the atmosphere over a given time horizon, relative to the radiative forcing that is caused by 1 kg of CO_2 over that same time horizion (Huijbregts et al., 2016). In this study, the hierarchic (H) perspective was adopted, which assumes a time horizon of 100 years.

For fossil resource scarcity, the characterization factor at the midpoint level is the Fossil Fuel Potential (FFP), which is defined as the ratio of the energy content of the fossil resource and the energy content of crude oil (Huijbregts et al., 2016). FFP is expressed in kg oil-eq.

These characterization factors are used to calculate the global warming (GW) and fossil resource scarcity (FRS) impacts for the CCU value chain.

The remaining 16 midpoint indicators are calculated as well and will be presented in the Appendix. In the Results, only the GW and FRS impact will be shown in detail.

4.2.4 Scenario analysis

The LCI was established for the whole plasma-catalytic CCU value chain, based on the performance of the DBD reactor in the laboratory. The LCIA then calculates the environmental impact for all 48 combinations, to select the most promising *reactor configuration* and *process parameters* based on the results from the laboratory. This serves the first goal of the LCA study: (1) Design.

For the second and third goal of the LCA, (2) MAI for separation and (3) Outlook, future improvements in the plasma catalysis technology need to be assumed and implemented in the plasma-catalytic CCU value chain. These projected technological improvements are now implemented in three technology development scenarios. This can also be seen as a scenario analysis, that helps us to interpret the results of the LCA.

The technological improvements are assumed to happen in two steps. First, the energy consumption of the DBD reactor is reduced. Second, the conversion rate and selectivity of the plasma-catalytic DRM in the DBD reactor are improved as well.

One of the greatest challenges for plasma-catalytic CO_2 conversion is increasing energy efficiency levels while maintaining high CO_2 conversion rates (Bogaerts et al., 2020). Therefore, the first round of projected technological improvement involves an increase in energy efficiency: the energy consumption of plasma catalysis was reduced by a factor of 10, resulting in energy efficiency levels between 2 and 20%. This assumption is based on the Review Article of Snoeckx and Bogaerts (2017b), who set an energy efficiency target of 60% for the indirect production of syngas in plasma to be competitive with conventional syngas production. For a direct one-step process, however, the energy efficiency target can be set up to two or three times lower. Hence, the energy efficiency target for the conversion of CO_2 and CH_4 into higher-value chemicals in a one-step process is set at 20%.

The second round of technological improvements combines improved energy efficiency with higher conversion rates and improved selectivity . In this scenario, maximum conversion rates for CO_2 and CH_4 of 80% are reached. This is based on the highest observed conversion rates for CO_2 and CH_4 conversion in a DBD reactor in the Review Article of Snoeckx and Bogaerts (2017b) and in the Review paper of Khoja et al. (2019). Moreover, a selectivity of 100% towards CH_3OCH_3 is assumed because this component currently has one of the highest market prices (**Table A.4.7**).

Table 4.3: Three different scenarios (Laboratory, Energy-Efficient and Selective) will be evaluated for the 48 different reactor configurations.

Scenario	Description	CO_2 conversion (%)	Energy efficiency (%)
1. Laboratory	The CO_2 & CH_4 conversion rate, energy consumption and product mix composition are based on the plasma catalysis' performance, as observed in the laboratory.	5 – 45 %	1.1 – 5.4 %
2. Energy-Efficient	The first round of technological improvements involves a reduction in the energy consumption by a factor 10, to reach the energy efficiency target put forward in literature.	5 – 45 %	11 – 54 %
3. Selective	The second round of technological improvements includes higher CO_2 and CH_4 conversion rates and improved selectivity. The CO_2 and CH_4 conversion rates are increased by 1.5 and the energy consumption is still reduced by a factor 10, compared to the laboratory. Because of the increased conversion rate, the energy efficiency is further increased. In this scenario, the CO_2 and CH_4 are fully converted into CH_3OCH_3.	7.5 – 67.5 %	16 – 80 %

This results in three different scenarios that are evaluated for the plasma-catalytic CCU value chain: (1) Laboratory, (2) Energy-Efficient, and (3) Selective. The assumed CO_2 conversion and energy efficiency levels in each scenario are summarized in **Table 4.3**. Each scenario will be evaluated for all 48 combinations. While the CO_2 conversion and energy efficiency ranges in the first scenario simply reflect the observations from the laboratory, assumptions had to be made for the Energy-Efficient and Selective scenarios.

To put these technological improvements into perspective, the results are also compared to two other, previously tested, plasma set-ups. First, the results are compared to the conversion of CO_2 and CH_4 in a DBD reactor with a discharge gap of 0.455 mm and a SiO_2 packing, based on previous experimental work from Uytdenhouwen et al. (2021). Second, the environmental impacts of a similar process in a Gliding Arc (GA) reactor are calculated as well. A GA reactor is a different type of plasma, which can generally achieve higher energy efficiency levels than a DBD reactor. However, it is more difficult to insert catalysts in a GA reactor, resulting in lower conversion rates (Bogaerts et al., 2020). Cleiren, Heijkers, Ramakers, and Bogaerts (2017) performed experiments to convert CO_2 and CH_4 in the GA reactor with different fractions of CH_4. Their results also show the CO_2 conversion, CH_4 conversion, energy consumption and product concentrations that are reached in the GA reactor.

Figure 4.6 summarises these two parts of the Outlook. On the one hand, LCIA results are shown based on experimental ('historical') data, for the GA reactor, the DBD reactor with gap size 0.455 mm and the DBD reactor with gap size 4.44 mm (Laboratory scenario). On the other hand, LCIA results will also be presented for the Energy-Efficient and Selective scenarios, based on projections from literature.

The evaluation of various scenarios to deal with the lab-scale nature of the technology is similar to the prospective LCA methodology developed by Thonemann and Schulte (2019). In their study, a four-step approach is proposed to perform a prospective LCA for emerging technologies: (1) the LCA is performed for the lab-scale technology, (2) assuming ideal conditions, the LCA is done again for the best-case scenario, (3) taking into account the technical limitations, the LCA is performed for the up-scaled process, and (4) the results are interpreted, comparing the results along the three LCAs and with other existing LCA studies. Similarly, we perform the LCA first for the Lab Performance, based on the laboratory data. The Energy-Efficient and Selective scenarios are not so much best-case and up-scaled scenarios but rather intend to show how potential developments of the technology in the future would affect the environmental assessment. Different to the approach from Thonemann and Schulte (2019), all three scenarios are assessed at the scale of a pilot plant. Because of the linearity and modularity in upscaling the DBD reactor, the lab-scale technology can be translated to the pilot-scale plant without changing the technology's performance. Choosing the same size for the three scenarios also increases the comparability of the three scenarios.

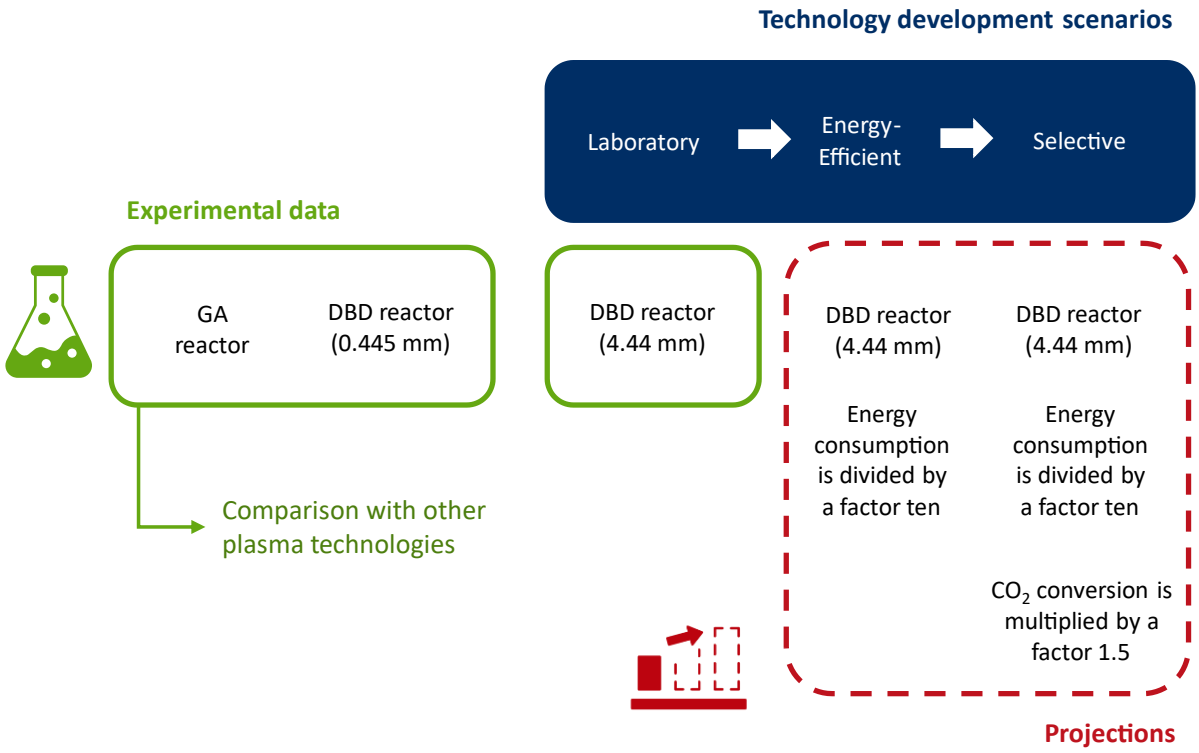


Figure 4.6: The Outlook for CO_2 conversion in plasma catalysis. Three technology development scenarios are analysed for the DBD reactor (4.44 mm). The Laboratory scenario is based on the experimental data, while the Energy-Efficient and Selective scenarios are based on future projections. The DBD reactor (4.44 mm) is also compared to two other plasma technologies, i.e. a GA reactor and a DBD reactor (0.455 mm) based on previous experimental data.

4.2.5 Techno-Economic Assessment

To achieve the final and fourth goal of this LCA study (Integration), a TEA is performed in this Chapter as well. This will allow us to compare the economic and environmental performance of the plasma-catalytic conversion of CO_2 into chemicals, and potentially identify trade-offs between both dimensions. The TEA framework developed by Lamberts-Van Assche et al. (2022), as presented in Chapter 3, is applied here to the 45 DBD reactor configurations. The Net Present Value (NPV), which describes the present value of all cashflows over the project's lifetime, is chosen as a metric to evaluate the economic feasibility of the technology. The main assumptions for the economic analysis are summarised in **Table 4.4**. The main differences with the TEA in Chapter 3 are in the price for the packing materials (200 €/kg here versus 88 €/kg in Chapter 3) and the end-products of the prices. In Appendix C, the prices from the end products are summarised in **Table A.4.7**.

Table 4.4: Main assumptions for the TEA.

Plant location	Belgium
Plant lifetime	20 years
Operational time	8000 h/yr
Discount rate	12%
Electricity cost	0.10 €/kWh
CO_2 capture cost	35 €/t CO_2
Packing material	200 kg

4.3 Results

In this section, the results of the LCIA are presented in three parts. First, the environmental impact scores for all 48 plasma set-ups in the Laboratory-scenario are calculated and compared. This will indicate which reactor configuration and process parameters are currently the most favourable in terms of environmental impacts (Design). Second, the 48 plasma set-ups are evaluated in the Energy-Efficient and Selective scenarios. The maximum acceptable impact (MAI) for the separation in the CCU value chain is then calculated. The evaluation of these future scenarios allows us to analyse how projected technological improvements would affect the environmental impacts (Outlook). Finally, the results of the Techno-Economic Assessment are contrasted with the results from the LCA (Integration).

4.3.1 Design

To analyse how the plasma catalysis configuration, i.e. the choice of packing material and space time, affects its environmental impacts, the Laboratory scenario is evaluated first.

Figure 4.7 (a) presents the GW impact as a function of the space time for the reactor configuration with the γ-Al_2O_3 packing, per process in the value chain, in the Laboratory scenario. The 'credits' for the avoided impacts from the conventional production processes of the chemicals in the product mix are presented apart from the other environmental impacts. These impacts are included, to represent the potential benefit of adopting the CCU route, in contrast to the conventional production route. However, the level of these avoided impacts is also subject to several assumptions. Hence, the credit is represented separately from the rest of the environmental impacts of the CCU value chain.

As explained earlier, the GW impact reflects how much radiative forcing is accumulated over a certain time horizon, because of the CCU value chain. Hence, the GW impact should be as low as possible.

Negative values for the GW impact would indicate that the CCU technology enables the reduction of this environmental impact, i.e. that the CCU value chain adds less GW impact than the avoided GW impact from the conventional production routes. From **Figure 4.7** (a), it can be seen that the impact from the energy supply (dark blue bars) outweighs all other impacts. The GW impact from the CO_2 and CH_4 that could not be recycled (grey bars) is also substantial, in particular at short space times (due to the lower conversion rates). The GW impact of the CO_2 capture, the materials for the DBD reactor and the packing material are very minor, compared to the impact from the energy supply for the CO_2 conversion. This figure also shows that the avoided impacts from the conventional production routes (green bars) are not nearly enough to counteract the impacts of the CCU production route.

Figure 4.7 (b) presents the net GW impact for all five packing materials, as a function of space time. The net GW impact is the sum of all environmental impacts in **Figure 4.7** (a), including the negative impacts from the avoided production routes. From **Figure 4.7** (b), it can be seen that the iron-based packing materials, 2% Fe_2O_3@γ-Al_2O_3 and 10% Fe_2O_3@γ-Al_2O_3, generate the highest net GW impact. The lowest impacts are observed for the configurations with the γ-Al_2O_3 packing, closely followed by the 2%CuO@γ-Al_2O_3 and 10%CuO@γ-Al_2O_3 packing.

Based on the results presented for the Laboratory-scenario in **Figure 4.7** (a) and (b), the most promising combination of *reactor configuration* and *process parameters* in terms of environmental impact, is a DBD reactor packed with γ-Al_2O_3, or CuO@γ-Al_2O_3 packing, and a space time of 5 to 10 s.

The reason that the combinations with γ-Al_2O_3 and CuO@γ-Al_2O_3 packings present lower net GW impacts than the Fe_2O_3@γ-Al_2O_3 packings can be found in the conversion rates that are reached with the different packings. **Figure A.4.2** presents the CO_2 conversion rate observed for all 48 combinations that were tested in the laboratory. From this figure, it can be seen that the combinations with γ-Al_2O_3 and CuO@γ-Al_2O_3 packing reach higher CO_2 conversion rates than the ones with Fe_2O_3@γ-Al_2O_3 packings. A higher CO_2 conversion rate means that more CO_2 is converted and utilised in the DBD reactor, and hence, more CO_2 can be captured to be treated annually. While the observed conversion rates are different for the five packings at the same space time, the SEI is (almost) the same for the five packings at each space time (Table 4.2). This means that, for the same input of energy, less CO_2 can be converted in the combinations with Fe_2O_3@γ-Al_2O_3 packings, than in the combinations with γ-Al_2O_3 and CuO@γ-Al_2O_3 packing. As a result, the impact from energy supply per kg of CO_2 captured (the functional unit) will be higher for the Fe_2O_3@γ-Al_2O_3 packings, explaining the elevated impacts.

In terms of *process parameters*, a shorter space time of 5 to 10 s should be preferred. Longer space times are associated with higher CO_2 conversion rates (**Figure A.4.2**). However, as the space time increases, not only the CO_2 conversion rate increases, but also the SEI (**Table 4.2** and **Figure A.4.4**). The adverse effect of the increased energy input outweighs the beneficial effect of the increased conversion rates.

Figure A.4.7, in Appendix 4.D, presents a very similar picture for the FRS impact. Higher values for FRS reflect the increasing depletion of fossil fuels, hence, the FRS impact should also be as low as possible. The FRS impact is dominated by the electricity supply, increases with longer space times, and is the lowest for the γ-Al_2O_3. The avoided impacts from the conventional production routes are more obvious in Figure A.4.7, but still insufficient to outweigh the additional burdens of the CCU route.

The results of the LCIA are also summarized in **Table A.4.8** and **Table A.4.9** in Appendix 4.D.

These results indicate that the enhanced catalytic activity, which is targeted by adding iron oxide or copper oxide to the γ-Al_2O_3 support, does not yet translate in reduced environmental impacts. The 10%Fe_2O_3@γ-Al_2O_3 packing generates environmental impacts that are more than 1.5 times greater

than the impacts for the γ-Al_2O_3 packing. In sum, based on the Laboratory-scenario, the most promising combination of *reactor configuration* and *process parameters* in terms of environmental impact, is a DBD reactor packed with γ-Al_2O_3, and a space time of 5 s.

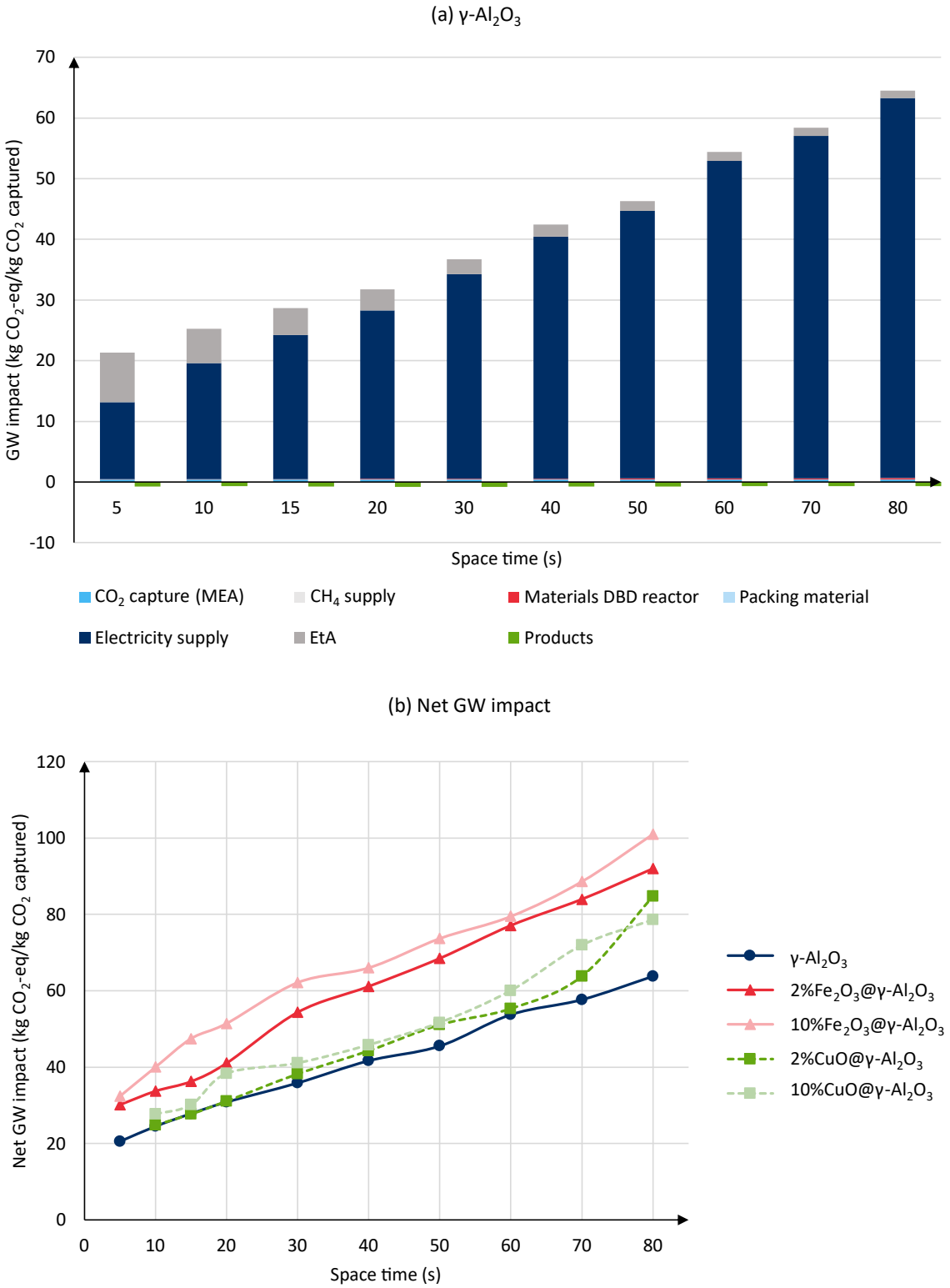


Figure 4.7: (a) GW impact for the *reactor configuration* with the γ-Al_2O_3 packing and (b) net GW impact for all five packing materials in the Laboratory scenario, with the electricity mix for Belgium in 2018.

The results for all 18 midpoint indicators are presented in **Figure A.4.8**, in Appendix 4.D.

4.3.2 Outlook & MAI for separation

To analyse how projected technological improvements from lab-scale to commercialisation would affect the environmental impacts, the Laboratory, Energy-Efficient and Selective scenarios will be compared in this section. Because plasma catalysis would only be put into operation in future years, the environmental impacts for the three scenarios are calculated and presented using the expected electricity mix for Belgium in 2030.

Figure 4.8 compares the Laboratory, Energy-Efficient and Selective scenarios for the γ-Al_2O_3 packing, assuming that the energy needs in the value chain are met by the electricity mix of Belgium in 2030. It can be seen from **Figure 4.8** that the technological improvements would result in large reductions in the environmental impacts.

The largest reduction is already observed from the Laboratory to the Energy-Efficient scenario, due to the reduced energy requirements in the Energy-Efficient scenario (the energy consumption was reduced tenfold from the Laboratory to the Energy-Efficient scenario (**Table 4.3**)). From the Energy-Efficient to the Selective scenario, the main change is observed for the avoided impacts of the products. This higher avoided impacts for the products can be attributed to the higher conversion rate and selectivity towards DME that is assumed in the Selective scenario (**Table 4.3**). Here, the credits for the avoided conventional production routes begin to balance the additional burdens of the CCU route, in particular in terms of fossil resource scarcity. This illustrates the potential of CCU to replace fossil fuels as a resource in the production of chemicals and hence, reduce our dependency on fossil fuels.

In the Laboratory and Energy-Efficient scenarios, it made no sense yet to calculate the MAI for separation, because the environmental burdens of the CCU route were much higher than the benefits (the avoided impacts). Hence, the MAI for separation would have been negative, which is not feasible in practice. In the Selective scenario, the MAI for separation can be calculated. **Figure 4.9** presents the maximum impact that the separation step can have, in terms of (a) GW and (b) FRS, in the Selective scenario, for the γ-Al_2O_3 packing.

Figure 4.9 (a) shows that the MAI for separation is still negative in terms of GW impact. Even in this Selective scenario, under the assumption of 90% separation rate, the MAI for the separation steps is still non-existent in terms of global warming. Hence, the bar representing the MAI for separation is shaded in **Figure 4.9** (a). **Figure 4.9** (b), on the other hand, shows that the MAI for separation in terms of fossil resource scarcity is positive for all space times. The MAI for separation reaches its maximum at a space time of 15 s. Here, the separation steps can have a MAI of 1.34 kg oil-eq per kg CO_2 captured.

To illustrate how the separation rate affects the calculated MAI for separation, the assumed separation rate is changed from 90% to 100%. The results are presented in Appendix 4.D, in **Figure A.4.9**. In this scenario, all unconverted CO_2 and CH_4 can be separated from the rest of the product mix and looped back to the inlet of the DBD reactor. Hence, the emission-to-air impacts are resolved. A higher separation rate also results in higher amounts of end-products, and consequently, also in increased avoided impacts. The results in **Figure A.4.9** indicate that, with this higher separation rate, a positive MAI for separation is now also observed in terms of GW impact, at least at space times up to 15 s. The highest MAI for separation in terms of GW amounts to 0.86 kg CO_2-eq per kg CO_2 captured, at a space time of 5 s. The higher separation rate also results in increases in the MAI for separation in terms of FRS. The MAI for separation now reaches its maximum at a space time of 5 s. Here, the separation steps can have a MAI of 2.12 kg oil-eq per kg CO_2 captured.

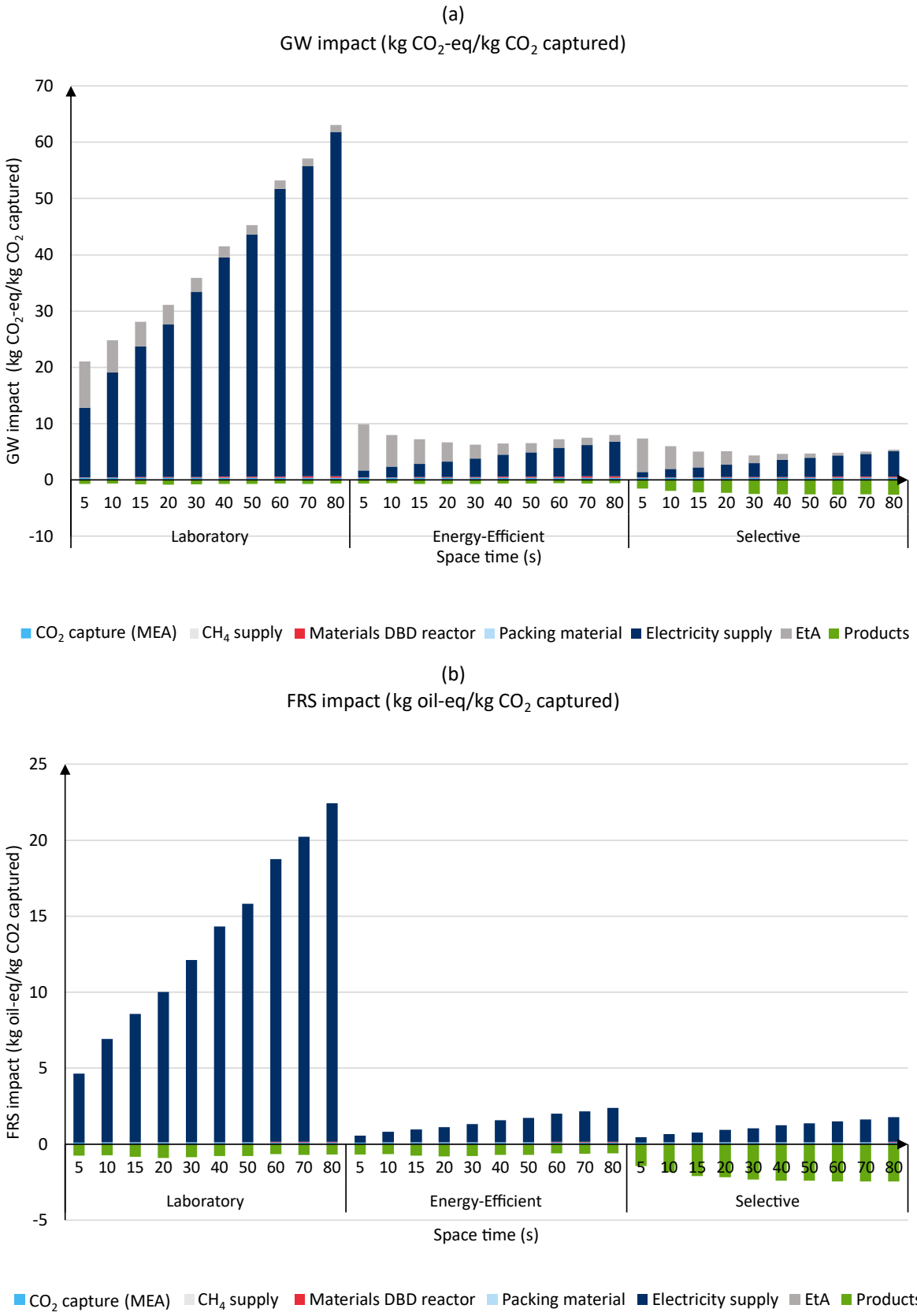


Figure 4.8: (a) Global warming and (b) fossil resource scarcity for the Laboratory, Energy-Efficient and Selective scenarios, with the electricity mix for Belgium in 2030.

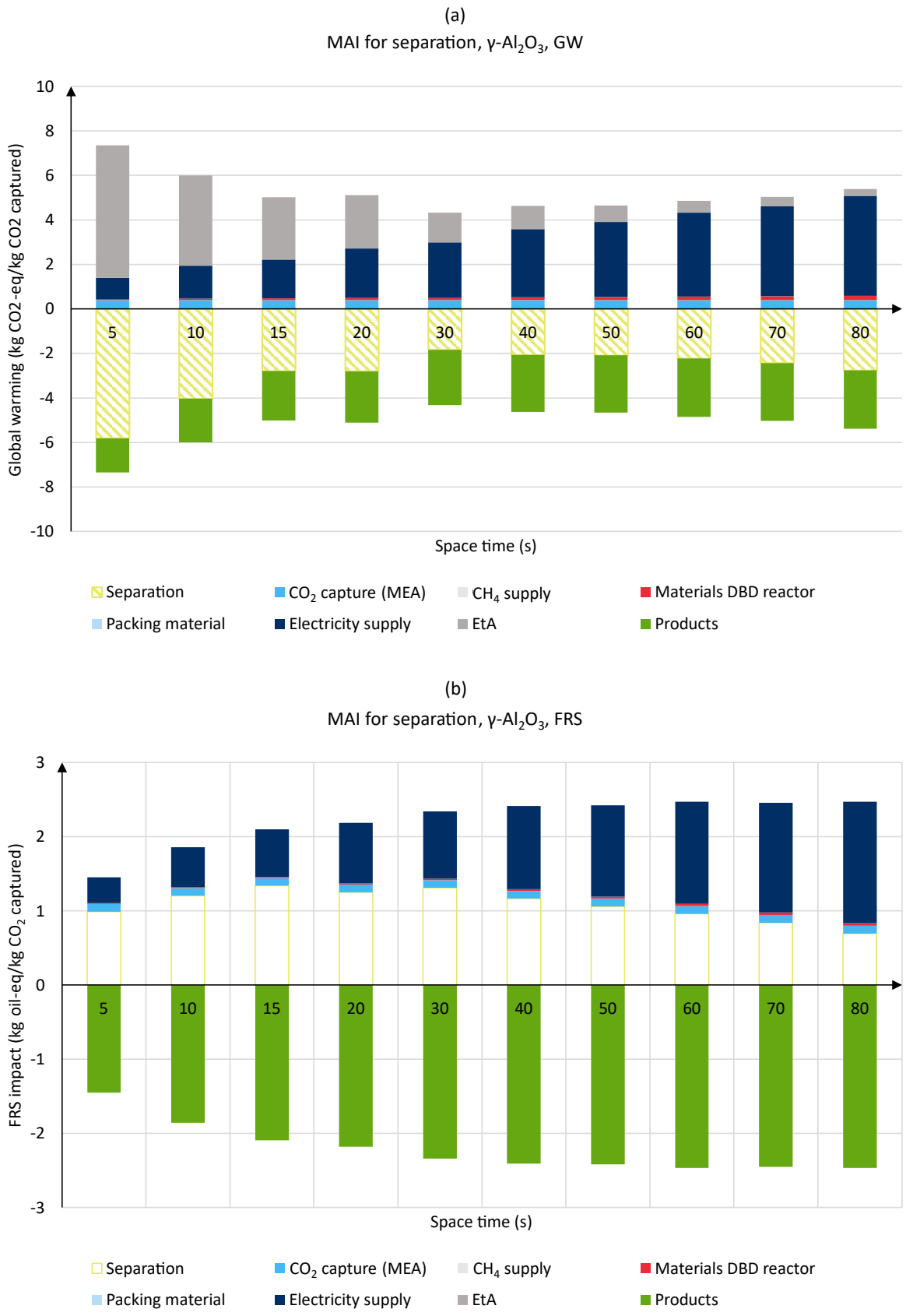


Figure 4.9: The MAI for separation, in terms of (a) global warming, and (b) fossil resource scarcity, in the Selective scenario, with the electricity mix for Belgium in 2030.

Finally, to illustrate how the plasma-catalytic DRM reactions have already evolved, the LCIA results based on previous experimental work for a DBD reactor with a smaller discharge gap and different packing material, and a GA reactor without packing material are also presented. This can be helpful to put into perspective how likely future improvements, due to technological changes, are and how influential they are for the environmental impacts. **Figure 4.10** compares the GW impact (a) and FRS impact (b) of the SiO_2-packed DBD reactor, the γ-Al_2O_3-packed DBD reactor (Laboratory), the GA reactor and the γ-Al_2O_3-packed DBD reactor (Selective).

The comparison of the SiO_2-packed DBD reactor with a gap size of 0.455 mm (Chapter 3) to the γ-Al_2O_3-packed DBD reactor with a gap size of 4.44 mm (Chapter 4) reveals the progress that has been made by reducing the gap size and changing the packing material. Both GW and FRS impact have been more than halved, due to these changes in the plasma configuration. **Figure 4.10** also reveals how the DBD reactors with different gap sizes have different impacts in different stages in the value chain. For the SiO_2-packed DBD reactor (gap size of 0.455 mm), the electricity supply dominates both the GW impact and FRS impact. Although the impact is still relatively small, the materials used in the DBD reactor contribute visibly to the GW impact of this DBD reactor. Due to the smaller gap size, lower flow rates can be reached in one tube; hence, more tubes are needed to reach that same total flow rate of 100 m^3/h. As a result, more materials are needed for the construction of the DBD reactor with a gap of 0.455 mm, compared to the DBD reactor with a gap size of 4.44 mm. For the γ-Al_2O_3-packed DBD reactor (gap size of 4.44 mm), the electricity supply is also the main contributor to the GW and FRS impact, although this impact is already three times smaller than in the DBD reactor with a gap of 0.455 mm. This reduced impact from the energy supply can be attributed to the reduced energy needs for the DBD reactors with a larger gap size. The impacts of the emissions-to-air (EtA), however, are much larger for the DBD reactor with the larger gap size. This is due to the lower conversion rates that are reached in this DBD reactor, compared to the DBD reactor with the smaller gap.

The GA plasma reactor presents even more promising results. The GW and FRS impact of the GA reactor are presented in **Figure A.4.10** in Appendix 4.D for different concentrations of CH_4. In **Figure 4.10**, only the GA reactor configuration with the lowest impact is presented. Thanks to its lower energy needs, the GA reaches almost net-zero GW and FRS impact.

Finally, the GW and FRS impact of the γ-Al_2O_3-packed DBD reactor in the Selective scenario are presented. The projected improvements in the energy efficiency and conversion rate result in greatly reduced environmental impacts, compared to the other DBD reactors. In comparison to the GA reactor, however, the DBD reactor still presents a higher GW impact than the GA reactor, even in this Selective scenario. The new DBD reactor can present a lower impact in terms of FRS. Due to the higher conversion rate and selectivity that can be reached with the DBD reactor, the benefits of the avoided fossil fuels are much larger than in the GA reactor.

This section presented the Outlook for the development of plasma catalysis as CO_2 conversion technology. To deliver environmental benefits, the technology will have to go through the presented technology development scenarios. The comparison of the DBD and GA reactor as potential plasma technologies showed that the GA reactor can present lower GW and FRS impacts, based on the current observations from the laboratory. The GA reactor has much lower energy requirements than the DBD reactor, which is the main reason for the lower environmental impacts. However, the conversion rates that can be reached are higher in the DBD reactor than in the GA reactor. As a result, the DBD reactor offers more potential to present avoided impacts from products, in particular in terms of FRS.

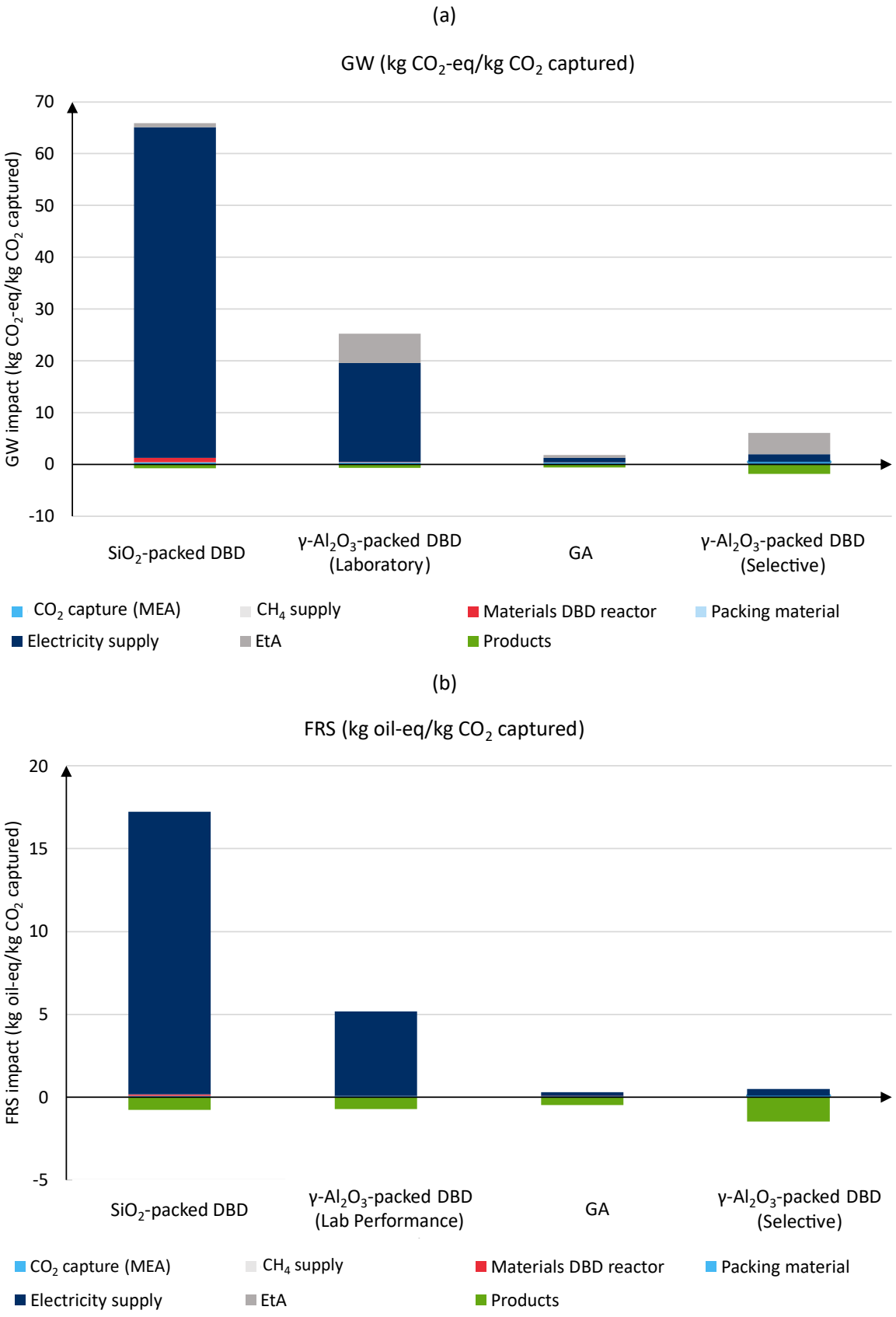


Figure 4.10: (a) Global warming and (b) fossil resource scarcity for the SiO_2-packed DBD reactor (10 s), the γ-Al_2O_3-packed DBD reactor (Laboratory – 10 s), the GA reactor (15% CH_4 concentration) and the γ-Al_2O_3-packed DBD reactor (Selective – 10 s) with the electricity mix of Belgium in 2018.

4.3.3 Integration

Finally, the paper also evaluates the performance of the plasma-catalytic conversion of CO_2 into chemicals from the economic perspective, to identify potential trade-offs between the economic and environmental evaluation.

Figure A.4.11 in Appendix 4.D presents the NPV for all 48 plasma configurations, per packing material and as a function of space time, both in the Laboratory and Selective scenarios. In the Laboratory scenario, the NPV is currently negative for all set-ups. The NPV decreases further with longer space time. No large differences between the five packing materials can be observed. However, in the Selective scenario, the NPV is negative for short space times at first, but increases as the space time lengthens. The NPV even reaches positive values for all five packing materials. In this Selective scenario, again, the discrepancy between the γ-Al_2O_3 and CuO@γ-Al_2O_3 packings and the Fe_2O_3@ γ-Al_2O_3 packings is observed.

To compare the environmental and economic performance, the GW impact and the NPV are plotted in one graph. **Figure 4.11** compares the GW impact to the NPV that is created per kg of CO_2 captured for all tested combinations. The different colours in **Figure 4.11** represent the different packing materials, and different dots from the same colours refer to different space times. The labels that indicate the space time are added for the γ-Al_2O_3 packing material, but similar patterns would be observed for the other packing materials. Four areas can be distinguished in this graph. In Area I, the NPV is negative and the GW is positive. Hence, these combinations are neither economically feasible nor environmentally desirable. Plasma setups in Area II now yield a positive NPV, but still generate a positive GW impact. In Area III, the GW impact is now negative, but the NPV is negative as well. Finally, in Area IV, the NPV created is positive and the GW impact generated is negative. Plasma configurations in Area IV are both economically feasible and environmentally desirable.

As can be seen from **Figure 4.11** (a), in the Laboratory scenario, and with the assumption that the energy needs are met by the electricity mix from 2018, all plasma configurations are in Area I and hence, they deliver both negative NPV and positive GW impact. From **Figure 4.11** (a), we can also observe that for the same GW impact, the γ-Al_2O_3 and copper oxide-based packing materials always deliver larger (i.e. less negative) NPV per kg of CO_2 captured than the iron oxide-based packings. **Figure 4.11** (b) presents the results for the Selective scenario, with the energy needs met by the electricity mix in 2030. Here, we observe a slightly different trend than in the Laboratory scenario. At short enough space times, both NPV and GW impact improve simultaneously when the space time increases: the NPV goes up and the GW impact goes down. However, at a space time of 30 s, a tipping point is observed. As the space time increases further, a trade-off between the economic and environmental performance emerges: while the NPV continues to improve, the GW impact now starts to deteriorate. **Figure 4.11** (b) also compares the different packing materials. As can be seen from **Figure 4.11** (b), the plasma configurations with iron oxide-based packings all present higher GW and lower NPVs per kg of CO_2 captured, than the γ-Al_2O_3 and copper oxide-based packings. The selection of the most optimal plasma set-up, based on **Figure 4.11**, will depend on the technology developer's preferences. If the developer or investor prefers to create more economic profits, a higher space time will be selected. If, on the other hand, the decision-maker prefers to minimize the environmental impact, the intermediate space time of 30 s will be selected, where the lowest GW impact is created, in combination with a positive NPV.

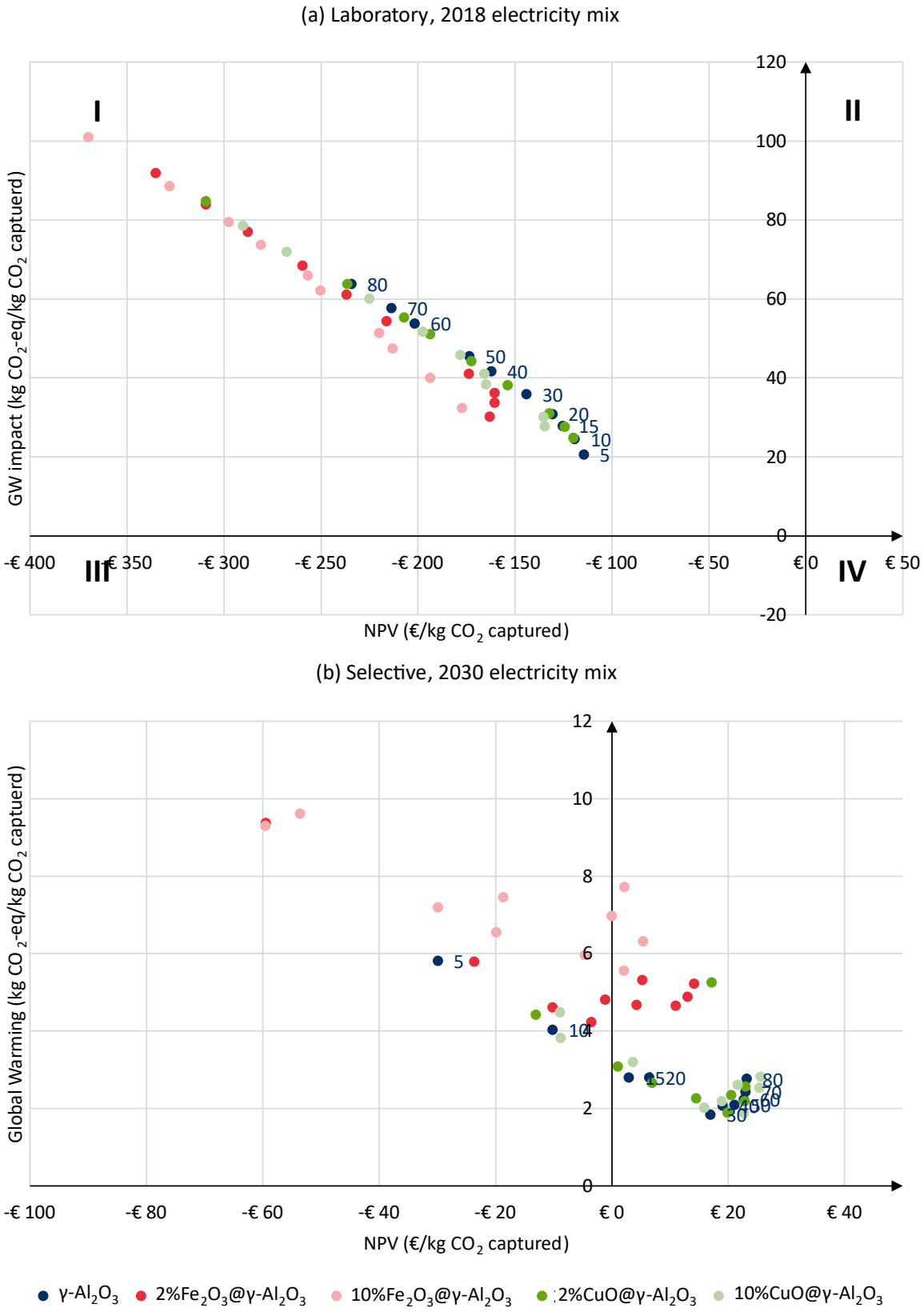


Figure 4.11: Global warming versus the NPV (EUR/kg CO_2 captured) for (a) the Laboratory scenario with the electricity mix of 2018, and (b), the Selective scenario with the electricity mix of 2030, for all five packing materials.

Figure 4.12 compares the FRS to NPV that is created per kg of CO_2 captured, both for the Laboratory and the Selective scenario. In the Laboratory scenario, all plasma configurations are in Area I, where a negative NPV and a positive FRS impact are created. In the Selective scenario, however, (almost) all plasma configurations result in a negative FRS. As a result, we can now find several setups with γ-Al_2O_3 and copper oxide-based packings, and even some set-ups with iron oxide-based packings, that yield both a positive NPV and negative FRS impact. This result again confirms that the greatest advantage of plasma catalysis as CCU technology lies in reducing fossil fuel dependency.

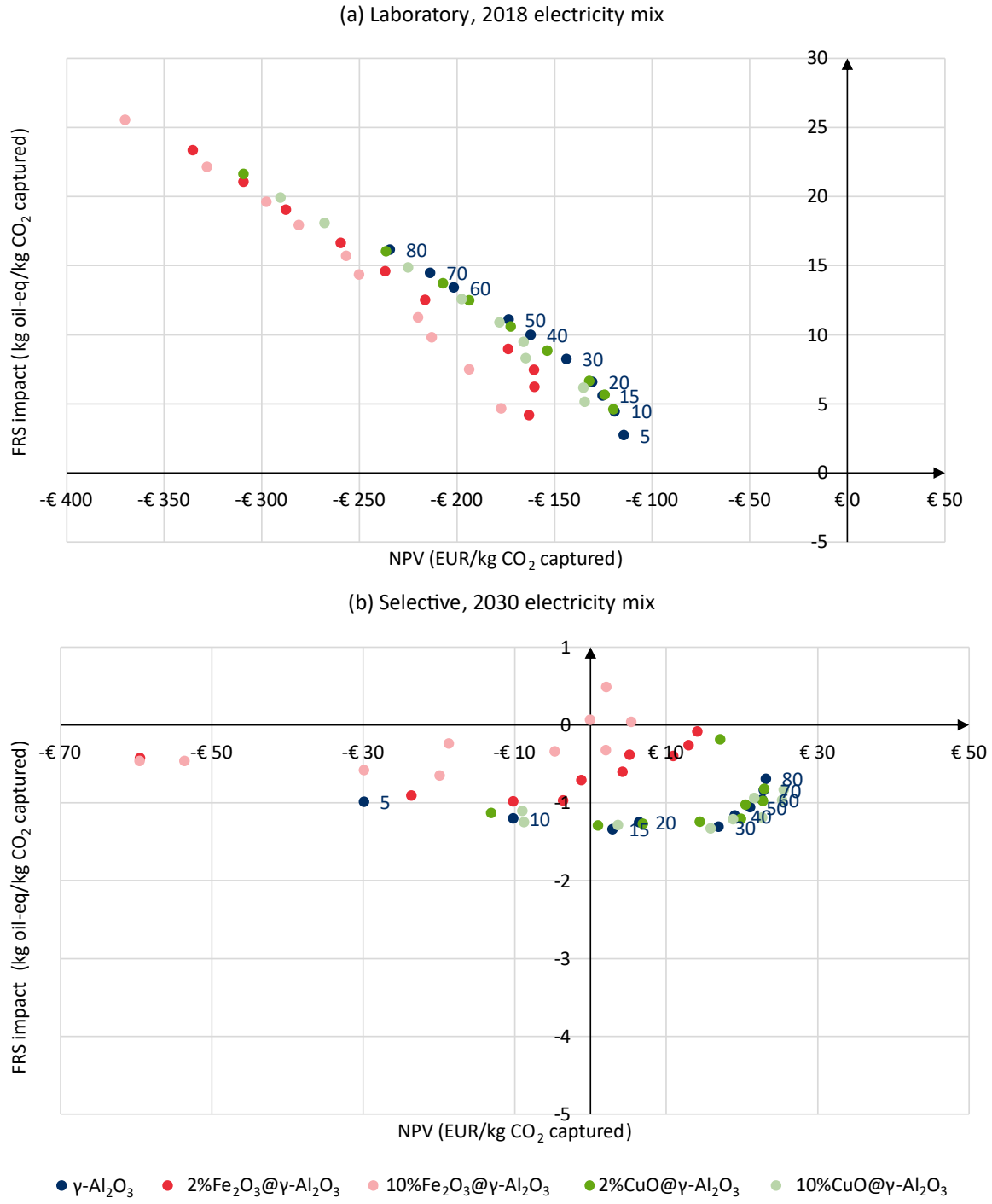


Figure 4.12: Fossil resource scarcity versus the NPV (EUR/kg CO_2 captured) for (a) the Laboratory scenario with the electricity mix of 2018, and (b), the Selective scenario with the electricity mix of 2030, for all five packing materials.

Figure 4.13 presents the energy efficiency (%) and CO_2 conversion rate (%) for those DBD reactor configurations that created both a positive NPV and a negative FRS. From **Figure 4.13**, it can be seen that lower conversion rates need to be compensated by higher energy efficiency levels and vice versa. This figure presents useful information for the technology developers, to understand which technical requirements need to be met before the technology is both profitable and environmentally beneficial. The minimum conversion rate that needs to be reached is approximately 25%, but this would have to be accompanied by an energy efficiency level of about 65%. While this CO_2 conversion rate is technically feasible in the current set-up, this energy efficiency level is very high for DBD plasmas. The minimum energy efficiency level observed in Figure 4.13 is approximately 20%, paired with a CO_2 conversion of about 30%. While CO_2 conversion rates of 30% (and higher) were observed in the experiments, the associated energy efficiency levels only reach about 2% currently.

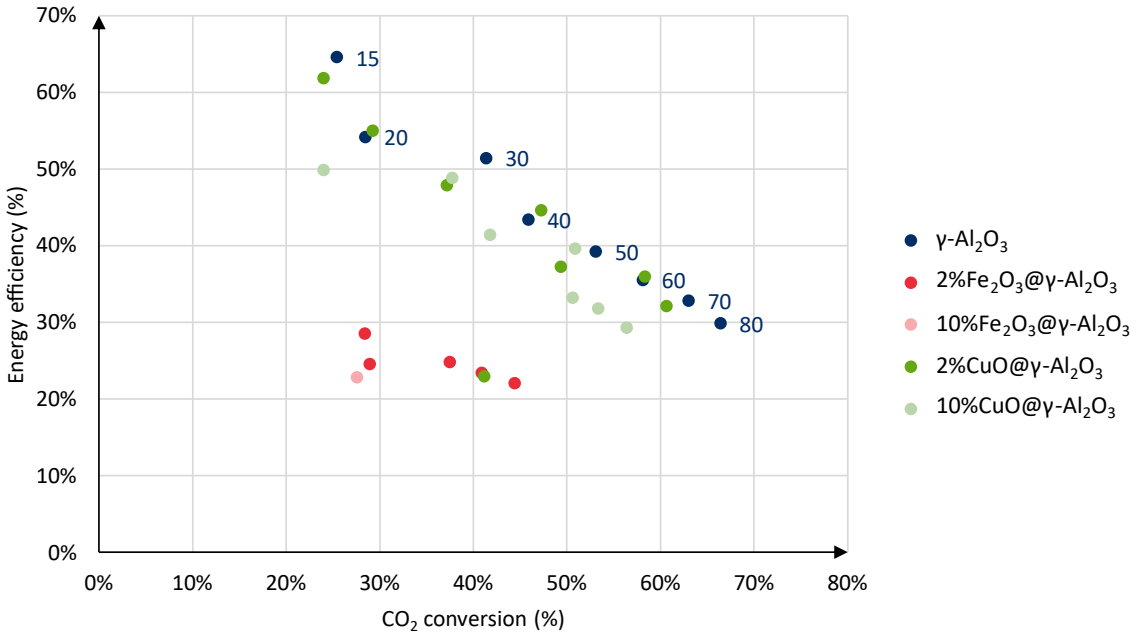


Figure 4.13: CO_2 conversion (%) and energy efficiency (%) levels for the DBD reactor configurations that result in a positive NPV (EUR/kg captured CO_2) and a negative FRS (kg oil-eq/ kg captured CO_2) in the Selective scenario (**Figure 4.12** (b)).

4.4 Discussion

This study performed an LCA for the plasma-catalytic DRM reactions in a DBD reactor, which is a promising technology for the chemical conversion of CO_2. Due to the lack of LCA studies for chemical CCU routes, as observed in the Introduction, it remains an open question whether chemical CCU routes can offer lower environmental impacts. This study calculated the environmental impacts of a CCU value chain, including the capture of CO_2, the conversion of CO_2 into chemicals in a DBD reactor and the avoided impacts from conventional production processes. Based on the results of the LCA, recommendations can be made for future research on the plasma-catalytic DRM reactions in the DBD reactor. First, one of the methodological choices that was made in this LCA is discussed.

The capture of CO_2 was included in the background system of the CCU value chain. The impact of CO_2 capture was based on the study of Giordano et al. (2018). They performed an LCA for the post-combustion capture of CO_2, using chemical absorption with MEA. In their study, the CO_2 is captured from the flue gases of a pulverized coal-fired power plant, with a capture ratio of 90%. The capture of

CO_2 from a pulverized coal-fired power plant is, however, not relevant in the context of Belgium or Flanders. No coal power plants are active anymore in this area. Nevertheless, the study of Giordano et al. (2018) was chosen because it provided the material and energy requirements of the CO_2 capture technology, per tonne of CO_2 separated. This enabled us to translate these material and energy flows into environmental impacts, in the LCIA. The main property of the CO_2 source that would affect the performance of the CO_2 capture technology is the CO_2 purity of the flue gases from that CO_2 source. The concentration of CO_2 in the flue gases of the pulverized coal-fired power plant investigated by Giordano et al. (2018) was rather low (13.5%). Hence, the included impacts for CO_2 capture are on the conservative side, as higher CO_2 concentration would generally facilitate the capture of CO_2. This concentration of CO_2 in the flue gases is in line with the CO_2 concentration of flue gases from a cement plant (15 – 34%) or a steel plant (21 -27%) (IEA, 2019c), which can be interesting CO_2 sources for CCU applications, and which also fit in a Belgian context.

The implications of this LCA study for CCU technologies in general and the future development of the DBD reactor for plasma-catalytic DRM reactions, in particular, are now discussed.

The LCA could not demonstrate any environmental benefits yet for the CCU value chain, based on the performance of the DBD reactor in the laboratory today. The energy requirements of the DBD reactor, to create the plasma and convert the highly stable CO_2 molecule, are the main cause for the high GW and FRS impact. Because the DBD reactor is still at an early stage of development, future technological developments were assumed and the environmental impacts were calculated again. Even in these future scenarios, the GW impact of the CCU value chain was still positive, indicating that the whole CCU value chain still accumulates radiative forcing (instead of removing it). However, the CCU value chain, with these future technological improvements, was able to present net benefits in terms of FRS impact. This observation can contribute to the debate in CCU literature on the motivation and incentive behind CCU technologies. Bruhn et al. (2016) argued that CCU technologies are not a solution to reduce CO_2 emissions and mitigate climate change, but rather a solution to reduce our dependency on fossil fuels (Bruhn et al., 2016). While conventional production processes need fossil fuels as the source of carbon, CCU processes use the captured CO_2 as a source of carbon. In other words, CCU routes allow the substitution of CO_2 for fossil fuels, as a source of carbon.

Another debate in the literature is the question of whether plasma catalysis research should be targeted at improving energy efficiency or improving the conversion rate. Based on the roadmap for plasma catalysis that was outlined by Bogaerts et al. (2020), the main challenge for the plasma-catalytic conversion of CO_2 in a DBD reactor is to improve the energy efficiency, without compromising the CO_2 conversion rate. In the current study, the evaluation of the three technology development scenarios showed that the greatest reduction in global warming impact was observed from the Laboratory to the Energy-Efficient scenario. These results indeed confirm the importance of improving the energy efficiency of the DBD reactor. However, the importance of improving the conversion rate, and the selectivity towards certain high-value chemicals, should not be underestimated. The integration of the TEA with the LCA (4.3.3.) revealed that the increased conversion rate and the improved selectivity towards dimethyl ether, as projected in the Selective scenario, were critical to finding a combination that combines environmental and economic benefits. The technology development from the Laboratory to the Energy-Efficient scenario was not sufficient to reach economic feasibility. Therefore, increasing the DBD reactor's energy efficiency is not the only challenge to tackle. To design a DBD reactor that delivers both environmental benefits and economic profits, it will be vital to improve the conversion rate and selectivity of the process as well.

The question can be raised whether the DBD reactor is the most suitable plasma technology to reach both higher energy efficiency levels and conversion rates. Alternative plasma technologies are the GA

or MW plasma. In their review of plasma technologies, Snoeckx and Bogaerts (2017a) report energy efficiency levels up to 20% for the DBD reactor, compared to a maximum of 70% in a GA reactor and 90% for the MW plasmas. However, GA and MW plasma are less suitable to combine with catalysts, which results in typically lower conversion rates and lower selectivity than the DBD reactor (Bogaerts et al., 2020). Conversion rates of 40 to 50% are commonly reported for the DBD reactor, while conversion rates of up to 20% are more common in GA and MW plasmas. With the right catalyst as packing material, chemicals such as higher hydrocarbons can be produced directly in the DBD reactor. While the GA and MW plasma cannot produce higher hydrocarbons in a one-step process, the presence of the catalyst in the DBD reactor allows the direct production of these higher-value chemicals. Producing higher hydrocarbons in a one-step process eliminates the need for Fischer-Tropsch process, which is usually energy-intensive. The ability to introduce packing materials remains one of the DBD's main advantages, which continues to stir interest in this technology.

In this LCA, not only the life cycle impacts of the processes in the DBD reactor were calculated, but also the impacts of CO_2 capture were considered. However, the impact of CO_2 capture was very small, compared to the other processes in the CCU value chain. The energy requirements of the CO_2 capture (98.3 kWh of electrical energy, 3.2 GJ of heat) are indeed only a fraction of the energy requirements of the DBD reactor (in the range of 5.6 to 86 GWh for the Laboratory scenario), which explains why the impact for CO_2 capture is so insignificant.

While the impacts from the CO_2 capture were included, the impacts that would be generated by the separation of the product mix were not included in this LCA. Instead, the separation and purification steps were treated, and the maximum acceptable impact (MAI) for separation was calculated. The MAI for separation reaches its maximum for the γ-Al_2O_3 packing at a space time of 15 s. Here, the separation can have a MAI of 1.34 kg oil-eq per kg CO_2 captured. To put this into perspective, this number should be compared to the impact observed in other LCA studies for the separation and purification of the end product. Aldaco et al. (2019) report steam consumption of 14.9 MJ per kg of formic acid, for the purification step. This translates into a fossil resource scarcity impact of 0.4 kg oil-eq per kg of CO_2 captured[13], well below the MAI of 1.34 kg oil-eq per kg CO_2 captured.

The calculated values for the MAI for separation of course depend on the assumptions made in the analysis. It depends e.g. on the chosen separation, as illustrated in **Figure 4.9** and **Figure A.4.9**, and on the chosen values for the avoided impacts from conventional production processes. The values for the included credits are listed in **Table A.4.6**, per kg of each component in the product mix. However, as discussed earlier in 4.2.2, the separation of all of the products present in the product fed at the outlet of the DBD reactor may not be needed. For example, as illustrated in **Figure 4.4**, the alcohols (ethanol (C_2H_5OH) and methanol (CH_3OH)) that are present in the product mix could be separated more easily from the rest of the mix, thanks to their higher boiling points. However, if we focus on the separation of the alcohols alone, the avoided impacts to be included in the LCIA should be adapted accordingly. As shown in **Table A.4.6**, the avoided impacts for the alcohols are on the lower side. In terms of going for the highest avoided impact, the focus should rather be on C_2H_2, H_2, C_2H_4 or CH_3OCH_3. Hence, if we would only separate the alcohols (C_2H_5OH and CH_3OH), this may lower the separation requirements, because of the difference in boiling points compared to the rest of the product mix (**Figure 4.4**), but it may also reduce the MAI for separation, because the avoided impacts will be lower (**Table A.4.6**).

[13] For the production of 1 kg of formic acid, 0.957 kg of CO_2 was needed. This results in a steam consumption of 15.57 MJ/kg CO_2. With 1 MJ equal to 0.2778 kWh, and an impact of 0.093 kg oil-eq/kWh (2030 electricity mix), the impact of 0.4 kg oil-eq/kg CO_2 was calculated.

The calculation of the MAI for separation also revealed that there is still no room for GWP impact, even in the Selective scenario, for the separation. The MAI for separation was calculated under the assumption that the energy needs of the DBD reactor and the CO_2 capture were met by the expected electricity mix for Belgium in 2030. This electricity mix still includes a considerable share of non-renewable energy, such as gas. If the energy requirements of the CO_2 conversion and CO_2 capture were met by 100% renewable energy, the GW impact could decrease considerably, creating scope for the separation steps. This is illustrated in **Figure A.4.13**, presenting the GW impact and the MAI for separation, if all of the energy needs are met by onshore wind energy. Adopting renewable energy would reduce the GW impact of the energy supply considerably. In this scenario, the MAI for separation can become positive, from a space time of 30 s. At shorter space times, the emissions to air still dominate, due to the lower conversion rates. Although it seems an optimistic scenario, it would in theory be possible to meet the energy needs of the CO_2 capture and CO_2 conversion with one wind turbine. A typical onshore wind turbine can produce more than 6 million kWh per year, whereas the energy requirements for the DBD reactor set-ups in **Figure A.4.13** vary from 0.56 million kWh to 9 million kWh per year. However, this would also involve an investment from the firm to build a wind turbine. Hence, to fully assess the feasibility of running the DBD reactor on wind energy by investing in a wind turbine for the CCU value chain, a TEA should also be performed again. This exercise simply means to illustrate what the (beneficial) effect would be on the environmental impact scores of the CCU value chain, if 100% renewable energy could be used to meet the energy requirements, instead of the electricity mix from Belgium.

To validate our results, the findings from this LCA study are also compared to the findings from previous LCA studies for plasma-based technologies. Stasiulaitiene et al. (2016) performed an LCA to compare the environmental impacts of plasma-based and conventional technologies to remove pollutants from flue gases. Their comparative LCA revealed that the plasma-based technology generally performs better in terms of acidification, eutrophication and human toxicity potential, while the conventional technology was preferred with respect to global warming impacts. The high electricity demand of the plasma-based technology was also identified as a barrier, which is consistent with our observations. King et al. (2021) also implemented a comparative LCA to evaluate the environmental impacts of a conventional SMR reactor and a DBD plasma reactor to produce hydrogen. In the scenario with the current electricity mix, the comparative LCA revealed no improvements for the DBD reactor, compared to the conventional SMR reactor. Even when a 100% green electricity mix was assumed, only moderate reductions in the environmental impacts were observed. Again, the main reason for this result was the increased energy requirements for the DBD reactor, compared to the conventional technology. Although the number of studies is limited for plasma-based technologies, each study comes to the same conclusion: the DBD reactor's high energy demand is the main contributor to its environmental impact. The results from this study confirm that the energy demand is the main source of its global warming impact and fossil resource scarcity, in its current state of technology development. However, in future technology development scenarios, the impact of the demand for energy is reduced significantly and the impact of other processes, start to weigh more on the environmental impacts. Moreover, we found that just reducing the energy requirements will not be sufficient to reach an environmentally desirable and economically feasible outcome. Improvements in the conversion rate and selectivity of the process will be indispensable as well to achieve both environmental benefits and economic gains.

The limitations of the study need to be recognised as well. First, this LCA study is largely based on experimental work for a technology at low TRL, and there is still a lot of uncertainty about how the technology might develop in the future. For this reason, the environmental impacts are always first calculated based on how the technology performs today in the laboratory (Laboratory scenario). This

scenario reflects the observations in the laboratory and consequently, this scenario deals with the lowest level of uncertainty. Second, primary data was only available for the plasma-catalytic conversion of CO_2 and CH_4 in the DBD reactor itself. All other processes (supply of CH_4, avoided products, …) were estimated based on data from literature. Third, the scope of this study was limited to Belgium. The Belgian electricity mix has its specific challenges. The electricity mix of Belgium in 2018, in the ecoinvent 3.8 database, still contains a high share of nuclear. In the future, nuclear energy is expected to phase out in Belgium. The EU reference scenario 2020 still assumes that nuclear energy will be completely phased out by 2030, and largely replaced by gas. However, the Ukranian war and subsequent energy crisis have revealed the vulnerability of the Belgian energy mix and its (future) dependency on gas. Hence, nuclear energy will probably still play a role in the Belgian electricity mix for longer than previously anticipated. As long as the higher share of nuclear energy does not hamper investment in renewable energy, this development can actually reduce the environmental impacts. Fourth and finally, the separation of the product mix at the outlet of the DBD reactor was treated as a black box and consequently, the potential environmental impacts of the separation steps were not yet included in the presented results. Instead, the MAI for separation' is calculated, indicating what the maximum acceptable environmental impact could be for the necessary separation steps. Nevertheless, the life cycle impacts presented for the CCU value chain will still be underestimated, because the separation is not included in the system boundaries.

4.5 Conclusions

This study performed an LCA for an emerging CCU technology, the plasma-catalytic conversion of CO_2 into chemicals in a DBD reactor. In the first phase of the LCA, four goals were: (1) Design, (2) MAI for separation, (3) Outlook, and (4) Integration. The main insights that were gained from the LCA are now summarised per goal.

To contribute to the R&D of plasma catalysis, this study aimed to investigate how the chosen reactor configuration (i.e. packing material) and process parameters (i.e. space time) affect the environmental performance. Performing the LCIA for all 48 combinations allowed us to compare the performance of the five different packing materials and the different space times. Based on the Laboratory scenario, a plasma catalysis set-up with a short space time and the γ-Al_2O_3 packing should be preferred to minimise the environmental impacts.

To present a future Outlook for plasma catalysis as emerging CCU technology, two other technology development scenarios are evaluated, i.e. the Energy-Efficient and Selective scenarios. The evaluation of the Laboratory, Energy-Efficient and Selective scenarios showed that the greatest reduction in environmental impacts was realised with the transition from the Laboratory to the Energy-Efficient scenario. If the energy consumption can be reduced by a factor of 10, as projected in the Energy-Efficient scenario, the environmental impacts will be reduced almost proportionally as well. Further improvements in the conversion rate, in the Selective scenario, do not have the same effect on the environmental impact.

The technology development pathways presented in the Energy-Efficient and Selective scenarios also allow us to reformulate our recommendations towards the technology developer in the laboratory. In all three scenarios, the γ-Al_2O_3 packing and copper oxide-based packings deliver the lowest impacts, while the iron oxide-based packing materials deliver the highest impacts, both in terms of global warming and fossil resource scarcity. In terms of space time, the recommendations are a bit more spread. The Laboratory scenario suggests focusing on short space times, whereas the Mature Performance reveals that an intermediate space time of 30 s results in the lowest impact.

The analysis of the Selective scenario also enabled us to calculate the 'space for separation'. Even in this advanced scenario, we found that there is no room for environmental impacts of the separation steps in terms of global warming. In terms of fossil resource scarcity, however, the space for separation was substantial.

To complete the Outlook for plasma catalysis in the DBD reactor, the LCA was also performed for a different type of plasma, the GA reactor. Compared to the GA, the DBD reactor presented higher global warming due to the higher energy requirements. However, the DBD reactor could potentially result in lower fossil resource scarcity, thanks to the higher conversion rates, that result in higher avoided impacts from the end products. The Energy-Efficient and Selective scenarios also highlighted the importance of including the avoided impacts of the products, that are otherwise produced in fossil-based production processes. Accounting for these avoided impacts can make the net impact negative, in particular for fossil resource scarcity. The greatest advantage for the plasma-catalytic DRM reactions in the DBD reactor lies indeed in reducing fossil fuel scarcity.

Finally, for the Integration of the economic and environmental perspective, the results from the LCA were plotted against the results from the TEA. The integration with the TEA confirmed that the iron oxide-based packings are the least promising for the conversion of CO_2 and CH_4 in the DBD reactor. From the integration with the TEA, we also learnt that improvements in the conversion rate are equally crucial to reach an economically and environmentally desirable technology.

Future research is needed to explore how the plasma catalysis technology performs for the production of one particular chemical. If the right packing can be found in the laboratory, that targets a high-value chemical such as dimethyl ether, the LCA study should be repeated. The functional unit can then be specified in line with the produced chemical.

In sum, this study helps steer the research in the laboratory towards the most optimal plasma catalysis configuration for the conversion of CO_2 and CH_4 in the DBD reactor, both from the environmental and the economic perspective. This study, in particular, formulates recommendations on the selection of packing materials and the choice of space time. The future challenge to tackle in the laboratory is designing a packing material tailor-made for plasma catalysis, that enables higher conversion rates and selectivity towards high-value chemicals, and lowers the energy requirements of the DBD reactor.

Appendix – Chapter 4

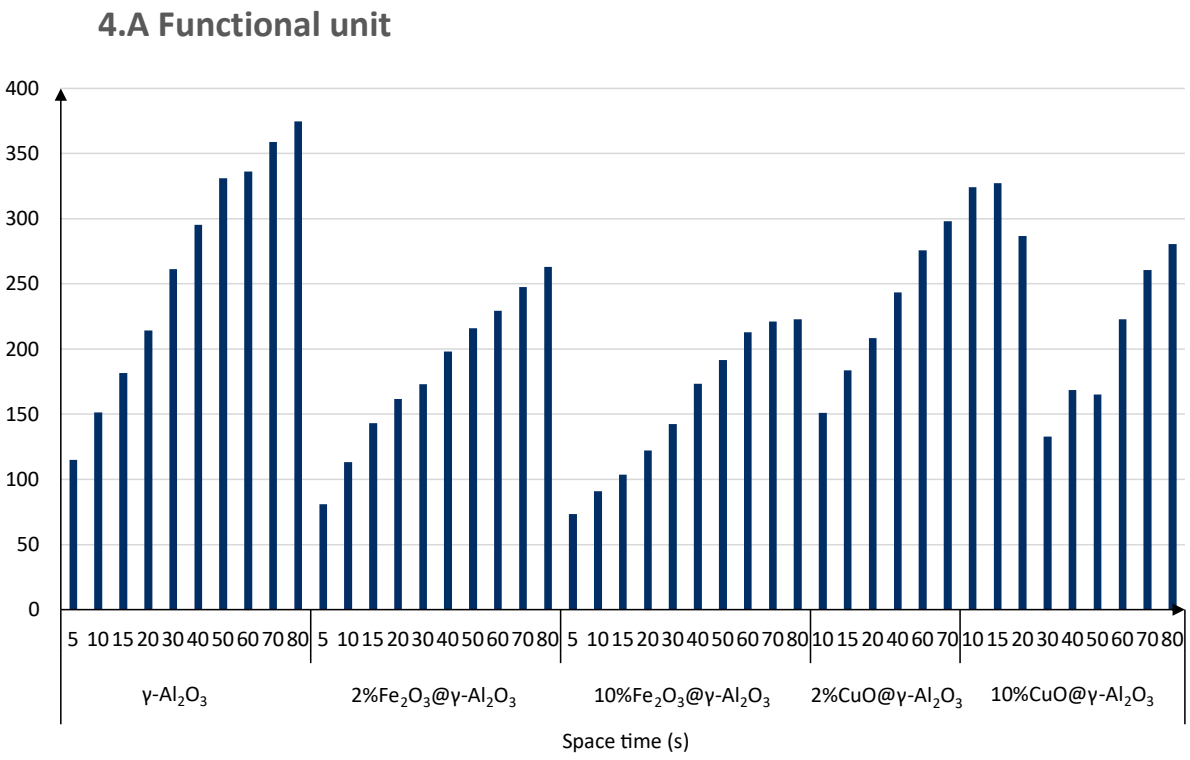


Figure A.4.1: Amount of CO_2 captured (t/year) as a function of space time for the pilot-size DBD reactor with a total feed of 50 m^3/h CO_2 and 50 m^3/h CH_4, for all five packing materials.

4.B Life Cycle Inventory

4.B.1 Technical parameters

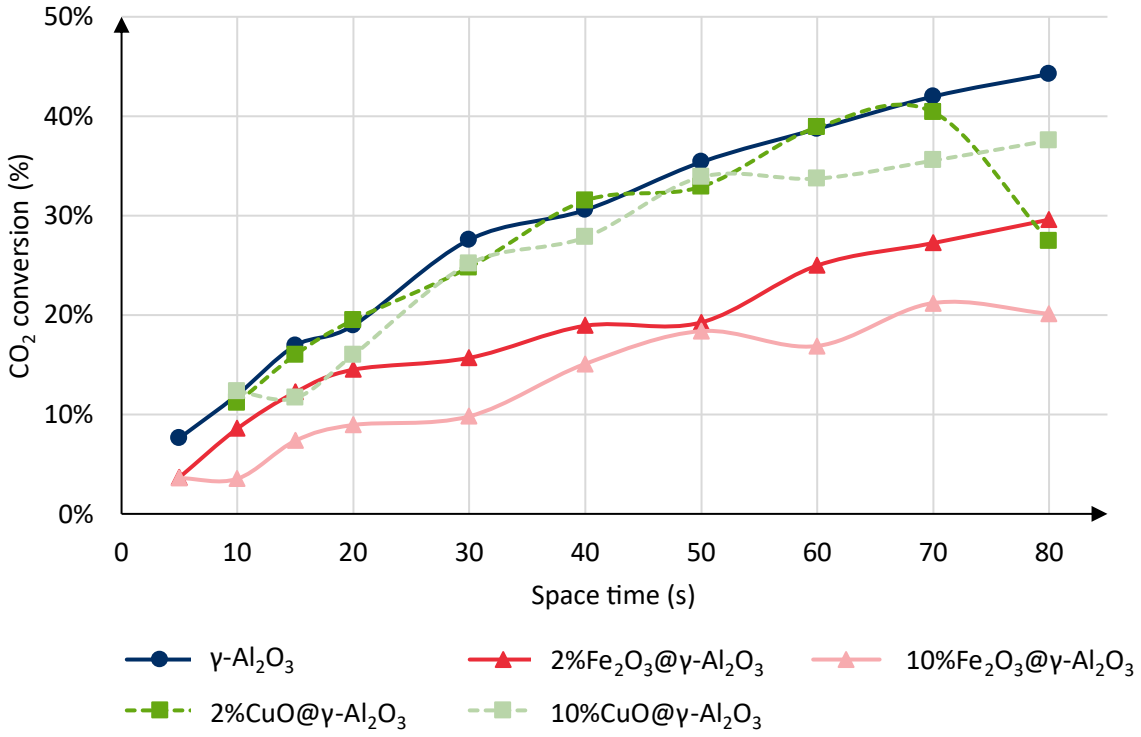


Figure A.4.2: CO_2 conversion (%) as a function of space time for the five packing materials.

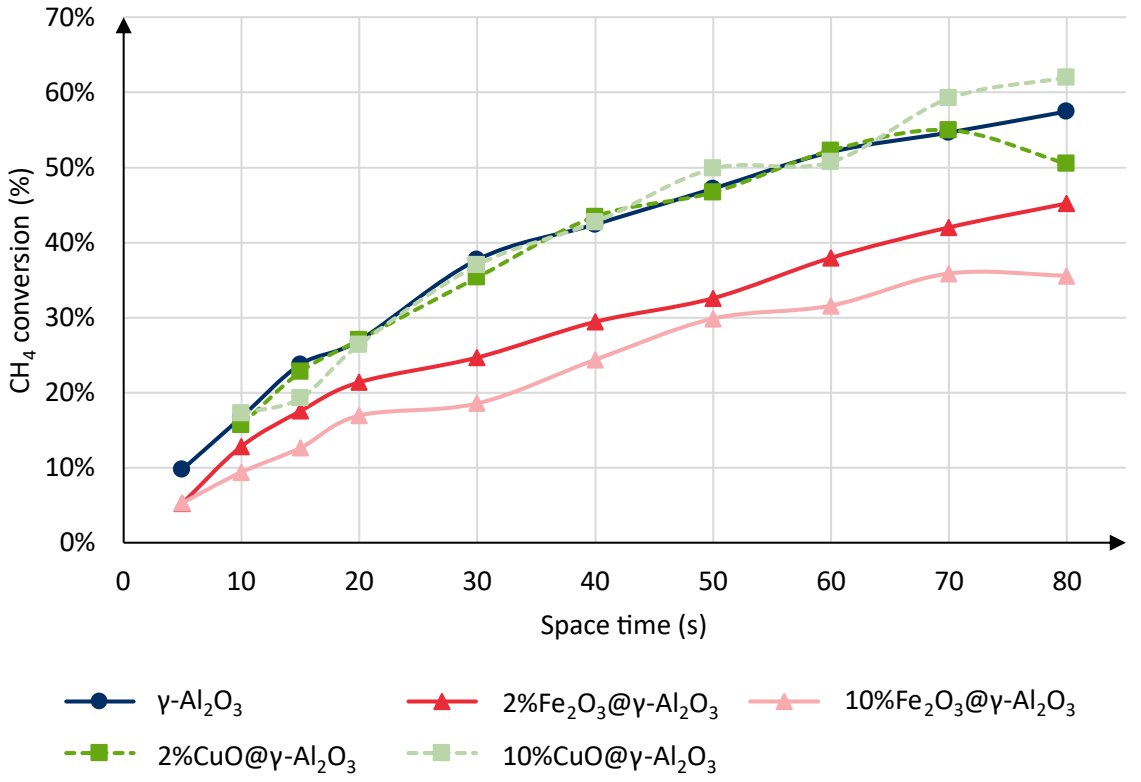


Figure A.4.3: CH_4 conversion (%) as a function of space time for the five packing materials.

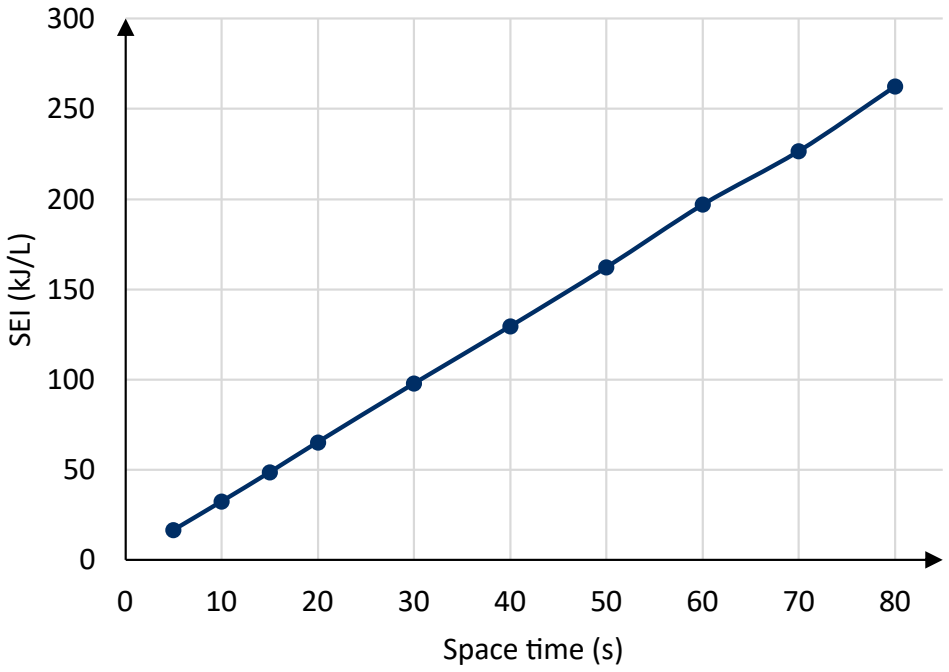


Figure A.4.4: Specific Energy Input (SEI) (kJ/L) for the γ-Al_2O_3 packing, as a function of space time.

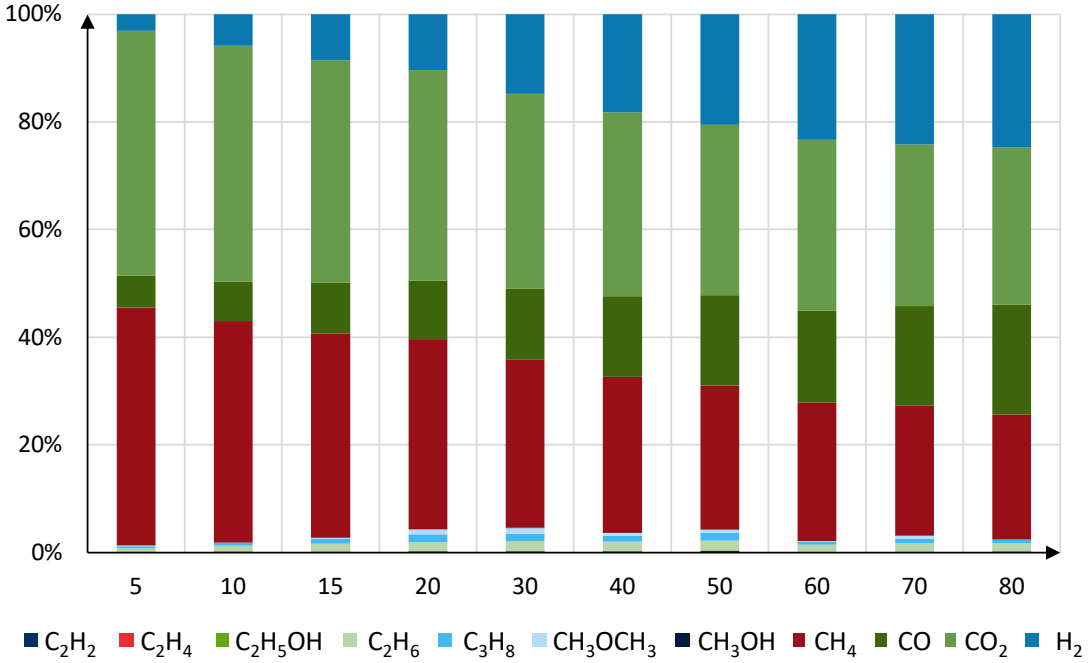


Figure A.4.5: The share of each component in the product mix (%) after the DBD reactor.

4.B.2 CO_2 capture using MEA

Table A.4.1: Parameters for the MEA absorption process, per tonne of CO_2 at the inlet of the capture system with a capture ratio of 90%, based on Giordano et al. (2018).

	Per tonne of CO_2 at inlet of CO_2 capture
Material requirements	
MEA	1.44 kg
Water	18.1 kg
Energy requirements	
Reboiler duty	3.2 GJ
Electrical energy	98.3 kWh
Air emissions	
H_2O	87.5
CO_2	99.9
Ar	54.8
N_2	3202.2
O_2	128.3
MEA	0.06
NH_3	0.03

These parameters are converted to the values per tonne of CO_2 captured, assuming the capture ratio of 90%. For example, if 1.44 kg MEA is needed to capture 0.9 tonne of CO_2, this implies that 1.6 kg MEA is consumed for the capture of 1 tonne of CO_2.

4.B.3 DBD reactor

Table A.4.2: Materials for 1 DBD tube.

Material	**Material in ecoinvent**	**Quantity (g)**
Aluminium oxide (dielectric barrier)	Aluminium oxide, non-metallurgical {IAI Area, EU27 & EFTA} | market for aluminium oxide, non-metallurgical | Cut-off, U	395
Stainless steel (inner electrode)	Steel, chromium steel 18/8 {GLO}| market for | Cut-off, U	650

Table A.4.3: The composition of the packing materials in SimaPro.

1 kg of packing material	Material	Material in ecoinvent	Quantity (kg)
γ-Al_2O_3	Aluminium oxide	Aluminium oxide, non-metallurgical {IAI Area, EU27 & EFTA} | market for aluminium oxide, non-metallurgical | Cut-off, U	1
2%Fe_2O_3@γ-Al_2O_3	Aluminium oxide		0.98
	Iron oxide	Iron ore concentrate {GLO} | market for iron ore concentrate | Cut-off, U	0.02
10%Fe_2O_3@γ-Al_2O_3	Aluminium oxide		0.90
	Iron oxide	Iron ore concentrate {GLO} | market for iron ore concentrate | Cut-off, U	0.10
2%CuO@γ-Al_2O_3	Aluminium oxide		0.98
	Copper oxide	Copper oxide {RER}| production | Cut-off, U	0.02
10%CuO@γ-Al_2O_3	Aluminium oxide		0.90
	Copper oxide	Copper oxide {RER} | production | Cut-off, U	0.10

4.B.4. Electricity mix

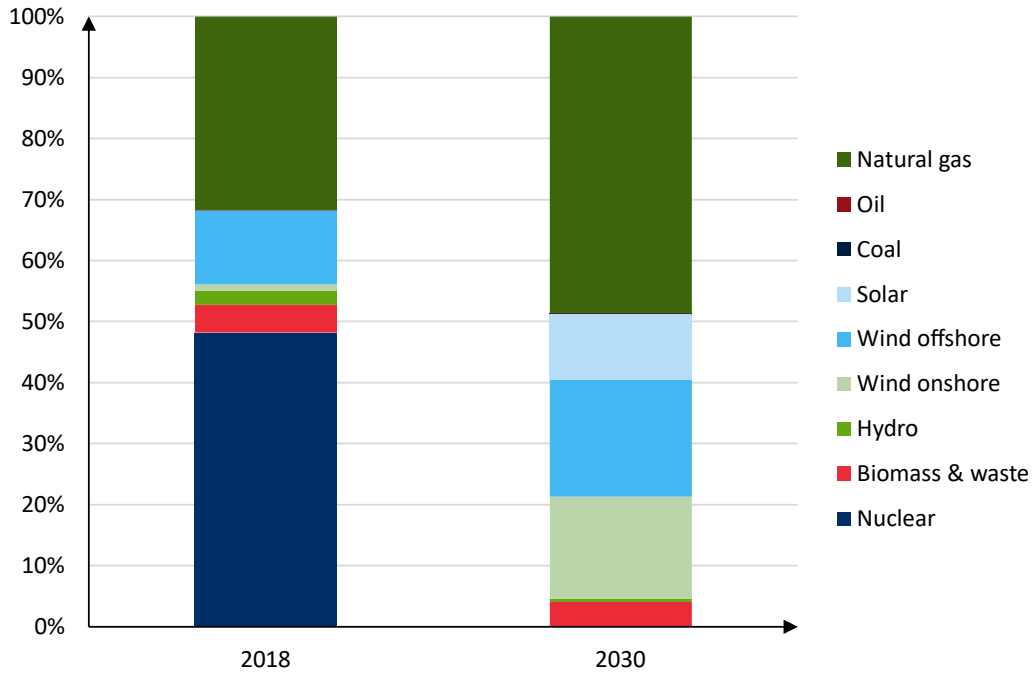


Figure A.4.6: The electricity mixes for Belgium in 2018, 2030 and 2040.

Table A.4.4: The simulation of 1 kWh of the electricity production mix for Belgium in 2030 in SimaPro.

Electricity, high voltage {BE} | … | Cut-off, U	**kWh**
electricity production, nuclear, pressure water reactor	0.000
heat and power co-generation, biogas, gas engine	0.027
treatment of municipal solid waste, incineration	0.013
electricity production, hydro, pumped storage	0.001
electricity production, hydro, run-of-river	0.004
electricity production, wind, 1-3MW turbine, onshore	0.167
electricity production, wind, 1-3MW turbine, offshore	0.192
electricity production, solar tower power plant, 20 MW	0.108
electricity production, hard coal	0.000
electricity production, oil	0.000
heat and power co-generation, natural gas, combined cycle power plant, 400MW electrical	0.017
electricity production, natural gas, combined cycle power plant	0.351
heat and power co-generation, natural gas, conventional power plant, 100MW electrical	0.039
electricity production, natural gas, conventional power plant	0.081

4.B.5. Substitution

Table A.4.5: Materials taken from the ecoinvent 3.8 database to represent the conventional production routes that can be avoided (or substituted) by the CCU production route.

Product	**Material in ecoinvent**
CO	Carbon monoxide {RER} | production | Cut-off, U
H_2	Hydrogen, gaseous {Europe without Switzerland}| hydrogen production, gaseous, petroleum refinery operation | Cut-off, U
C_2H_2	Acetylene {RER}| acetylene production | Cut-off, U
C_2H_4	Ethylene {RER} | ethylene production, average | Cut-off, U
C_2H_6	Ethane {RoW} | natural gas production | Cut-off, U
C_3H_8	Propane {RoW} | natural gas production | Cut-off, U
C_2H_5OH	Ethanol, without water, in 99.7% solution state, from ethylene {RER} | ethylene hydration | Cut-off, U
CH_3OH	Methanol {GLO}| production | Cut-off, U
CH_3OCH_3	Dimethyl ether {RER}| production | Cut-off, U

Table A.4.6: GW and FRS impact for the conventional production routes, for 1 kg of product produced, with the electricity mix for Belgium in 2018.

Product	**GW impact for 1 kg of product**	**FRS impact for 1 kg of product**
CO	1.18	0.95
H_2	1.61	3.24
C_2H_2	3.01	0.81
C_2H_4	1.51	1.43
C_2H_6	0.58	1.61
C_3H_8	0.51	1.43
C_2H_5OH	1.21	0.96
CH_3OH	0.66	0.75
CH_3OCH_3	1.31	1.20

4.C Techno-Economic Assessment

Prices for the end-products are listed in **Table A.4.7**. The price data is corrected for inflation using the Harmonised Index of Consumer Prices (HICP) for the European Union (Eurostat, 2023c). To convert prices in US $ to €, an exchange rate of 0.91 €/$ was adopted. If data was found, the annual production volumes are also presented in **Table A.4.7**.

Table A.4.7: Market study of end-products for the Techno-Economic Assessment.

Product	Price (€$_{2022}$/t)	Reference	Production (Mt/y)	Reference
CO	400	(Bushuyev et al., 2018; Lu & Jiao, 2016; van Rooij et al., 2017)[a]		
H_2	3960	(IEA, 2019a)		
C_2H_2	850[b]	(Hort & Taylor; Trotuş, Zimmermann, & Schüth, 2014)		
C_2H_4	850	(CarbonNext, 2017; Pacheco et al., 2021)[a]	24.5[c]	(CarbonNext, 2017)
C_2H_6	160[d]	(EIA, 2023b)		
C_3H_8	150[e]	(EIA, 2023a)		
C_2H_5OH	680	(CarbonNext, 2017; Pacheco et al., 2021)[a]	80.00[f]	(Chauvy et al., 2019)
CH_3OH	360	(Nyári et al., 2020)[g]	65.00[f]	(Chauvy et al., 2019)
CH_3OCH_3	3960	(Fernández-Dacosta et al., 2018; Pacheco et al., 2021)[a]	11.40[f]	(Chauvy et al., 2019)

[a] The average price was calculated from these references.

[b] No price could be found for acetylene (C_2H_2). Hort and Taylor mention that it has a relatively high price, which has resulted in efforts to replace actelyne by other, cheaper intermediates. Trotuş et al. (2014) stated ethylne (C_2H_4) has become a more important feedstock than C_2H_2. Based on these statements, we made the conservative assumption that C_2H_2 has the same price as C_2H_4.

[c] Production and imports in EU 28.

[d] 64 $ cents per gallon.

[e] 6.9. $ per million BTU.

[f] Global production.

[g] Nyári et al. (2020) used the 10-year average (2009 – 2019) of the European price, provided by Methanex.

4.D Results

4.D.1 Design

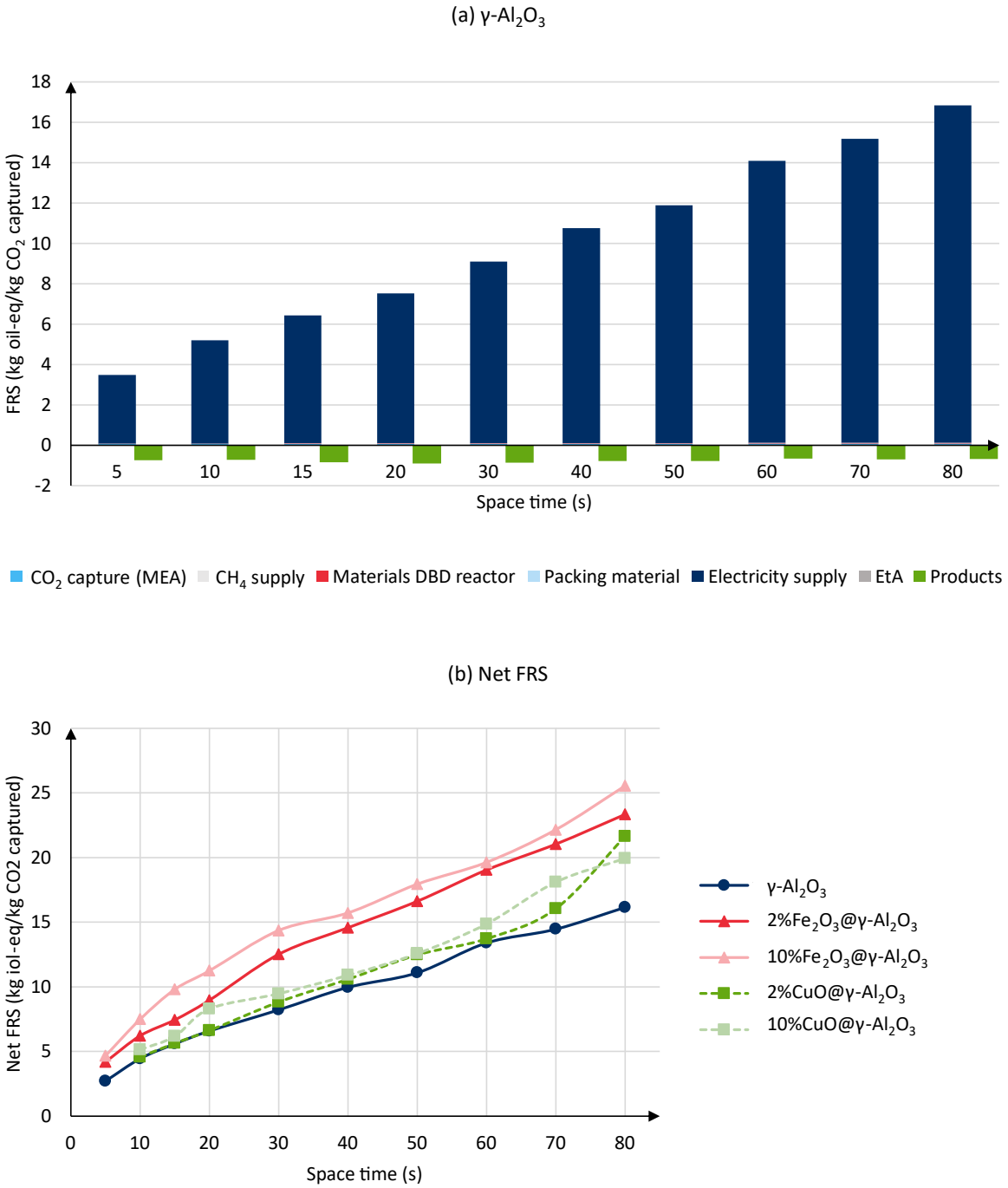


Figure A.4.7: (a) Fossil resource scarcity for the reactor configuration with the γ-Al_2O_3 packing and (b) net fossil resource scarcity for all five packing materials in the Laboratory scenario, with the electricity mix for Belgium in 2018.

Table A.4.8: GW impact (kg CO_2-eq per kg CO_2 captured) for the DBD reactor with γ-Al_2O_3 packing, in the Laboratory scenario, with electricity mix for Belgium in 2018

Space time	CO_2 capture (MEA)	CH_4 supply	Materials DBD reactor	Packing material	Electricity supply	EtA	Products
5	0.403	0.000	0.052	0.001	12.694	8.187	-0.743
10	0.403	0.000	0.078	0.001	19.091	5.659	-0.686
15	0.403	0.000	0.098	0.001	23.756	4.387	-0.770
20	0.403	0.000	0.111	0.002	27.778	3.443	-0.838
30	0.403	0.000	0.136	0.002	33.698	2.463	-0.800
40	0.403	0.000	0.160	0.002	39.890	1.990	-0.732
50	0.403	0.000	0.179	0.002	44.092	1.622	-0.731
60	0.403	0.000	0.211	0.003	52.310	1.518	-0.649
70	0.403	0.000	0.231	0.003	56.439	1.331	-0.692
80	0.403	0.000	0.253	0.003	62.642	1.212	-0.674

Table A.4.9: FRS impact (kg oil-eq per kg CO_2 captured) for the DBD reactor with γ-Al_2O_3 packing, in the Laboratory scenario, with electricity mix for Belgium in 2018

Space time	CO_2 capture (MEA)	CH_4 supply	Materials DBD reactor	Packing material	Electricity supply	EtA	Products
5	0.079	0.000	0.010	0.000	3.387	0.000	-0.748
10	0.079	0.000	0.015	0.000	5.093	0.000	-0.724
15	0.079	0.000	0.019	0.001	6.338	0.000	-0.835
20	0.079	0.000	0.021	0.001	7.411	0.000	-0.912
30	0.079	0.000	0.026	0.001	8.990	0.000	-0.864
40	0.079	0.000	0.031	0.001	10.642	0.000	-0.777
50	0.079	0.000	0.034	0.001	11.763	0.000	-0.779
60	0.079	0.000	0.041	0.001	13.955	0.000	-0.667
70	0.079	0.000	0.044	0.001	15.057	0.000	-0.711
80	0.079	0.000	0.049	0.001	16.712	0.000	-0.682

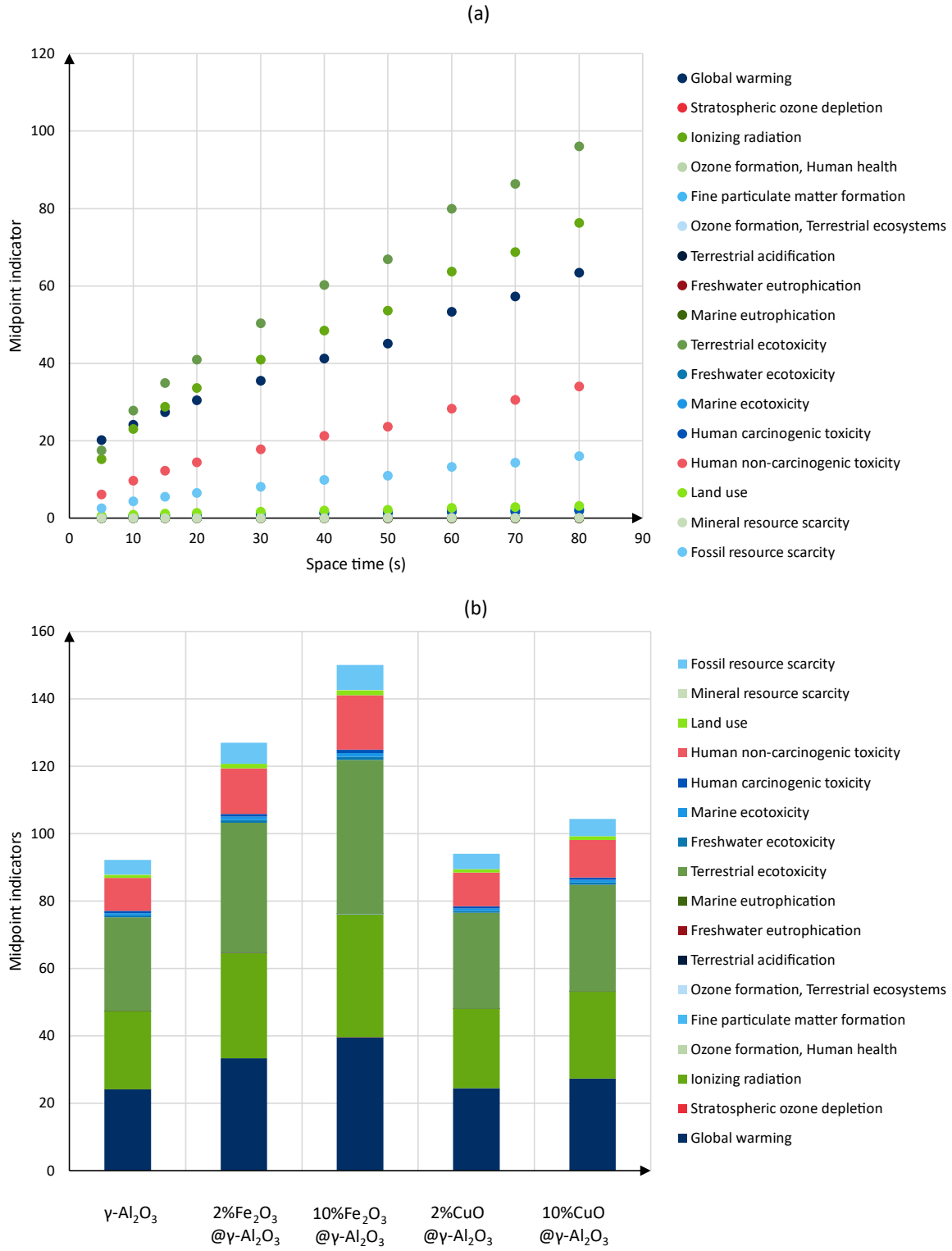


Figure A.4.8: All 18 midpoint indicators in the Laboratory scenario (a) as a function of space time for the γ-Al_2O_3 packing, and (b) for all five packing materials at a space time of 10 s.

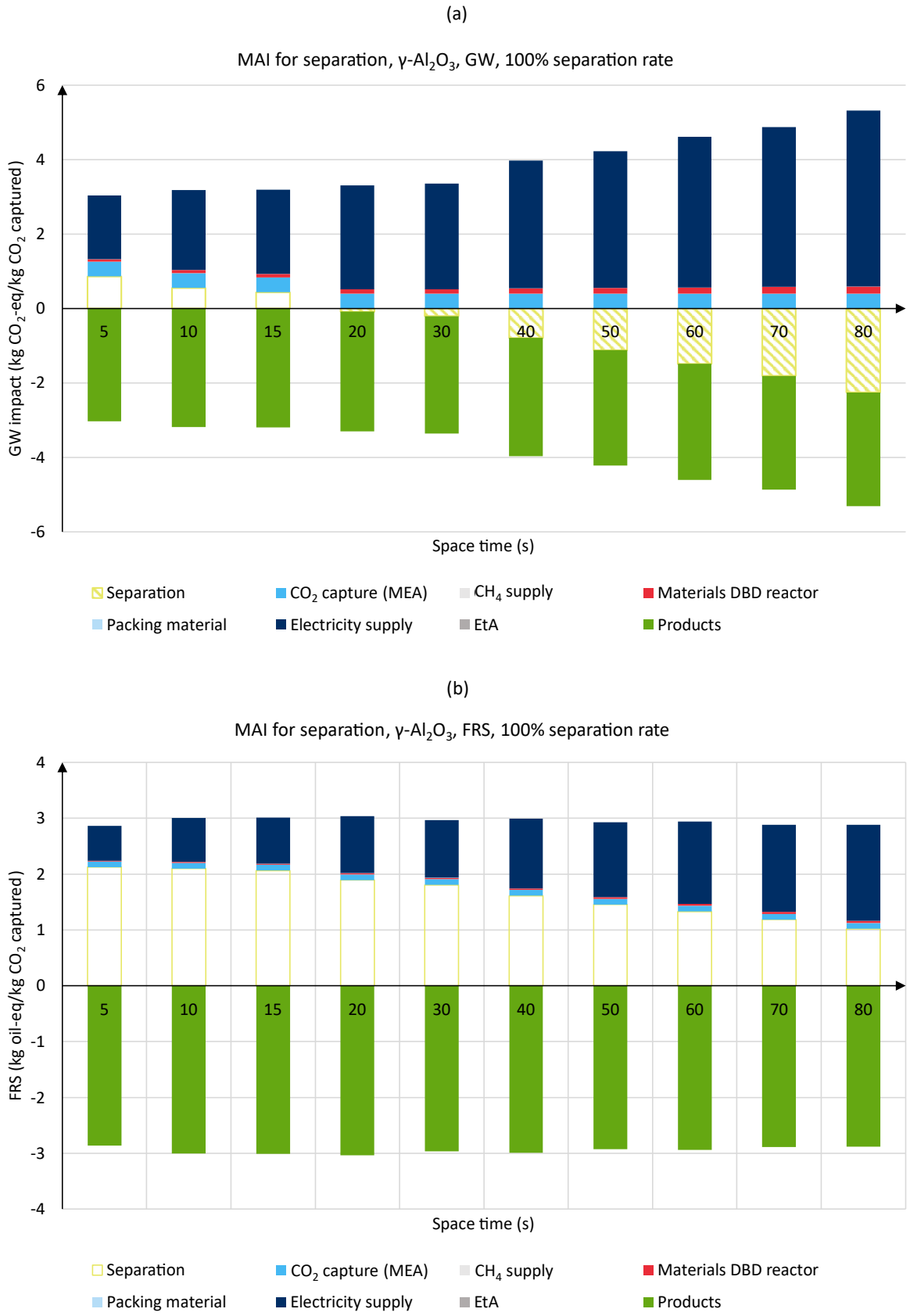


Figure A.4.9: The MAI for separation, in terms of (a) GW, and (b) FRS, in the Selective scenario, with the electricity mix for Belgium in 2030, with a separation rate of 100%.

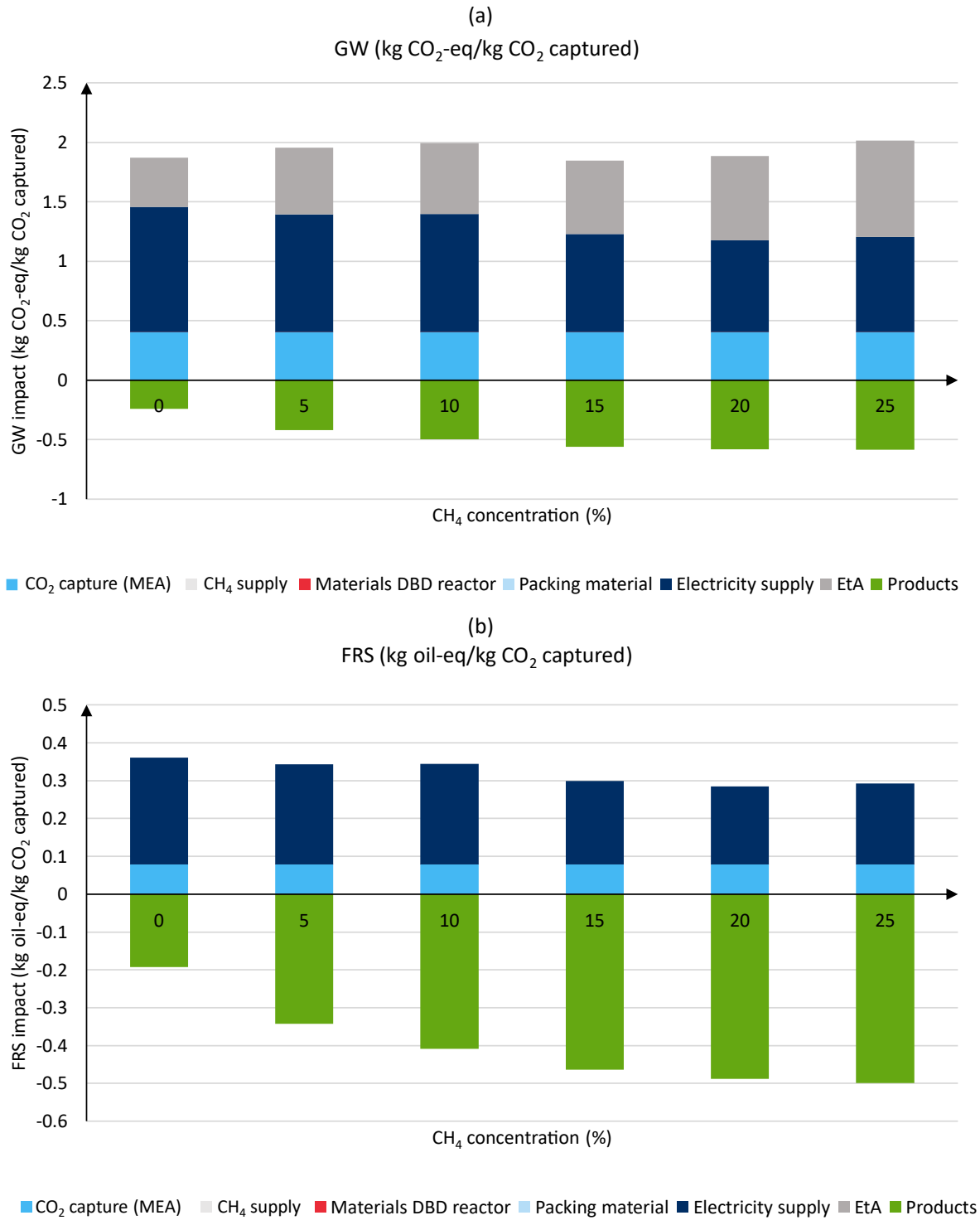


Figure A.4.10: (a) Global warming and (b) fossil resource scarcity for GA reactor, as a function of the CH_4 concentration (%), with the electricity mix of Belgium in 2018.

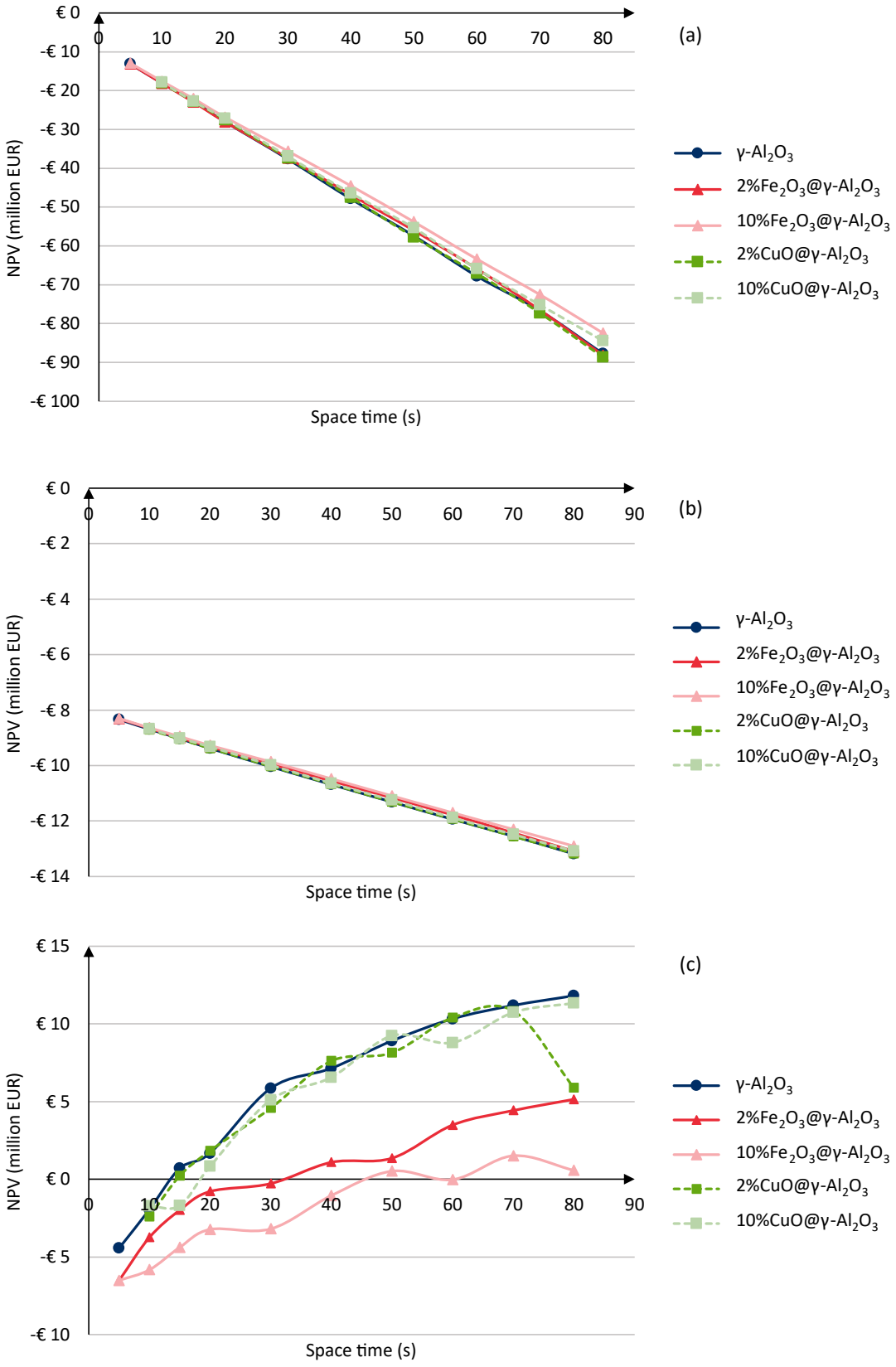


Figure A.4.11: The NPV (million EUR) as a function of space time for the five packing materials, in (a) the Laboratory, (b) the Energy-Efficient, and (c) the Selective scenario.

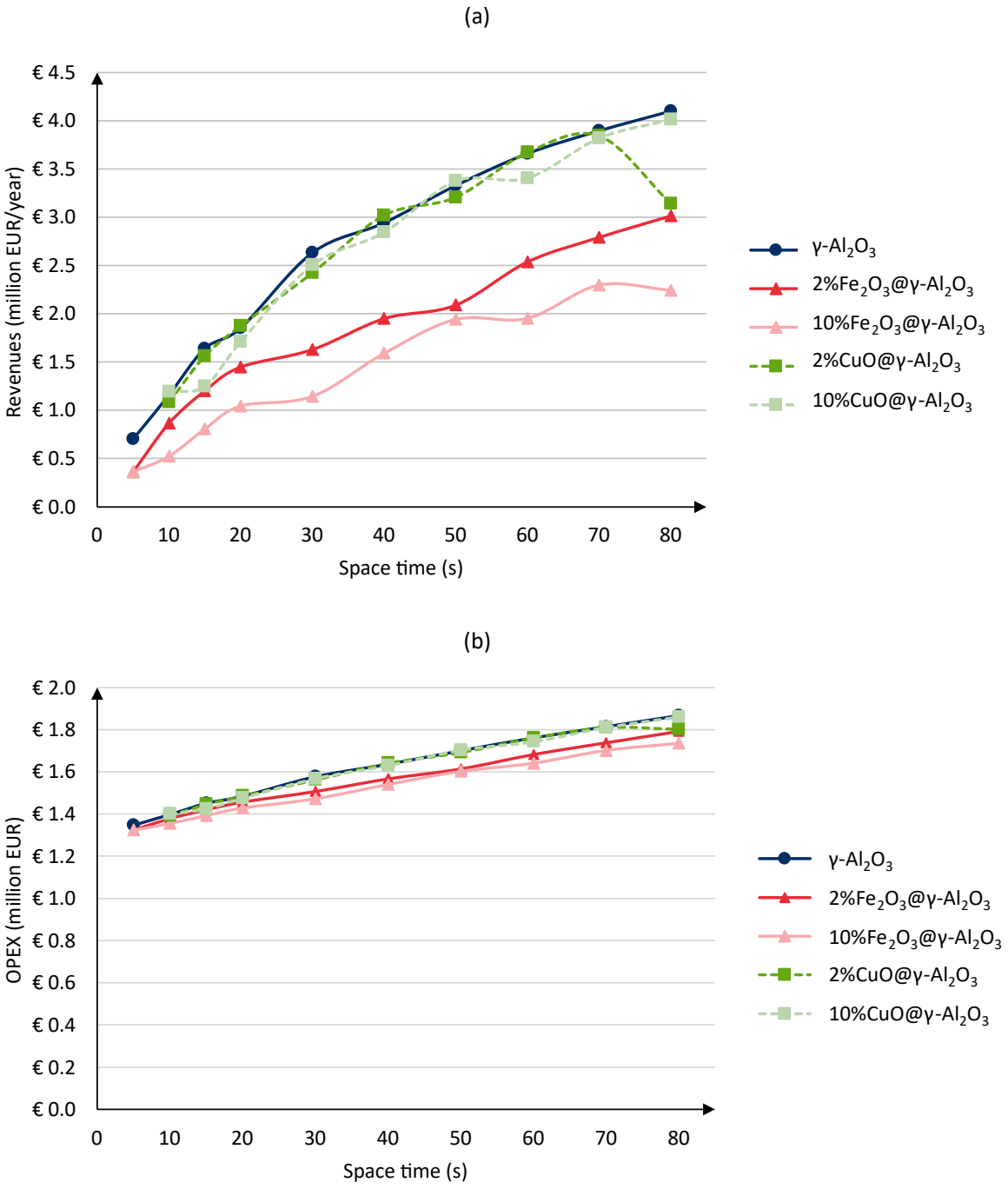


Figure A.4.12: (a) Revenues (million EUR/year) and (b) OPEX (million EUR/year) as a function of space time for the five packing materials in the Selective scenario.

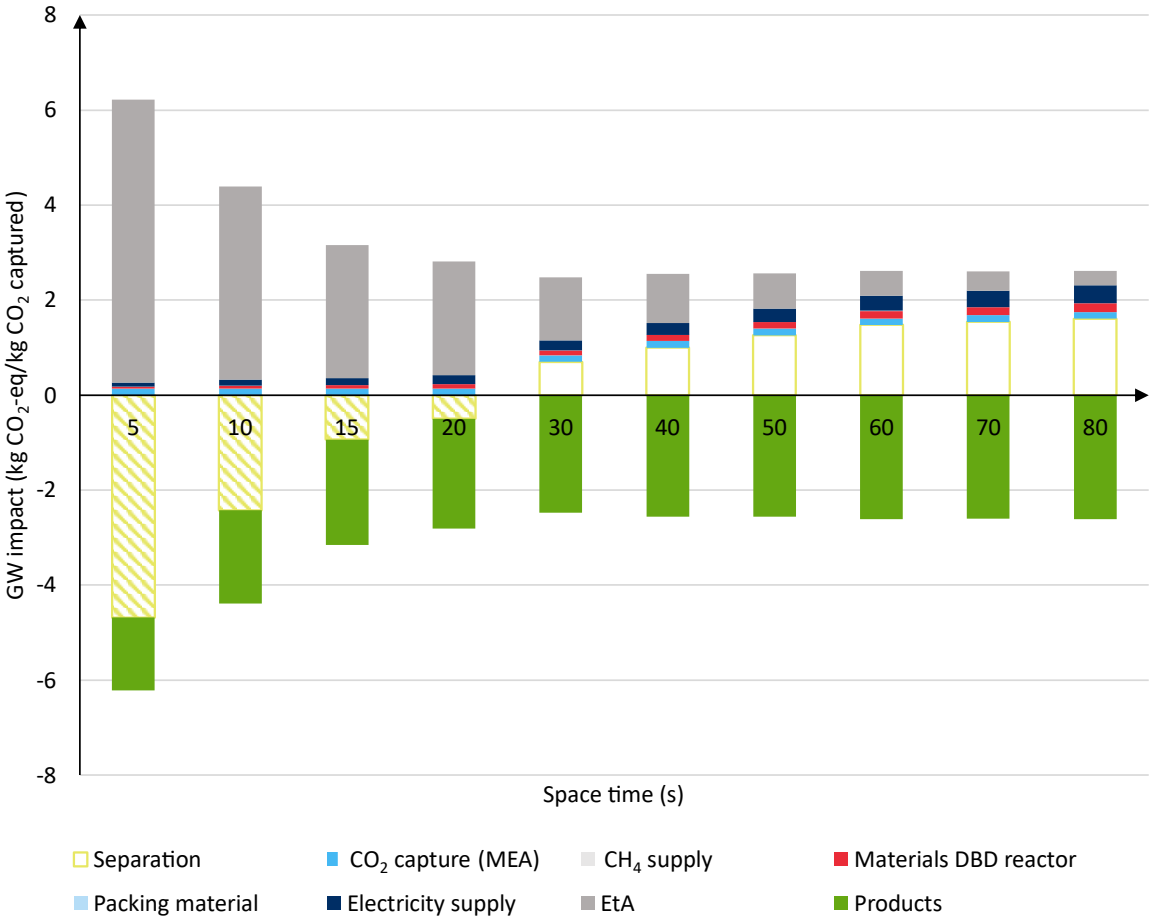


Figure A.4.13: The MAI for separation in terms of GW impact, for the DBD reactor with the γ-Al_2O_3 packing in the Selective scenario, with onshore wind energy.

5

Using Real Options Thinking to Value Investment Flexibility in Carbon Capture and Utilization Projects: a Review

Carbon capture and utilization (CCU) is one of the key technologies that may help to reduce industrial emissions. However, the deployment of CCU is hampered by various barriers, including high levels of technical, policy and market uncertainty. The real options theory (ROT) provides a method to account for these uncertainties and introduce flexibility in the investment decision by allowing decisions to be changed in response to the evolution of uncertainties. ROT is already being applied frequently in the evaluation of renewable energy or carbon capture and storage (CCS) projects, e.g., addressing the uncertainty in the price of CO_2. However, ROT has only found a few applications in the CCU literature to date. Therefore, this paper investigates the specific types of uncertainty that arise with the utilization of CO_2, identifies the types of real options present in CCU projects and discusses the applied valuation techniques. Research gaps are identified in the CCU literature and recommendations are made to fill these gaps. The investment decision sequence for CCU projects is shown, together with the uncertainties and flexibility options in the CCU projects. This review can support the real options-based evaluations of the investment decisions in CCU projects to take into account managerial flexibility and uncertainty.

Parts of this chapter have been published in:

Lamberts-Van Assche, H., & Compernolle, T. (2022). Using Real Options Thinking to Value Investment Flexibility in Carbon Capture and Utilization Projects: A Review. *Sustainability, 14*(4), 2098. Retrieved from https://www.mdpi.com/2071-1050/14/4/2098

Takeaway messages

- The development of and investment in CCU projects is hampered by many sources of uncertainty.
- ROT provides a framework to take these uncertainties into account in the investment decision and allow the firm to delay its decision.
- The existing literature on ROT for CCU projects I screened, to assess the types of uncertainties, options and methods that have been used before.
- One interesting observation was how technological uncertainty, i.e. the unknown technological development of CCU in the future, was most often described by learning curves. Learning curves are deterministic methods to forecast the technological process, by describing the expected reductions in e.g. investment or operating costs.
- In the literature study, one study was found that used a Poisson process to describe breakthroughs in the CCU technology. A Poisson process is a stochastic jump process, suited to describe the discrete nature of technological breakthroughs.

5.1 Introduction

Mitigating climate change is one of the biggest challenges that humankind is facing in the 21st century. The search for low-carbon, or even carbon-negative, solutions to reduce CO_2 emissions is ongoing. Carbon capture and utilization (CCU) technologies can be part of these low-carbon solutions helping to address climate change. Whereas carbon capture and storage (CCS) technologies capture the CO_2 from a CO_2-emitting process and store it permanently underground, CCU technologies use the captured CO_2 as a resource to create valuable products or services (IEA, 2022a). Utilizing CO_2 to create products generates additional revenues, thus lowering the net costs of reducing emissions (Hepburn et al., 2019). Although the concepts of CCS and CCU are often intermingled, the rationale behind both technologies is completely different. CCS contributes directly to climate change mitigation by capturing and permanently storing CO_2 emissions underground. CCU, on the other hand, can help to reduce the dependency on fossil fuels by using already emitted CO_2 as a substitute and can play a role in the transition to using renewable energy systems (Bruhn et al., 2016). The absence of a viable business case for CCS, due to its high costs and lack of incentives, has hindered its deployment. Contrary to CCS, CCU pathways could provide sufficient economic incentives through the cost savings from the reduction in fossil resources and the revenue from sold products.

CCU is generally classified into two categories: (1) the direct use of CO_2, where the CO_2 molecule is not chemically altered (non-conversion) and (2) the transformation of CO_2 through chemical or biological processes (conversion) (IEA, 2021a). Examples of the first category are CO_2-enhanced oil recovery (CO_2-EOR), where the captured CO_2 is injected into oil reservoirs to increase the production of oil, or the direct use of CO_2 in the soft drink industries (Chauvy et al., 2019; C.-H. Huang & Tan, 2014). An example of the second category is the conversion of CO_2 into methanol by using geothermal energy, in Iceland (CRI, 2022). When it comes to CO_2 conversion, three broad categories are identified: mineralization, chemical-based conversion and bio-based conversion routes.

Hepburn et al. (2019) estimate that CCU pathways could reach a total CO_2 utilization potential of 2.5 Gt of CO_2 per year by 2050. However, there are several challenges in taking CO_2 utilization to the market. The major challenge is the high stability of the CO_2 molecule, resulting in high energy requirements that are needed to break the bonds and convert the CO_2 (Ashford & Tu, 2017). Other challenges are the low technology maturity of CCU technologies, the lack of clear climate policies and regulatory frameworks for CCU, high investment costs, the need for green and cheap hydrogen and public acceptance of CCU (Fan, Xu, Yang, Zhang, & Li, 2019; Hepburn et al., 2019). These barriers hinder investments in CCU technologies, making it less likely that CCU projects will be scaled up soon. To investigate the economic feasibility of CCU projects, CCU researchers have resorted to techno-economic assessments (TEAs) (Lamberts-Van Assche & Compernolle, 2021). A TEA integrates technical and economic feasibility evaluations into one systematic study. The most common evaluation criteria in these TEAs for CCU is the net present value, which is based on the costs and revenue over the project's lifetime. However, these traditional valuation methods do not consider the ability to adjust investment decisions or defer investment to a later phase (Trigeorgis, 1996). Moreover, these traditional methods completely fail to capture the value of the additional flexibility that CCU installations may provide to existing plants, e.g., the ability to switch between energy sources, inputs or outputs. Hence, these traditional methods will likely underestimate the true value of CCU projects and will lead to sub-optimal investment decisions.

The review presented in this Chapter focuses on an alternative method, which recognizes the irreversibility and flexibility of CCU investments: the real options theory (ROT). While traditional valuation methods only address uncertainties in a sensitivity analysis, ROT is based on the idea that projects or decisions can be changed in response to the evolution of uncertainties in the ever-changing world (Martínez Ceseña, Mutale, & Rivas-Dávalos, 2013). To evaluate investment decisions in low-carbon energy systems, real options theory is currently the most frequently used valuation method in the presence of uncertain future revenues or costs and managerial flexibility (Yu, Wei, Tang, Mi, & Pan, 2016). Martínez Ceseña et al. (2013) reviewed the real options studies for (renewable) electricity generation projects. The authors observed that ROT has the potential to increase the feasibility of these projects as it allows us to introduce and value flexibility in the investment decision. Schachter and Mancarella (2016) provided a critical analysis of the application of ROT to value investment flexibility in smart grids and low-carbon energy systems. Ginbo, Di Corato, and Hoffmann (2021) reviewed the applications of ROT in investment decisions for climate change adaptation and mitigation projects and showed that ROT is particularly relevant for renewable energy projects because of its high risks and irreversibility. Kozlova (2017) reviewed the existing ROT studies for renewable energy projects and observed a variety of real options models. This illustrates the need for a critical review of the real options methodology and the evaluation methods for renewable energy projects in general. Similar to renewable energy projects, CCU projects are also characterized by high uncertainty, risk and irreversibility of the investment. Hence, ROT is also highly relevant for CCS projects. Agaton (2021) performed a bibliometric analysis, screening the CCS literature for real options applications. The literature search resulted in 67 studies, which were reviewed for the different types of uncertainties, options and valuation techniques that were applied to CCS projects.

The above-listed literature overview shows how ROT is already well developed and frequently applied in the evaluation of (renewable) energy projects and CCS projects. Real options methods have already been adopted in 67 studies to value CCS projects, together with their flexibilities, uncertainties and risks (Agaton, 2021). Although CCU and CCS projects share some similarities, their main differences should be recognized as well: (1) with CCS, the CO_2 is stored permanently, whereas the utilized CO_2 is only stored temporarily in CCU-based products; (2) CCS can store large quantities of CO_2, allowing for CO_2 capture from ambient air, while the demand for CO_2 in CCU pathways is limited by the demand for the products (chemicals, fuels); and (3) the economic incentive for CCS remains weak due to the high costs and the lack of revenue, whereas CCU projects create revenue by producing chemicals or fuels. Due to these differences, the evaluation of investment decisions in CCU projects through real options-based analyses can be significantly different from the real options-based studies for CCS projects. Nevertheless, the application of ROT to evaluate CCU investment decisions remains highly relevant because of the unique types of flexibilities, risks and uncertainties present in CCU pathways. Therefore, this review aims to screen the existing ROT studies for CCU projects and explore the common sources of uncertainty, types of real options and valuation techniques. Both the direct use of CO_2 (non-conversion) and the transformation of CO_2 through chemical or biological processes (conversion) are in the scope of this review study. CO_2-EOR, an example of the direct use of CO_2, is often considered to be in the grey zone between CCS and CCU: the CO_2 is injected into oil reservoirs to increase the production of oil (CCU) and is permanently stored in these reservoirs afterwards (CCS) (Bruhn et al., 2016). This study includes CO_2-EOR as a CCU route for the sake of completeness. This Chapter is organized as follows. Section 5.2 presents the Materials and Methods for this review. Section 5.3 explores the general principles of real options analysis. In Section 5.4, the existing applications of ROT in the CCU literature are reviewed in detail. Section 5.5 discusses the remaining research gaps in the CCU literature and expresses recommendations to fill these gaps based on ROT studies in other research fields. The review article ends with Conclusions.

5.2 Materials and Methods

Before exploring the CCU research, in particular, the basic principles of real options theory were summarized. To understand the real options theory properly, the renowned handbooks of Dixit and Pindyck (1994) and Trigeorgis (1996) were consulted. The different methods used to value real options, sources of uncertainty and real options types are listed in Section 5.3.

Next, a literature review on the applications of ROT for novel CCU technologies was performed. Literature searches were completed in the Web of Knowledge and Scopus databases to retrieve all papers that performed a real options analysis in a CCU context. The first search query combined different variations of the term "carbon capture and utilization" and the term "real options".[14] These searches in the Web of Knowledge and Scopus databases resulted in 10 and 11 papers, respectively. Seven duplicates were identified and removed and four more papers were deleted because they were out of scope (one was a review paper and three other papers were deleted because they only investigated CCS, not CCU). The second search query focused on real options studies for CO_2-EOR.[15] This search query led to 8 and 15 results in the Web of Knowledge and Scopus database, respectively. Of the 23 papers that were retrieved, only nine unique papers were found to fit the scope of this study. Assembling the results from the first and second search queries created a literature set of 13 unique studies. Finally, four additional papers that were previously known to the authors for their application of real options in CCU projects were added (Compernolle et al., 2017; Deeney, Cummins, Heintz, & Pryce, 2021; Greig & Uden, 2021; J.-Q. Li et al., 2020). The selection of the literature set is shown in **Figure 5.1**, resulting in a literature set of 17 papers was established. This literature set was screened for several features that were relevant for the application of real options analysis to their study:

- Year and country;
- Type of CCU technology: direct use of CO_2 or CO_2 conversion;
- Business model: non-cooperative or cooperative;
- Research focus: project valuation (optimal timing or valuing flexibility), policy appraisal and business model comparison;
- Uncertainty source and modelling;
- Type of real options;
- Valuation technique.

The features of ROT applications in the CCU literature are discussed in detail in Section 5.4. Hence, this section describes how the existing real options studies for CCU projects were performed, e.g. which choices were made concerning the type of options and the type of uncertainties.

To evaluate whether the existing real options studies for CCU projects cover all the relevant challenges for CCU projects, the following questions are asked in this Chapter:

(1) What types of uncertainties, that are relevant for CCU projects, are not yet addressed?
(2) What types of options are not yet included in the existing real options studies for CCU projects, although they could be highly valuable for CCU projects?
(3) What valuation techniques are the most suitable to address these research objectives and types of uncertainties?

[14] The first search query was ("carbon capture and utili?ation" OR "CO_2 utili?ation" OR "CO_2 use" OR "carbon dioxide utili?ation" OR "CCU" OR "CCUS") AND ("real options").
[15] The second search query was ("EOR" OR "enhanced oil recovery") AND ("real options").

Drawing on the experience from real options studies in other research areas, and based on the challenges that have been identified in the CCU literature before, these questions will be answered in Section 5.5. Finally, the investment decision sequence is presented for CCU projects, incorporating the real options that can be present and summarizing all sources of uncertainty.

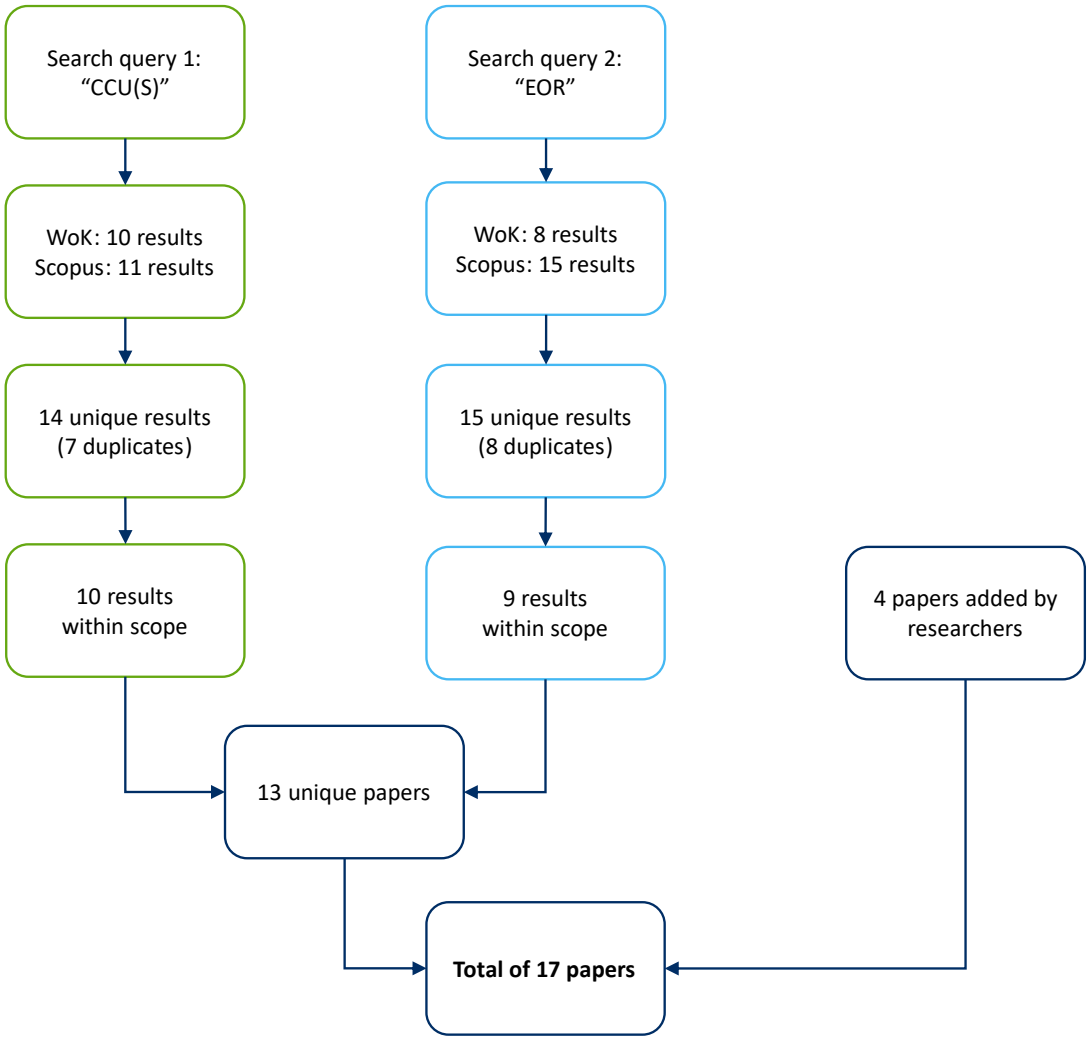


Figure 5.1: Literature set selection.

5.3 The principles of Real Options Theory (ROT)

The term "real options" was claimed for the very first time in 1977 by Myers [21] in a study on the issues of corporate debt. Myers (1977) defined real options as "opportunities to purchase real assets on possibly favourable terms" (p. 163). The opportunities for firms to buy real assets were given this name because of the analogy with financial options. Financial options allow the option holder to buy or sell the financial asset at a fixed price and date in the future. Only if conditions are favourable will option holders exercise their right to buy or sell that financial asset at the agreed-upon terms. Firms with an investment opportunity face a similar dilemma: they have the right, but not the obligation, to invest and acquire the asset in the future (Dixit & Pindyck, 1994).

In general, the majority of investment decisions have three characteristics in common: (1) the investment is, at least partially, irreversible, meaning that (part of) the investment cost is sunk; (2) the future returns from the investment are uncertain; and (3) decision-makers have some flexibility in the timing of investment (Dixit & Pindyck, 1994). While the classic net present value (NPV) valuation framework ignores these typical features of investments, the real options theory (ROT) recognizes the ability of decision-makers to adapt the project or technology in response to changes and developments in the real world (Martínez Ceseña et al., 2013). In other words, ROT allows for a "now-or-later" decision: investors do not only have to decide whether to invest or not, but also when to invest (Ginbo et al., 2021). Applying ROT to real-life investment decisions (1) acknowledges the fact that the initial costs are (partially) sunk, (2) deals with uncertainties on the future returns of the investment by modelling the future evolution of these uncertainties and (3) introduces various flexibility options into the investment decision, for example, flexibility in the timing of the investment decision, by calculating the value of waiting. In other words, ROT acknowledges the fact that decision-makers have the flexibility to adapt their decisions to changing circumstances, which could improve the potential gains and limit the expected losses of the investment (Trigeorgis, 1996). Moreover, the higher the uncertainty and variability in the payoffs of the investment, the higher the value of having the option to invest. The intuition is as follows: if a firm has the right—but not the obligation—to invest, more uncertainty and variability in the project payoffs will only increase the potential payoffs from the project whilst leaving the potential losses unchanged (the option to invest will not be exercised at unfavourable conditions) (Dixit & Pindyck, 1994).

The remainder of this section expands on the failure of classic NPV valuation techniques, presents the strengths of ROT and lists the main solution methods of ROT.

5.3.1 The failure of classic NPV valuation

Most investment decisions are evaluated by simply calculating the NPV of the project, i.e., the present value of the difference between the revenue and costs. If the NPV is greater than zero, the investment should be made. If the NPV is smaller than zero, the project is expected to lose money and hence, the investment should not be undertaken.

However, this simple NPV rule is based on two implicit assumptions, which may not be valid in a real-life setting. First, the NPV rule implicitly assumes that the investment is reversible, meaning that part of the costs can be recovered if the investment turns out to be less profitable than expected. For reversible investments, the presence of uncertainty does not influence the investment decision: if the project becomes unprofitable later due to unexpected changes, the expenditures can still be recovered (Davis & Cairns, 2017). Second, for an irreversible investment, the NPV rule is only valid if the investment decision is a "now-or-never" decision, i.e., you have to decide now whether or not to invest because you will not be able to invest in the future (Dixit & Pindyck, 1994). However, most investment decisions do not meet these conditions. In general, most investments are irreversible to some extent and have the possibility of delaying or staging the investment. To understand why the NPV rule fails in this case, the analogy with financial options is outlined.

Firms facing irreversible investments with the possibility of delay are holding an option: the firm has to right—not the obligation—to invest at some moment in the future. As long as the firm does not make the investment expenditure, it can wait for more information and still change its decision, if desirable. Since waiting allows the firm to collect more information on the future rewards of the investment and reduces the uncertainty of the investment, waiting is valuable to the firm. However, once the investment is made, the firm gives up the possibility to wait and to change its decision if

(market) conditions worsen. Hence, investing involves a "lost option value", which should be included as an opportunity cost in the investment decision (Dixit & Pindyck, 1994).

Whereas the classic NPV decision rule is to invest when the NPV is greater than zero, the improved decision rule should be to invest only when the NPV is greater than the lost option value. ROT provides a framework to value the lost option value or value of waiting and to incorporate it into investment decisions. In sum, ROT adds the time dimension to the decision, thereby making the investment decision dynamic.

5.3.2 Real Options valuation techniques

To introduce the time dimension into the investment decision and to include uncertainty and flexibility in the timing of the investment, Dixit and Pindyck (1994) outline two mathematical tools: DP and contingent claims analysis. Dynamic programming (DP) splits the whole sequence of investment decisions into two periods: the immediate decision (i.e., now) and the value of all subsequent decisions (i.e., all periods thereafter). By applying recursive optimization methods and comparing the stopping value with the continuation value for each period, the optimal investment decision can be found. Contingent claims analysis is based on the idea of a replicating portfolio: to value a new asset, a portfolio of existing assets is assembled that could replicate the return and risk of the new asset. While DP treats the discount rate exogenously, the contingent claims analysis ensures that the discount rate equals the return the investor could have earned on different assets with similar risks.

DP is a mathematical recursive optimization method, breaking decisions that span over different periods into sub-problems and finding the optimal decision by working backwards from the last period to the initial decision period (Dixit & Pindyck, 1994). To decide whether to invest now or later, the value of investing now is compared to the continuation value, which is the value of waiting and making the investment in one of the future periods. Intuitively, once the stopping value exceeds the continuation value, it is optimal to invest immediately. At each period, the stopping value and the continuation value are calculated by using one of the be-low-listed methods for real option valuation, e.g. PDE or Monte Carlo simulations (Kozlova, 2017). In sum, DP provides an optimization method to value flexibility options and define the optimal timing of the investment. However, advanced mathematical techniques are needed to solve the problem (Machiels, Compernolle, & Coppens, 2021).

DP and contingent claims analysis are the two main approaches in ROA. To find solutions, using either DP or contingent claims analysis, different methods can be used. Four different methods are distinguished for real option valuation: partial differential equations (PDEs), lattice (or tree-based) models, simulation techniques, and fuzzy set-based approaches (Agaton, 2021; Kozlova, 2017). While PDE can deliver analytical solutions, the other methods result in numerical solutions. Analytical solutions are exact (closed-form) solutions for the problem, while numerical solutions are found for problems where an exact solution does not exist and the solution has to be approximated (Sorsimo, 2015).

PDE can be defined to find the value of the real option. A PDE is an equation that holds an unknown function of two or more variables and the partial derivative of this unknown function with respect to these variables (Lewis, Onder, & Prudil, 2022). DP can be solved analytically using PDE.

Lattice models or trees are probably the easiest and most intuitive models to value real options. Trees are a simple visualization of how the asset can evolve in the future. Lattice models are discrete-time models, where the value of the asset is evaluated at each step. The binomial tree model is the most commonly used and most simple lattice model, which has one type of uncertainty and the value of the asset can only take two alternative values at each node (up or down). Lattice models allow the

"real options" to be exercised at any chosen time (~American call option), i.e., it evaluates at each node whether the exercise value of the option is greater than the continuation value of the option or not. Lattice models are quicker and more intuitive to grasp, however, they become increasingly complex when more periods and more uncertainties are involved (Schachter & Mancarella, 2016). In sum, lattice models are very effective when only one uncertainty is involved and they can be used to estimate the value of several real options.

Simulation techniques produce distributions with expected values of the project, taking into account the different sources of uncertainty. Monte Carlo simulations allow for different stochastic processes with different probability distributions, thus allowing many different types of uncertainty to be captured in the analysis. Hence, Monte Carlo simulations are suited to solving investment problems with different types of real options and with different sources of uncertainties (Agaton, 2021). However, Monte Carlo simulations only present today's value of the option and are thus incapable of identifying the optimal timing of investment (Schachter & Mancarella, 2016). Monte Carlo simulations are particularly useful for valuing European-type options. However, most real options are American-type options that can be exercised at any time. The features of recursive optimization and DP can be integrated into Monte Carlo simulations to allow the valuation of American-type options as well (Cheah & Garvin, 2009).

The fuzzy sets-based approach is a modern technique to value real options, however, it has not been widely implemented in valuing real options yet (Kozlova, 2017). For engineering design or scheduling problems, fuzzy sets are already being used to describe uncertainties and imprecise information for projects (J. Wang & Hwang, 2007). These approaches also model the distribution of value projects. Fuzzy sets preserve some of the advantages of simulation techniques (e.g., different uncertainties and options) while reducing the computational time requirements (Kozlova, 2017). **Table 5.1** summarizes the above-mentioned valuation techniques of real options with their main characteristics.

Table 5.1: The main characteristics of the four methods for real options valuation, based on (Cheah & Garvin, 2009; Dixit & Pindyck, 1994; Kozlova, 2017; Machiels et al., 2021; Schachter & Mancarella, 2016).

	PDE	**Lattice Models**	**Simulation**	**Fuzzy Sets**
Type of solution	Analytical	Numerical	Numerical	Numerical
Outcome	Value of real options	Value of real options	Distribution of project values	Distribution of project values
Number of uncertainties	1–2	1	> 1	> 1
Number of options	1	> 1	> 1	> 1
Continuous/ discrete	Continuous	Discrete	Continuous/discrete	Continuous
American-/European-type	European	American	European (and American)	European (and American)
Computation time	Low	Low	High	Low

5.3.3 Uncertainty sources

ROT values the managerial flexibility to adjust decisions in response to new information or changing conditions. If everything were 100% certain, new information would not change a project's performance. Hence, the presence of uncertainties that affect a project's performance is a condition for the application of ROT (Martínez Ceseña et al., 2013). Even more so, the present uncertainties can be a potential source of value to the project: a higher uncertainty in a project's payoffs increases the value of being flexible and being able to adjust your decisions. In the presence of managerial flexibility, if the uncertainty increases, the potential payoffs from a project also increase while the potential losses will remain the same (Dixit & Pindyck, 1994). Five main sources of uncertainty are generally distinguished in the ROT literature:

1. Technological uncertainty: Technological or technical uncertainty describes the uncertainty regarding the amount of time, effort and materials needed to complete a project or regarding the performance of the technology once it is in operation (Dixit & Pindyck, 1994). This uncertainty can only be resolved by actually undertaking the project. However, technical (or endogenous) uncertainties can generally be reduced by active learning (Savolainen, 2016). In other words, these uncertainties can be—to some extent—controlled and managed within a project. Examples of technological uncertainties are the level of energy efficiency, raw material consumption and technological progress;
2. Market uncertainty: Market uncertainties refer to the lack of knowledge regarding how a given market will evolve in the future (Hoskisson & Busenitz, 2001). While technical uncertainties are often endogenous to a project, the majority of market uncertainties are exogenous: the source of the uncertainty is external to the project and cannot be controlled or affected by the project. Examples of market uncertainty are product prices, demand uncertainty and electricity prices;
3. Policy uncertainty: Regulations imposed by the government can affect the performance of a project. The prospect of policy changes and the unpredictability of these changes create an additional source of uncertainty (Dixit & Pindyck, 1994). Policy uncertainty refers to the uncertainty that is created when the timing or level of taxes, subsidies or environmental regulations is not yet fixed;
4. Impact uncertainty: Besides providing a product or service, a project also has (unintended) effects on its environment (Coppens, Van Acker, Machiels, & Compernolle, 2021). These effects are called externalities and they are not valued in a market. It is often very difficult to estimate or forecast the effects that projects have on their wider environment, which gives rise to impact uncertainty;
5. Societal uncertainty: Public perception and acceptance can influence the success of a project and create an additional source of uncertainty. For example, wind energy or CCS projects suffered from a lack of social acceptance, which hindered the uptake of these technologies (Katrin Arning, Offermann-van Heek, Sternberg, Bardow, & Ziefle, 2020).

In Section 5.4, we will review whether these sources of uncertainty are also investigated in ROA studies for CCU projects.

5.3.4 Real Options

Analogue to financial options, real options refer to the right—but not the obligation—of a firm to undertake a certain investment or acquire a tangible, "real" asset (Dixit & Pindyck, 1994). The higher the degree of uncertainty in a project, the higher the value of having these "real" options, which add

the flexibility to respond to uncertain future outcomes. Trigeorgis (1996) distinguished six main types of real options:

1. Option to delay or defer: Instead of facing a now-or-never decision, investors can delay their investment to a future period. At each period, they re-evaluate the project and decide whether they should continue (wait for more information), invest immediately or abandon the project completely. The option to delay allows the decision-maker to wait until the uncertainty is resolved or reduced;
2. Option to stage (time-to-build investment): This option is more subtle than the option to delay. Instead of postponing their investment as a whole, the investment is split up into different phases. First, a partial investment is made, and only when the project's performance meets a certain standard is the second investment undertaken, etc. By staging the investment over time and splitting it into a series of smaller investments, the investor can abandon the project at any stage. This option is particularly important in R&D industries because R&D is typically performed to gain new insights into the technology's performance, which helps the decision-maker to decide whether or not to make further investments (Deeney et al., 2021);
3. Option to scale (expand or contract): In response to changing market conditions, the scale of production can be either expanded or downsized. To alter the scale of production when a project is already running, additional costs have to be incurred. Firms could also choose to design projects modularly, such that the project could be scaled easily without incurring high additional costs;
4. Option to abandon: This allows managers to (temporarily) shut down the plant when market conditions are weaker than expected. By abandoning the project, additional losses can be avoided;
5. Option to switch: This refers to the built-in flexibility to change the input or output, depending on current market conditions. Firms should be willing to pay a premium for projects with built-in flexibility to either change the input to the cheapest future input or switch output to the most valuable future output;
6. Option to grow (compound option): The growth option refers to early investments that lead the way to future opportunities. While these early projects may not be profitable yet, they may be crucial to unlocking future investments. For example, the infrastructure and experience developed for the early project may serve as a stepping stone for the next generations of that product or process. These growth options are again particularly relevant for R&D-heavy industries.

5.4 ROT in the CCU literature

As explained in the materials and methods section, a literature search was performed to retrieve all studies in CCU research that implement real options thinking when evaluating investment decisions. This literature search revealed the lack of ROT studies in CCU projects: only 17 studies presented a ROT approach to evaluating the investment decision in a new CCU project. Moreover, the majority of these studies investigated a CCU technology that involves the direct use of CO_2. Only two studies were found for a CCU conversion route. **Table 5.2** provides a summary of the ROT studies in the CCU literature. As can be seen from **Table 5.2**, this literature set only contained recent studies from between 2014 and 2021. The majority of ROT studies were performed in China. China's high share in coal-fired power plants is responsible for an increased interest in CCU technologies, aiming to mitigate the CO_2 emissions from these power plants.

Table 5.2: A summary of ROT applications in the CCU literature, ranked chronologically.

Reference	Direct use or Conversion	Technology	Year	Location
X. Zhang et al. (2014)	Direct use	CO_2-EOR	2014	China
Abadie, Galarraga, and Rübbelke (2014)	Direct use	CO_2-EOR	2014	Northwestern Europe
Compernolle et al. (2017)	Direct use	CO_2-EOR	2017	Northwestern Europe
Welkenhuysen et al. (2017)	Direct use	CO_2-EOR	2017	Northwestern Europe
X. Wang and Zhang (2018)	Direct use	CO_2-EOR	2018	China
L. Yang, Xu, Yang, Fan, and Zhang (2019)	Direct use	CO_2-EOR	2019	China
Fan et al. (2019)	Direct use	CO_2-EOR	2019	China
W. Zhang and Liu (2019)	Conversion	Industrial and food utilization	2019	China
Yao et al. (2019)	Direct use	CO_2-EOR	2019	China
Fan et al. (2020)	Direct use	CO_2-EOR and EWR	2020	China
J.-Q. Li et al. (2020)	Direct use	EWR	2020	China
Zhu, Yao, and Zhang (2020)	Direct use	CO_2-EOR	2020	China
W. Zhang et al. (2021)	Direct use	CO_2-EOR, ECBM, bio-conversion and chemical synthesis	2021	China
Compernolle and Thijssen (2021)	Direct use	CO_2-EOR	2021	Northwestern Europe
Deeney et al. (2021)	Conversion	CO_2-to-methane (Sabatier)	2021	Northwestern Europe
Lin and Tan (2021)	Direct use	CO_2-EOR	2021	China
Bi et al. (2021)	Direct use	CO_2-EOR	2021	China

5.4.1 Research objectives in CCU projects

Real options analyses can be implemented for different reasons. In the reviewed literature set, four main research objectives were observed:

1. Project valuation—optimal timing (OT) of the investment: ROT can be applied to value or evaluate the CCU project and to investigate when would be optimal to invest in that CCU technology. In other words, the investment threshold levels of particular economic or technical parameters, such as CO2 price, can be determined. Moreover, the application of real options can help to demonstrate how the presence of different uncertainties affects these threshold levels. Twelve papers from the reviewed literature set investigated the optimal timing of investments by determining the investment threshold levels of CO_2 price (Compernolle & Thijssen, 2021; Compernolle et al., 2017; Fan et al., 2020; J.-Q. Li et al., 2020; Lin & Tan, 2021; Welkenhuysen et al., 2017; W. Zhang & Liu, 2019; X. Zhang et al., 2014), oil price (Abadie et al., 2014; Compernolle & Thijssen, 2021; Compernolle et al., 2017; Lin & Tan, 2021), and/or CO_2 utilization rate (W. Zhang & Liu, 2019). Yao et al. (2019) calculated the investment probability in the CCU project over different stages of the project;
2. Project valuation—valuing flexibility (VF): Besides determining the optimal timing of the investment, project valuation by real options analysis can also include the valuation of the flexibility that is embedded into the investment decision. The value of the real options themselves was estimated in four studies in the literature set. X. Zhang et al. (2014) valued the cost-saving effect of pre-investing in a carbon capture facility. (Abadie et al., 2014) explicitly calculated the option value of being able to delay the investment to a later phase. X. Wang and Zhang (2018) estimated the value of the compound option by calculating the difference between the static (or passive) NPV and the dynamic NPV (that includes the compound real options). Finally, Deeney et al. (2021) benchmarked the real options-based value of the R&D investment against a static NPV that did not include any flexibility;
3. Policy appraisal: The applications of ROT can also help evaluate how different policy instruments affect the timing or level of investments in CCU projects, subject to uncertainty. To evaluate the effectiveness of different policy incentives, the real options-based value of CCU investments was calculated under different government subsidy modes or levels in seven papers from the literature set (Compernolle et al., 2017; Fan et al., 2020; Fan et al., 2019; Lin & Tan, 2021; L. Yang et al., 2019; W. Zhang et al., 2021; Zhu et al., 2020);
4. Business model: The evaluation of different business models can demonstrate how investments in CCU projects can be optimized. The CCU value chain involves different processes, from CO2 capture to CO_2 utilization, with different partners being responsible for each process. The business model describes how the avoided carbon taxes, the costs and the revenue from the CO_2-based product are distributed among the different stakeholders in the CCU value chain. How these stakeholders cooperate can affect investment decisions in CCU projects. Zhu et al. (2020) investigated three different business models between a coal-fired power plant (CFPP) and an oil producer with different contract terms: a fixed CO_2 price; an oil-indexed CO_2 price; and a joint venture contract. Compernolle and Thijssen (2021) compared the investment thresholds for a CFPP (CO_2 capture) and an oil producer (CO_2-EOR) on a stand-alone basis with their investment thresholds in a joint venture.

These research objectives are listed in **Table 5.3**. The most common research objective was determining the optimal timing of the investment (10 papers), followed by policy appraisal (seven papers).

Table 5.3: The addressed research objectives, business model and research findings in the CCU literature set.

References	Research objective	Business Model	Research findings
(X. Zhang et al., 2014)	Project valuation (OT + VF)	Non-cooperative	Critical CO_2 price and investment probability
(Abadie et al., 2014)	Project valuation (OT + VF)	Non-cooperative	Critical oil price
(Compernolle et al., 2017)	Project valuation (OT) + policy appraisal	Non-cooperative + contract terms	Critical CO_2 and oil price
(Welkenhuysen et al., 2017)	Project valuation (OT)	Non-cooperative	Critical CO_2 price
(X. Wang & Zhang, 2018)	Project valuation (VF)	Non-cooperative	Value of compound option and critical CO_2 price
(L. Yang et al., 2019)	Policy appraisal	Vertical integration	Comparison of three subsidy modes and critical oil price
(Fan et al., 2019)	Policy appraisal	Non-cooperative	Comparison of three subsidy modes
(W. Zhang & Liu, 2019)	Project valuation (OT)	Non-cooperative	Critical CO_2 price and CO_2 utilization rate
(Yao et al., 2019)	Project valuation (OT)	Non-cooperative	Investment probability
(Fan et al., 2020)	Project valuation (OT) + policy appraisal	Non-cooperative	Critical CO_2 price
(J.-Q. Li et al., 2020)	Project valuation (OT)	Non-cooperative	Critical CO_2 price
(Zhu et al., 2020)	Business model + policy appraisal	Contract terms + joint venture	NPV under different business models and CO_2 price
(W. Zhang et al., 2021)	Policy appraisal	Non-cooperative	Critical government subsidy level
(Compernolle & Thijssen, 2021)	Business model + project valuation (OT)	Non-cooperative + joint venture	Critical CO_2 and oil price
(Deeney et al., 2021)	Project valuation (VF)	Non-cooperative	Value of compound option and critical CO_2 price
(Lin & Tan, 2021)	Project valuation (OT) + policy appraisal	Vertical integration	Critical CO_2 and oil price
(Bi et al., 2021)	Project valuation (OT)	Non-cooperative	Unknown (Full paper unavailable to the authors.)

The investigated business models are also listed in **Table 5.3**. Non-cooperative investments refer to separate investment decisions by the different stakeholders in the CCU value chain, e.g., the CO_2 capture and CO_2 utilization plants. When contract terms are settled, some price agreements are made between the different stakeholders. In a joint venture, the CCU partners collaborate and the costs and revenue are distributed between the different stakeholders. In a vertically integrated business model, one investor integrates and operates all steps in the CCU value chain as a whole (Lin & Tan, 2021; L. Yang et al., 2019).

5.4.2 Uncertainty sources and modelling in CCU projects

Although the CCU landscape is diverse, covering both mature technologies (e.g., CO_2-EOR) and emerging technologies (e.g., CO_2-based fuels or chemicals) (Hepburn et al., 2019), all CCU projects are subject to many different types of uncertainty or risk. The sources of uncertainty that are addressed in the reviewed literature set are listed below, listed per uncertainty type defined in Section 5.3.3. Moreover, the techniques used to model the evolution of these uncertainties are summarized as well.

The CO_2 price

The major identified source of uncertainty in CCU projects is CO_2 price, which remains hard to predict. The evolution of the CO_2 price in the EU Emissions Trading System (ETS) is driven by both policy pressures and market forces. The CO_2 reduction targets set by the EU increase pressure on the carbon market, pushing the CO_2 price upwards. Other price drivers are oil and electricity prices, which provide signals reflecting the demand for oil and electricity and, consequently, also influence the "demand" for CO_2 emissions (P. Li, Zhang, Yuan, & Hao, 2021). As CO_2 price is subject to both policy and market forces, it is included as a separate type of uncertainty for CCU projects. The majority of the reviewed studies (13) described the evolution of the price of CO_2 using a Geometric Brownian Motion (GBM), where the CO_2 price follows a non-stationary stochastic process with constant drift and variance (Abadie et al., 2014; Compernolle & Thijssen, 2021; Compernolle et al., 2017; Deeney et al., 2021; Fan et al., 2020; Fan et al., 2019; J.-Q. Li et al., 2020; Lin & Tan, 2021; X. Wang & Zhang, 2018; Yao et al., 2019; W. Zhang et al., 2021; W. Zhang & Liu, 2019; X. Zhang et al., 2014). Zhu et al. (2020) included CO_2 price as an uncertain parameter in a sensitivity analysis and Welkenhuysen et al. (2017) treated the CO_2 price as a stochastic parameter in a Monte Carlo simulation.

The effect of CO_2 price uncertainty on the level and timing of CCU investments differs in the literature set. Compernolle et al. (2017) found that uncertainty in the price of CO_2 emission allowances delays CCU investment. The CO_2 price and oil price thresholds to invest in CO_2-EOR were higher in the real options-based analysis compared to the traditional NPV approach. This study also showed that lower CO_2 price uncertainty reduced the oil price threshold level for CO_2-EOR investment. Lin and Tan (2021)found that an increase in the volatility of CO_2 price (i.e. more uncertainty) leads to a reduction in the value of CCU investments and, hence, delays the investment. X. Wang and Zhang (2018) on the other hand, observed that the critical CO_2 price is lowered, based on a compound real options model. The threshold may be lowered because investors focus more on the future potential revenue that may follow when considering the compound option. J.-Q. Li et al. (2020) concluded that the uncertainty in CO_2 emission rights is the most decisive factor in investment decisions. In this study, a higher uncertainty in the CO_2 price induced earlier investment.

Technological uncertainty

Technological uncertainties are particularly important for low-maturity CCU technologies, which are still in the development phase. In the reviewed literature set, four different technological uncertainties were observed: the rate of technological progress or learning; residual lifetime; running time; and the EOR recovery factor or EOR efficiency rate.

Eight studies introduced technological progress in the investment analysis (Deeney et al., 2021; Fan et al., 2019; Lin & Tan, 2021; X. Wang & Zhang, 2018; L. Yang et al., 2019; W. Zhang et al., 2021; W. Zhang & Liu, 2019; X. Zhang et al., 2014). In the majority of these studies (i.e. seven), the technological progress was described through learning curves. Defining a learning curve is a method to forecast technological progress, expressing the reduction in investment costs or O&M costs that are expected for this project through technological improvements. In the eight study, the technological progress was modelled by a Poisson process. Deeney et al. (2021) described the number of technological breakthroughs for an R&D investment using a Poisson process. While a learning curve is a deterministic method to describe the effect of technological progress, the Poisson process is a stochastic method.[16] J.-Q. Li et al. (2020) and X. Zhang et al. (2014) investigated the influence of residual lifetime in a sensitivity analysis. Welkenhuysen et al. (2017) included the EOR recovery factor as a stochastic parameter in a Monte Carlo simulation. Zhu et al. (2020) also investigated the impact of the uncertain EOR efficiency rate. However, they split the evolution of the EOR rate into three periods, and in each period, the EOR rate was described by a different GBM. Remarkably, the uncertainty in the CO_2 utilization or CO_2 conversion rate was not investigated in the reviewed literature set.

Market uncertainty

Due to the dominance of CO_2-EOR as a CCU technology in the literature set, the most common source of market uncertainty was oil price. Six studies characterized the evolution of oil price by a GBM (Compernolle & Thijssen, 2021; Compernolle et al., 2017; L. Yang et al., 2019; Yao et al., 2019; X. Zhang et al., 2014; Zhu et al., 2020), one study included different levels of oil price in a sensitivity analysis (Fan et al., 2020), another study included oil price as a stochastic parameter in a Monte Carlo simulation (Welkenhuysen et al., 2017) and two studies described the evolution of oil price by a mean reversion process (Abadie et al., 2014; Lin & Tan, 2021). One study, in particular, applied the Ornstein–Uhlenbeck model (Lin & Tan, 2021), which is the most simple mean reverting process. For commodity prices, this mean-reverting process may be more realistic than the GBM, which can wander far from the starting point (Dixit & Pindyck, 1994). Electricity price was treated as an uncertain parameter in three studies, either through a mean reverting process (Abadie et al., 2014) or by including it in a scenario analysis (Fan et al., 2020; J.-Q. Li et al., 2020). Thirdly, the coal price was included as market uncertainty and described by a GBM in three studies (Fan et al., 2019; X. Wang & Zhang, 2018; Yao et al., 2019). Fourthly, the price of CO_2 that can be used for industrial utilization or food-grade utilization was also described by a GBM in one study (W. Zhang & Liu, 2019). Finally, the product price was included in one study as market uncertainty. The price of natural gas, serving as a proxy for methane, was described by the Ornstein–Uhlenbeck model in Deeney et al. (2021). These market uncertainties can have different effects on the value and timing of CCU investments. Lin and Tan (2021) observed that higher volatility in oil prices leads to reductions in CCU investments and delays the investment timing. Compernolle et al. (2017) and Abadie et al. (2014) found that the oil price threshold is significantly higher when the option to delay is included compared to the traditional NPV approach.

Policy uncertainty

Governments can affect CCU projects by granting subsidies, imposing new CO_2 emission reduction targets on the industry or changing the cap on the number of emission allowances of the EU ETS. As CO_2 price is driven by both market and policy uncertainty, it was identified as a separate type of uncertainty. Seven studies from the reviewed literature set investigated the effect of government

[16] A deterministic process always gives the same result for a particular set of input variables, whereas a stochastic process can give varying results for the same set of input variables. In other words, no randomness is involved in a deterministic process, while randomness is accounted for in stochastic processes.

subsidies on CCU investments by including different modes or levels of government subsidy in a scenario or sensitivity analysis (Fan et al., 2020; Fan et al., 2019; J.-Q. Li et al., 2020; X. Wang & Zhang, 2018; L. Yang et al., 2019; W. Zhang et al., 2021; X. Zhang et al., 2014). W. Zhang et al. (2021) calculated the critical government subsidy level to stimulate CCU investment and found that government subsidies alone are not sufficient to incentivize investments in CCU technologies.

Impact and societal uncertainty

CCU projects may reduce CO_2 emissions, having a clear impact on the environment. Katrin Arning et al. (2020) observed that the perceived risks and benefits of CCU technologies influence the social acceptance rate. However, none of the studies in the reviewed literature set included any type of impact or societal uncertainty. The uncertainty sources that were included in the CCU literature set are summarized in **Table 5.4**.

Table 5.4: The identified sources of uncertainty in the real options studies for CCU technologies.

Type of uncertainty	Uncertainty source	# studies	References
CO_2 price		15	(Abadie et al., 2014; Compernolle & Thijssen, 2021; Compernolle et al., 2017; Deeney et al., 2021; Fan et al., 2020; Fan et al., 2019; J.-Q. Li et al., 2020; Lin & Tan, 2021; X. Wang & Zhang, 2018; Welkenhuysen et al., 2017; Yao et al., 2019; W. Zhang et al., 2021; W. Zhang & Liu, 2019; X. Zhang et al., 2014; Zhu et al., 2020)
Technological uncertainty	Technological progress	8	(Deeney et al., 2021; Fan et al., 2019; Lin & Tan, 2021; X. Wang & Zhang, 2018; L. Yang et al., 2019; W. Zhang et al., 2021; W. Zhang & Liu, 2019; X. Zhang et al., 2014)
	EOR rate	2	(Welkenhuysen et al., 2017; Zhu et al., 2020)
	Residual lifetime	2	(J.-Q. Li et al., 2020; X. Zhang et al., 2014)
	Running time	1	(X. Zhang et al., 2014)
Market uncertainty	Oil price	10	(Abadie et al., 2014; Compernolle & Thijssen, 2021; Compernolle et al., 2017; Fan et al., 2020; Lin & Tan, 2021; Welkenhuysen et al., 2017; L. Yang et al., 2019; Yao et al., 2019; X. Zhang et al., 2014; Zhu et al., 2020)
	Electricity price	3	(Abadie et al., 2014; Fan et al., 2020; J.-Q. Li et al., 2020)
	Coal price	3	(Fan et al., 2019; X. Wang & Zhang, 2018; Yao et al., 2019)
	Product price	1	(Deeney et al., 2021)
Policy uncertainty	Government subsidy	7	(Fan et al., 2020; Fan et al., 2019; J.-Q. Li et al., 2020; X. Wang & Zhang, 2018; L. Yang et al., 2019; W. Zhang et al., 2021; X. Zhang et al., 2014)

5.4.3 Real options in CCU projects

In the reviewed literature set, only three different types of options were observed: the option to delay (nine); the option to abandon (two); and the option to grow (two).

In general, investors with an option to delay can choose to invest immediately or postpone the investment to a later period. As many CCU technologies are still in development, it can be very useful to delay the investment decision and wait until more information is known (on technological performance, market conditions or policy regulations). The option to delay or defer the CCU investment was investigated in 14 studies (Abadie et al., 2014; Bi et al., 2021; Compernolle & Thijssen, 2021; Compernolle et al., 2017; Fan et al., 2020; Fan et al., 2019; J.-Q. Li et al., 2020; Lin & Tan, 2021; Welkenhuysen et al., 2017; L. Yang et al., 2019; Yao et al., 2019; W. Zhang et al., 2021; W. Zhang & Liu, 2019; X. Zhang et al., 2014).

Two studies investigated the option to abandon the CCU project when the economic performance is unfavourable. Zhu et al. (2020) assumed that the CO_2-EOR operators hold the option to abandon the project if the payoff turns out to be negative. The value of the abandonment option is then equal to the avoided negative cashflows. Welkenhuysen et al. (2017) also included the option for CO_2-EOR projects to abandon oil fields. The oil production curves of oil fields typically increase at first, reach a peak and then decline again until production is no longer beneficial.

The more complex option to grow or compound was implemented in three studies. X. Wang and Zhang (2018) established a compound real options model to take into account the phased nature of CCS investment decisions from the perspective of a CFPP. Investing in a CO_2 capture unit opens up the opportunity to invest in the CO_2-EOR activity in a second phase. Deeney et al. (2021) modelled an R&D investment opportunity as a compound real options structure: at the end of the early phase of the R&D, the decision had to be made to start the late phase of the R&D or not. (Yao et al., 2019) investigated the investment decision in a coal-to-liquid (CTL) plant, possibly combined with a CCS plant. The decision sequence was split into different phases, where the investor had to decide first whether to build the CTL plant or not, followed by the decision to retrofit the CCS plant or not. If the plants were built, there was still the choice to operate the plants or not. Hence, the investment decisions made in the first stages (building the CTL/CCS plant or not) opened up future growth options.

In the reviewed literature set, no stage, scale or switch options were observed. However, each of these options could be valuable in CCU projects. The option to switch input or output is particularly relevant for CCU projects. Due to the variety in CO_2 sources, the ability to switch input would allow CCU projects to use flue gases from different sources with different CO_2 concentration levels. The flexibility to switch output from the current product to the most expensive product at that time could also improve the economic feasibility of CCU projects.

5.4.4 Valuation techniques in CCU projects

Three main valuation techniques were observed in the reviewed literature set: Monte Carlo simulations (seven); lattices (seven); and PDE (two). The Black–Scholes model or fuzzy sets-based approaches were not observed in the literature set. The Monte Carlo simulations were used for different research objectives: to determine the optimal timing (five); to value flexibility (two); to compare business models (one); and to evaluate policy instruments (two). The Monte Carlo simulations were also used for the three different types of options: the option to delay (three); the option to abandon (two); and the option to grow (one). Hence, Monte Carlo simulations seem to fit the different research objectives and the different types of options.

Table 5.5: A summary of the investigated technology, sources of uncertainty, types of real options and valuation techniques in the reviewed CCU literature set.

References	Technology	Uncertainty				Real Options			Valuation
		CO_2 Price	Technological	Market	Policy	Delay	Abandon	Grow	
X. Zhang et al. (2014)	CO_2-EOR	X ^{GBM}	x ^{LC}	X ^{GBM}	x ^{SA}	X			Lattice (trinomial tree)
Abadie et al. (2014)	CO_2-EOR	X ^{GBM}		X ^{GBM}		X			Simulation (MC)
Compernolle et al. (2017)	CO_2-EOR	X ^{GBM}		X ^{GBM}		X			PDE
Welkenhuysen et al. (2017)	CO_2-EOR	X	X	X		X	X		Simulation (MC) and lattice
X. Wang and Zhang (2018)	CO_2-EOR	X ^{GBM}	x ^{LC}	X ^{GBM}	x ^{SA}			X	Lattice (binomial tree)
L. Yang et al. (2019)	CO_2-EOR		x ^{LC}	X ^{GBM}	x ^{SA}	X			Lattice (trinomial tree)
Fan et al. (2019)	CO_2-EOR	X ^{GBM}	x ^{LC}	X ^{GBM}	x ^{SA}	X			Lattice (trinomial tree)
W. Zhang and Liu (2019)	CO_2 conversion	X ^{GBM}	x ^{LC}	X ^{GBM}		X			Simulation (MC)
Yao et al. (2019)	CO_2-EOR	X ^{GBM}		X ^{GBM}		X		X	Simulation (MC)
Fan et al. (2020)	CO_2-EOR and EWR	X ^{GBM}		x ^{SA}	x ^{SA}	X			Lattice (trinomial tree)
J.-Q. Li et al. (2020)	EWR	X ^{GBM}	x ^{SA}	x ^{SA}	x ^{SA}	X			Lattice (trinomial tree)
Zhu et al. (2020)	CO_2-EOR	x ^{SA}	X ^{GBM}	X ^{GBM}			X		Simulation (MC)
W. Zhang et al. (2021)	CO_2-EOR and CO_2 conversion routes	X ^{GBM}	x ^{LC}		x ^{SA}	X			Lattice (binomial tree)
Compernolle and Thijssen (2021)	CO_2-EOR	X ^{GBM}		X ^{GBM}		X			PDE
Deeney et al. (2021)	CO_2-to-methane (Sabatier)	X ^{GBM}	X ^{P}	X ^{OU}				X	Simulation (MC and random tree)
Lin and Tan (2021)	CO_2-EOR	X ^{GBM}	x ^{LC}	X ^{OU}		X			Simulation (MC)
Bi et al. (2021)	CO_2-EOR					X			

X: the uncertainty was modelled as a stochastic process; x: the uncertainty was modelled as a deterministic process; GBM: the uncertainty was modelled as a stochastic process, described by a GBM; LC: the technological progress is modelled using a learning curve, which describes the reduction in investment and/or O&M costs; SA: the uncertainty was only included as a parameter in a sensitivity or scenario analysis; P: the technological breakthroughs were described by a Poisson process; OU: the oil price/natural gas price (a proxy for methane) were described by the Ornstein–Uhlenbeck model.

The lattice models could also be implemented for different goals: to find the optimal timing (three); to value flexibility (two); and to evaluate policy instruments (four). Both binomial and trinomial trees were built in the literature set. The use of lattice models seems particularly attractive for valuing the option to delay (six) because trees allow an intuitive comparison of different timing alternatives (Fan et al., 2020; Fan et al., 2019; J.-Q. Li et al., 2020; W. Zhang et al., 2021). One study used a binomial tree to value the compound option (X. Wang & Zhang, 2018).

Finally, PDE was observed in two studies, for various research objectives: defining the optimal timing (wo) and in combination with policy appraisals (one) or business model comparisons (one). In these two studies, dynamic programming was used to investigate the option to delay.

This brief overview demonstrates that different valuation techniques can be used for various research objectives and types of options. PDE and lattice models seem to be the most obvious techniques to model the option to delay, while Monte Carlo simulations can be more easily implemented for different types of options.

Table 5.5 summarizes the types of uncertainties, the types of real options and the valuation techniques that were implemented in the reviewed literature set. A capital X indicates that the uncertainty was modelled as a stochastic process, while a lowercase x indicates that the uncertainty was modelled deterministically. How the uncertainty was modelled is indicated in the superscript: GBM refers to Geometric Brownian Motion; SA to sensitivity or scenario analysis; LC to learning curve models; P to the Poisson process; and OU to the Ornstein–Uhlenbeck model. **Table 5.5** shows how different uncertainties were combined with different types of options and how different valuation techniques were used to value the same type of option. This demonstrates the wide variety of methods that are currently present in the CCU literature.

5.5 Research gaps and recommendations

The application of ROT to evaluate investment decisions in novel CCU projects is a relatively new but promising branch in the literature. In this section, the observed research gaps in the previous sections are summarized and several recommendations are made to gain more insights into ROT in future studies. These recommendations are based on real options analyses in other research areas, e.g., CCS, (renewable) energy and climate change policy. First of all, it is remarkable that the vast majority of ROT studies in the CCU literature focused on the direct use of CO_2. Only two studies addressed investment decisions for CO_2 conversion routes. However, the CO_2 conversion routes are also affected by different sources of uncertainty, which restrains firms from investing in these novel CCU projects. Hence, ROT studies can be very valuable in gaining more insights into how these uncertainties affect the optimal investment timing.

5.5.1 Uncertainty sources

Figure 5.2 illustrates how the investment decision sequence for CCU projects may look. In **Figure 5.2**, all sources of uncertainty are summarized, both for the CO_2 capture and the CO_2 utilization phases. The uncertainties that were already observed in the reviewed literature set are indicated with asterisks (*).

The CO_2 price

The vast majority of reviewed papers included CO_2 price as the main source of uncertainty. The CO_2 price uncertainty was included because it affects the revenue from CCU investments. By capturing and utilizing CO_2, CO_2 emissions into the atmosphere are avoided and thus, the carbon taxes that should

otherwise be paid can be avoided as well. Note that this reasoning assumes that the captured and utilized CO_2 would be counted as "avoided CO_2 emissions" in the carbon trading mechanism. However, in the current EU ETS framework, only permanently stored CO_2 counts as "avoided CO_2"(European Commission, 2012). Hence, it may be insightful to also model the inclusion or exclusion of CCU pathways in the EU ETS framework (or other carbon trading mechanisms) as a source of uncertainty. Even if carbon taxes can be seen as revenue for CCU projects, how carbon price evolution should be described is still up for debate. In sum, two major gaps concerning CO_2 price uncertainty have been identified:

- Current feasibility studies do not acknowledge the uncertainty of whether a carbon tax would be avoided or not. The uncertainty about the eligibility of CCU in the EU ETS framework (or other carbon trading mechanisms) should be recognized;
- The vast majority of the real options-based studies assumed that carbon prices follow a GBM. However, the behaviour of carbon prices in the EU is volatile and prone to jumps (Flora & Vargiolu, 2020). Hence, other stochastic models could be more appropriate.

Two recommendations are made to fill these gaps, based on how carbon price uncertainty is treated in other fields:

- Blyth et al. (2007) investigated how uncertain climate change policies affect investment decisions in power generation. In this study, carbon price was used as a proxy for climate change policy. Their model allows the carbon price to change in two distinct ways: (1) carbon prices fluctuate due to changes in demand and supply on the carbon market. This stochastic nature of carbon markets can be described by GBM and (2) the carbon price is also affected by discrete policy-related interventions. These events can be modelled by jump processes, describing the sudden changes in carbon prices. The use of a GBM with a jump process to describe CO_2 price evolution was also suggested in CCS investment studies (Patiño-Echeverri, Morel, Apt, & Chen, 2007; Zhu & Fan, 2011). Hence, the combination of a GBM to describe the stochastic nature of the carbon price with a discrete jump process to describe sudden policy changes could model the evolution of carbon prices more accurately;
- Flora and Vargiolu (2020) analysed how the price dynamics in the EU ETS affect low-carbon investments. They suggest using a more general stochastic model than a GBM because carbon price behaviour is still very volatile, uncertain and very prone to jumps. The Variance Gamma has been found to describe the carbon price evolution better than a traditional GBM.

Technological uncertainty

Technological progress was the main identified source of technological uncertainty in the reviewed literature set. Seven (out of eight) studies described technological improvements using a learning curve model. Besides technological learning, the EOR rate was often included as an uncertain factor as well. Nevertheless, two research gaps could be identified:

- A clear lack of studies investigating technological uncertainties that are specific to CO_2 utilization routes was observed. The major challenge for CCU is the high stability of the CO_2 molecule, resulting in high energy consumption (Ashford & Tu, 2017). Moreover, the technical risks associated with the installation and upscale of CCU plants slow down investments (IEA, 2020a). For the conversion of CO_2, in particular, the CO_2 conversion rate and the energy efficiency are often decisive parameters. However, none of these parameters was included as a source of uncertainty in the literature set;
- Most CCU technologies (e.g., CO_2-based fuels or chemicals) are still novel and emerging (Hepburn et al., 2019), requiring further development and pilot-scale projects to demonstrate

the feasibility of those projects (Z. Zhang et al., 2020). Hence, the majority of CCU projects (i.e., CO_2 conversion routes) possess R&D characteristics. As R&D projects are typically characterized by sudden breakthroughs, the use of learning curve models may not be suited for CCU projects that are still in the R&D phase.

Three recommendations are made to address technological uncertainty in CCU projects better:

- Future research should try to map the evolution of the CO_2 conversion rate or energy efficiency and find a stochastic model that fits the progress of these parameters better. Alternatively, instead of trying to model these technological uncertainties, real options analysis could also be applied to define the critical thresholds that should be surpassed before investing in a CCU project. In the current literature set, researchers mostly determined the critical CO_2 and/or oil price levels (**Table 5.3**);
- Instead of using learning curve models, Poisson processes should be used to simulate technological breakthroughs that are typical for R&D projects (Deeney et al., 2021);
- J. Wang and Yang (2012) described how to incorporate flexibility into the management of R&D projects under risk. They observed that technological uncertainty, contrary to market uncertainty, cannot be resolved by waiting. Instead, the uncertainty about the technical performance of the new technology can only be resolved by investing in follow-up stages of the R&D process. This has some implications for the value of the option to delay investment, which we will discuss in Section 5.5.2.

Market uncertainty

At the CO_2 source, which was often an electricity producer or a coal-fired power plant, coal prices and electricity prices were identified as market uncertainties. The CO_2 utilization phase often entailed CO_2-EOR, hence, the oil price was included as market uncertainty in the literature set as well. Two major gaps have been identified concerning market uncertainty:

- Most CO_2 conversion routes have high energy requirements due to the stability of the CO_2 molecule (Ashford & Tu, 2017). Hence, the electricity price can be a dominant factor in the operational expenditures of CCU projects. Electricity price was only included as revenue in the literature set, while it can also be a cost for CCU plants;
- For CO_2-EOR CCU projects, the oil price was included as market uncertainty in six studies as being the price of the product. In CCU conversion routes, on the other hand, CO_2 is generally converted into a chemical or fuel. Although the price of this end product would also influence investment decisions, it was not included as uncertainty in the literature set.

Two recommendations are made on how to treat these market uncertainties in future research:

- Electricity price should be included as a source of uncertainty at the CO_2 utilization phase due to the high energy consumption levels of CO_2 conversion routes. The review of Agaton (2021) regarding CCS projects revealed that both mean-reverting processes and GBMs were used to model electricity processes. The evolution of electricity prices can indeed be modelled using a mean-reverting process or a GBM, depending on the goal of the study. Dixit and Pindyck (1994) addressed the question of whether to use mean-reverting processes or GBMs for the prices of commodities. In their example, data for the oil prices over the past 120 years were analyzed. Using the oil price for the whole timeframe, their test revealed that the oil prices are mean reverting. However, if only the oil price data for the past 30 to 40 years was analyzed, no mean reverting trend could be detected. Hence, whether GBM or mean-reverting

processes should be used to model the electricity prices, depends on the timeframe (short-term versus long-term) and goal of the study;

- Although product price could be an important source of uncertainty for CCU projects, this uncertainty was rarely included. For CO_2-EOR projects, a GBM was used to describe the evolution of the oil price. However, for CO_2 conversion routes, many different potential products can be identified whose price does not necessarily follow a GBM. Future research should include product prices as uncertainties for CO_2 conversion as well and should try to find the stochastic model that best describes the product price evolution.

Policy uncertainty

In the literature set, only one type of policy uncertainty was addressed: government subsidy uncertainty, which can refer to subsidies for the CO_2 capture plant or the CO_2 utilization plant. However, inclusion in or exclusion from the EU ETS framework is an important source of policy uncertainty that should be analysed as well. Two gaps have been identified concerning policy uncertainty in CCU projects:

- Uncertainty about the level of government subsidy was generally only addressed in a scenario or sensitivity analysis;
- The uncertainty about the eligibility of CCU routes in carbon trading mechanisms was not acknowledged nor addressed in investment analysis for CCU projects.

Based on similar challenges in CCS literature, this gap could be addressed as follows. Instead of investigating the impact of different subsidy schemes or levels in a sensitivity analysis, the uncertainty about the subsidy level could be modelled through Poisson processes. Subsidy modes depend on policy interventions, which are often discrete. CCS projects are also prone to policy uncertainty and the impact of different subsidy modes, in particular. Hence, C. Huang, Chen, Tadikamalla, and Gordon (2021) modelled the uncertainty of subsidies by a Poisson jump process in their evaluation of a CCS technology to characterize the uncertain timing and level of government subsidies.

Impact and societal uncertainty

Similar to the findings of Agaton (2021), who observed the lack of research on social acceptance uncertainty in CCS projects, this review has shown that impact and societal un-certainties were not addressed in the current literature set. Nonetheless, both types of uncertainty could have a substantial impact on the feasibility and desirability of CCU projects. As demonstrated by the public protests against CCS projects, public acceptance is a necessary condition for the successful rollout of CCU technologies (Katrin Arning et al., 2020). One of the major risks that fuels the protest against CCS is the risk of CO_2 leakages from the storage reservoir. Narita and Klepper (2016) modelled CO_2 leakage as a probabilistic event that may occur at a certain hazard rate. Hence, feasibility studies should not only include the economic and environmental impact but should also address the public acceptance of the CCU technology (Katrin Arning et al., 2020). Surveys in Germany and the UK have shown that the public is not yet familiar with CCU, but they show a generally positive attitude towards CCU (K. Arning et al., 2019; Perdan, Jones, & Azapagic, 2017). The low public awareness of CCU only increases the uncertainty: will the public acceptance increase further or go down as awareness increases? How this societal uncertainty could be included in investment analysis is an interesting and challenging task for future research.

5.5.2 Real options

This section discusses which types of real options could be found in different phases of the investment decision for a CCU value chain.

Figure 5.2 illustrates where the different options are situated in the investment decision sequence for CCU projects. First, the decision has to be made whether to build a CO_2 capture now, later or never. Once CO_2 can be captured, the investment in a CCU plant can be considered. As the investment in the CO_2 capture plant is a prerequisite for the CCU plant to be built, we call this a compound option. The option to delay or defer the investment occurs before the investment is made, while the options to abandon, (temporarily) suspend, switch or scale are only available after the investment has been made. In the reviewed literature set, only three types of real options were analysed: the option to delay; the option to abandon; and the compound option. The delay or timing option provides the flexibility to invest at the optimal moment. The option to abandon was also present in the literature set. Due to the low maturity of CCU technologies, it can be valuable to be able to abandon the project if the technology does not perform as desired. The compound option, although more complex, was analysed for three CCU projects. Due to the interlinked steps in the CO_2 value chain, investing in one technology may serve as a stepping stone for a novel technology in the next step of the supply chain. The options to scale or switch were not investigated once in the literature set, although both are relevant for CCU projects. Hence, two major gaps have been identified. First, real options-based studies for CCU projects currently lack insights into how the flexibility in the CCU technology itself could add value to a project. For example, the CCU technology could be flexible in terms of input (CO_2 source, electricity source) or output (products). This type of flexibility has not yet been investigated or valued in the reviewed literature set. Second, although technical risks associated with the upscale of technologies are one of the main barriers to CCU commercialization, the value of the option to scale up in a later phase has not been analysed yet. Three recommendations are made to fill these gaps:

- The flexibility to switch inputs or outputs could be very valuable for CCU technologies. In practice, flue gases from polluting plants are often used as a CO_2 source. These flue gases have different compositions and thus, CO_2 may be contaminated with nitrogen (N_2), methane (CH_4), etc. Hence, the input may vary depending on the CO_2 source. The option to switch outputs could also be very profitable. If the CCU route could produce a different output with the same input, the products with the highest market value at that moment could be targeted. For example, the option to switch between a higher production of wood chips or the production of energy for sale in a bioenergy cogeneration project was analysed with a real options approach (de Oliveira, Brandao, Igrejas, & Gomes, 2014). The researchers observed that the option to switch added significant value to the project. Moreover, the CCU technology in itself can provide a switch option to the producer: the flexibility to switch between the old polluting production process and the low-carbon CCU production process. For example, Flora and Vargiolu (2020) investigated the option to switch electricity production from being fossil fuel-intensive to low-carbon sources of energy. In sum, we strongly recommend evaluating the option to switch in future studies as it may increase the desirability of CCU routes;
- The option to scale the production level of CCU plants should be analysed as well. For example, Enders, Scheller-Wolf, and Secomandi (2010) investigated the option to scale the production level of a natural gas plant. They found that the possibility to scale the plant increases the value of the natural gas significantly;
- Besides these options that can be foreseen in the investment decision sequence of a CCU project, the CCU technology itself can provide flexibility in a system. In the presence of uncertain fossil fuel prices, CCU technologies may offer an advantage because the utilized CO_2 often replaces fossil fuels as a resource in conventional production processes. For example, Davis and Owens (2003) applied ROT to estimate the value of renewable energy technologies in the presence of uncertain fossil fuel prices. Renewable energy systems can serve as backup technologies when fossil fuel prices increase severely. The authors used GBMs to represent

the changes in fossil fuel prices and renewable electricity prices and tried to capture the value of the flexibility that renewable energy systems can provide in real options-based analysis. Similarly, CCU technologies may serve as a backup technology for fossil fuel-based processes when fossil fuel prices rise significantly.

5.6 Conclusions

This review article aimed to explore the application of ROT to introduce and value flexibility in investment decisions regarding CCU projects. CCU projects comprise different phases, from the capture of CO_2 to the utilization of CO_2, and can unite different agents in the CCU value chain. Hence, many different types of uncertainties and flexibility options can be identified in CCU value chains. Although real options analysis could be very relevant for CCU projects, the literature search revealed a limited number of 17 ROT applications in CCU projects. Moreover, the majority of the literature set focused on the direct use of CO_2 (15 studies), while only two studies investigated the investment decisions for CO_2 conversion routes.

In the reviewed literature set, the price of CO_2 was identified as the main source of uncertainty. Oil price (ten), technological progress (eight) and government subsidies (seven) were also frequently observed as uncertainty sources in the literature set.

Concerning real options, the option to delay the investment decision was the most common type of option in the literature set. Only two other types of real options were observed in the literature set: the option to abandon and the growth option. Remarkably, the options to switch or the option to stage were never included, although these could constitute valuable flexibility options for CCU technologies.

Several recommendations have been made to improve the insights that can be gained from real options-based analyses for CCU projects. First, the CO_2 price uncertainty should not only address the level of CO_2 price but also the eligibility of CCU technologies in carbon trading mechanisms. Second, technological uncertainty should be addressed more in-depth and in different ways in future ROA studies for CCU projects. In the presented literature set, the technological progress in CCU projects was mostly modelled through a learning curve, which is a deterministic method. The Poisson process, which is a stochastic process, could be more fitting to model technological progress, as it helps describe the discrete nature of technological breakthroughs. Besides, the uncertainty of the CO_2 conversion rate or the energy efficiency of CO_2 conversion routes should also be included. Third, the importance of product price as a market uncertainty should not be neglected for CO_2 conversion technologies. Fourth, policy uncertainty should not only be addressed in a sensitivity analysis but can also be simulated through Poisson jump processes to characterize the uncertain timing and level of government subsidies. Finally, the flexibility embedded in CCU technology should be recognized and valued correctly. For example, the flexibility to switch output or the flexibility to switch from a fossil fuel-based process to a CCU-based process should be included properly in economic feasibility studies.

In sum, this review article has shown that a real options analysis can be very valuable for CCU projects to introduce flexibility and uncertainty into investment decisions, thereby making the decisions more realistic. Future research should also apply ROT to investment decisions for CO_2 conversion routes as these are also characterized by different types of uncertainties. Introducing flexibility into the decision pathways of CO_2 conversion routes could reduce existing barriers for investors.

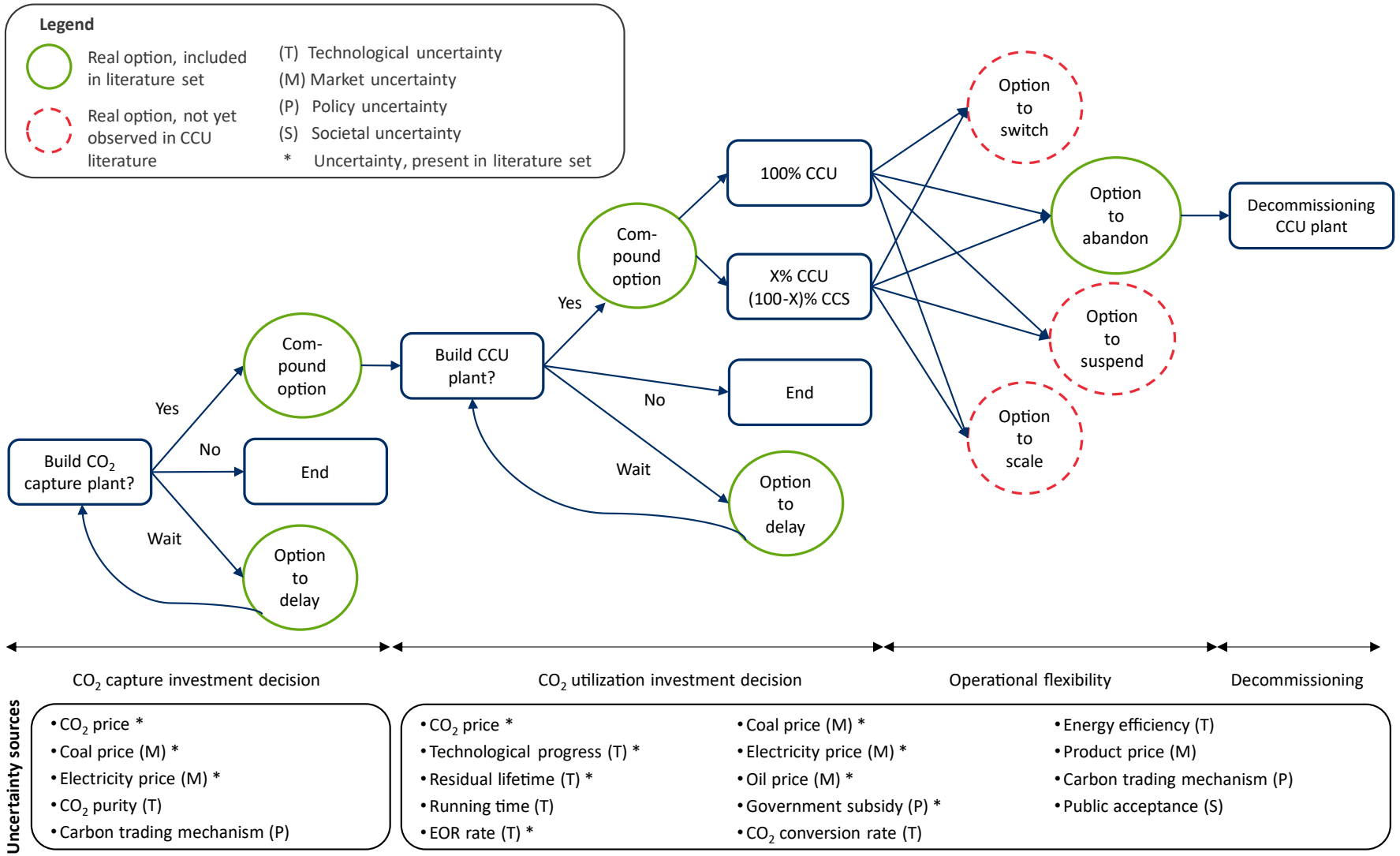


Figure 5.2: Real options in the investment decision sequence for a CCU value chain. Real options that were not yet observed in the literature set are indicated by dashed circles. The sources of uncertainty in each step are listed below. Uncertainty sources observed in the literature set are indicated with *.

6

CO_2 Storage Or Utilization? A Real Options Analysis Under Market and Technological Uncertainty

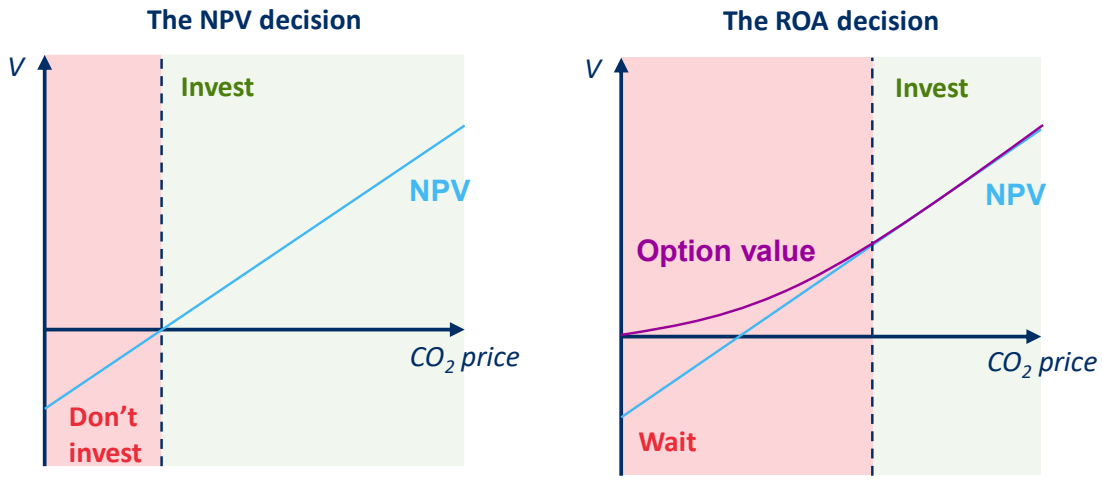
Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU) are considered essential solutions to reduce greenhouse gas (GHG) emissions worldwide. A crucial difference between the two is that CCS is already a mature technology, while CCU is still in the R&D phase. Hence, firms are confronted with a dilemma, where they have to choose between either the mature CCS, the emerging CCU, or the installation of both in a Carbon Capture Utilization and Storage (CCUS) system. In this study, we analyse different strategies that the firm can pursue and determine the optimal investment timing. In doing so, we take into account both technological uncertainty, i.e. the unknown time-to-market of CCU, and market uncertainty, i.e. the CO_2 price. Three different CCUS value chains in the cement industry are analysed. We find that the anticipated arrival of profitable CCU technologies in the future does not delay investments in CCS in the current period. Investments in CCS and CCU can be accelerated by reducing the volatility of the CO_2 price, or by increasing the growth rate of the CO_2 price. Finally, we find that a higher fraction of CO_2 emissions that can be used in CCU, results in sooner adoption of CCS today.

Takeaway messages

- Firms are confronted with a choice between the mature CCS, the emerging CCU or the integration of both in a CCUS value chain.
- Two uncertainties complicate this investment decision: (1) the volatile CO_2 price in the EU ETS (market uncertainty) and (2) the unknown time before CCU is also a mature solution (technological uncertainty).
- Real options analysis can help firms identify the optimal timing, defined by the CO_2 price threshold, to invest in these technologies.
- The firm can choose between a variety of adoption strategies, with different combinations of CCS and CCU and different sequences of investing in these technologies.
- Four real options models are built to accommodate this variety of adoption strategies.
- The application to the cement industry shows that (1) volatility in the CO_2 price delays investments in both CCS and CCU, (2) investments in CCS are not delayed by the anticipated arrival of CCU in a future period, and (3) investments in CCS are even accelerated when a higher portion of the CO_2 emissions can be used in the (future) CCU value chain.

Why Real Options Analysis?

- Firms generally make their investment decision based on the NPV of a project. If the NPV is greater than zero, the firm will invest. If the NPV is negative, the firm will not invest.
- However, the NPV criterium is flawed. It does not take into account uncertainty and it presents a now-or-never decision to the firm: invest now (NPV > 0), or never (NPV < 0).
- With real options analysis, the value of waiting is taken into account. When future prices are uncertain, it can be valuable for the firm to wait for more information. This creates a value of waiting. Hence, the investment decision becomes a now-or-later decision for the firm.
- The option value includes this value of waiting. Instead of investing when the NPV is greater than zero, the NPV should now be greater than the value of waiting.
- The comparison of the NPV and the ROA decision reveals that the investment decision is made at different CO_2 price levels.



6.1 Introduction

Despite the growing sense of urgency to tackle climate change, the CO_2 emission levels still rose by 6% in 2021. This is in stark contrast with the ambitious goals from the European Union, which has expressed the ambitions to emit 55% less greenhouse gas (GHG) emissions by 2030, compared to 1990, and to become the first climate-neutral continent by 2050 (European Commission, 2022). Besides investments in renewables, increased energy efficiency and alternative transport modes, the EU's long-term vision to become climate-neutral by 2050 also includes Carbon Capture and Storage (CCS) to abate the remaining CO_2 emissions (European Commission, 2018a). CCS captures, transports and finally stores the CO_2 permanently underground, either on- or offshore. In addition to CCS, the European Commission also recognizes a role for Carbon Capture and Utilization (CCU) in the pathway to climate neutrality (European Commission, 2021). CCU uses the captured CO_2 as a valuable commodity and transforms it into marketable products (e.g. fuels, chemicals, building materials), which generates additional revenues. Finally, both technologies can also be integrated into a Carbon Capture Utilization and Storage (CCUS) value chain.

CCS and CCU are expected to play an important role in the transition to a climate-neutral society. In their latest report, the Intergovernmental Panel on Climate Change (IPCC) also recognizes CCS and CCU to be crucial for reaching the targets in the Paris Agreement (IEF, 2022).-Despite their central role in many mitigation strategies, the deployment of both CCS and CCU remains too slow. CCS projects are delayed because of their high costs, a lack of public acceptance and clear policy support (Bui et al., 2018). CCU is lagging even further in terms of deployment. Most CCU technologies are not yet ready to be commercialized, and their expansion to a commercial scale would require high volumes of renewable energy and green hydrogen in the future (European Commission, 2023b). In sum, various economic, technical and societal barriers currently hamper the deployment of both CCS and CCU.

To solve some of these barriers and further support the deployment of CCS and CCU technologies, the European Commission has established different policy initiatives. For example, the CCS Directive provides a legal framework to guarantee the safe storage of CO_2 and the Renewable Energy Directive includes incentives to increase the production of fuels by CCU. Since 2015, CO_2 capture and storage installations are included in the EU Emission Trading System (ETS), meaning that captured and safely stored CO_2 is considered as not-emitted under the EU ETS, providing the main incentive for CCS investments (European Commission, 2023a).

The novelty of CCS and CCU, together with the identified barriers and the possibility to combine CCS and CCU adds to the complexity of the investment decision for CCS, CCU or CCUS projects. To decide whether or not to invest in these projects, the technical, economic and environmental feasibility should be analysed. The most commonly applied methods to do so are Techno-Economic Assessments (TEAs) and Life Cycle Assessments (LCAs).[17] While the results from the TEAs are technology-specific, the majority of the studies indicate that the costs of both CCS and CCU, in particular energy costs, are still substantial. A comparison of the environmental impacts of CCS and CCU revealed that CCS projects on average create lower global warming potential (GWP) than CCU projects, while CCU performs better than CCS on other environmental impact categories (Cuéllar-Franca & Azapagic, 2015). One common concern in all studies is the high level of uncertainty about the future performance of CCS

[17] A review of economic feasibility studies for CCU projects can be found in (Lamberts-Van Assche & Compernolle, 2021) and a review of the costs for CCS in the industrial sector can be found in (Leeson, Mac Dowell, Shah, Petit, & Fennell, 2017). Cuéllar-Franca and Azapagic (2015) compare the life cycle environmental impacts of both CCS and CCU technologies over 27 LCA studies in total.

and CCU projects. The most common method in TEAs and LCAs to address the uncertainty is a sensitivity analysis, both for CCS (van der Spek et al., 2020) and CCU (Lamberts-Van Assche & Compernolle, 2021) projects. While sensitivity analysis allows one to assess how and which variables affect the result the most, it does not enable the decision-maker to integrate uncertainty into an investment decision. In sum, TEA (and LCA) studies typically only consider a deterministic setting and hence, can only advise to either adopt the technology now, if it is profitable, or never, if it is too costly. The uncertainties and risks of the real-world setting are typically neglected in this type of assessment.

To include these uncertainties and risks properly, there is a growing stream of literature that analyses investment decisions in CCS or CCU technologies in a dynamic framework, taking managerial flexibility into account.[18] Real options analysis presents a method to value flexibility in investment decisions, acknowledging the fact that decision-makers can delay investment decisions in practice (Dixit & Pindyck, 1994). Finally, the investment decision in CCS and CCU solutions can also be affected by the policies that are pursued. Castillo Castillo and Angelis-Dimakis (2019) use stakeholder engagement to identify three main policy needs to promote the development of CO_2 utilization: (1) market regulation, (2) support for early development of CCU and (3) provide incentives and guidance for further deployment. Greaker and Rosendahl (2008) find that an increasingly strict environmental policy on the polluter leads to more competition in the CCS sector and will reduce abatement costs. The CO_2 price in the EU ETS can also be affected by policymakers, by changing the emissions cap and the number of emissions allowances issued. The CO_2 price is even the most commonly investigated source of uncertainty in real options analyses for investment decisions in CCU projects (Lamberts-Van Assche & Compernolle, 2022). Despite the growing number of studies on CCS or CCU investments, the existing literature does not yet address all complexities associated with these investment decisions.

First, CCS and CCU should not only be considered as two stand-alone solutions but also as technologies that are compatible and can be integrated into one CCUS installation. To avoid a mismatch between the scale of the CO_2-emitting plant, on the one hand, and the scale of the CO_2 utilization plant, on the other hand, a CCUS value chain is created (Monteiro & Roussanaly, 2022). Hence, the possibility to combine CCS and CCU is included in our real options model.

Second, CCS and CCU are at different levels of maturity. While CCS has reached the highest Technology Readiness Level (TRL) of 9 and large-scale CCS projects exist, CCU technologies are mostly still at the lab or prototype scale (TRL 4-5) (Bui et al., 2018). This discrepancy in maturity confronts firms with a complex decision problem. On the one hand, if the firm adopts CCS today, the firm can start reducing its CO_2 emissions immediately. On the other hand, if the firm decides to wait for the arrival of CCU, the firm holds the option open to adopt the technology with the expected larger profits. In other words, the firm needs to anticipate the arrival of more profitable technologies (i.e. CCU) in the future, while making investment decisions for existing technologies (i.e. CCS) today. Although the effect of technological progress on investments in CCU projects has been investigated before, these studies did not consider the case where one technology is already mature and the other is not. The majority of these studies use learning curve models to describe technological progress, assuming a continuous decline in the costs (Lin & Tan, 2021; L. Yang et al., 2019; W. Zhang et al., 2021; X. Zhang et al., 2014). Deeney et al. (2021), however, model the technological innovation for a CCU project in the R&D phase by a Poisson process, to mimic the sudden arrival of breakthroughs. In our real options model, the Poisson process is also used to simulate the breakthrough of CCU as a mature technology.

[18] See Agaton (2021) and Lamberts-Van Assche and Compernolle (2022) for an extensive review of real options applications in CCS and CCU respectively

These two complexities, the possibility of a CCUS value chain and the different maturity of CCS and CCU, have so far not been addressed simultaneously in the literature. This study fills this gap by allowing the decision-maker the choice between CCS and CCU individually, and the combination of both (CCUS), even when one of these technologies is not yet available at present. The goal of this study is to build a model that enables the decision-maker to identify the optimal timing to invest in CCS, CCU or CCUS. This 'optimal timing to invest' is defined by the critical CO_2 price threshold that needs to be surpassed in the EU ETS before the investment is made. Therefore, a real options model is built that aims to find this optimal timing to invest and that includes (1) technological uncertainty, i.e. the unknown time-to-market of CCU, and (2) market uncertainty, i.e. the CO_2 price in EU ETS. The real options model is then applied to potential CCUS chains in the cement industry. The cement industry is a major source of CO_2 emissions, responsible for 6 to 7% of global CO_2 emissions (Monteiro & Roussanaly, 2022). About two-thirds of the cement industry's CO_2 emissions are unavoidable, highlighting the need for CCUS to reduce these CO_2 emissions (IEA, 2019b).

Applying our framework to the cement industry results in the following findings. We find that the investment threshold for CCS in the current period is lowered in the prospect of a more profitable CCU technology in a future period. However, how soon the arrival of CCU is expected, does not affect the investment threshold to a large extent. A higher growth rate of the CO_2 price lowers the barriers to investing in CCS and CCU, while a higher volatility in the CO_2 price increases the investment thresholds.

Our main contributions can be summarized as follows. First, this study adds to the existing literature by recognizing the complementary nature of CCU and CCS and showing how this affects the investment decision in both CCU and CCS individually and CCUS jointly. Second, firms that consider the flexibility in the timing of the investment and the technological and market uncertainties present, will delay their investment in CCS and CCU. This is the optimal decision for a firm considering their economic interest, but it may not be the most desirable decision from the societal perspective. Third, and adjacent to the previous finding, policymakers should guarantee more predictability and a higher growth rate in the CO_2 price in the EU ETS, if they want to minimize the delay in CCUS investments. Finally, both firms and policymakers should realize that the anticipation of a more attractive CCU solution in the future accelerates investments in CCS today. This means that the development of CCU technologies should be supported, as it will facilitate investments in CCS technologies and hence, initiate the abatement of CO_2 emissions sooner.

The remainder of the article is organized as follows. The following section presents the set-up of the four real options models, one for each possible investment strategy. Section 6.3 presents the results of the real options models, for three CCUS value chains in the cement industry. In Section 6.4, we analyse how the investment thresholds shift in response to changes in certain parameters of the model, e.g. the arrival rate of CCU and the volatility in the CO_2 price. The results are discussed in Section 6.5 and our conclusions are given in Section 6.6.

6.2 The model set-up

We consider a risk-neutral, profit-maximizing firm that emits CO_2 and needs to surrender emission allowances under the EU ETS. To reduce its CO_2 emissions and the associated emission allowances that need to be bought, the firm is considering an investment in CCS, CCU, or CCUS. We propose a dynamic framework to find the firm's optimal strategy to reduce its payments in the EU ETS, under both technological (the unknown time-to-market of CCU) and market uncertainty (the CO_2 price). This framework is built using a real options approach, that acknowledges the flexibility in the firm's investment decisions and includes the present uncertainties. This setup is similar to the well-cited

work of Grenadier and Weiss (1997), which develops a real options model to find the optimal investment decision for a firm confronted with a sequence of innovations. In the current study, the sequence of innovations is presented by CCS (the existing technology) and CCU (the future innovation). The present study provides the first framework to acknowledge that the existing and future innovations are not necessarily mutually exclusive, but can also be combined.

The unknown arrival of CCU in the future is a source of technological uncertainty. We consider a firm that does not influence or accelerate the arrival of CCU by investing in R&D: the R&D process is exogenous to the firm. We model the firm's perceived probability of CCU arriving in the next period by a Poisson jump process. Due to the R&D nature of CCU projects, the discrete jumps of a Poisson process are fit to describe breakthroughs in the CCU project (Deeney et al., 2021). A Poisson process with intensity λ means that the probability of CCU maturing in the next period equals λdt.

The CO_2 price in the EU ETS presents a source of market uncertainty. Since January 2020, the price of emissions allowances in the EU has increased from less than 25 euros per tonne of CO_2 to almost 85 euros per tonne of CO_2 in August 2023. The carbon price level is driven by various forces, including policy measures, commodity prices or geopolitical events. We assume that the CO_2 price evolution follows a Geometric Brownian Motion (GBM) (see e.g. (Abadie et al., 2014; Compernolle & Thijssen, 2022; Compernolle et al., 2017; X. Zhang et al., 2014)) and is described as follows

$$dE = \alpha\, E\, dt\, + \sigma\, E\, dz, \tag{6.1}$$

with E the price for an emission allowance per tonne of CO_2 in the EU ETS, or simply the CO_2 price, α the drift or growth rate, σ the variance or volatility, and dz the increment of a Wiener process. In the real options model, the CO_2 price is included as a revenue per tonne of CO_2 stored or utilized: the assumption is that both the stored CO_2 and the utilized CO_2 are considered as not-emitted in the EU ETS and consequently, no allowances need to be surrendered anymore for the stored or utilized CO_2. In practice, not all utilized CO_2 is considered not-emitted in the EU ETS. In May 2023, the EU ETS regulations were revised to mirror the ambitious climate targets of the EU. Under the current EU ETS directive, the obligation to surrender emission allowances is lifted for CO_2 emissions that are captured and transported for permanent storage (Article 12(3a)), and for CO_2 emissions that have been utilised in such a way that they are permanently chemically bound (Article 12(3b)) (European Commission, 2023c). Hence, the present study includes an optimistic scenario where utilized CO_2 is always considered as not-emitted in the EU ETS, independent of the utilization route.

A profit-maximizing firm will only invest in emission abatement projects when the CO_2 price is high enough, resulting in higher cost savings. The investment decision in CCS, CCU or CCUS will be triggered by threshold CO_2 prices, which we denote by E^*_{ccs}, E^*_{ccu} and E^*_{ccus}, at which the firm is indifferent between waiting or investing in CCS, CCU and CCUS respectively. To determine the optimal investment time, the first step is to identify the optimal strategy when CCU is mature and ready to install. Once we have determined the conditions under which each adoption strategy is optimal in the presence of CCU, we can start analysing what happens before CCU arrives. Therefore, the real options model to analyse the investment strategy is split into two stages: one before and one after the arrival of the CCU technology. To identify the variety of technology adoption strategies that are possible over both stages, we need to understand the features of each abatement technology first.

The CCS technology captures and stores all CO_2 permanently underground.[19] To put CCS into operation, the firm needs to pay a one-time investment cost for the capture facility, a capture cost per tonne of CO_2 and a transport and storage fee to a third party. Hence, we assume that the firm invests in and builds the CO_2 capture plant on-site, but 'outsources' the transport and subsequent storage of CO_2 to a third party. This third party could e.g. be the Longship project, which will be the first cross-border transport and storage infrastructure network, offering the storage of CO_2 underground in Norway.

The CCU solution does not store the CO_2 underground but utilizes and converts the CO_2 into valuable products. Because the amount of CO_2 that can be used and converted is limited - both due to market and technical limitations - not all CO_2 will be captured and converted (Markewitz et al., 2012). Hence, the firm will still need to buy emission allowances for the remaining CO_2 emissions. To adopt CCU, the firm needs to incur sunk investment costs for the capture facility and the utilization plant and needs to pay a capture cost and utilization cost per tonne of CO_2 used. Because the CO_2 is now converted into products, the firm will also receive revenues from the sales of those CO_2-based products. Finally, the CCUS technology option combines both CCS and CCU. The part of the CO_2 emissions that can be used and converted is sent to the utilization plant on-site. The remaining part of the CO_2 emissions is transported to the storage site to be stored underground. Hence, all CO_2 emissions are avoided. The firm needs to pay investment costs for both the capture facility and the utilization plant and needs to pay capture costs for all CO_2, the transport and storage fee for the part that is stored and the utilization cost for the fraction of CO_2 emissions that is used.

To simplify the framework, we only consider the direct CO_2 emissions from the firm and consider them as 'not-emitted' in the EU ETS when they are either captured and stored or captured and utilized. We do not consider other, additional CO_2 emissions that could be created in the CCUS value chain (e.g. due to the energy needed to capture the CO_2).

Table 6.1 summarizes the characteristics of the three abatement technologies. **Figure 6.1** visualizes the value chain for each abatement technology. With CCS, the captured CO_2 is transported and stored underground, whereas the captured CO_2 is used on-site and converted into products in the CCU route. The CCUS route integrates both the storage and utilization of CO_2 into one value chain. With the CCS and CCUS value chain, all CO_2 emissions are captured from the CO_2 source. In the CCU route, only part of the CO_2 emissions can be captured and used.

Table 6.1: Comparison of the three abatement technologies: CCS vs. CCU vs. CCUS.

	CCS	**CCU**	**CCUS**
Goal	CO_2 storage	CO_2 utilization	CO_2 storage & utilization
Emission allowances	0	>0	0
Investment costs	Capture facility	Capture facility Utilization plant	Capture facility Utilization plant
Variable costs	Capture costs Transport & storage fee	Capture costs Utilization cost	Capture costs Transport & storage fee Utilization cost
Revenues		CO_2-based product	CO_2-based product

[19] In the literature, the assumption of a 90% capture rate has become standard. However, capture rates will need to go beyond 90%, to reach climate targets. Capture rates up to 98% are feasible at relatively low marginal costs (Brandl, Bui, Hallett, & Mac Dowell, 2021). In this study, we assume that 100% of the CO_2 is captured and stored.

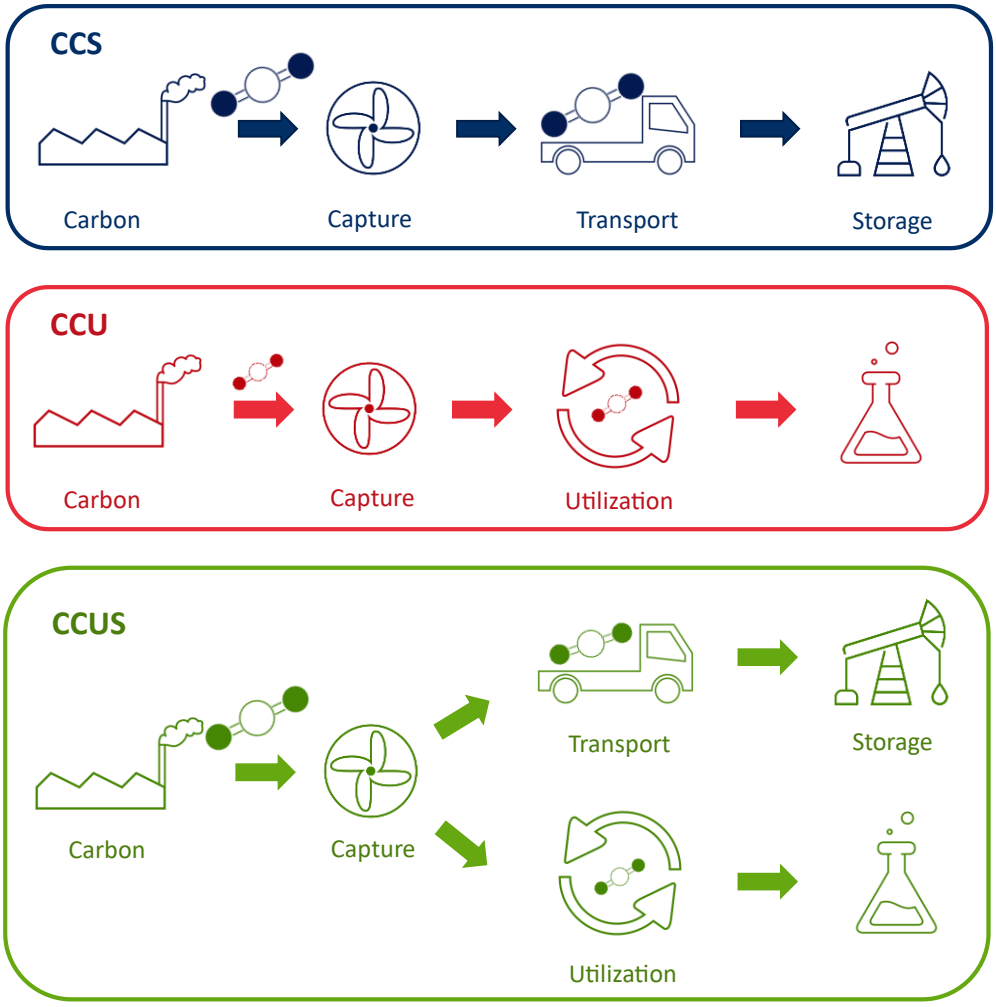


Figure 6.1: The CCS, CCU and CCUS value chains.

In this paper, six possible technology adoption strategies can be identified, considering the two-staged nature of the investment problem and the characteristics of each technology (**Table 6.1**). In Stage 1, the firm has only two options: invest in CCS, or wait. If the firm adopted CCS in Stage 1, the firm can hold on to CCS (S.1) or adopt CCU in Stage 2 (S.2), to reach the hybrid CCUS solution. If the firm waited in Stage 1, the firm can still decide to invest in CCS alone (S.3), invest in CCUS simultaneously (S.4), adopt CCU and CCS in a sequential order (S.5) or invest in CCU immediately when it arrives (S.6) in Stage 2. **Figure 6.2** summarizes the various decisions that are possible over both strategies, resulting in these six adoption strategies.

To determine the optimal decision in Stage 1 (invest in CCS or wait), the firm needs to understand the consequences of its decision today on its future opportunities. If the firm invests in CCS in Stage 1, it can stick with CCS alone or invest in CCU as well in Stage 2. Only if CCUS results in a higher project value than CCS, the firm should also invest in CCU in Stage 2. If the firm waited in Stage 1, more strategies are still available to the firm, as summed up in **Figure 6.2**.

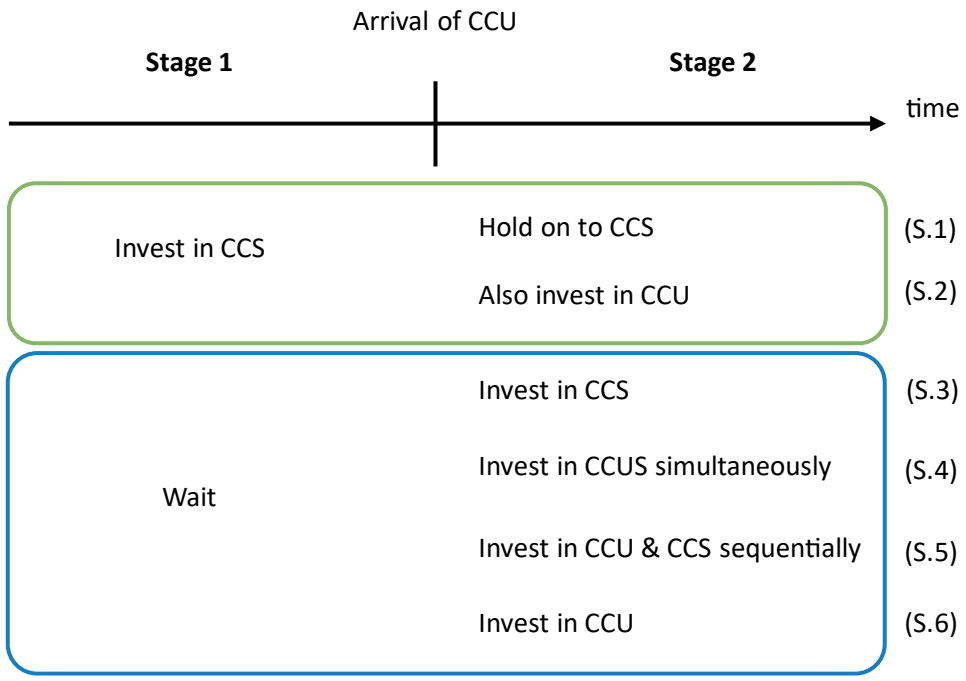


Figure 6.2: The combination of actions possible over Stages 1 and 2, resulting in six technology adoption strategies.

A comparison of the project values of CCS, CCU and CCUS enables us to identify the optimal adoption strategy in Stage 2, after waiting in Stage 1. The present value V of each abatement technology over an infinite time horizon, taking into account the expected growth rate α in the CO_2 price E, is expressed as follows

$$V_{ccs} = \frac{Q_{co_2}}{\rho - \alpha} \cdot E - \frac{Q_{co_2}}{\rho} \cdot (C_c + C_{ts}) - I_c, \tag{6.2}$$

$$V_{ccu} = \frac{q \cdot Q_{co_2}}{\rho - \alpha} \cdot E + \frac{q \cdot Q_{co_2}}{\rho} \cdot \left(P_p \cdot X - C_c - C_u\right) - I_c - I_u, \tag{6.3}$$

$$V_{ccus} = \frac{Q_{co_2}}{\rho - \alpha} \cdot E - \frac{Q}{\rho} \cdot C_c - \frac{(1-q) \cdot Q_{co_2}}{\rho} \cdot C_{ts} + \frac{q \cdot Q}{\rho}\left(P_p \cdot X - C_u\right) - I_c - I_u, \tag{6.4}$$

where ρ represents the discount rate (with $\rho > \alpha$)[20], Q_{co_2} represents the amount of CO_2 emissions from the firm, C_c the capture cost per tonne of CO_2, C_{ts} the transport and storage fee per tonne of CO_2, q the fraction of the CO_2 emissions that can be utilized, P_p the price for the CO_2-based product, X the conversion factor from CO_2 to the product and C_u the utilization cost per tonne of CO_2. The investment costs for the capture and utilization plant are respectively I_c and I_u.

Figure 6.3 plots the present values of the cash flows that are generated by CCS, CCU and CCUS as a function of the CO_2 price. The present values of each technology (CCS, CCU or CCUS) are ranked relative to each other in four different scenarios, when it is optimal for the firm to (a) invest in CCS alone, (b) invest in CCS and CCU simultaneously, (c) adopt CCU and CCS sequentially, at different CO_2 prices, and (d) invest in CCU immediately.

[20] The assumption $\rho > \alpha$ is made to ensure the finiteness of the PVs.

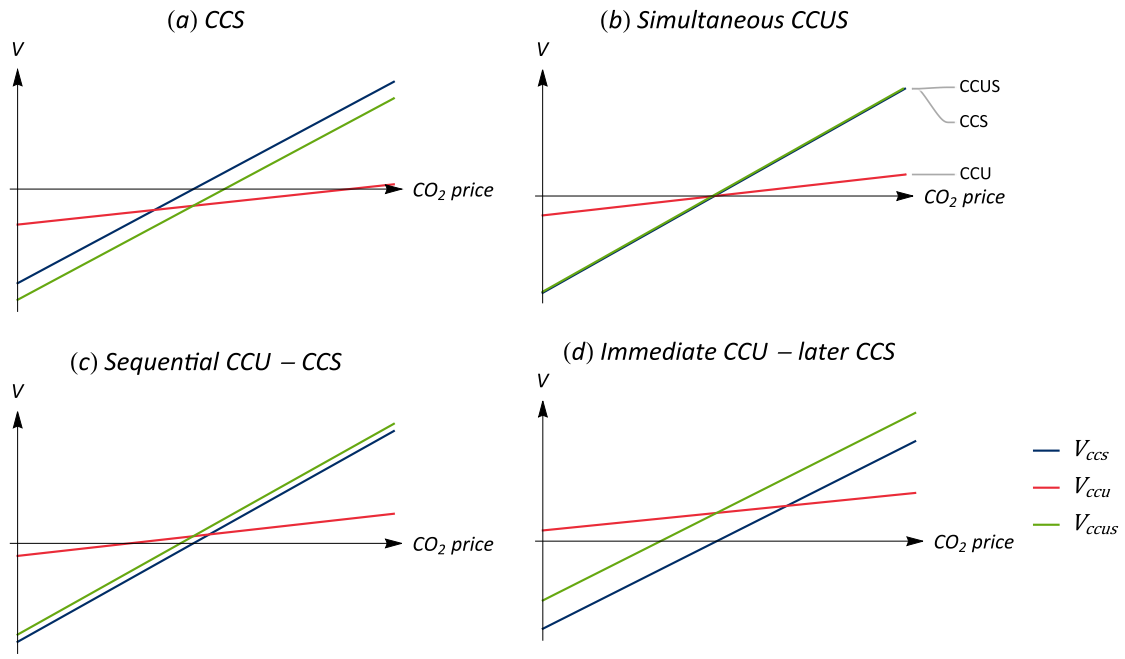


Figure 6.3: The present values of CCS, CCU and CCUS in four scenarios where it is optimal to (a) invest in CCS alone, (b) invest in CCUS simultaneously, (c) invest in CCU and CCS sequentially, or (d) invest in CCU immediately and in CCS later. These scenarios reflect adoption strategies (S.3) – (S.6).

These scenarios reflect the adoption strategies (S.3) – (S.6) that were presented in **Figure 6.2**, where the firm waits in Stage 1 until CCU arrives. If the firm invests in CCS in Stage 1, the present value of CCU alone (red line) is no longer relevant. **Figure 6.3** (a) then represents the scenario where the firm should hold on to CCS (S.1). **Figure 6.3** (b) – **Figure 6.3** (d) present scenarios where the firm should also invest in CCU (S.2) since the present value of CCUS is higher than the present value of CCS.

Based on **Figure 6.3**, we can derive the conditions under which each of these strategies is optimal. We do so by comparing the investment cost for the utilization plant I_u to the net benefits of CCU, denoted by F. These net benefits represent the cashflows that are generated by operating CCU, in addition to CCS. Hence, F equals the revenues for the CO_2-based product ($P_p \cdot X$), plus the avoided transport and storage costs (C_{ts}), minus the utilization costs (C_u).

Figure 6.4 plots the investment cost for the utilization plant I_u against the net cashflows F from operating CCU, to draw the four optimal regions and their boundary conditions. When the investment cost I_u for the utilization plant is high and the net CCU cashflows F are low, the optimal adoption strategy for the firm is to invest in CCS alone (blue). When the investment cost decreases or the net benefits of CCU increase slightly, it is optimal for the firm to invest in CCUS simultaneously (dark red). At further declining I_u or increasing F, the attractiveness of CCU rises. In the light red area, the firm will invest sequentially in CCU and CCS: first in CCU alone, and later, at higher CO_2 prices, also in CCS. Finally, as I_u becomes lower and F continues to rise, the firm will invest in CCU immediately when it arrives (independent of the CO_2 price) and later invest in CCS (green). Similar to **Figure 6.3**, the regions (a) – (d) reflect the optimal adoption strategies (S.3) – (S.6) from **Figure 6.2**. However, we can also observe the optimal regions for adoption strategies (S.1) – (S.2) in **Figure 6.4**. In region (a) (blue), the firm should hold on to CCS, while the firm should also invest in CCU in regions (b) – (d) (red and green).

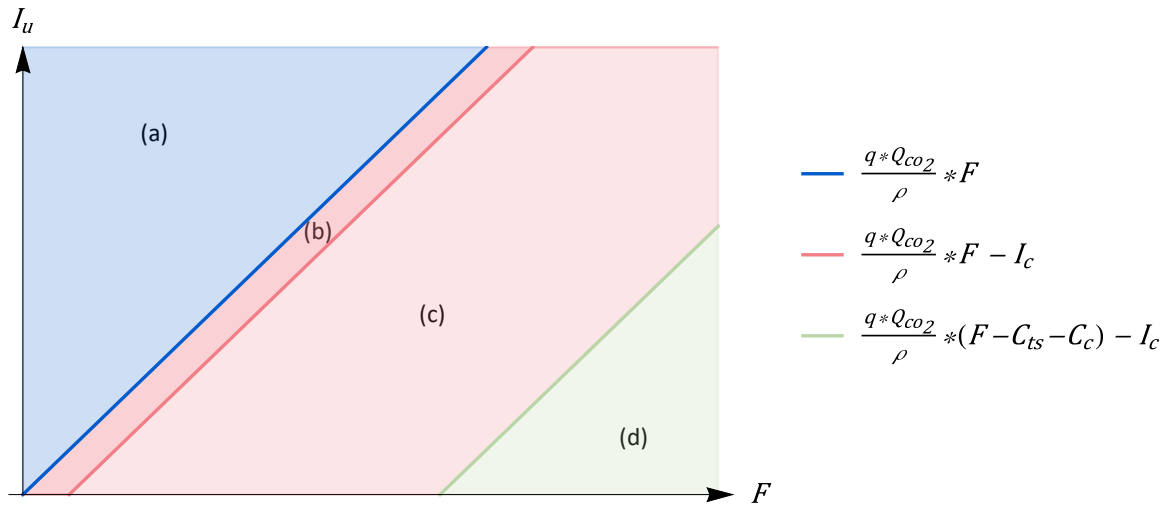


Figure 6.4: The definition of the regions in which it is optimal in Stage 2 to invest in (a) CCS (blue); (b) CCUS simultaneously (dark red); (c) CCU and CCS sequentially (light red); (d) immediately in CCU, followed by CCS (green), after the firm waited in Stage 1. The regions are defined by the investment cost for the utilization plant I_u and the net benefits F of CCU.

Whether the firm already invested in CCS in Stage 1 or is still waiting when CCU enters the market will depend on the arrival time of CCU and the profitability of both CCS and CCU. To model these dynamics, a real options approach is necessary. In the next sections, we perform a rigorous real options analysis to identify the CO_2 price thresholds for each abatement technology in both stages, $E^*_{ccs,1}$, $E^*_{ccu,2}$, $E^*_{ccs,2}$ and $E^*_{ccus,2}$. These investment thresholds are not simply the break-even points of the present value curves in **Figure 6.3**, but also take into account the value of flexibility due to the uncertainty in the CO_2 price. As a result, these 'real options' investment thresholds can either be lower or higher than the traditional investment thresholds. Because the optimal adoption strategy and required investment thresholds are different in each region from **Figure 6.4**, the real options models are developed separately for each region in the following sections.

6.2.1 Model 1: CCS

In Model 1, we analyse the optimal investment timing for the blue region in **Figure 6.4**, where CCS yields the highest return for the firm. As shown in **Figure 6.3**, CCS can reach break-even at the lowest CO_2 price and always returns the highest value afterwards. To find the optimal timing to invest in CCS, the firm needs to determine the CO_2 price threshold $E^*_{ccs,1}$. Using the dynamic programming technique, as described in Dixit and Pindyck (1994), we can solve this investment decision problem and find the threshold $E^*_{ccs,1}$. Model 1 describes how to find the optimal timing to invest in CCS, either in Stage 1 (before CCU arrives) or in Stage 2 (after CCU arrives). Hence, Model 1 develops the adoption strategies (S.1) and (S.3) from **Figure 6.2**.

When $E > E^*_{ccs,1}$, it is optimal to invest in CCS and the firm obtains the project value V_{ccs} (6.2):

$$F_1(E) = \frac{Q_{co_2}}{\rho - \alpha} \cdot E - \frac{Q_{co_2}}{\rho} \cdot (C_c + C_{ts}) - I_c, \tag{6.5}$$

As long as $E \leq E^*_{ccs,1}$, it is optimal for the firm to wait with the investment and hold on to the option to invest in CCS. The first step to finding this option value is the preparation of the Bellman equation (Dixit & Pindyck, 1994):

$$\rho \cdot F_1(E) = \lim_{dt \to 0} \frac{1}{dt} \cdot \mathbb{E}[dF_1]. \tag{6.6}$$

The second step is to apply Ito's Lemma, which is used to determine $E[dF_1]$. The Bellman equation in (6.6) is expanded using Ito's Lemma, resulting in the Ordinary Differential Equation (ODE):

$$\frac{1}{2}\sigma^2 \cdot E^2 \cdot F_1''(E) + \alpha \cdot E \cdot F_1'(E) - \rho \cdot F_1(E) = 0. \tag{6.7}$$

The solution of (6.7) is given by (6.8), which reflects the value of the option to invest in CCS.

$$F_1(E) = A_1 \cdot E^{\beta_1}. \tag{6.8}$$

The optimal CO_2 price threshold to invest in CCS, $E^*_{ccs,1}$, and the constant A_1 are obtained analytically by applying value-matching and smooth-pasting between (6.5) and (6.8). The solution procedure is presented in Appendix 6.A. Then $E^*_{ccs,1}$ and A_1 are equal to:

$$E^*_{ccs,1} = \frac{\beta_1}{\beta_1 - 1}\left(\frac{\rho - \alpha}{\rho} \cdot (C_c + C_{ts}) + \frac{\rho - \alpha}{Q_{co_2}} \cdot I_c\right), \tag{6.9}$$

$$A_1 = \frac{Q_{co_2}}{\rho - \alpha} \cdot \frac{1}{\beta_1}\left(\frac{\beta_1}{\beta_1 - 1}\left(\frac{\rho - \alpha}{\rho} \cdot (C_c + C_{ts}) + \frac{\rho - \alpha}{Q_{co_2}} \cdot I_c\right)\right)^{\beta_1}. \tag{6.10}$$

In sum, as long as the CO_2 price is lower than $E^*_{ccs,1}$, the value of waiting (6.8) is greater than the project value (6.5). Once the CO_2 price crosses the threshold $E^*_{ccs,1}$, the firm invests: the option value and the project value coincide.

6.2.2 Model 2: Simultaneous CCUS

Next, we assume that the firm is operating in the dark red region in **Figure 6.4**, where it is optimal to invest in CCUS. In Model 2, CCU starts to play a role, and hence, the unknown arrival of CCU now needs to be considered. The investment decision is split into two stages: one before and one after CCU arrival. In Stage 1, before CCU arrives, the firm might decide to not wait any longer and invest in CCS already. We will show that there exists a CO_2 price $E^*_{ccs,1}$ that triggers optimal investment in CCS in Stage 1, taking into account the expected arrival of CCU in the future. In Stage 2, once CCU has arrived, a new investment decision problem emerges. If CCU arrives and the firm already invested in CCS in Stage 1, the firm adopts CCU immediately upon its arrival. If, however, CCU arrives and the firm did not invest yet in Stage 1, we will show that there exists a CO_2 price $E^*_{ccus,2}$ that triggers optimal investment in CCUS in Stage 2. The outlined sequence of actions in Model 2 corresponds to adoption strategies (S.2) and (S.4) in **Figure 6.2**: investing in CCS in Stage 1 and in CCU when it arrives (S.2) and investing in CCUS simultaneously in Stage 2 (S.4).

Figure 6.5 summarizes this two-staged problem from Model 2, with a different type of investment decision in each stage. Depending on the stage and depending on the actions that were previously taken, the firm will face a different type of investment decision, with different CO_2 price thresholds to be found.

Four different value functions are identified:

- $F_1(E)$: Initially, the firm is in Stage 1, where the CCU technology has not yet entered the market. Hence, the firm holds an option to invest in CCS and an option to adopt CCU, once it leaves the R&D phase and enters the market as well.
- $\phi_1(E)$: If the CO_2 price exceeds the threshold $E^*_{ccs,1}$ before the CCU technology arrives, the firm will invest in CCS first. The firm then holds the value function $\phi_1(E)$, which represents the value of operating CCS and the option to adopt CCU, once CCU enters the market.
- $\phi_2(E)$: The firm has invested in CCS and now the CCU technology becomes available, i.e. the firm transitions from Stage 1 to Stage 2. The firm now holds the value function $\phi_2(E)$, which is the value of operating CCUS.
- $F_2(E)$: If, on the other hand, the CCU technology enters the market before the CCS technology is adopted, the firm transitions to Stage 2 first. The firm now holds the value function $F_2(E)$, which includes an option to invest in CCUS simultaneously.

These value functions and the optimal investment thresholds are now analysed through backward induction, starting in Stage 2. We will now apply the dynamic programming technique, as described in Dixit and Pindyck (1994), to find the option value and the investment thresholds $E^*_{ccs,1}$ and $E^*_{ccus,2}$.[21]

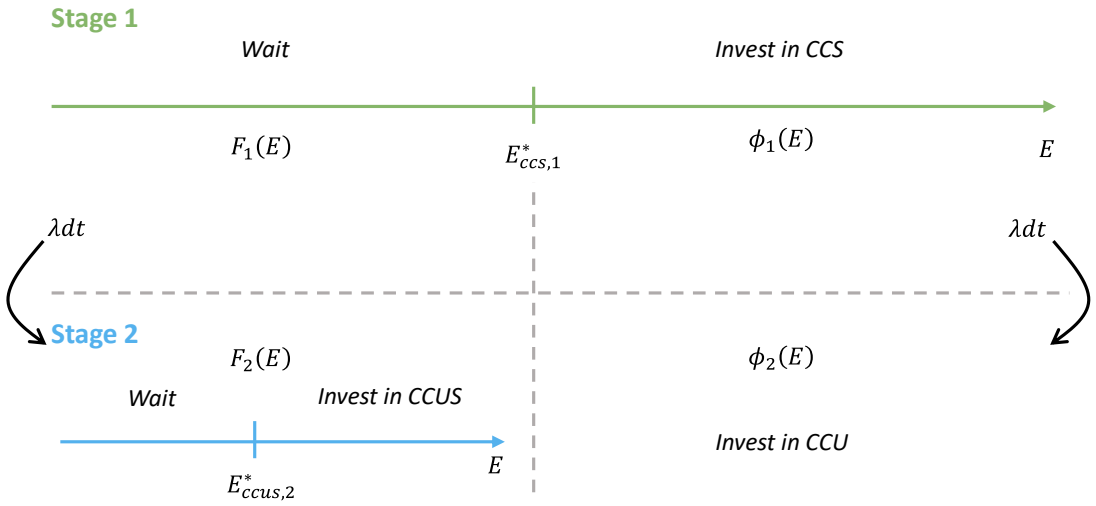


Figure 6.5: The two-staged decision problem for the firm, in Model 2.

Stage 2

In Stage 2, the CCU technology is mature and ready to install, leaving the firm with only one source of uncertainty: the CO_2 price uncertainty.

We first assume that the firm invests in CCS in Stage 1 and is now operating CCS (upper right box in **Figure 6.5**). In this case, all CO_2 emissions are captured and stored. Hence, no more emission allowances need to be paid and the CO_2 price uncertainty is completely resolved as well. As a result, when CCU arrives (lower right box in **Figure 6.5**), the firm will immediately adopt the CCU technology. The firm's value then equals the value of operating CCUS, V_{ccus}:

[21] To simplify notation and improve readability throughout this Chapter, the same notation for the value functions in Stage 1 and 2 and the CO_2 price thresholds is used over the different models. However, the interpretation of these value functions and the calculation of the CO_2 price thresholds can differ between the four models.

$$\phi_2(E) = \frac{Q_{co_2}}{\rho - \alpha} \cdot E - \frac{Q_{co_2}}{\rho} \cdot C_c - \frac{(1-q)Q_{co_2}}{\rho} * C_{ts} + \frac{q \cdot Q_{co_2}}{\rho} \cdot \left(P_p \cdot X - C_u\right) - I_c - I_u. \quad (6.11)$$

If, on the other hand, the firm waited in Stage 1, a new optimal investment problem starts in Stage 2. In this case (lower left box in **Figure 6.5**), it is optimal to invest in CCUS simultaneously. The threshold $E^*_{ccus,2}$ characterizes the optimal time to invest.

When $E > E^*_{ccus,2}$, the firm invests in CCUS and gains the project value V_{ccus} (6.4).

As long as $E \leq E^*_{ccus,2}$, the firm waits and holds on to the option to invest in CCUS. Using similar steps as described in Dixit and Pindyck (1994), the option value can be derived. First, the Bellman equation for this option value in Stage 2 is

$$\rho \cdot F_2(E) = \lim_{dt \to 0} \frac{1}{dt} \cdot \mathbb{E}[dF_2]. \quad (6.12)$$

The Bellman equation in (6.12) is now expanded using Ito's Lemma, which results in the ODE

$$\frac{1}{2}\sigma^2 \cdot E^2 \cdot F_1''(E) + \alpha \cdot E \cdot F_1'(E) - \rho \cdot F_1(E) = 0. \quad (6.13)$$

This ODE is similar to the ODE in Model 1 (6.7) and hence, the same steps are followed to find its solution. The value of the option to invest in CCUS can be found in (A.6) and the optimal investment threshold $E^*_{ccus,2}$ and the constant A_1 are given by:

$$E^*_{ccus,2} = \frac{\beta_1}{\beta_1 - 1}\left(\frac{\rho - \alpha}{\rho} \cdot \left(C_c + (1-q) \cdot C_{ts} - q \cdot (P \cdot X - C_u)\right) - \frac{\rho - \alpha}{Q_{co_2}} \cdot (I_c + I_u)\right), \quad (6.14)$$

$$A_1 = \frac{Q_{co_2}}{\rho - \alpha} \cdot \frac{1}{\beta_1} \cdot \left[\frac{\beta_1}{\beta_1 - 1}\left(\frac{\rho - \alpha}{\rho} \cdot \left(C_c + (1-q) \cdot C_{ts} - q \cdot (P \cdot X - C_u)\right) - \frac{\rho - \alpha}{Q_{co_2}} \cdot (I_c + I_u)\right)\right]^{1-\beta_1}. \quad (6.15)$$

The proof for these equations can be found in Appendix 6.B.1.

Stage 1

In Stage 1, the timing of the CCU arrival is still unknown and the firm needs to consider both the market and technological uncertainty in its investment decision. Similar to Model 1, the firm wants to find the threshold $E^*_{ccs,1}$, which defines the optimal investment timing in CCS. Unlike Model 1, the firm now also needs to take the value of the option to invest in CCU(S) in Stage 2 into account.

When $E > E^*_{ccs,1}$ before CCU arrives (upper right in **Figure 6.5**), the firm invests in CCS and earns the project value $V_{ccs}(E)$ (6.2). As described before, the firm will adopt CCU when it arrives in this case. As a result, $\phi_1(E)$ needs to reflect both the value of operating CCS now and the value of operating CCU once it arrives:

$$\phi_1(E) = \frac{Q_{co_2}}{\rho - \alpha} \cdot E - \frac{Q_{co_2}}{\rho} \cdot (C_c + C_{ts}) - I_c +$$

$$\frac{\lambda}{\lambda+\rho}\cdot\left(\frac{q\cdot Q_{co_2}}{\rho}\cdot\left(P_p\cdot X+C_{ts}-C_u\right)-I_u\right). \tag{6.16}$$

The expression for $\phi_1(E)$ contains the expected profit from operating both CCS and CCU. However, the value from operating CCU is adjusted by the term $\frac{\lambda}{\lambda+\rho}$, since CCU has not arrived yet.

As long as $E \leq E^*_{ccs,1}$ (upper left box in **Figure 6.5**), it is still optimal to wait with the investment. The firm now holds an option to invest in CCS (before CCU arrives) and to invest in CCU simultaneously (once CCU arrives).

Let $F_1(E)$ denote the value of the option that the firm is holding in Stage 1, along with all future options. To describe $F_1(E)$, we follow similar steps as in Dixit and Pindyck (1994) (p. 202-205) and Sendstad and Chronopoulos (2020). When $E \leq E^*_{ccs,1}$, no profits are earned yet. With a probability λdt, CCU arrives in the next short time interval dt. The firm then moves to Stage 2 and holds the option worth $F_2(E)$ (A.7). With a probability $1-\lambda dt$, CCU does not arrive yet and the firm continues to hold $F_1(E)$. This gives the following dynamics for the value function $F_1(E)$ over a small interval of time dt:

$$F_1(E)=(1-\lambda dt)\cdot\mathbb{E}[F_1(E+dE)]e^{-\rho dt}+\lambda dt\cdot\mathbb{E}[F_2(E+dE)]e^{-\rho dt}. \tag{6.17}$$

Expanding the right-hand side of this equation using Ito's Lemma (A.10), results in the ODE

$$\frac{1}{2}\sigma^2\cdot E^2\cdot F_1''(E)+\alpha\cdot E\cdot F_1'(E)-\rho\cdot F_1(E)+\lambda\cdot\left(F_2(E)-F_1(E)\right)=0. \tag{6.18}$$

The main difference with the previous ODE in (6.7) and (6.13) is the additional term $\lambda\cdot\left(F_2(E)-F_1(E)\right)$, which is added to reflect that the value of the option can switch from $F_1(E)$ to $F_2(E)$ if CCU arrives while the firm waits. Because of this additional term $\lambda\cdot F_2(E)$, the solution for $F_1(E)$ will consist of a homogeneous and a particular solution. Note that $F_2(E)$ is defined differently over two CO_2 price intervals, i.e. $E\leq E^*_{ccus,2}$ and $E>E^*_{ccus,2}$. Hence, we must solve (6.18) separately for these two price intervals as well. The solution for $F_1(E)$ is indicated in (6.19). The first part of $F_1(E)$, $C_1\cdot E^{\delta_1}$, reflects the option to invest in CCS alone, prior to CCU arrival, while the second part within brackets reflects the option to invest in CCUS, after CCU arrival.

$$F_1(E)=C_1\cdot E^{\delta_1}+ \tag{6.19}$$

$$\begin{cases} A_1\cdot E^{\beta_1}+B_1\cdot E^{\delta_1}\ if\ E\leq E^*_{ccus,2}, \\ \dfrac{\lambda}{\lambda+\rho-\alpha}\dfrac{Q_{co_2}}{\rho-\alpha}\cdot E+\dfrac{\lambda}{\lambda+\rho}\left[-\dfrac{Q_{co_2}}{\rho}\cdot C_c-\dfrac{(1-q)Q_{co_2}}{\rho}\cdot C_{ts}+\dfrac{q\cdot Q_{co_2}}{\rho}\cdot\left(P_p\cdot X-C_u\right)-I_c-I_u\right] \\ +B_4\cdot E^{\delta_2}\ if\ E>E^*_{ccus,2}. \end{cases}$$

The first term on the top part of (6.19) represents the option to invest in CCUS, adjusted via the second (negative) term because CCU has yet to arrive. The first terms on the bottom part represent the value of operating CCUS, adjusted by λ. The final term indicates the likelihood that the CO_2 price may drop back to a level below $E^*_{ccus,2}$, before the CCU technology arrives. Threshold $E^*_{ccus,2}$ and the constant A_1 were given in (6.14) and (6.15). The constants B_1 and B_4 are determined analytically through value-matching (A.11) and smooth pasting conditions (A.12) at the threshold $E^*_{ccus,2}$. The terms δ_1 and δ_2

are the positive and negative roots of the quadratic equation $\frac{1}{2}\sigma^2\delta^2 + \left(\sigma - \frac{1}{2}\sigma^2\right)\delta - (\rho + \lambda) = 0$. The constant C_1 and the investment threshold $E^*_{ccs,1}$ are found by applying value-matching and smooth-pasting at the threshold $E^*_{ccs,1}$, where $F_1(E)$ and $\phi_1(E)$ should match.

6.2.3 Model 3: Sequential CCU – CCS

Next, consider the region where it is optimal to invest in CCU and CCS sequentially (light red region in **Figure 6.4**). The real options model for this scenario is very similar to Model 2, with one major difference: instead of finding one investment threshold $E^*_{ccus,2}$, the firm now needs to identify two thresholds $E^*_{ccu,2}$ and $E^*_{ccs,2}$. Model 3 describes the optimal timing to invest in CCS and CCU for adoption strategies (S.2) and (S.5) in Figure 2.

Figure 6.6 summarizes the firm's decision problem for Model 3. The sole difference with Model 2 is in $F_2(E)$, which now describes the value of the option to invest in CCU and CCS sequentially. Analogous to Model 2, the optimal investment thresholds $E^*_{ccs,1}$, $E^*_{ccu,2}$ and $E^*_{ccs,2}$ are determined through backward induction. In this section, only the differences with Model 2 will be highlighted.

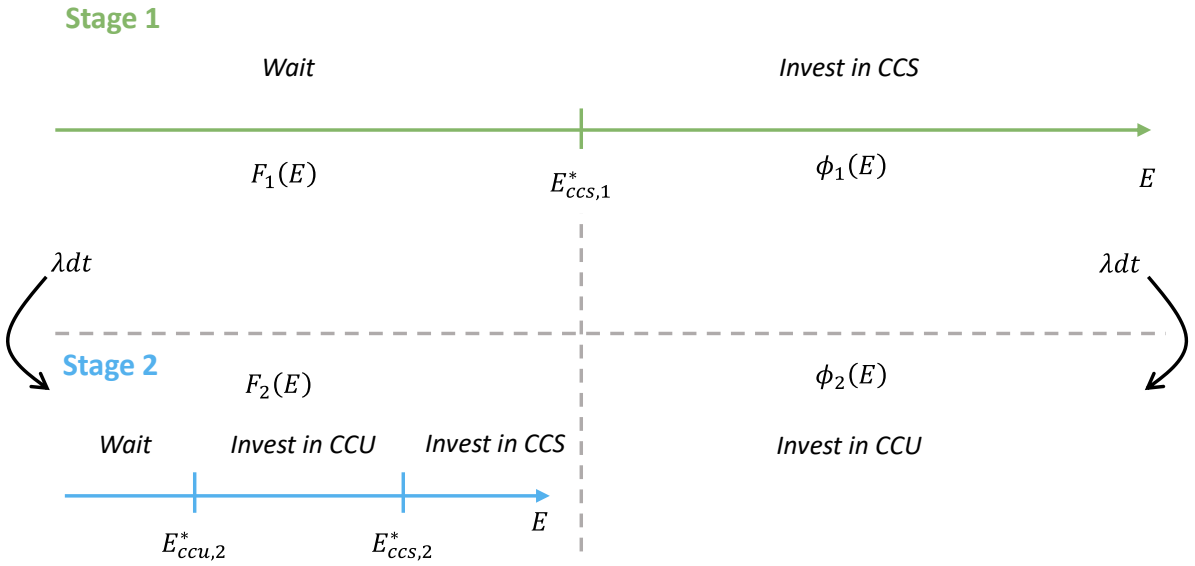


Figure 6.6: The two-staged decision problem for the firm, in Model 3.

Stage 2

If the firm adopted CCS in Stage 1 (lower right corner in **Figure 6.6**, it will immediately install CCU in Stage 2, as discussed before. The firm obtains $\phi_2(E)$, equal to the value of operating CCUS V_{ccus} (6.4).

If, on the other hand, the firm waited in Stage 1 until CCU entered the market (lower left corner in **Figure 6.6**), the firm's optimal strategy is now to adopt CCU and CCS sequentially. Therefore, the firm now needs to find two investment thresholds (instead of one) to determine the optimal timing of the investments in respectively CCU and CCS: $E^*_{ccu,2}$ and $E^*_{ccs,2}$.

As long as $E \leq E^*_{ccu,2}$, the firm continues to wait and holds the option to invest in CCU and CCS sequentially. The Bellman equation (6.12) and the resulting ODE (6.13) are identical to the solutions in Model 2, when $E \leq E^*_{ccus,2}$. The solution for the ODE when $E \leq E^*_{ccu,2}$ is $F_2(E) = A_1 \cdot E^{\beta_1}$.

When $E > E^*_{ccu,2}$, the firm invests in CCU but continues to postpone the investment in CCS. This results in a new Bellman equation that includes the profits from operating CCU:

$$\rho \cdot F_2(E) = \pi_{ccu} + \lim_{dt \to 0} \frac{1}{dt} \mathbb{E}[dF_2]. \tag{6.20}$$

Expanding this new Bellman equation (6.20) using Ito's lemma, we obtain the ODE

$$\frac{1}{2}\sigma^2 \cdot E^2 \cdot F_2''(E) + \alpha \cdot E \cdot F_2'(E) - \rho \cdot F_2(E) + \pi_{ccu} = 0. \tag{6.21}$$

The general solution of this ODE will now consist of a homogeneous and a particular solution, due to the additional term π_{ccu}. Hence, the solution for the ODE in (6.21) is

$$F_2(E) = D_1 \cdot E^{\beta_1} + \frac{q \cdot Q_{co_2}}{\rho - \alpha} \cdot E + \frac{q \cdot Q_{co_2}}{\rho} \cdot \left(P_p \cdot X - C_c - C_u\right) - I_c - I_u, \tag{6.22}$$

where the first part reflects the option to invest in CCS and the second part reflects the expected present value of the profits from operating CCU.

Finally, when $E > E^*_{ccs,2}$, the firm also adopts CCS and starts operating CCUS. The value function $F_2(E)$ now equals the CCUS profits in (6.4).

The solution for $F_2(E)$ over the three CO_2 price intervals is shown in

$$F_2(E) = \tag{6.23}$$

$$\begin{cases} A_1 \cdot E^{\beta_1} & if\ E < E^*_{ccu}, \\ D_1 \cdot E^{\beta_1} + \frac{q \cdot Q_{co_2}}{\rho - \alpha} \cdot E + \frac{q \cdot Q_{co_2}}{\rho} \cdot \left(P_p \cdot X - C_c - C_u\right) - I_c - I_u & if\ E^*_{ccu,2} \le E \le E^*_{ccs,2}, \\ \frac{Q_{co_2}}{\rho - \alpha} \cdot E - \frac{Q_{co_2}}{\rho} \cdot C_c - \frac{(1-q) \cdot Q_{co_2}}{\rho} \cdot C_{ts} + \frac{q \cdot Q_{co_2}}{\rho} \cdot \left(P_p \cdot X - C_u\right) - I_c - I_u & if\ E > E^*_{ccs,2}. \end{cases}$$

The solutions for $E^*_{ccu,2}$ and $E^*_{ccs,2}$ are found via value-matching ((A.13) and (A.15)) and smooth pasting ((A.14) and (A.16)) conditions between the three branches of (6.23). The solutions for the constants A_1 and D_1 can be found in Appendix 6.C.1.

$$E^*_{ccu,2} = \frac{\beta_1}{\beta_1 - 1} \cdot \left(\frac{\rho - \alpha}{\rho} \cdot \left(C_c + C_u - P_p \cdot X\right) + \frac{\rho - \alpha}{q \cdot Q_{co_2}} \cdot (I_c + I_u) \right), \tag{6.24}$$

$$E^*_{ccs,2} = \frac{\beta_1}{\beta_1 - 1} \cdot \frac{\rho - \alpha}{\rho} \cdot (C_c + C_{ts}). \tag{6.25}$$

The CO_2 price investment threshold for CCU depends on the capture costs, utilization costs, the product price, the conversion rate and the investment costs for the capture facility and the utilization plant (6.24). The investment threshold for CCS, when the firm is already operating CCU, is only affected by the capture costs and the transport and storage fee (6.25). Note that the investment for the capture plant I_c does not affect the threshold for CCS, as this investment cost was already incurred to adopt CCU.

Stage 1

In stage 1, CCU is still in the R&D phase and it is yet unknown when CCU will enter the market.

When $E > E^*_{ccs,1}$ before CCU arrives (upper right corner in **Figure 6.6**), the firm invests in CCS and obtains the profits from operating CCS (6.2). Because the CO_2 price uncertainty is now resolved, the firm will also adopt CCU immediately when it arrives. Hence, $\phi_1(E)$ equals the sum of the profits from CCS and the expected profits from CCU in the future, as shown in Model 2 (6.16).

As long as $E \leq E^*_{ccs,1}$ (upper left corner in **Figure 6.6**), the firm waits and holds the option to invest in CCU and CCS. Following the steps from Dixit and Pindyck (1994), results in the same ODE as in Model 2 (6.18). However, $F_2(E)$ is now defined over three different intervals, i.e. $E \leq E^*_{ccu,2}$, $E^*_{ccu,2} < E \leq E^*_{ccs,2}$, and $E > E^*_{ccs,2}$. The solution for $F_1(E)$ over all CO_2 price intervals is presented in (6.26). The first part, $C_1 \cdot E^{\delta_1}$, again reflects the option to invest in CCS before CCU arrives, while the second part reflects the option to invest in CCU and CCS sequentially after CCU arrived. The first term in the top part of (6.26) represents the option to invest in CCU, adjusted for the unknown arrival timing of CCU by the second term. The first two terms in the middle part of (6.26) represent the expected present value of the CCU profits. The third term ($D_1 \cdot E^{\beta_1}$) reflects the option to invest in CCS, adjusted via the fourth term ($B_2 \cdot E^{\delta_1}$) because CCU hasn't arrived yet. The fifth term ($B_3 \cdot E^{\delta_2}$) accounts for the possibility that the CO_2 price drops below $E^*_{ccu,2}$ before CCU arrives. The first two terms in the bottom part of (6.26) are the expected profits from operating CCUS, adjusted for the possibility that the CO_2 price drops below $E^*_{ccs,2}$ by the third term. The constants A_1 and D_1 and the investment thresholds $E^*_{ccu,2}$ and $E^*_{ccs,2}$ are the same as in $F_2(E)$. The constants B_1, B_2, B_3, and B_4 are found by applying the value-matching and smooth-pasting conditions between the three branches of $F_1(E)$ (A.20)-(A.23). The constant C_1 and the threshold $E^*_{ccs,1}$ are obtained by applying value matching and smooth pasting to $F_1(E)$ and $\phi_1(E)$ at $E^*_{ccs,1}$.

$$F_1(E) = C_1 \cdot E^{\delta_1} + \tag{6.26}$$

$$\begin{cases} A_{1,seq} \cdot E^{\beta_1} + B_1 \cdot E^{\delta_1} \quad if\ E \leq E^*_{ccu,2}, \\ \dfrac{\lambda}{\lambda+\rho-\alpha}\dfrac{Q_{co_2}}{\rho-\alpha} \cdot E + \dfrac{\lambda}{\lambda+\rho}\left[-\dfrac{Q_{co_2}}{\rho} \cdot C_c - \dfrac{(1-q)Q_{co_2}}{\rho} \cdot C_{ts} + \dfrac{q \cdot Q_{co_2}}{\rho} \cdot \left(P_p \cdot X - C_u\right) - I_c - I_u\right] \\ + D_1 \cdot E^{\beta_1} + B_2 \cdot E^{\delta_1} + B_3 \cdot E^{\delta_2} \quad if\ E^*_{ccu,2} < E \leq E^*_{ccs,2}, \\ \dfrac{\lambda}{\rho+\lambda-\alpha} \cdot \dfrac{q * Q_{co_2}}{\rho-\alpha} \cdot E + \dfrac{\lambda}{\lambda+\rho} \cdot \left[-\dfrac{Q_{co_2}}{\rho} \cdot C_c - \dfrac{(1-q)Q_{co_2}}{\rho} \cdot C_{ts}\right. \\ \left. + \dfrac{q \cdot Q_{co_2}}{\rho} \cdot \left(P_p \cdot X - C_u\right) - I_c - I_u\right] + B_4 \cdot E^{\delta_2} \quad if\ E > E^*_{ccus,2} \end{cases}$$

6.2.4 Model 4: Immediate CCU – later CCS

Finally, we analyse the optimal investment timing in the blue area in **Figure 6.4**, where the firm immediately invests in CCU, once it arrives. In Stage 1, the firm invests in CCS if $E > E^*_{ccs,1}$. In Stage 2, the firm adopts CCU immediately upon its arrival. When the CO_2 price continues to rise, the incentive to avoid all CO_2 becomes larger, and the firm will also adopt CCS in Stage 2. This possible sequence of investment decisions matches adoption strategies (S.2) and (S.6) in **Figure 6.2**.

Figure 6.7 shows how the investment decision problem in Model 4 evolves over both stages.

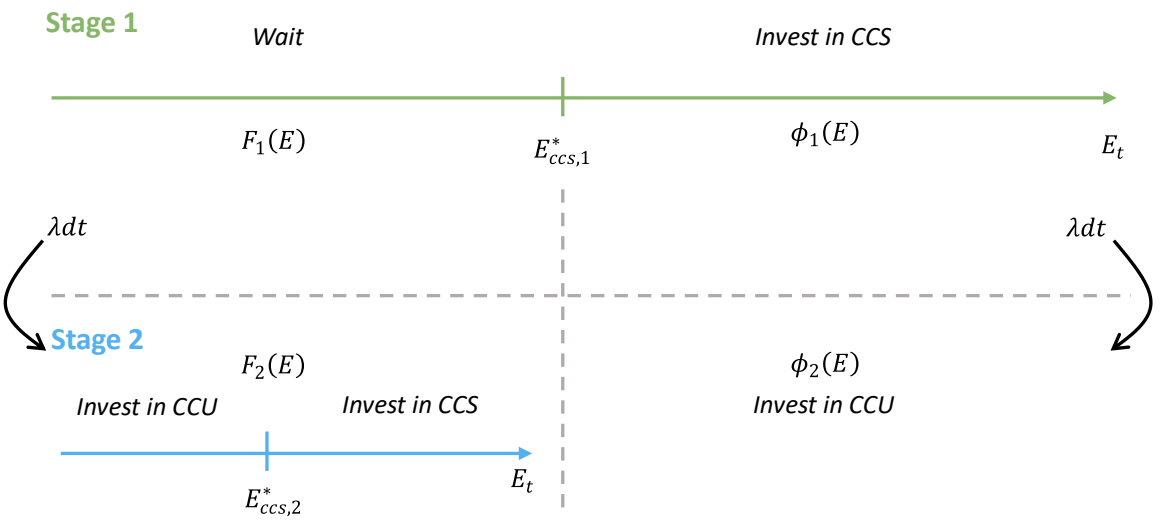


Figure 6.7: The two-staged decision problem for the firm, in Model 4.

The value functions $\phi_1(E)$ and $\phi_2(E)$ are the same as in Models 2 and 3, while the value functions $F_1(E)$ and $F_2(E)$ are defined slightly different compared to the previous models:

- $F_1(E)$: the firm holds an option to invest in CCS and an option to invest in CCU, once it arrives, followed by CCS investment, when the CO_2 price is high enough.
- $F_2(E)$: if CCU matures before the firm invested in CCS, the firm will immediately invest in CCU and hold an option to invest in CCS later, when CO_2 prices continue to rise.

The optimal investment thresholds $E^*_{ccs,1}$ and $E^*_{ccs,2}$ are again determined using backward induction.

Stage 2

If the firm already invests in CCS in Stage 1 (lower right corner in **Figure 6.7**), the firm's value function $\phi_2(E)$ again equals the expected present value of the CCUS profits (6.4). Even if the firm did not yet invest in CCS, the firm is now triggered to invest in CCU when it arrives, independent of the CO_2 price. Hence, there is only one investment threshold, $E^*_{ccs,2}$.

The investment threshold $E^*_{ccs,2}$ will define the optimal timing for the investment in CCS. The Bellman equation is

$$\rho \cdot F_2(E) = \pi_{ccu} + \lim_{dt \to 0} \frac{1}{dt} \cdot \mathbb{E}[dF_2(E)]. \tag{6.27}$$

which is the same Bellman equation as in Model 3, when $E^*_{ccu,2} < E \leq E^*_{ccs,2}$ (20). As a result, the ODE in (6.21) and the solution for this ODE (6.22) are also the same as in Model 3. We get the following expression for $F_2(E)$ in Model 4

$$F_2(E) = \tag{6.28}$$

$$\begin{cases} A_1 \cdot E^{\beta_1} + \dfrac{q \cdot Q_{co_2}}{\rho - \alpha} E + \dfrac{q \cdot Q_{co_2}}{\rho} \cdot \left(P_p \cdot X - C_c - C_u\right) - I_c - I_u & if\ E \leq E^*_{ccs,2}, \\ \dfrac{Q_{co_2}}{\rho - \alpha} \cdot E - \dfrac{Q_{co_2}}{\rho} \cdot C_c - \dfrac{(1-q) \cdot Q_{co_2}}{\rho} C_{ts} + \dfrac{q \cdot Q_{co_2}}{\rho} \cdot \left(P_p \cdot X - C_u\right) - I_c - I_u & if\ E > E^*_{ccs,2}. \end{cases}$$

The threshold $E^*_{ccs,2}$ and the constant $A_{1,imm}$ are obtained through value-matching and smooth-pasting at the threshold. Since these conditions are the same as in Model 3 ((A.15) and (A.16)), the

investment threshold $E^*_{ccs,2}$ and the constant $A_{1,imm}$ are also identical to the threshold $E^*_{ccs,2}$ (6.25) and the constant $A_{1,seq}$ (A.17) in Model 3.

Stage 1

In Stage 1, the arrival timing of CCU is still unknown and the firm needs to determine the optimal investment timing for CCS.

When $E > E^*_{ccs,1}$, the firm invests in CCS and obtains $\phi_1(E)$ (6.16), representing the expected profits from operating CCS and CCU.

As long as $E \leq E^*_{ccs,1}$, the firm waits and holds the option to invest in CCS (before CCU arrives) and the option to invest in CCU when it arrives, and CCS at high enough CO_2 prices. The Bellman equation is

$$\rho \cdot F_1(E) = \frac{1}{dt}\mathbb{E}[dF_1(E)].. \tag{6.29}$$

Expanding the Bellman equation by applying Ito's Lemma, results in the same ODE as in Models 3 and 2 (18). Since $F_2(E)$ is defined over two different CO_2 price intervals, $F_1(E)$ must be solved for these intervals separately, i.e. $E \leq E^*_{ccs,2}$ and $E > E^*_{ccs,2}$. The solution for $F_1(E)$ over both CO_2 price intervals is presented in (6.30).

$$F_1(E) = C_1 \cdot E^{\delta_1} + \tag{6.30}$$

$$\begin{cases} A_1 \cdot E^{\beta_1} + \dfrac{\lambda}{\lambda+\rho-\alpha}\dfrac{q \cdot Q_{co_2}}{\rho-\alpha} \cdot E + \\ \dfrac{\lambda}{\lambda+\rho} + \dfrac{q \cdot Q_{co_2}}{\rho} \cdot \left[\left(P_p \cdot X - C_c - C_u\right) - I_c - I_u\right] + B_1 \cdot E^{\delta_1} \quad if\ E \leq E^*_{ccs,2}, \\ \dfrac{\lambda}{\lambda+\rho-\alpha}\dfrac{Q_{co_2}}{\rho-\alpha} \cdot E + \dfrac{\lambda}{\lambda+\rho} \cdot \left[-\dfrac{Q_{co_2}}{\rho} \cdot C_c - \dfrac{(1-q) \cdot Q_{co_2}}{\rho} \cdot C_{ts} + \right. \\ \left. \dfrac{q \cdot Q_{co_2}}{\rho} \cdot \left(P_p \cdot X - C_u\right) - I_c - I_u\right] + B_4 \cdot E^{\delta_2} \quad if\ E > E^*_{ccs,2}. \end{cases}$$

The first part, $C_1 \cdot E^{\delta_1}$, again reflects the option to invest in CCS, before CCU arrives. The second part, between brackets, represents the option to invest in CCU and CCS, once CCU has arrived. Analogous to the previous models, the term $B_1 \cdot E^{\delta_1}$ is added to adjust for the unknown arrival of CCU and the term $B_4 \cdot E^{\delta_2}$ accounts for the possibility that the CO_2 price again drops below $E^*_{ccu,2}$ before CCU arrives. The constants B_1 and B_4 are found via the value-matching and smooth pasting conditions between the two branches of $F_1(E)$ (A.24) - (A.25). The constant C_1 and the threshold $E^*_{ccs,1}$ are obtained by applying value matching and smooth pasting to $F_1(E)$ and $\phi_1(E)$ at $E^*_{ccs,1}$.

6.3 A numerical example: the cement industry

In this section, the real options models are applied to three CCUS scenarios that were developed by Monteiro and Roussanaly (2022). These scenarios connect the cement industry to potential CCUS chains, to reduce its CO_2 emissions. Three alternative CCU chains are analyzed: the production of ethanol, food-grade CO_2 or polyol. The CO_2 emissions from an average cement plant are used. This cement plant produces 1.36 Mt cement per year and emits 771,000 tonnes of CO_2 annually. However, the cement plant emits more CO_2 than can be utilized in any of these scenarios, either due to market size or to availability of other raw materials. Therefore, CCU should be integrated with CCS in a CCUS

chain, if the aim is to abate all CO_2 emissions from the cement plant. The investigated CCS chain includes the CO_2 capture using monoethanolamine (MEA) and the subsequent geological storage of CO_2 in a deep saline aquifer. The economic feasibility of these CCUS scenarios for the cement industry is then investigated by Monteiro and Roussanaly (2022). Their results show that the economic feasibility of the CCUS chain depends on the chosen CCU-product.

Hence, these investigated CCUS scenarios in connection to the cement industry fit within the framework of the real options model that was developed in this Chapter. The estimated costs, product price and technical parameters for each CCUS scenario are summarized in **Table 6.2**. More detailed information about these assumptions can be found in Appendix 6.E.

The three CCUS scenarios differ in the investments for the utilization plant I_u, the utilization costs C_u, the price of the product P_p, the conversion factor from CO_2 to final product X and the arrival rate λ. The ethanol production route has the lowest maturity level, which results in a slower arrival rate λ than the food-grade CO_2 or polyol production route.

Figure 6.8 shows the present values from the investment in CCS, CCU or CCUS for each scenario from **Table 6.2**. In the ethanol CCUS scenario, the CCS technology always yields the highest value, compared to CCUS and CCU. When the CO_2 is used as food-grade CO_2, the CCU solution reaches break-even first, closely followed and overtaken by the CCUS chain. In the polyol CCUS chain, CCU already yields a positive present value at a zero CO_2 price. **Figure 6.8** reflects how the differences in costs and revenues, as listed in **Table 6.2**, cause variations in which of the technologies presents the most profitable solution. This will also affect the optimal adoption strategy of the firm for each scenario.

Table 6.2: Description of three CCUS scenarios for the cement industry: ethanol production (fuel), food-grade CO_2 production (direct use of CO_2) and polyol production (chemical). The numbers for the three scenarios are based on Monteiro and Roussanaly (2022), unless indicated otherwise.

	Ethanol	**Food-grade CO_2**	**Polyol**	**Unit**	**Reference**
TRL	5	9	9		
Q_{co_2}	771,000	771,000	771,000	t CO_2/year	
q	3.1	6.5	7.5	%	
I_c	15,000,000	15,000,000	15,000,000	€	(Gardarsdóttir, Normann, Skagestad, & Johnsson, 2018)
I_u	22,600,000	16,000,000	21,000,000	€	
C_c	69	69	69	€/ton CO_2	
C_{ts}	20	20	20	€/ton CO_2	(Jang, Kim, Kim, & Lee, 2016)
C_u	656	100	603*	€/ton CO_2	*(Fernández-Dacosta et al., 2017)
P_p	633	150	1400	€/ton	
X	0.525	1	5		
ρ	8	8	8	%	(Gardarsdóttir et al., 2019)
α	0.05	0.05	0.05		(Compernolle et al., 2017)
σ	0.2	0.2	0.2		(Compernolle et al., 2017)
λ	0.2	0.5	0.5		

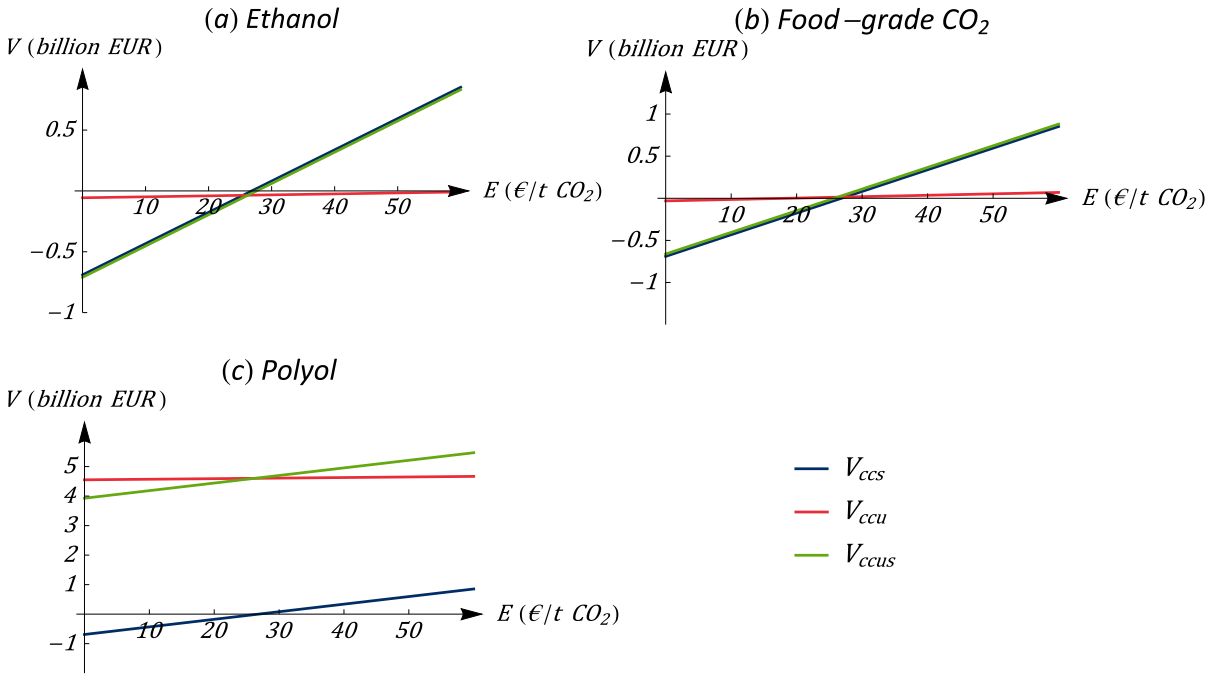


Figure 6.8: The present values of the CCS (blue), CCU (red) and CCUS (green) solutions in each CCUS scenario based on Monteiro and Roussanaly (2022).

Figure 6.9 presents the positioning of each CCUS scenario in its optimal region (**Figure 6.4**).

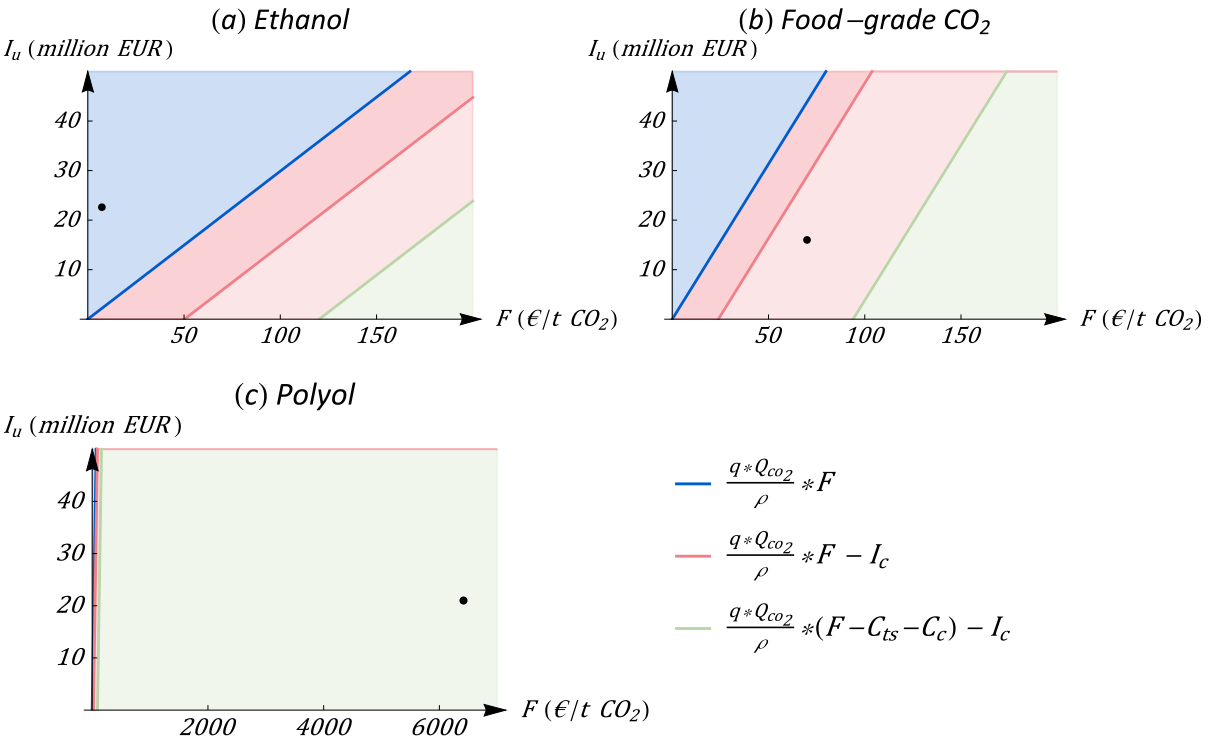


Figure 6.9: The optimal region for each CCUS scenario (a) ethanol (q = 0.031), (b) food-grade CO_2 (q = 0.065), and (c) polyol (q = 0.075) represented by the black dot.

In the ethanol CCUS scenario, it is the most profitable to invest only in CCS (Model 1). For the food-grade CO_2 CCUS chain, the optimal strategy is to adopt CCU and CCS sequentially (Model 3). Finally, the polyol CCUS chain is in the green region, where CCU is so profitable that the firm will immediately adopt CCU upon arrival. When the CO_2 price reaches a certain threshold, the firm will also abate the remaining CO_2 emissions with CCS (Model 4). Following the Models 1, 3 and 4, we can now calculate the actual CO_2 price levels at which the firm should invest in each technology.

6.3.1 Model 1: Ethanol

Model 1, as developed in 6.2.1., is applied to the ethanol CCUS chain to identify the optimal investment timing. Because the investment in CCS always results in a higher value than the investment in CCU or CCUS (**Figure 6.8** (a)), only one CO_2 price threshold needs to be found: $E^*_{ccs,1}$, the CO_2 price threshold to invest in CCS. **Figure 6.10** shows the results of Model 1 for the ethanol CCUS chain. The firm should invest in CCS once the CO_2 price exceeds 96.35 €/t CO_2.

6.3.2 Model 3: Food-grade CO_2

Because of the higher fraction of CO_2 that can be used, q, the lower investment costs, I_u, and higher conversion rate, X, it can be valuable to invest in CCU in the food-grade CO_2 CCUS chain. **Figure 6.8** shows how the sequential CCU-CCS adoption strategy is optimal, once the CCU technology is mature. Therefore, Model 3, as developed in 6.2.3., is now applied to the food-grade CO_2 CCUS chain to identify the optimal investment timing. Three CO_2 price thresholds need to be found: $E^*_{ccs,1}$, the CO_2 price threshold to invest in CCS in Stage 1, $E^*_{ccu,2}$ and $E^*_{ccs,2}$, the CO_2 price thresholds to invest in Stage 2 in CCU and CCS, respectively. **Figure 6.11** shows the results of Model 3 for the food-grade CO_2 CCUS chain. In Stage 1, the firm should invest in CCS once the CO_2 price exceeds 94.84 €/t CO_2. In Stage 2, the firm should invest in CCU as soon as the CO_2 price crosses 66.63 €/t CO_2. If the CO_2 price rises further and also exceeds 94.25 €/t CO_2, the firm should also adopt CCS to abate the remaining CO_2 emissions.

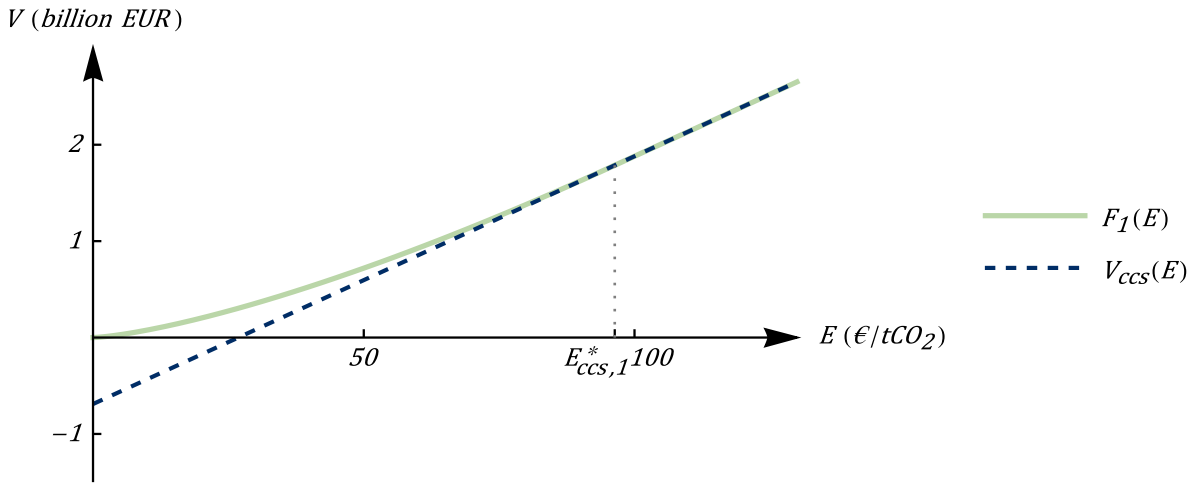


Figure 6.10: The option value $F_1(E)$ (light blue) and the present value of CCS V_{ccs} (dark blue) for the ethanol CCUS chain.

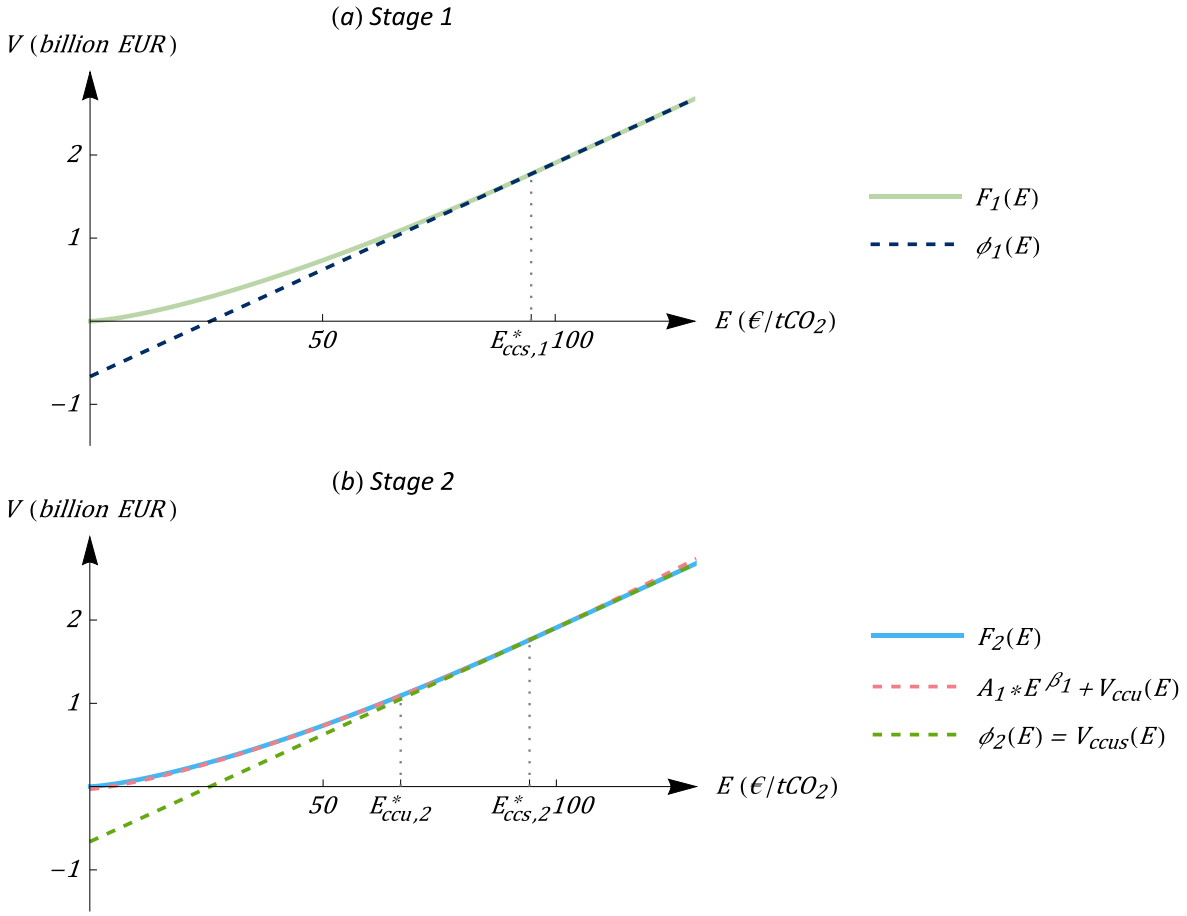


Figure 6.11: (a) The option value $F_1(E)$ (green) and the present value of investing in CCS and CCU, once it arrives, $\phi_1(E)$ (dark orange) in Stage 1 and (b) the option value $F_2(E)$ (light blue), the value of having the option to invest in CCS and investing in CCU $A_1 \cdot E^{\beta_1} + V_{ccu}$ (E) (light red) and the present value of CCUS V_{ccus} (green) in Stage 2 for the food-grade CO_2 CCUS chain.

6.3.3 Model 4: Polyol

Although the polyol CCUS chain involves higher investment cost I_u and higher utilization costs C_u than the food-grade CO_2 CCUS chain, it still presents a more attractive business case for CCU due to the higher product price, P_p, and higher conversion factor, X. For the polyol CCUS chain, the investment in CCU pays off, even when the CO_2 price equals zero, as can be seen in **Figure 6.8**. Hence, we can apply Model 4, as developed in 6.2.4., to the polyol CCUS chain to identify the optimal investment timing. Two CO_2 price thresholds need to be found: $E^*_{ccs,1}$ and $E^*_{ccs,2}$, the CO_2 price threshold to invest in CCS in Stage 1 and Stage 2 respectively. **Figure 6.12** shows the results of Model 4 for the polyol CCUS chain. In Stage 1, the firm should invest in CCS once the CO_2 price exceeds 94.73 €/t CO_2. In Stage 2, the firm should adopt CCS as well, in addition to CCU, when the CO_2 price crosses 94.25 €/t CO_2.

The calculated CO_2 price thresholds for each CCUS scenario are summarized in **Table 6.3**. It can be seen from **Table 6.3** that the investment thresholds for CCS in Stage 1 for the three CCUS chains differ. Since the costs and revenues of CCS are the same in all three CCUS chains, the discrepancy between the investment thresholds for CCS in Stage 1 is explained by the difference in the availability and profitability of CCU.

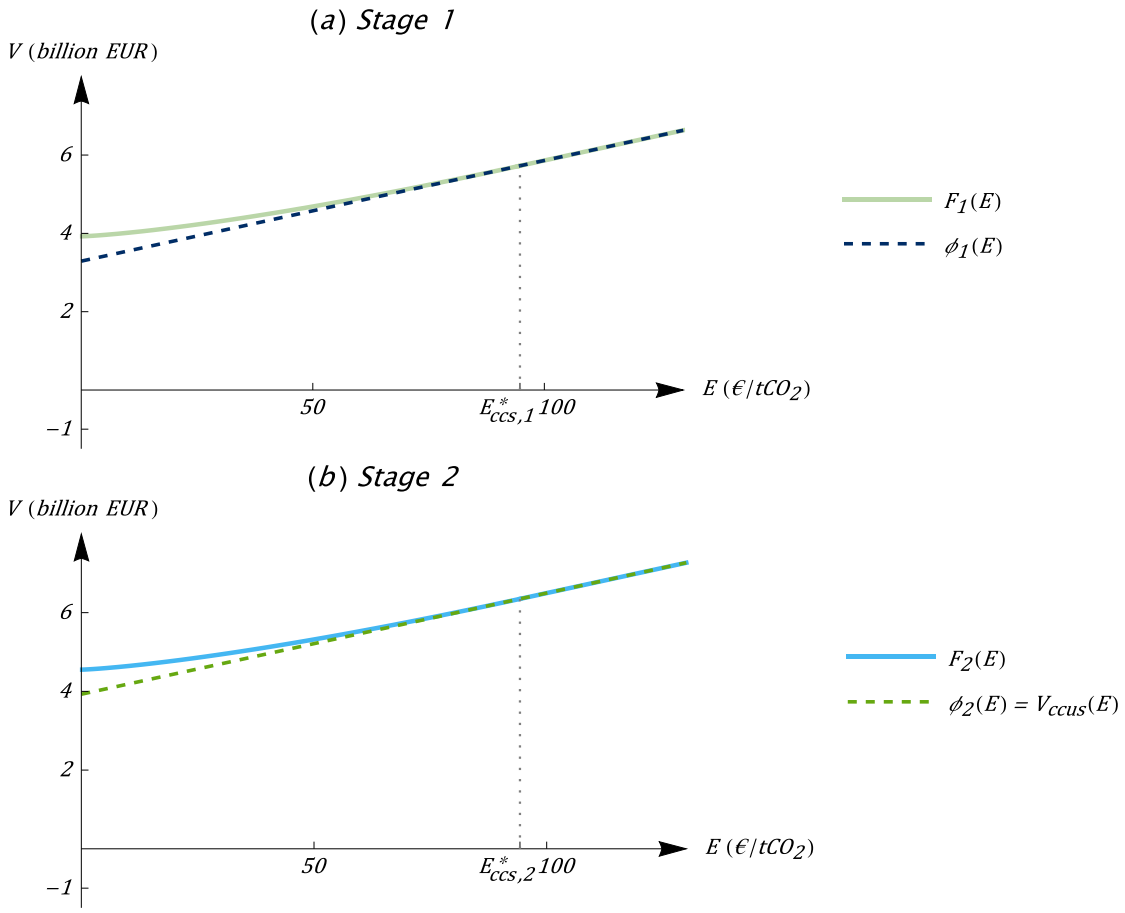


Figure 6.12: (a) The option value $F_1(E)$ (green) and the present value of investing in CCS and CCU, once it arrives, $\phi_1(E)$ (dark blue) in Stage 1 and (b) the option value $F_2(E)$ (light blue) and the present value of CCUS V_{ccus} (green) in Stage 2 for the polyol CCUS chain.

Table 6.3: The CO_2 price thresholds in Stage 1 and Stage 2 for the three CCUS scenarios in the cement industry: ethanol production, food-grade CO_2 production and polyol production.

	Ethanol	**Food-grade CO_2**	**Polyol**	**Unit**
$E^*_{ccs,1}$	96.35	94.84	94.73	€/t CO_2
$E^*_{ccu,2}$	-	66.63	-	€/t CO_2
$E^*_{ccs,2}$	-	94.25	94.25	€/t CO_2

In the ethanol CCUS scenario, the arrival rate λ of the CCU solution is lower due to its lower TRL. Moreover, the CCS technology is always more profitable than the CCU route in the ethanol CCUS scenario (**Figure 6.10**), in contrast to the food-grade CO_2 and polyol CCUS chain. From the values in **Table 6.3**, it can be concluded that when the investor expects a more attractive CCU solution in the future, than the existing CCS solution today, the CO_2 price investment threshold for CCS in Stage 1 will be lower and consequently, the investment in CCS will be accelerated. Although this may be counterintuitive, a logical explanation can be given for this result. A more profitable CCU technology makes the integrated CCUS chain more attractive as well. Hence, the investor is triggered sooner to do the investment for CCS, because the investments for the CO_2 capture will also pay off in the future for the CCU route.

Besides the differences in the investment threshold for CCS in Stage 1, it can also be seen from **Table 6.3** how the investment threshold for CCS decreases from Stage 1 to Stage 2, for the food-grade CO_2 and polyol CCUS scenarios. Although the decrease is very small, it shows that the investment in CCU, ahead of the investment in CCS, lowers the threshold to adopt CCS as well.

Finally, **Table 6.3** reveals that the CO_2 price threshold to invest in CCS in Stage 2 is the same for the food-grade CO_2 and the polyol CCUS chain. Once the investment for CCU is made, the investment trigger for CCS only depends on parameters specific for CCS, i.e. the cost for CO_2 capture (C_c) and the transport and storage fee (C_{ts}), as can be seen in equation (6.25). These cost parameters are the same for the food-grade CO_2 and polyol CCUS chain and consequently, $E^*_{ccs,2}$ is identical for both.

In sum, two main insights can be drawn from this table: (1) the investment threshold for CCS in Stage 1 is lowered in the prospect of a more profitable CCU technology in a future period, and (2) investment in CCU, before the investment in CCS, lowers the investment threshold for CCS.

Table 6.4 shows the CO_2 price levels that should be reached to invest in CCS, CCU or CCUS in each CCUS scenario, based on a traditional NPV calculation. The CO_2 price thresholds to invest in CCU and CCUS for the polyol CCUS-chain are equal to zero, reflecting the fact that these technologies are already profitable, even when the CO_2 price equals zero. A comparison of **Table 6.3** and **Table 6.4** leads to the conclusion that the investment thresholds from the real options analysis are much higher than the CO_2 price levels that the firm would demand based on NPV analysis. As can be seen, the inclusion of uncertainty and the flexibility to choose the timing of investment delays investments in CCS and CCU.

Table 6.4: The NPV CO_2 price thresholds to invest in CCS, CCU and CCUS for the three CCUS scenarios in the cement industry: ethanol production, food-grade CO_2 production and polyol production.

	Ethanol	**Food-grade CO_2**	**Polyol**	**Unit**
CCS	26.84	26.84	26.84	€/t CO_2
CCU	70.70	18.56	0[22]	€/t CO_2
CCUS	27.63	25.75	0	€/t CO_2

6.3.4 Expected time to invest

While the calculated investment thresholds in **Table 6.3** indicate at which CO_2 price level the firm should invest in the CCS, CCU or CCUS chain, it does not reflect how long it may take before the firm invests in any of these abatement technologies. The calculated thresholds can be translated into the 'expected time to investment', that is the expected time before the optimal CO_2 price threshold is hit. We follow the approach presented by Wong (2007) to calculate the expected time to investment:

$$\mathbb{E}(T) = \frac{ln(E^*/E_0)}{\alpha - \sigma^2/2}. \tag{6.31}$$

with E^* the optimal CO_2 price threshold, E_0 the CO_2 price today, α the assumed drift in the CO_2 price and σ the variance in the CO_2 price. Based on the price for emission allowances in the EU ETS in August 2023, we assume a value of 85 €/t for E_0. Together with the optimal investment thresholds from **Table 6.3**, the expected time to investment is calculated and summarized in **Table 6.6**. For the investigated

[22] In fact, these thresholds are even negative (-2361 €/t for CCU and -152.83 €/t for CCUS), indicating that the firm could even afford to pay a price for the CO_2 that is being utilized in the polyol CCU(S) chain. However, negative CO_2 prices in the EU ETS would imply that firms get paid for emitting CO2, which would not make sense. Hence, these thresholds are set to zero in **Table 6.4** .

CCUS chains in the cement industry, the expected time to investment in CCS is between 3.44 and 4.18 years, depending on the CCU-route. With the current set of parameter values, the expected time to investment for CCU is 0 years for the food-grade CO_2 CCU chain, indicating that an investor would immediately invest in CCU if this CCU technology would arrive today.

In comparison, based on the estimated NPV CO_2 price thresholds in **Table 6.5**, a potential investor would invest today in all of these CCUS chains, because the CO_2 price today (85 €/t) is higher than any of these thresholds. This again illustrates how the inclusion of uncertainty and flexibility delays the investment in CCS and CCUS in our framework.

Table 6.6: The expected time to investment in years for CCS and CCU for the three CCUS scenarios in the cement industry: ethanol, food-grade CO_2 and polyol.

	Ethanol	**Food-grade CO_2**	**Polyol**	**Unit**
$E^*_{ccs,1}$	4.18	3.65	3.61	€/t CO_2
$E^*_{ccu,2}$	-	0	-	€/t CO_2
$E^*_{ccs,2}$	-	3.44	3.44	€/t CO_2

6.4 Comparative statics

In this section, we investigate how the investment thresholds change when the level of technological uncertainty, the market uncertainty, and the cost and revenue parameters of the technologies vary. The values from the three CCUS chains in Section 6.3 are used as the base case values for Models 1, 3 and 4 (**Table 6.2**).

6.4.1 The arrival rate of CCU does not influence investment in CCS

The unknown time-to-market of CCU is the source of technological uncertainty in the model. The unknown arrival timing is characterized by the arrival rate λ, which is equivalent to an average waiting time of $1/\lambda$ years. Intuitively, the expected arrival rate could influence the optimal investment timing for CCS in the first stage.

Figure 6.13 shows how the investment thresholds $E^*_{ccs,1}$, $E^*_{ccu,2}$, and $E^*_{ccs,2}$ change when the arrival rate λ is varied from 0 to 1. This means that the average waiting time for CCU varies from infinitely long to one year.

In Stage 2, the CCU technology is mature and the uncertainty about the arrival timing is resolved. Hence, λ does not affect the investment thresholds in Stage 2 ($E^*_{ccu,2}$ and $E^*_{ccs,2}$). In Stage 1, the expected arrival of CCU could affect the incentive to invest in CCS. In Model 1, where CCS is always the optimal solution, the arrival rate of CCU does not affect the investment threshold either. In Models 3 and 4, a higher λ results in a decrease in the CCS investment threshold in Stage 1. Hence, the sooner CCU is expected, the lower the investment threshold is for CCS. However, the absolute effect of λ on the CCS investment threshold is very small, as can be seen in **Figure 6.13**. In sum, when CCU arrives - next year, in 10 years or in 100 years - barely changes the investment decision for CCS.

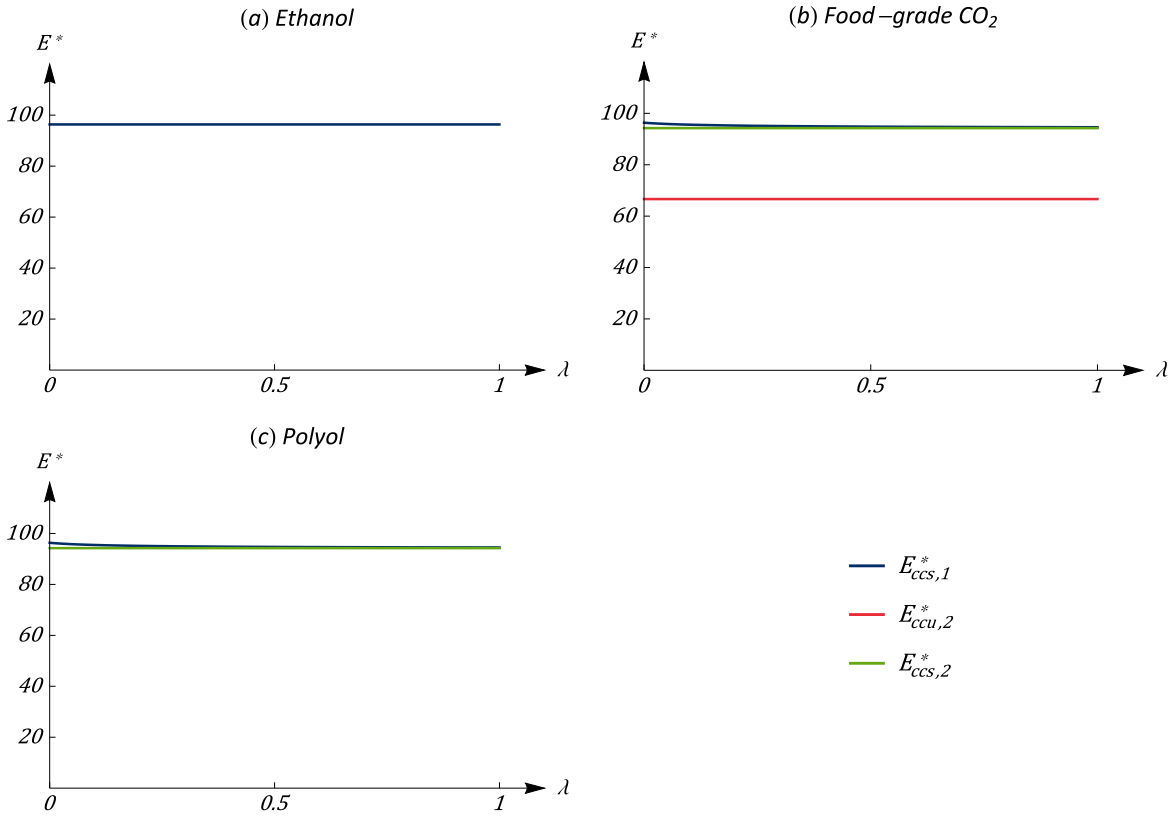


Figure 6.13: The influence of λ on the investment thresholds E^* for the three CCUS scenarios in 6.3.

6.4.2 Volatile carbon prices delay investments

The market uncertainty is characterized by the CO_2 price, which evolves in the future according to the GBM, described in (1). The drift rate α describes the expected growth rate of the CO_2 price in each time interval and the variance parameter σ defines the standard deviation per time interval. It is valuable to analyze how variations in α and σ would affect the resulting investment thresholds.

The drift rate α is varied between 0 and 0.07, to ensure that the condition $\rho > \alpha$ remains fulfilled (Dixit & Pindyck, 1994). **Figure 6.14** presents the influence of α on the investment thresholds in the three scenarios. This figure reveals that a higher α results in lower investment thresholds: firms are triggered to invest sooner in CCS and CCU, due to higher expected prices in the future. The effect of a higher α is similar for all models and over both stages.

The influence of σ on the investment thresholds is presented in **Figure 6.15**. In contrast to the growth rate α, a higher volatility σ now increases the investment thresholds. Higher uncertainty in the CO_2 price results in higher investment thresholds and thus delayed investments in CCS an CCU. This is a standard result in real options theory: the options are more valuable due to the higher uncertainty, hence, firms like to keep their options open for a longer time. This result illustrates that uncertainty generates a value of waiting. From **Figure 6.15** (b), it can be seen that the CO_2 price thresholds for CCS (blue and green curves) and CCU (red curve) diverge when σ increases further. This effect can be attributed to CCU's lower dependency on the CO_2 price as source of revenues, compared to CCS, because (1) a smaller amount of CO_2 emissions is captured with CCU, and (2) other revenues are generated with CCU as well.

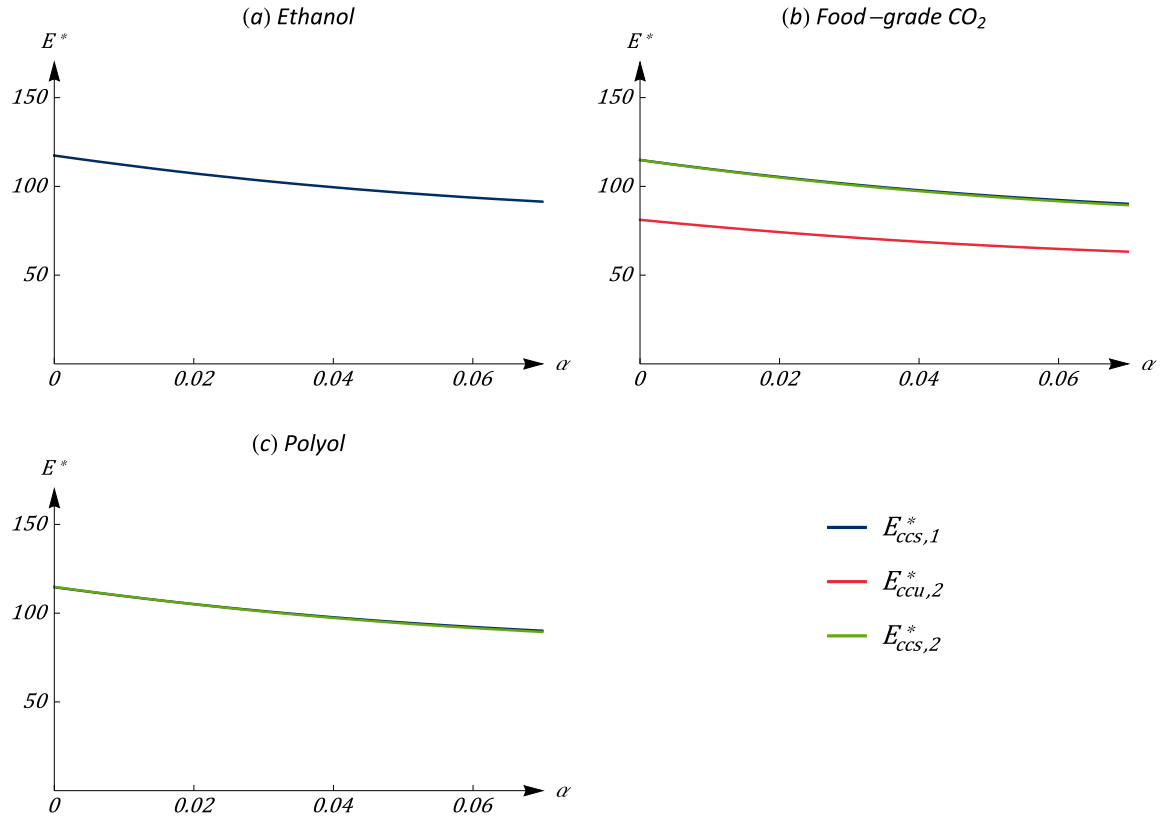


Figure 6.14: The influence of α on the investment thresholds E^* for the three CCUS scenarios in 6.3.

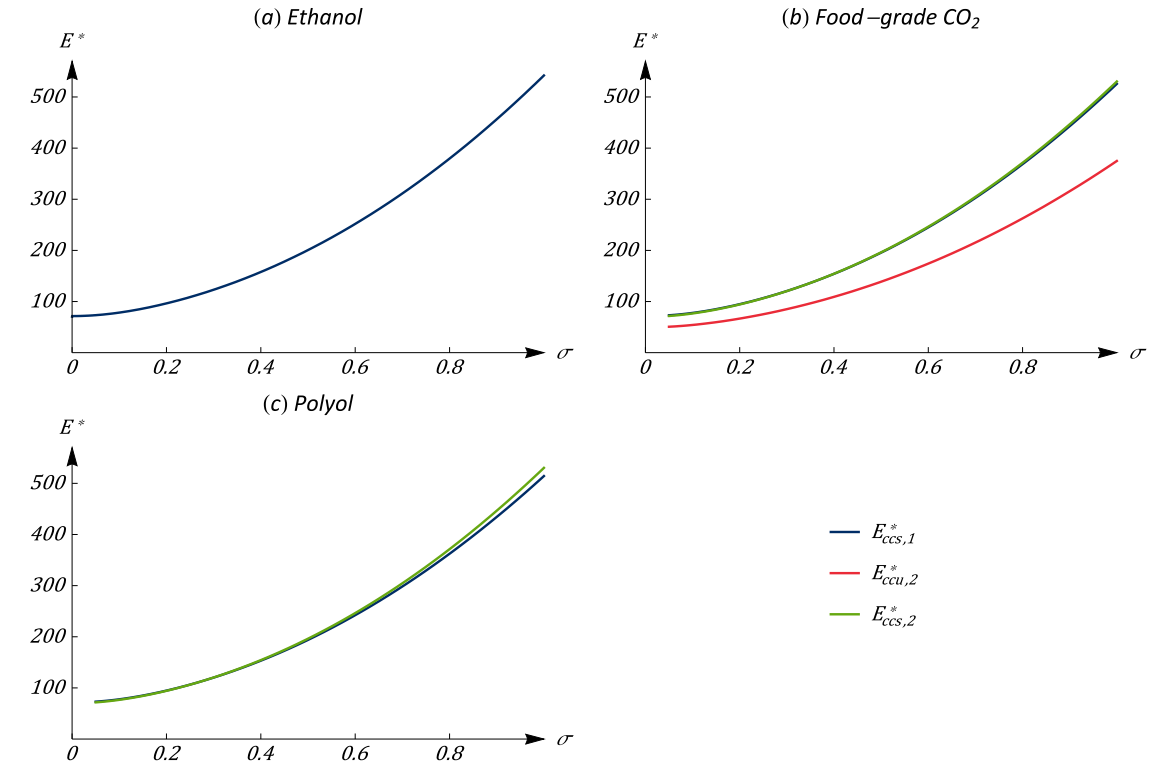


Figure 6.15: The influence of σ on the investment thresholds E^* for the three CCUS scenarios in 6.3.

6.4.3 A higher fraction of CO_2 used stimulates investment in CCS

A crucial difference between CCS and CCU lies in the scale on which CO_2 emissions can be stored or used. The storage of CO_2 emissions can be implemented on a very large scale without running into technical or market limitations, whereas the use of CO_2 is limited to the market for the CO_2-based product. The parameter q describes the fraction of the CO_2 that can be used in the CCU route. **Figure 6.16** presents the influence of q on the CO_2 price thresholds to invest in CCS and CCU in the three scenarios.[23] When the investment in CCS alone is the optimal strategy, the fraction of CO_2 that can be used q does not affect the investment threshold (**Figure 6.16** (a)).

When it is optimal to invest in CCU and CCS consecutively, the fraction q clearly affects the incentive to invest in CCU: the more CO_2 can be used, the lower the CO_2 threshold to invest in CCU. The CO_2 price drops to a level below 20 €/t CO_2 for values of q higher than 0.2. Moreover, q now also influences the CO_2 price threshold to invest in CCS in the first stage (**Figure 6.16** (b)). The influence of q on the CO_2 price threshold to invest in CCS in Stage 1 is still present when it is optimal to invest in CCU the moment it matures (**Figure 6.16** (c)). Although the fraction of CO_2 that can be used affects the incentive to invest in CCS before CCU arrives, this effect disappears once the investment in CCU is made: the CO_2 price threshold for CCS in Stage 2 is not affected by the parameter q, both in **Figure 6.16** (b) and **Figure 6.16** (c).

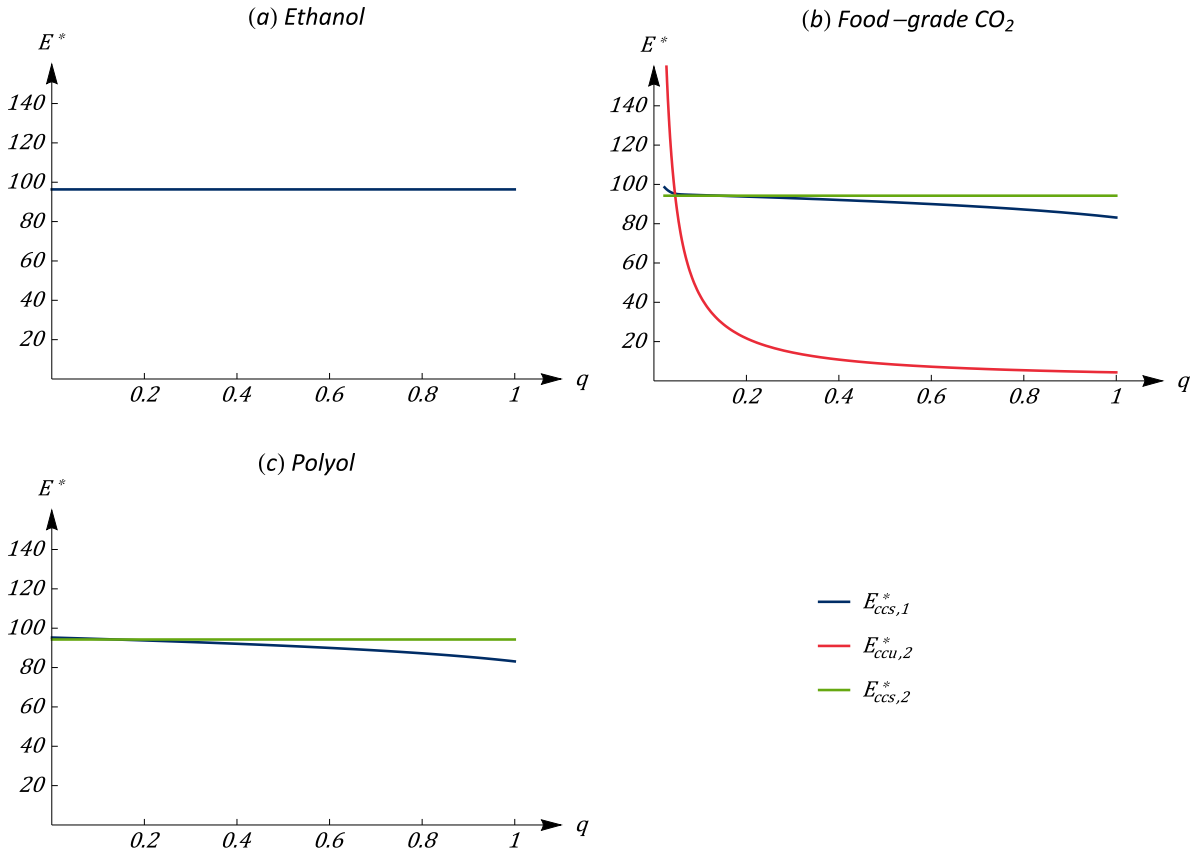


Figure 6.16: The influence of q on the investment thresholds E^* for the three CCUS scenarios in 6.3.

[23] The parameter q was varied between 0 and 1, 0.024 and 1, and 0.0006 and 1 for respectively the ethanol, food-grade CO_2 and polyol scenarios, to ensure that the conditions for each model remain fulfilled.

The investment cost for the capture plant I_c, which needs to be incurred for both the CCS and CCU technologies, is the trigger here. When more CO_2 can be used in the CCU route, the investment cost for the capture plant is also carried more by the CCU technology. As a result, firms that anticipate the arrival of a profitable CCU technology in the future, also anticipate that the investment cost for the capture plant will be supported by the CCU route and hence, they require a lower CO_2 price to invest in CCS in Stage 1. In Stage 2, however, firms already carried out the investment for the capture plant, for the CCU route. As a result, it does not matter anymore how much CO_2 is used or stored: the investment cost I_c no longer affects the CO_2 price to invest in CCS. These intuitive explanations are confirmed by the expressions for the threshold $E^*_{ccs,2}$ (6.25) in Models 3 and 4, where the parameter q is not included, and for the threshold $E^*_{ccu,2}$ (6.24), where the investment costs are indeed divided by the amount of CO_2 emission that can be used.

6.4.4 When to invest in CCS is mostly determined by its costs

The present values of the abatement technologies over the infinite time horizon are also determined by the investment costs, operational costs, the conversion rate, and the price of the product. While changing these parameter values, we will move from one region to another in **Figure 6.4** and the optimal adoption strategy will change. The investment costs in the capture plant, I_c, and the utilization plant, I_u, the utilization costs, C_u, the transport and storage fee, C_{ts}, the conversion rate, X and the price of the product, P_p, are all varied over the four regions in **Figure 6.4**. **Figure 6.17** demonstrates how the investment threshold in Stage 1 $E^*_{ccs,1}$ changes when these parameters are varied over the four regions. The food-grade CO_2 CCUS chain is the starting point and is indicated by the black dot in **Figure 6.17**.

Figure 6.17 (a) and (b) show the influence of the investment costs I_c and the transport and storage costs C_{ts}. The investment threshold $E^*_{ccs,1}$ for CCS in Stage 1 rises when the investment cost for the capture plant I_c or the transport and storage fee C_{ts} increases. For the investment cost I_c, we observe a kink at the boundary between the light red and dark red region in **Figure 6.17** (a). The effect of I_c on the threshold $E^*_{ccs,1}$ is larger in the dark red region, where it is optimal to invest simultaneously in CCUS. Note that the cost I_c would have to become negative, to end up in the green area. The effect of the utilization cost C_u and the investment cost for the utilization plant I_u are displayed in **Figure 6.17** (c) and (d). The effect on $E^*_{ccs,1}$ depends on the region. When the instant CCU adoption strategy is optimal (green), the costs C_u and I_u do not affect the threshold $E^*_{ccs,1}$. In the sequential CCU-CCS adoption strategy (light red), at first, the threshold remains constant. However, the investment threshold $E^*_{ccs,1}$ starts to increase slightly, when we approach the next region. When the firm should invest in CCUS simultaneously (dark red), the threshold $E^*_{ccs,1}$ increases more sharply. Nevertheless, the absolute effect remains rather small, as the threshold only varies from approximately 94 to 96 euros per tonne of CO_2. In the CCS region (blue), the investment threshold again remains unchanged. Finally, **Figure 6.17** (e) and (f) reveal the effect of the product price P_p and the conversion factor X on the threshold $E^*_{ccs,1}$. Both parameters affect the threshold $E^*_{ccs,1}$ similarly as C_u and I_u.

In sum, **Figure 6.17** reveals that the cost parameters of the CCS technology, i.e. I_c and C_{ts}, affect the threshold to invest in CCS in Stage 1 the most. The parameters that are specific to the CCU technology, i.e. C_u, I_u, P_p and X, only affect the CO_2 price threshold to invest in CCS in Stage 1 minimally. **Figure 6.17** (c) - (e) shows that the CO_2 price only varies between 94 and 97 €/t CO_2.

In **Figure 6.17**, we adjust the selected adoption strategy to the changed parameter assumptions. **Figure A.6.5** demonstrates how the threshold would change when we do not change the adoption strategy and only consider one adoption strategy. When the conversion rate X is varied between 0

and 1, we can now observe that the CO_2 price threshold to invest in CCS changes from 125 €/t CO_2 to 95 €/t CO_2. We conclude that adjusting the chosen adoption strategy to changing circumstances helps to flatten out the effect on the investment threshold.

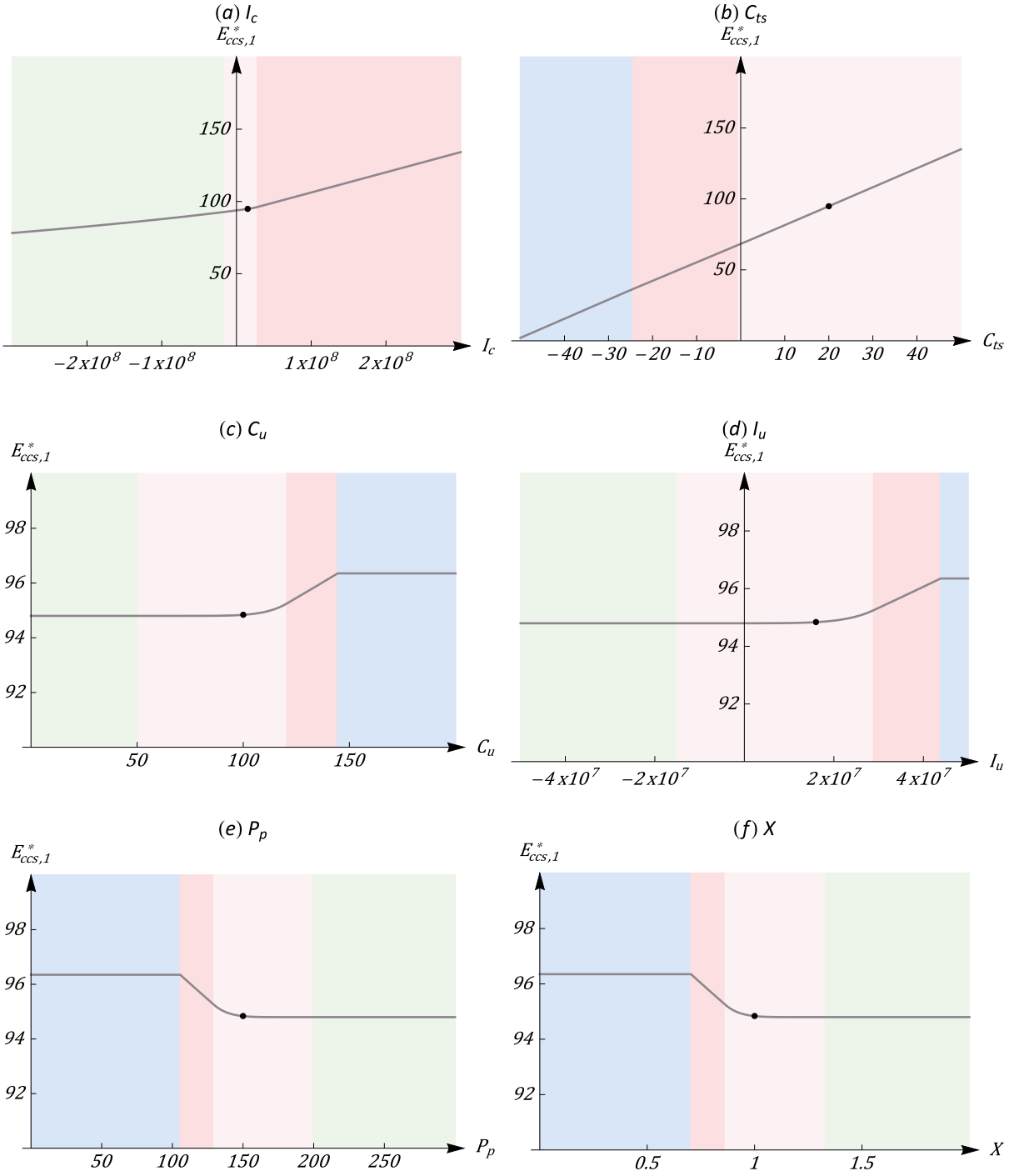


Figure 6.17: The influence of (a) I_c, (b) C_{ts}, (c) C_u, (d) I_u, (e) P_p, and (f) X on the investment thresholds $E^*_{ccs,1}$. The blue, dark red, light red and green areas reflect the optimal regions for respectively the CCS, simultaneous CCUS, sequential CCU-CCS, and instant CCU adoption strategy. The black dots represent the base case, i.e. the food-grade CO_2 (**Table 6.2**).

6.5 Discussion

Our work demonstrates the need to develop individual real options models to accommodate the different adoption strategies that are optimal under varying conditions. Grenadier and Weiss (1997) paved the way by identifying four different adoption strategies when a firm is confronted with a sequence of two technological innovations. We extended their work by allowing one technological innovation to replace the other and by allowing the co-existence of both innovations. While Grenadier and Weiss (1997) found that slow innovation (i.e. low λ) resulted in earlier adoption of the existing technology, we observe the effect of the innovation pace λ on the investment in the existing technology (CCS) to be minimal. In contrast to the findings of Grenadier and Weiss (1997), we observed that the investment threshold for the existing technology (i.e.CCS) in Stage 1 is lowered in the prospect of a more profitable innovative technology (i.e. CCU) in a future period. This difference in findings can be explained by the fact that in the current study, the new technological innovation does not necessarily replace the existing technology but can complement it.

The potential of coupling CCS and CCU was indeed investigated explicitly in this study. Whether CCU and CCS are complementary or competitive solutions has been debated before in literature. While some argue that CCU can serve as a stepping stone towards CCS, by valorising the captured CO_2 and reducing the high costs associated with CCS (Ampelli et al., 2015; Hepburn et al., 2019), others claim that CCU will not be able to reduce the costs of CCS and that it will only distract the attention from CCS, because of the limited scale on which CCU can be implemented (Mac Dowell et al., 2017). Within the theoretical framework of the presented real options models, we find that having the possibility to invest in CCU in the future does not reduce the willingness to invest in CCS today. On the contrary, we observed that the CO_2 price threshold to invest in CCS was lowered when the firms anticipated the arrival of a profitable CCU technology in the route. In this study, the limitations of the scale of CCU were taken into account. Whether it is the market size of the CCU-product, or the availability of other raw materials, the scale on which CO_2 can be utilized is generally much smaller than the CO_2 emissions. This was considered in the CCUS scenarios for the cement industry, where only a fraction of the CO_2 emissions could be utilized in the CCU route.

Another important finding was that higher volatility of the CO_2 price in the EU ETS, described by σ, resulted in delayed investments in CCS. This finding is consistent with that of Compernolle et al. (2017) and Lin and Tan (2021), who found that higher CO_2 price uncertainty resulted in higher investment thresholds. This highlights the need for EU policymakers to provide a stable framework for the EU ETS. A study on the behaviour of the carbon price in the EU ETS demonstrated how a steep increase in the volatility of the carbon price is expected by the end of a trading period (Seifert, Uhrig-Homburg, & Wagner, 2008). Combined with the results of our real options analysis, this implies that firms will postpone their investments in carbon abatement solutions further as the end of the next trading period (2030) approaches. Hence, policymakers must be transparent and try to smooth the transition from one trading period to another, to lower the expected volatility in the carbon price.

In this study, we considered the possibility of combining both CCS and CCU in one value chain, to mitigate all CO_2 emissions of one plant. Hence, we assumed that all CO_2 emissions used in the CCU route are also accounted as not-emitted in the EU ETS. In practice, only CO_2 emissions that are captured and permanently stored, or that have been utilised in such a way that they are permanently chemically bound are exempted from paying emission allowances (European Commission, 2023c). This means that the ethanol, food-grade CO_2 and polyol CCU-routes do not qualify (yet) for this exemption. Hence, the assumptions made for the real options model presented an optimistic scenario for CCU inclusion in the EU ETS. In the future, we expect that the EU ETS directives will also include more

provisions for CCU technologies as well. In further investigations, it might be possible to investigate different scenarios with different proportions of the CO_2 used that is exempted from payments in the EU ETS.

In sum, these findings suggest that firms will delay their investment in CCS or CCU when they are confronted with uncertainty about the carbon price and when they have the flexibility to postpone their investment decision. An implication of this is that the abatement of CO_2 emissions is postponed, which is not desirable from the societal perspective. As indicated by previous research, early action to mitigate climate change is needed, as well as to contain the cost of mitigation (Bosetti, Carraro, & Tavoni, 2012). This is an important issue for future research. Therefore, a future study that includes the environmental impact (and cost) of the delayed abatement of CO_2 emissions is suggested. Combining both economic and environmental perspectives into the real options analysis is an interesting and challenging issue for future research.

6.6 Conclusions

In this study, we show how to tackle the technological and market uncertainties that are present while making investment decisions for CCS and CCU technologies. Moreover, the possibility of combining CCS and CCU in an integrated CCUS installation is investigated as well. To do so, we develop a real options model that determines the optimal timing to invest in CCS and CCU, while taking into account the unknown arrival of CCU and the CO_2 price uncertainty. The real options analysis reveals three main findings. First, the presence of technological and market uncertainties, accounted for in the real options model, increases the barriers to investing in CCS or CCU. Second, when the firm anticipates the arrival of a more attractive CCU solution in the future, it will not postpone the investment in CCS. On the contrary, the investment threshold for CCS in Stage 1 is lowered in the prospect of a more profitable CCU technology in a future period. Whether this new CCU technology arrives next year or only in ten years, does not affect the investment threshold for CCS to a great extent. Third, higher uncertainty in the CO_2 price, i.e. higher σ, increases the investment thresholds, while a higher trend in the CO_2 price, i.e. higher α, decreases the investment thresholds for CCS and CCU. Hence, this study confirms the observation from previous papers (Compernolle et al., 2017; Lin & Tan, 2021) that higher uncertainty in the CO_2 price delays the investment in CCS or CCU.

This study generates useful insights, both for firms that want to invest in CCUS technologies and for policymakers that want to reduce the barriers to investing in these solutions. Based on the real options analysis, the expected time to invest for the CCS and CCU technologies varied between 3.5 and 4 years, depending on the CCUS chain. Based on the NPV, however, the expected time to invest is now. Firms that consider the value of waiting will indeed delay their investment in CCS and CCU technologies when they purely consider their economic interests. The real options analysis also revealed that the prospect of a profitable CCU route in a future period reduces the investment threshold for CCS in the current period. Hence, firms should make efforts to investigate the potential of CCU routes in the future. From the policymaker's perspective, three recommendations can be formulated based on the results. First, policymakers should aim to ensure stability and predictability in the CO_2 price, to lower the volatility σ of the CO_2 price. Reducing the market uncertainty will lower the CO_2 price investment thresholds for CCS, CCU and CCUS. Second, they should also commit to an increasing growth rate in the CO_2 price in the EU ETS. When firms expect higher growth rates for the CO_2 price in the future, they are more likely to invest in CCS, CCU and CCUS sooner. Finally, policymakers should realize that CCU and CCS can be complementary solutions. We find that the anticipation of more profitable CCU technologies in the future did not delay investments in CCS today. Firms will even invest in CCS at slightly lower CO_2 prices today and hence, initiate the abatement of CO_2 emissions sooner.

Appendix – Chapter 6

6.A Model 1

The general solution for the ODE in (6.7) yields $F_1(E) = A_1 \cdot E^{\beta_1} + A_2 \cdot E^{\beta_2}$, where β_1 and β_2 are respectively the positive and negative roots of the quadratic equation $\frac{1}{2}\sigma^2\beta^2 + \left(\alpha - \frac{1}{2}\sigma\right)\beta - \rho = 0$, and A_1 and A_2 are constants that remain to be determined. If the CO_2 price equals zero, it will remain zero according to (6.1), and, since then there is no reason for the firm to abate, the option value should equal zero as well. Since $F_1(0) = 0$ and $\beta_2 < 0$, it follows that $A_2 = 0$ (otherwise, $F_1(0) \to \infty$). Hence, the value of the option in the waiting region equals

$$F_1(E) = A_1 \cdot E^{\beta_1}, \text{ with} \tag{A.1}$$

$$\beta_1 = \frac{-\alpha + \frac{1}{2}\cdot\sigma^2 + \sqrt{\left(\alpha - \frac{1}{2}\cdot\sigma^2\right)^2 + 2*\sigma^2*\rho}}{\sigma^2}. \tag{A.2}$$

Combining the expected present value of operating CCS (6.2) and the value of waiting (A.1) yields the expression for $F_1(E)$:

$$F_1(E) = C_1 \cdot E^{\delta_1} + \tag{A.3}$$

$$\begin{cases} A_1 \cdot E^{\beta_1} \; if \; E \leq E^*_{ccs,1}, \\ \frac{Q_{co_2}}{\rho - \alpha} \cdot E - \frac{Q_{co_2}}{\rho} \cdot (C_c + C_{ts}) - I_c \; if \; E > E^*_{ccs,1}. \end{cases}$$

When the CO_2 price equals the investment threshold $E^*_{ccs,1}$, the firm is indifferent between investing and waiting. Following (Dixit & Pindyck, 1994), the optimal investment threshold $E^*_{ccs,1}$ and the constant A_1 are now determined analytically by applying value-matching and smooth-pasting conditions to the two branches of (A.3). These conditions are indicated in (A.4) and (A.5):

$$A_1 \cdot \left(E^*_{ccs,1}\right)^{\beta_1} = \frac{Q_{co_2}}{\rho - \alpha} \cdot E^*_{ccs,1} - \frac{Q_{co_2}}{\rho} \cdot (C_c + C_{ts}) - I_c, \tag{A.4}$$

$$A_1 \cdot \beta_1 \cdot \left(E^*_{ccs,1}\right)^{\beta_1 - 1} = \frac{Q_{co_2}}{\rho - \alpha}. \tag{A.5}$$

The value matching condition in (A.4) simply states that at the threshold, the value of waiting (left-hand side) should equal the value of the investment (right-hand side). The smooth pasting condition in (A.5) stipulates that the slope of both curves should also be equal at the threshold. Solving this system of equations yields a solution for $E^*_{ccs,1}$ and A_1, as presented in equations (6.9) and (6.10). **Figure A.6.1** summarizes the investment decision for the firm in Model 1.

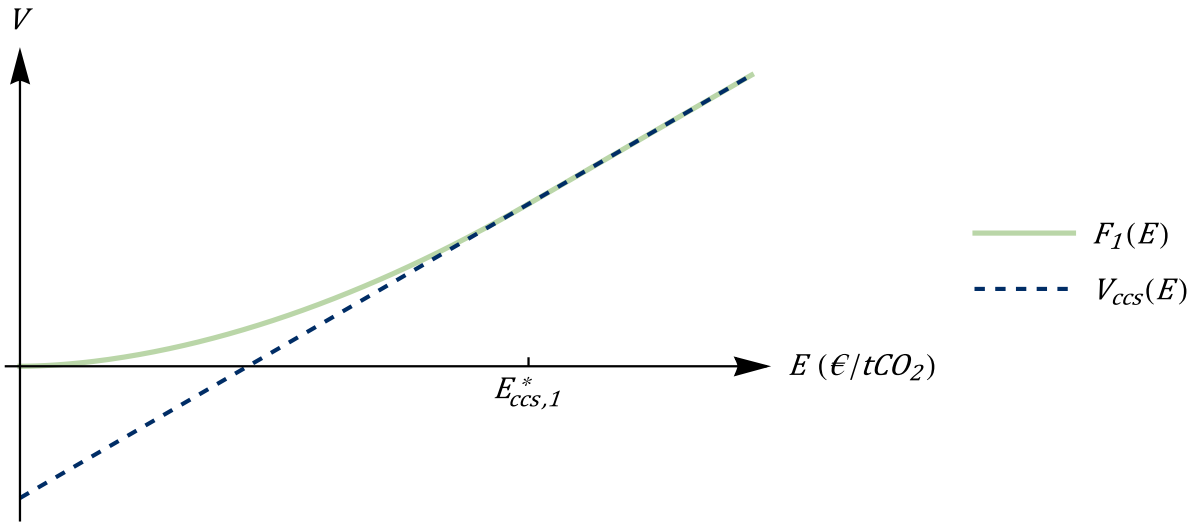


Figure A.6.1: The firm's investment decision problem, in Model 1.

6.B Model 2

Model 2 finds the optimal timing to invest in CCS in Stage 1 and in CCUS in Stage 2, when the optimal strategy is to invest simultaneously in CCUS.

6.B.1. Stage 2

The value of the option to invest in CCUS is given by

$$F_2(E) = A_1 \cdot E^{\beta_1}. \tag{A.6}$$

Combining the expressions for $F_2(E)$ in the stopping region, i.e. the expected present value of operating CCUS (6.11), and in the waiting region, i.e. (A.6), characterizes $F_2(E)$ for all E:

$$F_2(E) = \tag{A.7}$$

$$\begin{cases} A_{1,sim} \cdot E^{\beta_1} \quad if\ E \le E^*_{ccus,2}, \\ \dfrac{Q_{co_2}}{\rho-\alpha} \cdot E - \dfrac{Q_{co_2}}{\rho} \cdot C_c - \dfrac{(1-q) * Q_{co_2}}{\rho} \cdot C_{ts} + \dfrac{q * Q_{co_2}}{\rho} \cdot \left(P_p \cdot X - C_u\right) - I_c - I_u \quad if\ E > E^*_{ccus,2}. \end{cases}$$

The solution for $F_2(E)$ is indicated in (A.7), where the threshold $E^*_{ccus,2}$ and the constant are obtained analytically via the value matching and smooth pasting conditions in (A.8) and (A.9):

$$B_{1,sim}\left(E^*_{ccus,2}\right)^{\beta_1} \tag{A.8}$$

$$= \frac{Q_{co_2}}{\rho-\alpha} E^*_{ccus,2} - \frac{Q_{co_2}}{\rho} \cdot C_c - \frac{(1-q)Q_{co_2}}{\rho} \cdot C_{ts} + \frac{q \cdot Q_{co_2}}{\rho}\left(P_p \cdot X - C_u\right) - I_c - I_u,$$

$$B_{1,sim}\left(E^*_{ccus,2}\right)^{\beta_1 - 1} = \frac{Q_{co_2}}{\rho-\alpha} \tag{A.9}$$

6.B.2. Stage 1

The dynamics of $F_1(E)$ were described in (6.17). Applying Ito's Lemma to find the derivative of $F_1(E)$ results in

$$dF_1(E) = \frac{1}{2}\sigma^2 \cdot E^2 \cdot F_1''(E)dt + \alpha \cdot E \cdot F_1'(E)dt + \sigma \cdot E \cdot F_2'(E)dz + \lambda\big(F_2(E) - F_1(E)\big)dt. \quad \text{(A.10)}$$

The resulting ODE is indicated in (6.18). Note that the solution of the homogeneous part ($\frac{1}{2}\sigma^2 \cdot E^2 \cdot F_1''(E) + \alpha \cdot E \cdot F_1'(E) + \sigma \cdot E \cdot F_2'(E) - (\rho + \lambda) \cdot F_1(E)$) is $F_1(E) = C_1 \cdot E^{\delta_1} + C_2 \cdot E^{\delta_2}$. Since $F_1(E) = 0$ and $\delta_2 < 0$, C_2 should again be equal to zero (otherwise, $F_1(0) \to \infty$). The particular solution is based on $F_2(E)$, adjusted by the term λ because CCU has yet to become available. The value matching and smooth pasting conditions at $E^*_{ccus,2}$ are indicated in (A.11) and (A.12).

$$B_1\big(E^*_{ccus,2}\big)^{\delta_1} + A_{1,sim}\big(E^*_{ccus,2}\big)^{\beta_1} = B_4\big(E^*_{ccus,2}\big)^{\delta_2} + \frac{\lambda}{\lambda+\rho-\alpha}\frac{Q_{co_2}}{\rho-\alpha}E^*_{ccus,2} + \frac{\lambda}{\lambda+\rho} \cdot \left[-\frac{Q_{co_2}}{\rho} \cdot C_c - \frac{(1-q) \cdot Q_{co_2}}{\rho} \cdot C_{ts} + \frac{q \cdot Q_{co_2}}{\rho} \cdot \big(P_p \cdot X - C_u\big) - I_c - I_u\right] \quad \text{(A.11)}$$

$$B_1\big(E^*_{ccus,2}\big)^{\delta_1-1} + A_{1,sim}\big(E^*_{ccus,2}\big)^{\beta_1-1} = B_4\big(E^*_{ccus,2}\big)^{\delta_2-1} + \frac{\lambda}{\lambda+\rho-\alpha}\frac{Q}{\rho-\alpha} \quad \text{(A.12)}$$

Solving this system of equations results in the solution for B_1, B_4, and $E^*_{ccus,2}$ (6.14).

Figure A.6.2 illustrates the value functions for the firm in Model 2. **Figure A.6.2** (a) shows how $F_1(E)$ and $\phi_1(E)$ match at the investment threshold $E^*_{ccus,1}$ in Stage 1. Similarly, in Stage 2, $F_2(E)$ and the value from operating CCUS (adjusted for its unknown arrival) converge at the investment threshold $E^*_{ccus,2}$.

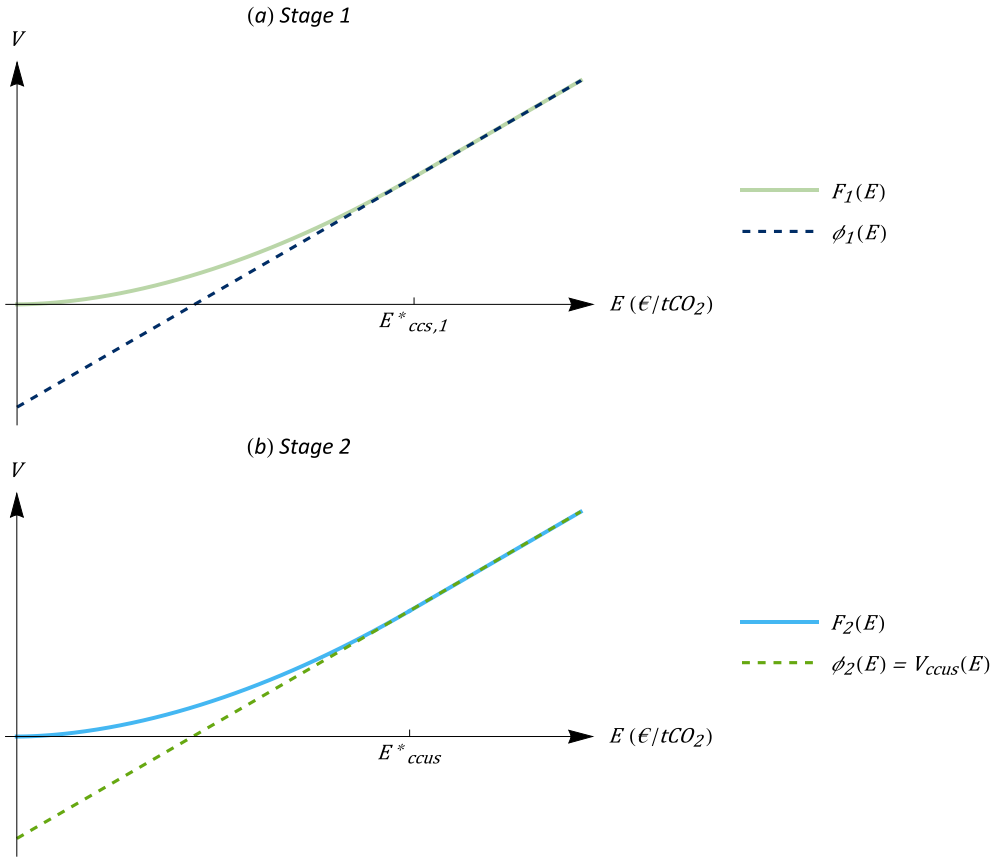


Figure A.6.2: The firm's investment decision problem in Stage 1 and Stage 2, in Model 2.

6.C Model 3

Model 3 finds the optimal timing to invest in CCS in Stage 1 and in CCU and CCS in Stage 2, when the optimal strategy is to invest sequentially in CCU and CCS.

6.C.1. Stage 2

The solution for $F_2(E)$ is indicated in (23). The thresholds $E^*_{ccu,2}$ and $E^*_{ccs,2}$ and the constants $A_{1,seq}$ and D_1 are determined analytically via the value-matching and smooth pasting conditions in (A.13), (A.14), (A.15), and (A.16).

$$A_{1,seq} \cdot \left(E^*_{ccu,2}\right)^{\beta_1} = \tag{A.13}$$

$$D_1 \cdot \left(E^*_{ccu,2}\right)^{\beta_1} + \frac{q \cdot Q}{\rho - \alpha} * E^*_{ccu,2} + \frac{q \cdot Q_{co_2}}{\rho} * \left(P_p * X - C_c - C_u\right) - I_c - I_u,$$

$$A_{1,seq} \cdot \beta_1 \cdot \left(E^*_{ccu,2}\right)^{\beta_1 - 1} = D_1 \cdot \beta_1 \cdot \left(E^*_{ccu,2}\right)^{\beta_1 - 1} + \frac{q \cdot Q_{co_2}}{\rho - \alpha}, \tag{A.14}$$

$$D_1 \cdot \left(E^*_{ccs,2}\right)^{\beta_1} + \frac{q \cdot Q_{co_2}}{\rho - \alpha} * E^*_{ccs,2} + \frac{q \cdot Q_{co_2}}{\rho} * \left(P_p * X - C_c - C_u\right) - I_c - I_u = \tag{A.15}$$

$$\frac{Q_{co_2}}{\rho - \alpha} E^*_{ccs,2} - \frac{Q_{co_2}}{\rho} \cdot C_c - \frac{(1-q)Q_{co_2}}{\rho} C_{ts} + \frac{q \cdot Q_{co_2}}{\rho}\left(P_p \cdot X - C_u\right) - I_c - I_u,$$

$$D_1 \cdot \left(E^*_{ccs,2}\right)^{\beta_1} + \frac{q * Q_{co_2}}{\rho - \alpha} = \frac{Q_{co_2}}{\rho - \alpha}. \tag{A.16}$$

The solutions for the constants $A_{1,seq}$ and D_1 are given by:

$$A_{1,seq} = D_1 + \tag{A.17}$$

$$\frac{q \cdot Q_{co_2}}{\rho - \alpha} \cdot \frac{1}{\beta_1} \cdot \left[\frac{\beta_1}{\beta_1 - 1} \cdot \left(\frac{\rho - \alpha}{\rho} \cdot \left(C_c + C_u - P_p \cdot X\right) + \frac{\rho - \alpha}{q \cdot Q_{co_2} Q} \cdot \left(I_c + I_u\right)\right)\right]^{1-\beta_1},$$

$$D_1 = \frac{(1-q)Q}{\rho - \alpha} \cdot \frac{1}{\beta_1} \cdot \left[\frac{\beta_1}{\beta_1 - 1} \cdot \frac{\rho - \alpha}{\rho} \cdot \left(C_c + C_{ts}\right)\right]^{1-\beta_1}. \tag{A.18}$$

6.C.2. Stage 1

The dynamics of $F_1(E)$ were described in (6.17). Applying Ito's Lemma to find the derivative of $F_1(E)$ results in

$$\begin{aligned} dF_1(E) = \frac{1}{2}\sigma^2 \cdot E^2 \cdot F_1''(E)dt + \alpha \cdot E \cdot F_1'(E)dt + \sigma \cdot E \cdot F_2'(E)dz \\ + \lambda\big(F_2(E) - F_1(E)\big)dt. \end{aligned} \tag{A.19}$$

The resulting ODE is indicated in (6.18). Note that the solution of the homogeneous part ($\frac{1}{2}\sigma^2 \cdot E^2 \cdot F_1''(E) + \alpha \cdot E \cdot F_1'(E) + \sigma \cdot E \cdot F_2'(E) - (\rho + \lambda) \cdot F_1(E)$) is $F_1(E) = C_1 \cdot E^{\delta_1} + C_2 \cdot E^{\delta_2}$. Since $F_1(0) = 0$ and $\delta_2 < 0$, C_2 should again be equal to zero (otherwise, $F_1(0) \to \infty$). The particular solution is based on $F_2(E)$, adjusted by the term λ because CCU has yet to become available.

The value-matching and smooth pasting conditions at respectively $E^*_{ccu,2}$ and $E^*_{ccs,2}$ are indicated in (A.20) - (A.23).

$$A_{1,seq} \cdot \left(E^*_{ccu,2}\right)^{\beta_1} + B_{1,seq} \cdot \left(E^*_{ccu,2}\right)^{\delta_1} = \tag{A.20}$$

$$\frac{\lambda}{\rho + \lambda - \alpha} \cdot \frac{q * Q}{\rho - \alpha} \cdot E^*_{ccu,2} + \frac{\lambda}{\lambda + \rho} \cdot \left[\frac{q \cdot Q_{co_2}}{\rho} \cdot (P * X - C_u - C_c) - I_c - I_u\right] +$$

$$D_1 \cdot \left(E^*_{ccu,2}\right)^{\beta_1} + B_{2,seq} \cdot \left(E^*_{ccu,2}\right)^{\delta_1} + B_{3,seq} \cdot \left(E^*_{ccu,2}\right)^{\delta_2}$$

$$A_{1,seq} \cdot \beta_1 \cdot \left(E^*_{ccu,2}\right)^{\beta_1 - 1} + B_{1,seq} \cdot \delta_1 \cdot \left(E^*_{ccu,2}\right)^{\delta_1 - 1} = \tag{A.21}$$

$$\frac{\lambda}{\rho + \lambda - \alpha} \cdot \frac{q \cdot Q_{co_2}}{\rho - \alpha} + D_1 \cdot \beta_1 \cdot \left(E^*_{ccu,2}\right)^{\beta_1 - 1} +$$

$$B_{2,seq} \cdot \delta_1 \cdot \left(E^*_{ccu,2}\right)^{\delta_1 - 1} + B_{3,seq} \cdot \delta_2 \cdot \left(E^*_{ccu,2}\right)^{\delta_2 - 1},$$

$$\frac{\lambda}{\rho + \lambda - \alpha} \cdot \frac{q * Q_{co_2}}{\rho - \alpha} \cdot E^*_{ccs,2} + \frac{\lambda}{\lambda + \rho} \cdot \left[\frac{q * Q_{co_2}}{\rho} \cdot \left(P_p * X - C_u - C_c\right) - I_c - I_u\right] + \tag{A.22}$$

$$D_1 \cdot \left(E^*_{ccs,2}\right)^{\beta_1} + B_{2,seq} \cdot \left(E^*_{ccs,2}\right)^{\delta_1} + B_{3,seq} \cdot \left(E^*_{ccs,2}\right)^{\delta_2} =$$

$$\frac{\lambda}{\rho + \lambda - \alpha} \cdot \frac{q * Q_{co_2}}{\rho - \alpha} \cdot E^*_{ccs,2} + \frac{\lambda}{\lambda + \rho} \cdot \left[-\frac{Q_{co_2}}{\rho} \cdot C_c - (1 - q) \cdot Q_{co_2} \cdot C_{ts} +\right.$$

$$\left.\frac{q * Q_{co_2}}{\rho} \cdot \left(P_p * X - C_u\right) - I_c - I_u\right] + B_{4,seq} \cdot \left(E^*_{ccs,2}\right)^{\delta_2},$$

$$\frac{\lambda}{\rho + \lambda - \alpha} \cdot \frac{q * Q_{co_2}}{\rho - \alpha} \cdot + D_1 \cdot \beta_1 \cdot \left(E^*_{ccs,2}\right)^{\beta_1 - 1} + B_{2,seq} \cdot \delta_1 \cdot \left(E^*_{ccs,2}\right)^{\delta_1 - 1} \tag{A.23}$$

$$+ B_{3,seq} \cdot \delta_2 \cdot \left(E^*_{ccs,2}\right)^{\delta_2 - 1} = \frac{\lambda}{\rho + \lambda - \alpha} * \frac{q * Q_{co_2}}{\rho - \alpha} \cdot E^*_{ccs,2} +$$

$$\frac{\lambda}{\lambda + \rho} \cdot \left[-\frac{Q}{\rho} \cdot C_c - (1 - q) \cdot Q_{co_2} \cdot C_{ts} + \frac{q \cdot Q_{co_2}}{\rho} \cdot \left(P_p \cdot X - C_u\right) - I_c - I_u\right] +$$

$$B_{4,seq} \cdot \delta_2 \cdot \left(E^*_{ccs,2}\right)^{\delta_2 - 1}.$$

Figure A.6.3 summarizes the investment decision for the firm in Model 3. **Figure A.6.3** (a) shows how $F_1(E)$ and $\phi_1(E)$ match at the investment threshold $E^*_{ccs,1}$ in Stage 1. **Figure A.6.3** (b) illustrates the threefold character of $F_2(E)$. At $E^*_{ccu,2}$, the value function $F_2(E)$ aligns with the expected profits of CCU and the option to invest in CCS (blue dashed line). When the CO_2 price rises further until $E^*_{ccs,2}$, the value function $F_2(E)$ collapses with the profits of CCUS (green dashed line).

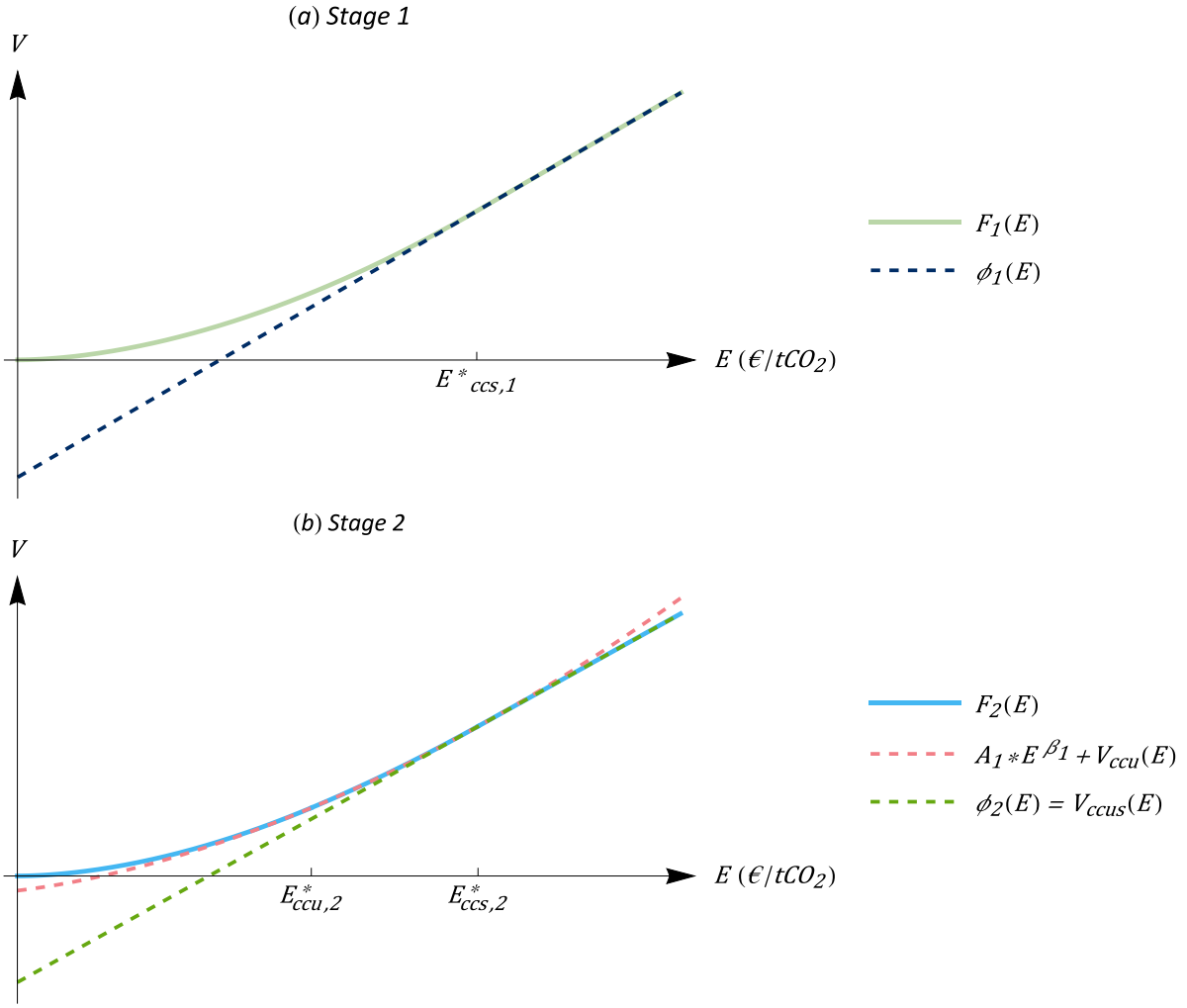


Figure A.6.3: The firm's investment decision problem in Stage 1 and Stage 2, in Model 3.

6.D Model 4

Model 4 finds the optimal timing to invest in CCS in Stage 1 and in CCS in Stage 2, when the optimal strategy is to invest immediately in CCU when it arrives, followed by CCS later.

6.D.1. Stage 1

The value-matching and smooth pasting conditions at $E^*_{ccs,2}$ are indicated in (A.24) - (A.25).

$$A_{1,imm} \cdot \left(E^*_{ccs,2}\right)^{\beta_1} + \frac{\lambda}{\lambda+\rho-\alpha} \cdot \frac{q \cdot Q_{co_2}}{\rho-\alpha} \cdot E^*_{ccs,2} + \tag{A.24}$$

$$\frac{\lambda}{\lambda+\rho} \cdot \frac{q \cdot Q_{co_2}}{\rho} \left[\left(P_p \cdot X - C_c - C_u\right) - I_c - I_u\right] + B_{1,imm} * \left(E^*_{ccs,2}\right)^{\delta_1} =$$

$$\frac{\lambda}{\lambda+\rho-\alpha}\frac{Q_{co_2}}{\rho-\alpha} * E^*_{ccs,2} + \frac{\lambda}{\lambda+\rho}\cdot\left[-\frac{Q_{co_2}}{\rho} * C_c - \frac{(1-q)\cdot Q_{co_2}}{\rho} * C_{ts}\right.$$

$$\left.+\frac{q\cdot Q_{co_2}}{\rho}\cdot\left(P_p\cdot X - C_u\right) - I_c - I_u\right] + B_{4,imm} * \left(E^*_{ccs,2}\right)^{\delta_2},$$

$$A_{1,imm}\cdot\beta_1\cdot\left(E^*_{ccs,2}\right)^{\beta_1-1} + \frac{\lambda}{\lambda+\rho-\alpha}\frac{q\cdot Q_{co_2}}{\rho-\alpha}\cdot E^*_{ccs,2} + B_{1,imm}\cdot\delta_1\cdot\left(E^*_{ccs,2}\right)^{\delta_1-1} \quad \text{(A.25)}$$

$$= \frac{\lambda}{\lambda+\rho-\alpha}\frac{Q}{\rho-\alpha} + B_{4,imm}\cdot\delta_2\cdot\left(E^*_{ccs,2}\right)^{\delta_2-1}.$$

We can summarize the investment decision for Model 4 in **Figure A.6.4**. In Stage 1, $F_1(E)$ and $\phi_1(E)$ match at the threshold $E^*_{ccs,1}$, as in Model 2. **Figure A.6.4** (b) shows the solution for Stage 2, where $F_2(E)$ collapses with the value of operating CCUS V_{ccus} at the threshold $E^*_{ccs,2}$.

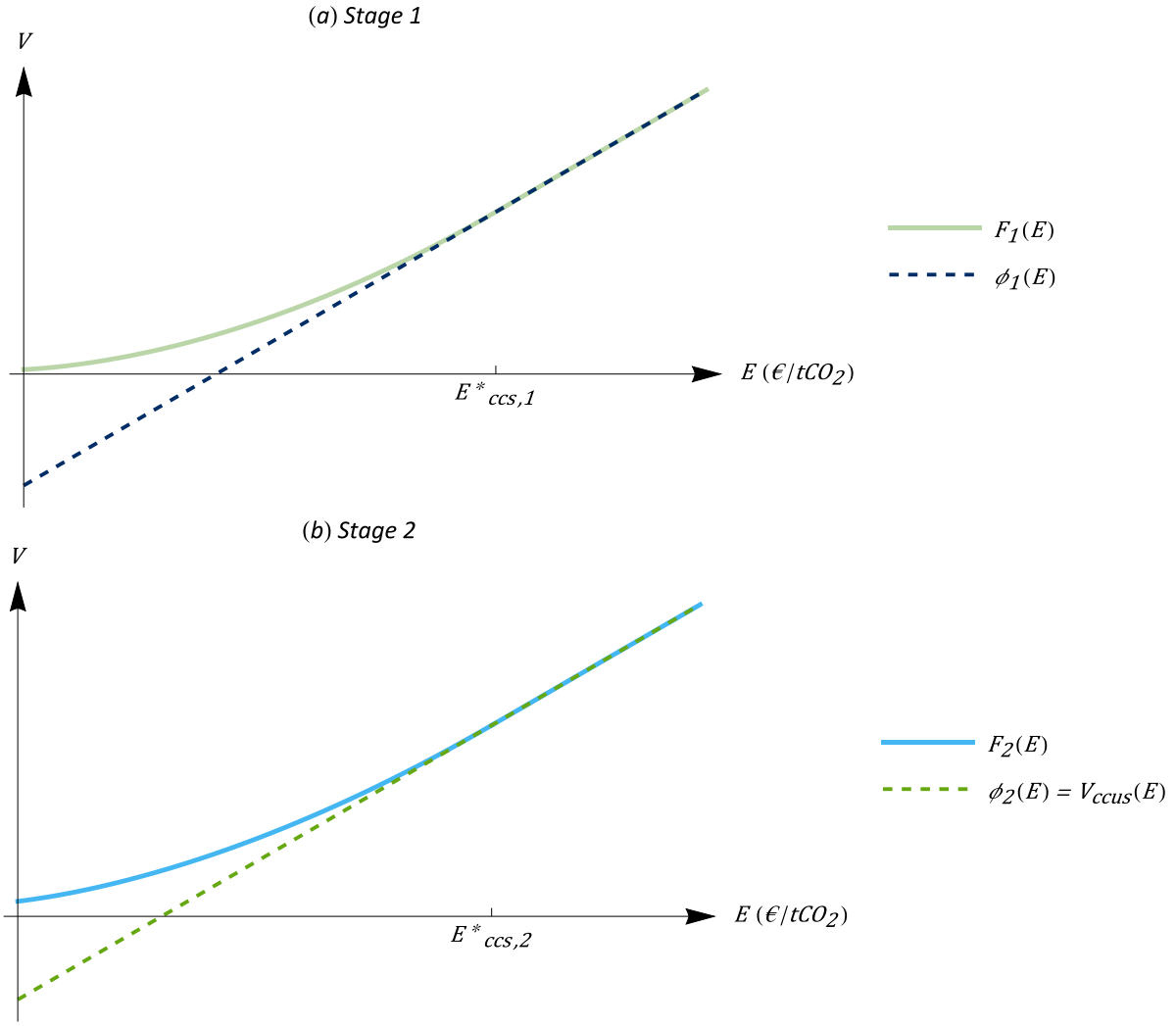


Figure A.6.4: The firm's investment decision problem in Stage 1 and Stage 2, in Model 4.

6.E CCUS chains in cement industry

Table A.6.1: Assumptions for the ethanol CCUS chain. The values are based on (Monteiro & Roussanaly, 2022), unless indicated otherwise.

	Symbol	Value	Unit	Remarks	Reference
Technology Readiness Level	TRL	5		This means that the technology is validated in the relevant environment.	
CO_2 emissions of cement plant	Q_{co_2}	771,000	t CO_2/year		
Ethanol production		12,500	t ethanol/year		
CO_2 emissions used for ethanol production		23,800	t CO_2 used/year		
Utilized fraction of CO_2 emissions	q	3.1	%	= (23,800 t CO_2 used/year) / (771,000 t CO_2/year)	
Investment cost for the CO_2 capture facility	I_c	15,000,000	€	The capital cost for a standard MEA-based CO_2 absorption process, applied to a highly concentrated CO_2 source, such as a cement plant, is estimated in the range of 10 to 20 €/t CO_2. The upper value is multiplied with the amount of CO_2 captured, and then rounded to 15 M€.	(Gardarsdóttir et al., 2018)
Investment cost for the utilization plant	I_u	22,600,000	€		
Operating cost CO_2 capture	C_c	50	€/ton CO_2 captured	Estimated cost for CO_2 capture of 69 €/t CO_2 avoided; converted to cost per tonne of CO_2 captured (504,000 t CO_2	

				avoided/year versus 694,000 t CO_2 captured/year)	
Transport and storage fee	C_{ts}	20	€/ton CO_2	Estimated cost for on- and offshore pipeline and storage of 28 €/t CO_2 avoided; converted to cost per tonne of CO_2 captured	
Operating cost for the utilization plant	C_u	345	€/ton CO_2 used	Estimated cost for the production of ethanol is 656 €/t ethanol produced; converted to cost per tonne of CO_2 used	
Product price	P_p	633	€/ton	Market value of ethanol	
Conversion factor from CO_2 to end-product	X	0.525		12,500 t ethanol /23,800 t CO_2 used	
Discount rate	ρ	8	%	Discount rate used in cost analysis for CO_2 capture from same reference cement plant	(Gardarsdóttir et al., 2019)
Drift	α	0.05		CO_2 price growth rate assumed for the GBM in a real options study to analyse investment decision in CO_2-EOR	(Compernolle et al., 2017)
Variance	σ	0.2		CO_2 price volatility assumed for the GBM in a real options study to analyse investment decision in CO_2-EOR	(Compernolle et al., 2017)
Arrival rate of CCU	λ	0.2		This reflects the expectation that CCU will mature in 5 years	This work

Table A.6.2.: Assumptions for the food-grade CO_2 CCUS chain. The values are based on (Monteiro & Roussanaly, 2022), unless indicated otherwise.

	Symbol	Value	Unit	Remarks	Reference
Technology Readiness Level	TRL	9		This means that the technology is proven in an operational environment. In other words, the technology is technically mature.	(Monteiro & Roussanaly, 2022)
CO_2 emissions of cement plant	Q_{co_2}	771,000	t CO_2/year		
Food-grade CO_2 production		50,000	t CO_2/year		
CO_2 emissions used for food-grade CO_2 production		50,000	t CO_2 used/year		
Utilized fraction of CO_2 emissions	q	6.5	%	= (50,000 t CO_2 used/year) / (771,000 t CO_2/year)	
Investment cost for the CO_2 capture facility	I_c	15,000,000	€	The capital cost for a standard MEA-based CO_2 absorption process, applied to a highly concentrated CO_2 source, such as a cement plant, is estimated in the range of 10 to 20 €/t CO_2. The upper value is multiplied with the amount of CO_2 captured, and then rounded to 15 M€.	(Gardarsdóttir et al., 2018)
Investment cost for the utilization plant	I_u	16,000,000	€		
Operating cost CO_2 capture	C_c	50	€/ton CO_2 captured	Estimated cost for CO_2 capture of 69 €/t CO_2 avoided; converted to cost per tonne of CO_2 captured (504,000 t CO_2	

				avoided/year versus 694,000 t CO_2 captured/year)	
Transport and storage fee	C_{ts}	20	€/ton CO_2	Estimated cost for on- and offshore pipeline and storage of 28 €/t CO_2 avoided; converted to cost per tonne of CO_2 captured	
Operating cost for the utilization plant	C_u	100	€/ton CO_2 used		
Product price	P_p	150	€/ton	The price of food-grade CO_2 is location-sensitive, but in the range of 80 to 150 €/t in Europe. In this study, we assumed the upper value of this range.	
Conversion factor from CO_2 to end-product	X	1		The captured CO_2 needs to be purified to food-grade CO_2 quality. We assume no losses in the purification step.	
Discount rate	ρ	8	%	Discount rate used in cost analysis for CO_2 capture from same reference cement plant	(Gardarsdóttir et al., 2019)
Drift	α	0.05		CO_2 price growth rate assumed for the GBM in a real options study to analyse investment decision in CO_2-EOR	(Compernolle et al., 2017)
Variance	σ	0.2		CO_2 price volatility assumed for the GBM in a real options study to analyse investment decision in CO_2-EOR	(Compernolle et al., 2017)
Arrival rate of CCU	λ	0.5		This reflects the expectation that the food-grade CO_2 CCU route will be available in 2 years. A higher arrival rate is assumed than for ethanol, because of the higher TRL.	This work

Table A.6.3.: Assumptions for the polyol CCUS chain. The values are based on (Monteiro & Roussanaly, 2022), unless indicated otherwise.

	Symbol	Value	Unit	Remarks	Reference
Technology Readiness Level	TRL	9		This means that the technology is proven in an operational environment. In other words, the technology is technically mature.	(Monteiro & Roussanaly, 2022)
CO_2 emissions of cement plant	Q_{co_2}	771,000	t CO_2/year		
Polyol production		288,000	t polyol/year		
CO_2 emissions used for food-grade CO_2 production		57,500	t CO_2 used/year		
Utilized fraction of CO_2 emissions	q	7.5	%	= (57,500 t CO_2 used/year) / (771,000 t CO_2/year)	
Investment cost for the CO_2 capture facility	I_c	15,000,000	€	The capital cost for a standard MEA-based CO_2 absorption process, applied to a highly concentrated CO_2 source, such as a cement plant, is estimated in the range of 10 to 20 €/t CO_2. The upper value is multiplied with the amount of CO_2 captured, and then rounded to 15 M€.	(Gardarsdóttir et al., 2018)
Investment cost for the utilization plant	I_u	21,000,000	€		
Operating cost CO_2 capture	C_c	50	€/ton CO_2 captured	Estimated cost for CO_2 capture of 69 €/t CO_2 avoided; converted to cost per tonne of CO_2 captured (504,000 t CO_2	

				avoided/year versus 694,000 t CO_2 captured/year)	
Transport and storage fee	C_{ts}	20	€/ton CO_2	Estimated cost for on- and offshore pipeline and storage of 28 €/t CO_2 avoided; converted to cost per tonne of CO_2 captured	
Operating cost for the utilization plant	C_u	603	€/ton CO_2 used		
Product price	P_p	1400	€/ton		
Conversion factor from CO_2 to end-product	X	5		288,000 t polyol/57,500 t CO_2 used	
Discount rate	ρ	8	%	Discount rate used in cost analysis for CO_2 capture from same reference cement plant	(Gardarsdóttir et al., 2019)
Drift	α	0.05		CO_2 price growth rate assumed for the GBM in a real options study to analyse investment decision in CO_2-EOR	(Compernolle et al., 2017)
Variance	σ	0.2		CO_2 price volatility assumed for the GBM in a real options study to analyse investment decision in CO_2-EOR	(Compernolle et al., 2017)
Arrival rate of CCU	λ	0.5		This reflects the expectation that the polyol CCU route will be available in 2 years. The same arrival rate is chosen as for food-grade CO_2, because of the same TRL.	This work

6.F Comparative statics

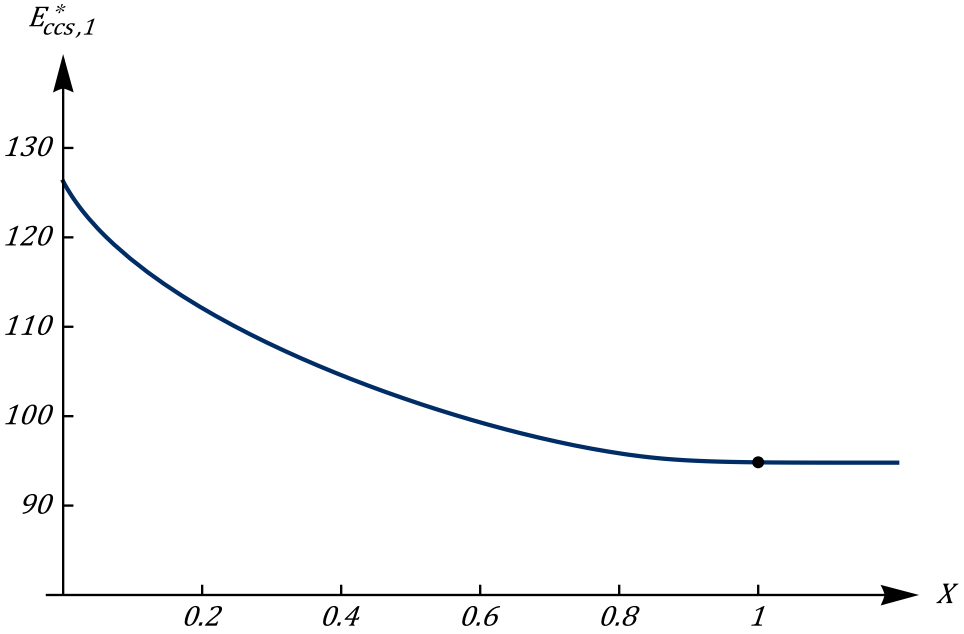


Figure A.6.5: The influence of X on the investment threshold $E^*_{ccs,1}$.

7

Conclusions

This chapter concludes this doctoral thesis by providing an answer to the research questions that were asked in Chapter 1 and summarising the main contributions to the field of CO_2 utilisation. The limitations of the research are acknowledged and opportunities for future research, to support the development of novel CCU technologies, are proposed. Finally, the potential for a CCUS value chain in Flanders is briefly discussed.

7.1 The research questions answered

This research aimed to analyse the economic feasibility and the environmental footprint of a novel CCU technology – plasma catalysis – and to investigate how uncertainty can affect the decision to invest in CCU(S) value chains. The economic and environmental assessments were performed in parallel with the technology's development in the laboratory. This created an opportunity to use the insights from the economic and environmental analyses and make more informed decisions for the next steps to be taken in the development of this novel technology.

This thesis was part of the PlasMaCatDESIGN project, which is centred around the search for the most optimal design of the catalyst for the conversion of CO_2 and CH_4 into higher-value chemicals. The catalyst is inserted as packing material in a DBD reactor to create a plasma-catalytic process. The CO_2 and CH_4 can flow through the DBD reactor, where the CO_2 and CH_4 molecules interact with the plasma. The bonds of the molecules are broken by the high reactivity of the plasma and then recombined again into other end products, guided by the presence of the catalyst. The PlasMaCatDESIGN project involved both academic and industrial partners, from varying disciplines. The interdisciplinary nature of the project was one of its strengths.

Researchers at VITO, UGent and UHasselt developed the supports, coating and catalytic nanoparticles for the packing beads to be inserted in the gap in the DBD reactor. These newly designed and developed packing beads were then tested in the laboratory at the University of Antwerp, for different combinations of *reactor configuration* and *process parameters*. This resulted in the creation of a comprehensive dataset, describing how the systematic variations in *reactor configuration* and *process parameters* affected the technical performance of the plasma-catalytic process. In this dataset, measurements are collected for several important parameters on the technical performance of the plasma catalysis technology, including the CO_2 conversion rate, which describes how much CO_2 is converted, the Specific Energy Input (SEI), which reflects how much plasma power is used relative to the flow rate in the reactor, and the product mix, displaying the concentrations of the different products at the outlet of the DBD reactor. Simultaneously, chemical scientists at the University of Antwerp tried to model the plasma chemistry and interactions, to suggest new pathways to be explored. The results from the experiments in the laboratory at the University of Antwerp were then used as input to perform the economic and environmental assessments. Thanks to the interdisciplinary approach in this project, the insights from the economic and environmental analyses

could immediately be used to support the selection of packing materials that should be developed and tested further. Moreover, the results of this dissertation can contribute to the identification of the remaining bottlenecks for the technology and can help to set future objectives for the development of plasma catalysis as CCU technology.

To contribute to the PlasMaCatDESIGN project and the development of packing materials from the field of environmental economics, four research questions were asked in Chapter 1, each addressing a different aspect of the development of a novel CCU technology.

7.1.1 An economically feasible configuration of the DBD reactor

The first research question addressed the economic aspect:

1. *How do variations in the design of the DBD plasma technology, for the plasma-catalytic conversion of CO_2, translate into economic impacts for the CCU value chain as a whole?*

To find an answer to this research question, a Techno-Economic Assessment (TEA)-tool was developed in Excel, that allowed us to translate the whole experimental dataset for the different combinations of *reactor configurations* and *process parameters* into economic metrics with one click. The development of this TEA-tool involved two main benefits. First, a TEA allows for translating the technical performance of a technology into economic metrics. This also means that a change in one of the technical parameters, e.g. energy consumed or conversion rate, will immediately be reflected in a change in the economic parameters. Hence, the development and use of the tool enabled us to evaluate how different combinations of *reactor configuration* and *process parameters* resulted in varying costs and revenues. Second, the TEA-tool was developed in such a way that its assumptions can easily be adjusted and that it can also still be deployed to analyze a new round of experiments in the future, with new combinations of *reactor configuration* and *process parameters.* The assumptions in the TEA, e.g. about the electricity price, product price or discount rate, can be adapted easily in the tool and the TEA can then be rerun for the whole set of combinations in one click. When a new set of *reactor configurations* and *process parameters* is analyzed in the future, the new dataset has to be uploaded in the TEA – perhaps some settings have to be changed about the dimensions of the DBD reactor, or new products (and their prices) would have to be added to the tool – and then the TEA could again be performed for this new round of experiments. Hence, the tool can continue to be used in the future, to generate insights for new variations in the design of the DBD reactor easily and quickly.

This TEA-tool has been applied to 83 different combinations of the DBD *reactor configuration* and *process parameters*: 35 set-ups of the DBD reactor with a gap of 0.455 mm (Chapter 3) and 48 configurations of the DBD reactor with a gap of 4.44 mm (Chapter 4). Each data point that was analyzed in the TEA represents a unique combination of gap size and packing material (*reactor configuration*) and feed ratio, space time and SEI (*process parameters*). The results indicate that none of these 83 DBD reactor configurations is currently economically feasible, based on their technical performance in the laboratory.

Combining the insights from both Chapter 3 and Chapter 4, **Figure 7.1** assembles the NPVs for all DBD reactor configurations with a feed of CO_2 and CH_4, which are 63 reactor configurations in total. The DBD reactor with a gap of 0.455 mm is represented by the triangular marks and the DBD reactor with a gap of 4.44 mm is represented by the circular marks. From **Figure 7.1**, it can be seen that the configurations with the smaller gap size of 0.455 mm have much lower NPVs than those with a gap size of 4.44 mm.

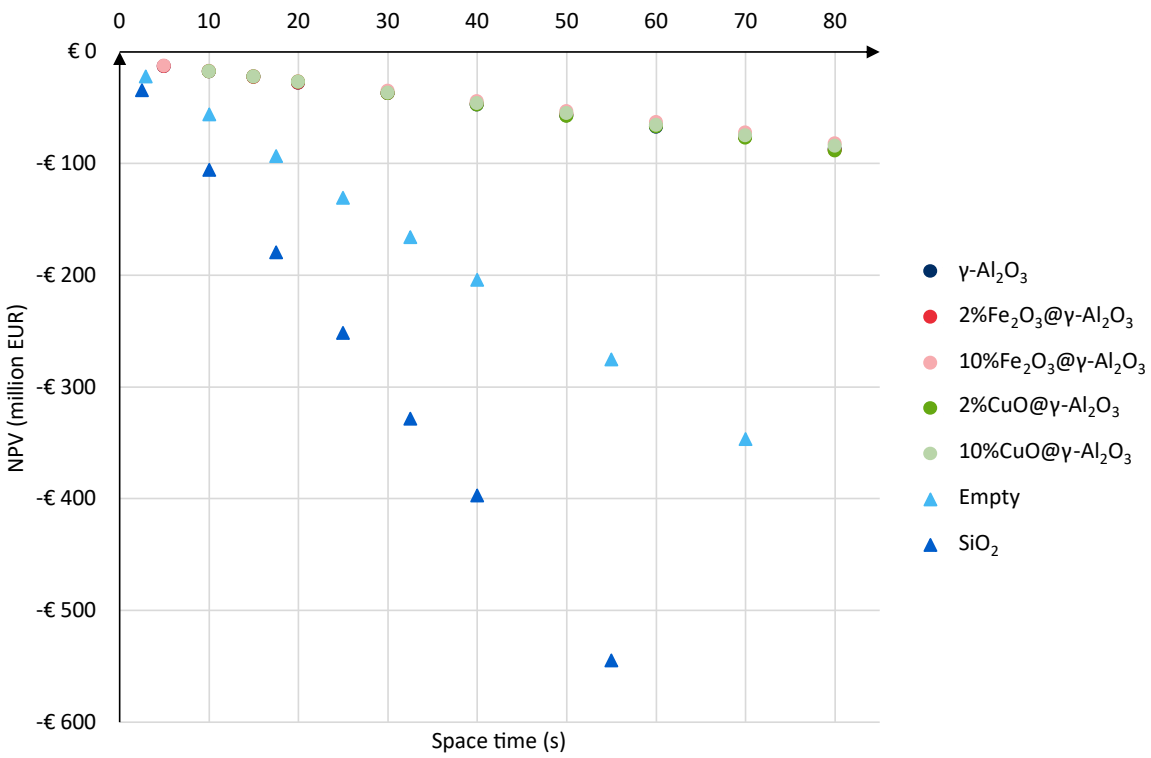


Figure 7.1: The NPV (million EUR) as a function of space time for the DBD *reactor configuration* with a gap size of 4.44 mm (circular marks) and with a gap size of 0.455 mm (triangular marks), for different packing materials.

This can be explained through **Figure 7.2**, which compares the CO_2 conversion rate (3.1) and the Specific Energy Input (SEI) (3.4) of these 63 DBD reactor configurations. **Figure 7.2** enables us to contrast the CO_2 conversion and SEI of the different *reactor configurations* and *process parameters* that were analysed in Chapters 3 & 4. This comparison brings forward several interesting observations. First of all, much higher CO_2 conversion rates are reached in the 0.455 mm reactor. The maximum CO_2 conversion rate in the 0.455 mm-reactor is 85.35% (55 s, SiO_2), in contrast to a maximum of 44.25% in the 4.44 mm-reactor (80 s, γ-Al_2O_3). However, these elevated CO_2 conversion rates for the 0.455 mm gap size are accompanied by higher levels of SEI as well. The corresponding SEI is more than 5 times higher in the 0.455 mm reactor (55 s, SiO_2) compared to the 4.44 mm reactor (80 s, γ-Al_2O_3).

The higher SEI can be explained through the difference in gap sizes. A smaller gap size reduces the available volume for the gas to interact with the plasma, i.e. the discharge (or reaction) volume is lower in a DBD reactor with a smaller gap size. When the discharge volume is reduced, the flow rate of the gas that can run through the reactor is also lower. The flow rates reached in one DBD tube range from 2.08 to 50 mL/min for the 0.455 mm gap size, and from 6.90 to 110.36 mL/min for the 4.44 mm gap size. This is illustrated in **Figure 7.3**. When looking back at the formula of the SEI, it becomes clear why the 0.455 mm reaches much higher levels of SEI:

$$SEI\left(\frac{kJ}{L}\right) = \frac{plasma\ power\ (W)}{Q\ (mL/min)} * 60\ (s/min). \tag{7.1}$$

The plasma power is kept constant for all experiments in both Chapters 3 & 4 at 30 W. Hence, the lower flow rates that can be reached in the DBD tubes with a gap size of 0.455 mm result in higher SEI.

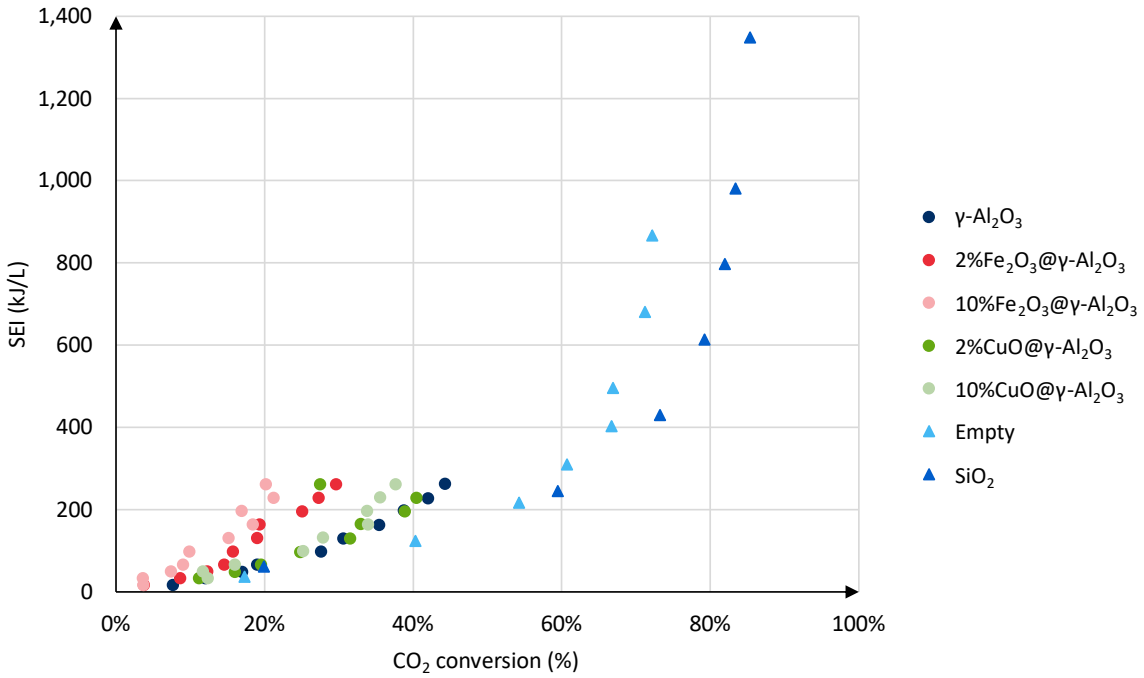


Figure 7.2: The CO_2 conversion (%) and SEI (kJ/L) for the DBD *reactor configuration* with a gap size of 4.44 mm (circular marks) and with a gap size of 0.455 mm (triangular marks), for different packing materials.

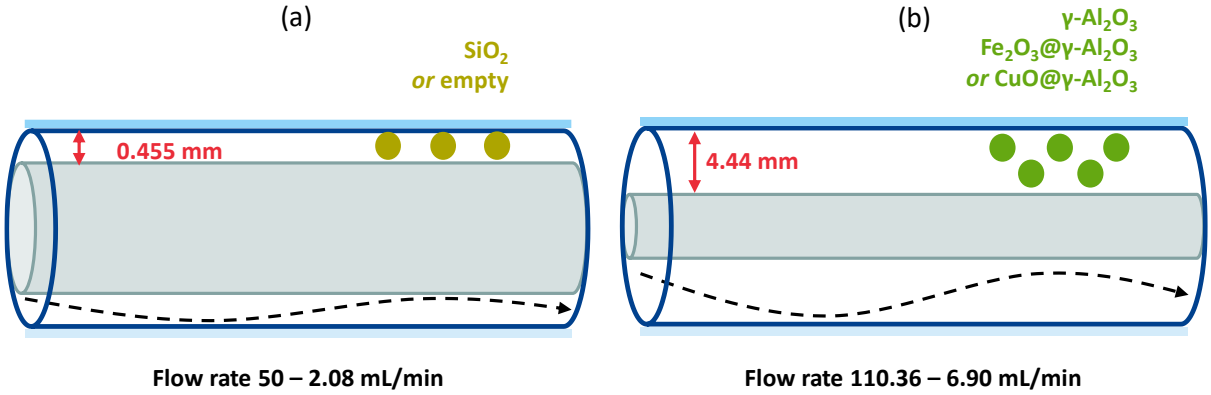


Figure 7.3: Comparison of the tested *reactor configuration* with a gap size of 0.455 mm in Chapter 3 (a) and a gap size of 4.44 mm in Chapter 4 (b).

These higher levels of SEI translate into higher levels of electricity consumption for the 0.455 mm reactor, and hence increased expenses for electricity, which explains the large differences observed in the NPV in **Figure 7.1**. In sum, the 0.455 mm reactor is not able to redeem its advantage of reaching higher CO_2 conversion rates, because it is accompanied by much higher energy consumption levels as well. Hence, we will focus the remainder of these Conclusions for the economic assessment on the DBD reactor with a gap size of 4.44 mm (Chapter 4).

In this DBD reactor, five different types of packing materials were introduced. Based on **Figure 7.1**, it is hard to distinguish between these five γ-Al_2O_3-based packing materials. **Figure A.4.11** presented the NPVs for these 48 reactor configurations separately. The NPVs are the highest at shorter space times. **Figure 7.4** presents the NPVs for the five γ-Al_2O_3-based packing materials at a space time of 5, 10 and

15 s. From this figure, it can be seen that the *reactor configuration* with the 10% Fe_2O_3@γ-Al_2O_3 results in the highest (that is, least negative) NPVs. However, the differences in NPV between the five tested packing materials are very small.

Taking a closer look at **Figure 7.2**, it can be seen that for the same level of SEI, the conversion rates reached with the Fe_2O_3@γ-Al_2O_3 packings are lower than the rates observed for the γ-Al_2O_3 and CuO@γ-Al_2O_3 packing materials. Due to these higher conversion rates, the γ-Al_2O_3 and CuO@γ-Al_2O_3 packings indeed generate higher revenues than the Fe_2O_3@γ-Al_2O_3 packings (Figure A.4.12 (a)). The reason that the set-ups with Fe_2O_3@γ-Al_2O_3 packings still result in slightly higher NPVs can be found in the power source efficiency[24]. This was measured to be 70% for the set-up with 10% Fe_2O_3@γ-Al_2O_3 and a space time of 5 s, compared to 66% for the set-up with the γ-Al_2O_3 packing at 5 s. Because of the importance of the electricity consumption (and the associated expenses), even this small difference in power source efficiency weighs more on the NPV than the elevated conversion rates that can be reached with the other packing materials. This was also illustrated in the sensitivity analysis in Chapter 3 (**Figure 3.11**).

In sum, the most optimal combination of *reactor configuration* and *process parameters* – that is, the one that results in the least negative NPV based on **Figure 7.1** – includes the combination of a larger gap size (4.44 mm), the mixed feed of CO_2 and CH_4, a short space time (5 s) and the 10% Fe_2O_3@γ-Al_2O_3 packing. However, the differences in NPV for the *reactor configuration* with a gap size of 4.44 mm are very small at similar space times. The higher power source efficiency that is observed for the combinations with the 10% Fe_2O_3@γ-Al_2O_3 packing explains why this packing results in slightly higher NPVs. Looking at the CO_2 conversion rates and the generated revenues, however, the optimal set-up would have a more intermediate space time (30 – 40 s) and include the γ-Al_2O_3 or the CuO@γ-Al_2O_3 packing materials.

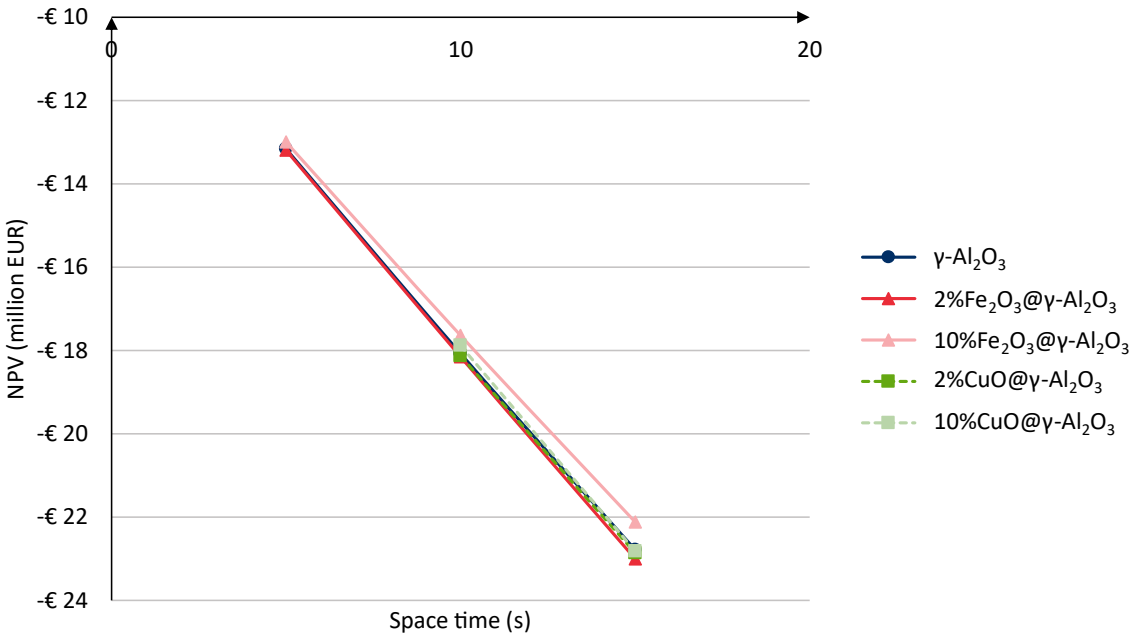


Figure 7.4: The NPV (million EUR) as a function of space time for the five packing materials, for selected space times of 5, 10 and 15 s.

[24] The power source efficiency describes how much of the supplied source power is effectively absorbed by the plasma – see Chapter 3.

In sum, the NPVs are currently negative, indicating that the performance of the plasma catalysis in the DBD reactor must be improved before it can be commercialized. Identifying the most optimal combination of *reactor configuration* and *process parameters* is not straightforward, due to the trade-off between the conversion rate and SEI.

7.1.2 An environmentally desirable configuration of the DBD reactor

The second research question in Chapter 1 addressed the environmental aspect:

2. *How do variations in the design of the DBD plasma technology, for the plasma-catalytic conversion of CO_2, translate into environmental impacts for the CCU value chain as a whole*?

To answer this research question, a Life Cycle Assessment (LCA)-tool was developed in Excel, similar to the TEA-tool, that allowed us to translate the whole experimental dataset for the different combinations of *reactor configurations* and *process parameters* into environmental impacts with one click. This LCA-tool was developed and applied in Chapter 4, to evaluate the environmental impacts of the *reactor configuration* with a gap size of 4.44 mm. The development of the LCA-tool is again associated with several advantages. First, performing an LCA allows us to evaluate the environmental impact of the conversion of CO_2 in the DBD reactor over its full life cycle. Processes such as electricity supply, CO_2 capture and the impact of materials are accounted for in the LCA. Second, the LCA methodology has several similarities with the TEA methodology. The technical backbone that was built for the TEA, i.e. the mass & energy balances, is the same for the LCA. Therefore, this saves some work for the construction of the LCA-tool. Third, similar to the TEA, changes in technical performance are again translated into changes in environmental impacts. Finally, similar to the TEA-tool, the LA-tool was developed in such a way that its assumptions can easily be adjusted and that it can also still be deployed to analyze a new round of experiments in the future, with new combinations of *reactor configuration* and *process parameters*.

This LCA-tool has been applied to 83 combinations of *reactor configuration* and *process parameters* in total: 35 configurations of the DBD reactor with a gap of 0.455 mm (from Chapter 3) and 48 configurations of the DBD reactor with a gap of 4.44 mm (Chapter 4). In sum, the development and use of the tool enabled us to evaluate how different combinations of *reactor configuration* and *process parameters* resulted in varying environmental impacts. One of the strengths of this dissertation lies indeed in the translation of the design of the technology into economic or environmental impacts, and the explicit evaluation of how changes in the design affect these indicators.

The results from the LCA indicate that none of the tested combinations of *reactor configuration* and *process parameters* is currently able to present a net negative environmental impact. The high energy consumption of plasma catalysis is the main contributor to the global warming (GW) and fossil resource scarcity (FRS) impact. **Figure 7.5** presents the GW impact for the 63 DBD reactor configurations with a feed of CO_2 and CH_4, based on the observed performance in the laboratory. Consistent with the results from the TEA, the DBD reactor configurations with a smaller gap size of 0.455 mm have a higher GW impact than those with a gap size of 4.44 mm. The higher energy consumption levels in the 0.455 mm-DBD reactor can again be identified as the trigger for this increased global warming impact. Hence, we will focus the remainder of these Conclusions for the environmental assessment on the DBD reactor with a gap size of 4.44 mm (Chapter 4).

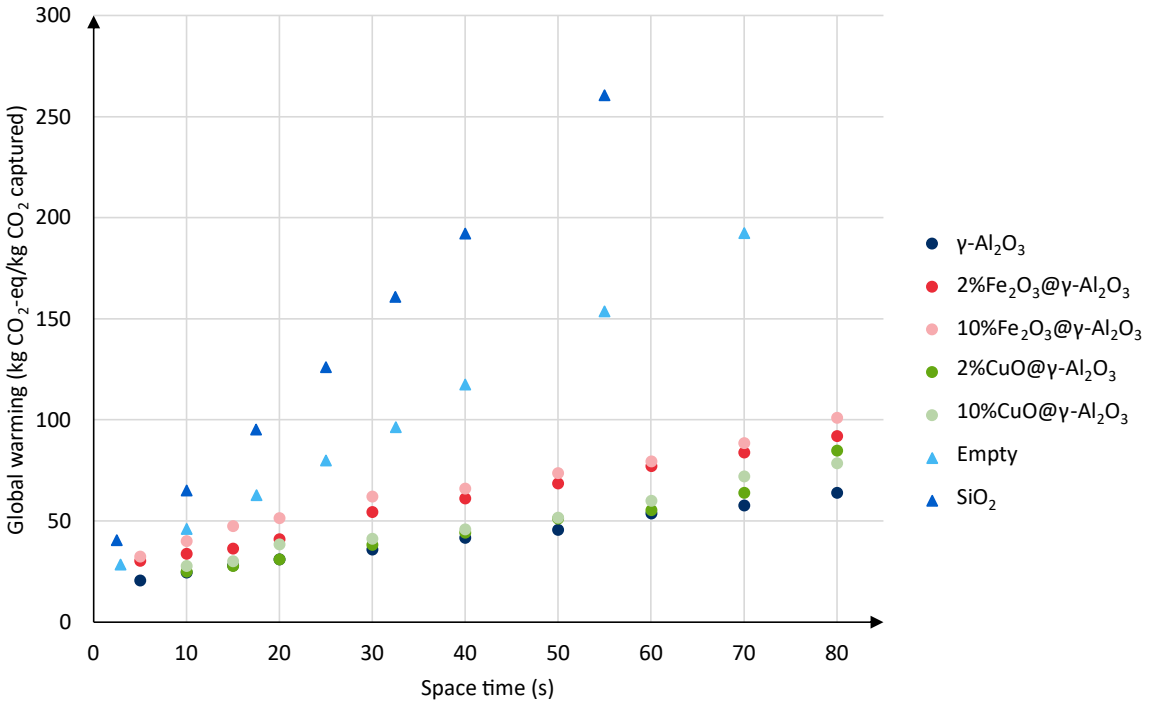


Figure 7.5: The global warming (kg CO_2-eq per kg of CO_2 captured) as a function of the space time for the DBD *reactor configuration* with a gap size of 4.44 mm (circular marks) and with a gap size of 0.455 mm (triangular marks), for different packing materials in the Laboratory scenario.

In contrast to the results of the TEA, where it was hard to distinguish between the five packing materials that were analysed based on the NPV, **Figure 7.5** gives clearer hints about the type of packing material to prefer from an environmental perspective. For each space time, the configurations with the Fe_2O_3@γ-Al_2O_3 packing materials generate the highest global warming per kg of CO_2 captured. The γ-Al_2O_3 and CuO@γ-Al_2O_3 packing materials present a more similar global warming impact. At a space time of 80 s, the ranking of packings is the clearest: the γ-Al_2O_3 packing generates the lowest global warming, followed by the 10%CuO, 2%CuO, 2% Fe_2O_3 and 10% Fe_2O_3 packings.

This ranking can be explained by the technical parameters presented in **Figure 7.2**. The CO_2 conversion rates are the highest for the *reactor configurations* with CuO@γ-Al_2O_3 and γ-Al_2O_3 packings, while the ones with a Fe_2O_3@γ-Al_2O_3 packing reach CO_2 conversion rates that are on average two times smaller (at similar space times). As a result, the *reactor configurations* with CuO@γ-Al_2O_3 and γ-Al_2O_3 packings can process more captured CO_2, because of the higher amount of CO_2 that can be converted. Since the environmental impacts are calculated per kg of CO_2 that is captured, this is reflected in **Figure 7.5**.

In Chapter 4, the LCA also included the assessment of three different technology development scenarios: (1) the Laboratory, based on the observations from the experiments, (2) the Energy-Efficient scenario, which included improvements in the energy efficiency of the technology, and (3) the Selective scenario, which combined the improvements in energy efficiency with an increase in the conversion rate. If we consider this final scenario, the role of the electricity supply in the environmental impact becomes less important and other processes start to contribute relatively more to the environmental impact. For example, the impact of CO_2 capture and the avoided impacts from the conventional production processes of the produced chemicals start to become visible in the global warming impact as well.

Based on GW impact in the Laboratory scenario, the optimal DBD plasma set-up includes the combination of a larger gap size (4.44 mm), the mixed feed of CO_2 and CH_4, a short space time (5 s) and the γ-Al_2O_3 packing material. In the Selective scenario, however, the global warming impact does not increase linearly with the space time. The lowest global warming impact is here observed for the DBD reactor configuration with a space time of 30 s and the γ-Al_2O_3 packing material. The lowest fossil resource scarcity, however, is observed at a space time of 15 s.

Figure 7.6 plots both the GW and the FRS impact into one graph, for the Selective scenario. From this figure, it is clear that the Fe_2O_3@γ-Al_2O_3 packing materials are not preferable from the environmental perspective: for the same global warming, these packing materials always present a higher fossil resource scarcity than the γ-Al_2O_3 and CuO@γ-Al_2O_3 packing materials, and vice versa, for the same fossil resource scarcity, a higher global warming impact is observed with the Fe_2O_3@γ-Al_2O_3 packing materials. For three combinations with the 10%Fe_2O_3@γ-Al_2O_3 packing, we even still found a positive fossil resource scarcity (space time of 60, 70 and 80 s).

The marks for γ-Al_2O_3 and CuO@γ-Al_2O_3 packing materials are much closer to each other. At first, when the space time lengthens from 5 to about 30 s, both global warming and fossil resource scarcity decrease. However, once the space time extends further to 80 s, both the global warming and fossil resource scarcity start to increase again. Depending on the objective of the CCU project, other choices for the combination of *reactor configuration* and *process parameters* can be made. If the main goal is to reduce global warming impact, the set-up with γ-Al_2O_3 packing at a space time of 30 s should be selected. If, however, the main objective is to limit fossil resource scarcity, set-up with γ-Al_2O_3 packing at a space time of 15 s should be chosen. In between these two marks, the set-up with 10% CuO@γ-Al_2O_3 packing (30 s) also presents both a low fossil resource scarcity and global warming impact.

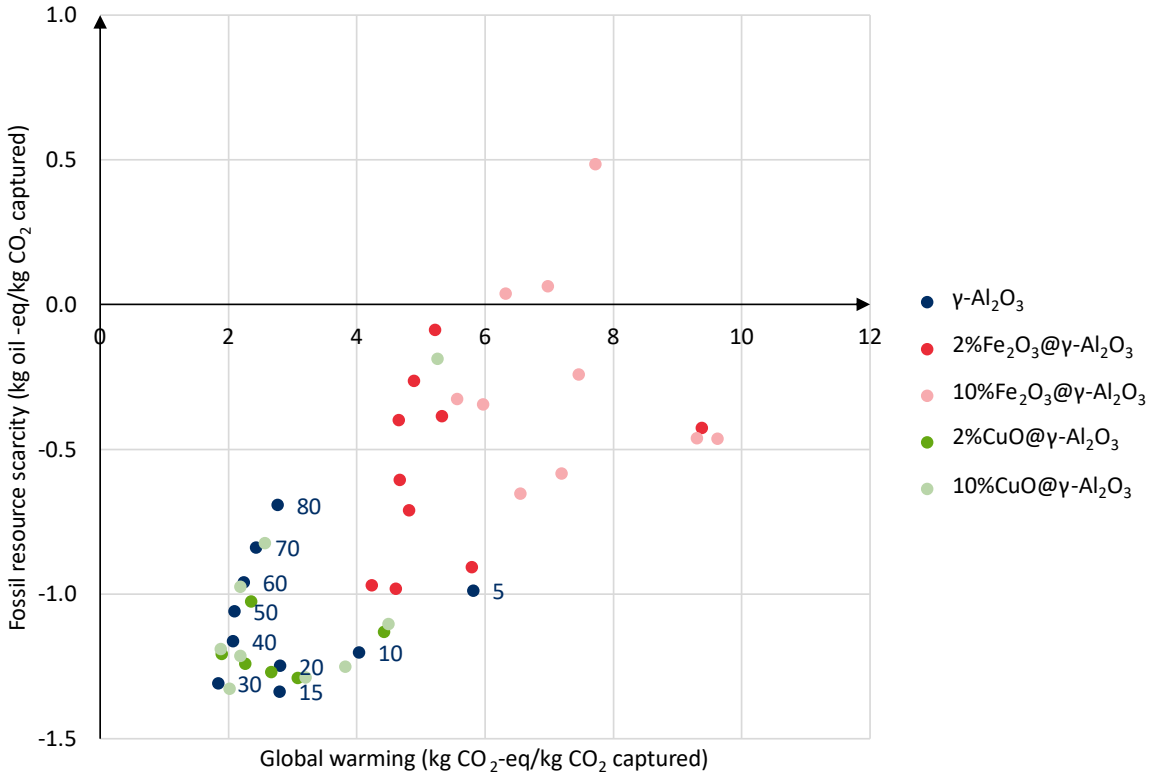


Figure 7.6: The global warming (kg CO_2-eq per kg of CO_2 captured) and the fossil resource scarcity (kg oil-eq per kg of CO_2 captured) for the DBD reactor with a gap size of 4.44 mm, for different packing materials in the Mature Performance scenario.

In sum, based on the performance in the Laboratory, both the global warming impact and the fossil resource scarcity of the technology are currently positive, indicating that the performance of plasma catalysis must be improved before it is environmentally desirable to invest in these technologies. While it was not straightforward to choose between the Fe_2O_3@γ-Al_2O_3 packing materials and the γ-Al_2O_3 and CuO@γ-Al_2O_3 packing materials based on the economic results, this choice is more evident from the environmental perspective. The results from the LCA indicate that *reactor configurations* with the Fe_2O_3@γ-Al_2O_3 packing materials always generate the highest environmental impacts. The choice between the γ-Al_2O_3 and CuO@γ-Al_2O_3 packing materials and the selection of the space time is less obvious. Depending on the preferences of the decision-maker, the optimal combination of *reactor configuration* and *process parameters* will be different. To minimize environmental impacts, the set-up should combine an intermediate space time of 15 to 30 s, with the γ-Al_2O_3 or CuO@γ-Al_2O_3 packing.

7.1.3 Integrating the economic and environmental perspectives

The third research question in Chapter 1 aimed to compare and integrate the economic and environmental results:

3. *What are the potential trade-offs between the economic and environmental impacts that could result in diverging design choices?*

To find an answer to this research question, the results from the TEA and the LCA were combined. The assessment of the economic and environmental performance separately could lead to diverging decisions in terms of the chosen *reactor configuration* and *process parameters*. Therefore, the economic and environmental indicators were pooled to help identify the set-up that can tick the most boxes. In contrast to other integrated assessment methods, the environmental and economic indicators were not aggregated into one weighted indicator. Aggregated indicators have the disadvantage of being more difficult to interpret, and depend on the chosen weights of each dimension. Instead, the NPV and global warming impact of the tested DBD reactor configurations were plotted against each other. **Figure 7.7** presents these economic and environmental indicators on the same graph for the *reactor configurations* with a gap size of 0.455 mm and 4.44 mm that were supplied with a mix of CO_2 and CH_4, based on their performance in the laboratory. These results indicate that none of the DBD reactor configurations that were tested in the laboratory is both economically feasible and environmentally desirable. Nevertheless, recommendations can be formulated to move towards a combination of *reactor configuration* and *process parameters* that is the most likely to become economically feasible and environmentally desirable in the future.

Figure 7.7 again illustrates the difference between the *reactor configurations* with a 0.455 mm and 4.44 mm gap size. Most of the set-ups with the 0.455 mm gap create much higher global warming and generate lower NPV, than the ones with a gap of 4.44 mm. However, because the results in **Figure 7.7** are now presented per kg of CO_2 captured, we can see that some of the set-ups with the 0.455 mm gap can generate NPVs and GW quite similar to the *reactor configurations* with a 4.44 mm gap size. This is due to the higher conversion rates that can be reached in the *reactor configurations* with the smaller gap size (**Figure 7.2**), allowing them to treat more captured CO_2. Nevertheless, the most promising results are still observed for the *reactor configuration* with the 4.44 mm gap. Hence, we will focus the remainder of this paragraph on the *reactor configuration* with a gap size of 4.44 mm.

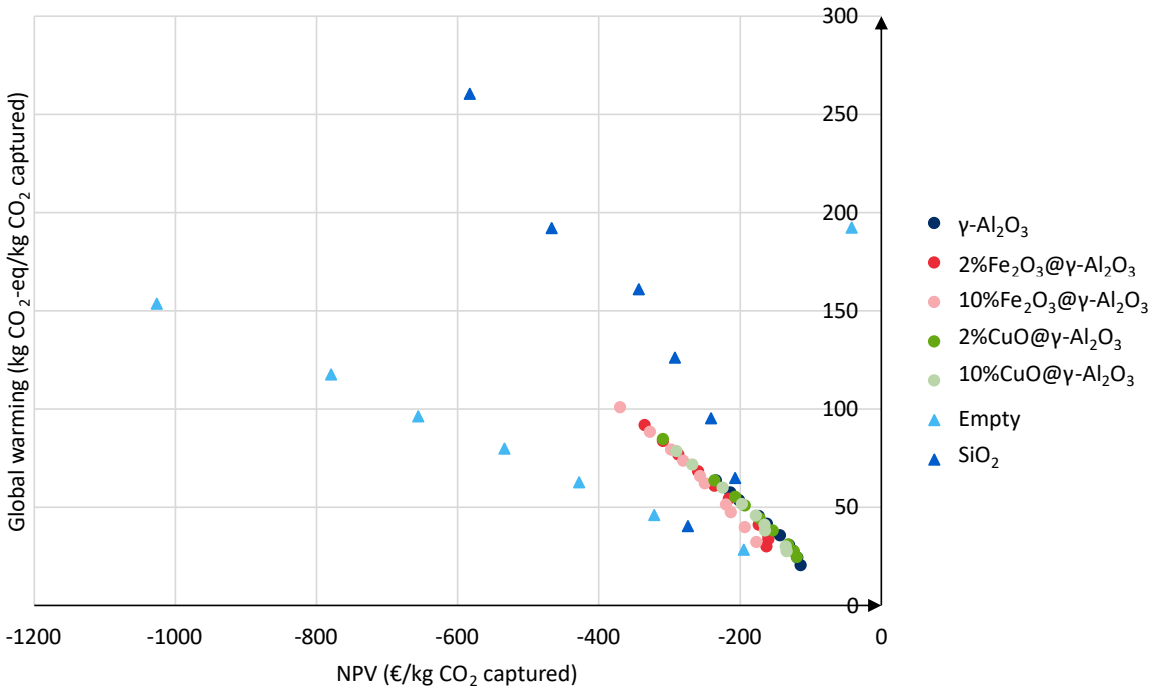


Figure 7.7: The global warming (kg CO_2-eq per kg of CO_2 captured) and the NPV (€ per kg of CO_2 captured) for the DBD reactor with a gap size of 4.44 mm (circular marks) and with a gap size of 0.455 mm (triangular marks), for different packing materials in the Lab Performance scenario.

To complete the choice of the *reactor configuration*, the packing material needs to be selected as well. The economic and environmental performance of the 4.44 mm-sized DBD reactor configurations were compared for different technology development scenarios in **Figure 4.11** (Chapter 4). In all two technology development scenarios (Laboratory and Selective), the Fe_2O_3@γ-Al_2O_3 packing materials presented a higher global warming impact than the γ-Al_2O_3 and CuO@γ-Al_2O_3 packing materials, for (almost) the same NPV per kg of CO_2 captured. As a result, the γ-Al_2O_3 and CuO@γ-Al_2O_3 packing materials should be preferred. Hence, to optimize the performance of the plasma catalysis for CO_2 conversion, both from the economic and environmental perspective, a *reactor configuration* with a gap size of 4.44 mm and γ -Al_2O_3 or CuO@γ-Al_2O_3 packings should be selected.

For the *process parameters*, the only remaining choice left is the length of the space time. Based on the performance of plasma catalysis in the Laboratory, the shortest space time of 5 s should be chosen. As the space time increases, the NPV (per kg of CO_2 captured) decreases further, while the global warming impact increases (Figure 4.11). When we consider the technological developments in the Selective scenario, the choice for the space time will differ. Up to a space time of 30 s, the NPV created per kg of CO_2 captured increases, while the global warming impact decreases. For space times longer than 30 s, a trade-off emerges between the economic and environmental perspectives: while the economic indicator continues to improve, the environmental indicator starts to deteriorate again for longer space times (Figure 4.11). These observations imply that the choice of space time depends on the technology development scenario and the decision-maker's preferences.

In sum, the plasma DBD set-up that seems the most likely to become economically feasible and environmentally desirable in the future involves a *reactor configuration* with a gap size of 4.44 mm and the γ-Al_2O_3 or CuO@γ-Al_2O_3 packing materials as catalysts. For the selection of *process parameters*, the type of feed and space time have to be discussed. A feed of both CO_2 and CH_4 offers the most possibilities in terms of end-products and also improves the CO_2 conversion rate. The

selection of space time is less evident. Based on the results from the tests in the Laboratory, the shortest space time should be selected, to minimize energy consumption and the associated costs and environmental impacts. However, when we assume that the DBD plasma will undergo various technological improvements in the future, the selection of the space time depends on the decision-maker's preferences. If the decision-maker focuses on the economic perspective, a longer space time of 70 to 80 s should be chosen. If the decision-maker attaches more importance to the environmental perspective, a space time of 30 s should be selected. These recommendations are based on the comparison of the global warming impact and the NPV per kg of CO_2 captured in the Selective scenario.

However, different choices may rise to the surface when the analysis is made with the NPV in absolute terms. Based on the current performance of the technology in the Laboratory, the *reactor configuration* and *process parameters* that currently yield the highest (i.e. least negative) NPV ànd the lowest global warming include the combination of a short space time (5 s) and the γ-Al_2O_3 packing material. Hence, when the NPV in absolute terms is considered as the economic criterium and GW per kg of CO_2 captured as the environmental criterium, a slightly different choice will be made.

In sum, none of the DBD reactor configurations is currently able to present both a positive NPV and a negative environmental impact, based on the technology's performance in the laboratory. The future projections in the Selective scenario allow for finding a reactor configuration that could yield both economic and environmental benefits (in terms of fossil resource scarcity). The comparison of the economic (NPV per kg of CO_2 captured) and environmental (GW per kg of CO_2 captured) criteria, reveals a clearer ranking for the packing materials. The *reactor configurations* with the Fe_2O_3@γ-Al_2O_3 packings present both lower economic and higher environmental impacts than the ones with γ-Al_2O_3, or CuO@γ-Al_2O_3 packings. Hence, future research for the plasma-catalytic conversion of CO_2 in the DBD reactor should focus on the latter two types of packings. However, the previous discussions also revealed that the choices made for the *reactor configuration* and *process parameters* depend on the objectives and preferences of the decision-maker, on the assumed technology development scenario and the chosen basis for comparison (in absolute terms, or per kg of CO_2 captured).

7.1.4 Investing in CCU under uncertainty

While TEA and LCA are sound methods to assess the technology as it performs today, or to evaluate how projected changes in the technology would change the results, these methods do not allow a dynamic perspective. Instead, these methods take snapshots: the performance of the technology is evaluated based on the information available at that moment. The investment decision is made now-or-never: when the NPV is greater than 0, the firm should invest, and otherwise not. In practice, however, it can often be interesting for firms to delay the investment decision and wait for more information to become available. Waiting can be particularly valuable when uncertainties are present. For example, it can be valuable for firms to postpone their investment decision and observe whether the market price of a product increases or decreases in the next period. Real options analysis presents a method to value flexibility in investment decisions, acknowledging the fact that decision-makers can and will delay investment decisions in practice (Dixit & Pindyck, 1994).

The fourth and final research question in Chapter 1 aimed to address this uncertainty that is inherent to investment decisions in novel CCU technologies and investigate how this would change the investment decision in CCUS technologies:

4. *How is the investment decision in CCUS technologies affected by technological uncertainty, i.e. the innovation pace in CCU, and market uncertainty, i.e. the CO_2 price in the EU ETS?*

In contrast to the first three research questions, the focus is not on the development of plasma catalysis as a novel CCU technology. With the final research question, the investment decision in novel CCU technologies is put into a broader perspective and compared against the investment decision in mature CCS technologies. The decision for a firm to either invest in the existing and mature CCS technology or wait for the developing but promising CCU technology is analysed. Why can this decision not be made by calculating the NPV, as in Chapter 3?

It would be possible to calculate the NPV for the existing CCS technology and the promising CCU technology today, based on our expectations for the CCU technology and based on the current CO_2 price in the EU ETS. The choice between CCS and CCU would then be determined by whichever has the highest NPV at that moment. However, two issues arise. First, the calculated NPVs do not incorporate the uncertainty on the CO_2 price in the EU ETS. This could be (partially) resolved by performing a sensitivity analysis, to investigate how the NPV changes in response to different CO_2 price levels. Second, the NPV would be calculated as if the CCU technology is already available today, while it is in practice not yet known when the CCU technology will be commercialized. Hence, this difference in availability over the years, i.e. CCS available from today versus CCU available from some future moment, should taken into account in the investment decision.

Hence, a new method was introduced in Chapter 6 to deal with these issues: real options analysis. In contrast to NPV, real options analysis enables us to calculate the value of waiting and to incorporate this in the investment decision. Real options models were developed in this thesis, to help firms identify the CO_2 price thresholds for investment in CCS, CCU or CCUS. These CO_2 price thresholds define the optimal timing to invest in CCS, CCU or CCUS and take into account the uncertainties that are present.

Two sources of uncertainty were selected; one technological and one market uncertainty. The unknown remaining time needed for the development of the CCU technology is the source of technological uncertainty that is taken into account in this thesis. The EU ETS currently includes provisions for captured CO_2 that is then transported for permanent storage (Article 12(3a) and for captured CO_2 that is then utilised in such a way that they are permanently chemically bound (Article 12(3b)) (European Commission, 2023c). Hence, the unknown future CO_2 prices in the EU ETS define the revenues that could be generated by the CCS or CCU technology and consequently, present a source of market uncertainty for the firm.

The real options models, developed in Chapter 6, were also applied to possible CCUS value chains in the cement industry. This allowed us to calculate the CO_2 price thresholds for investment in CCS, CCU or CCUS, for this specific case. Moreover, these CO_2 price thresholds were also converted into an expected time to investment, to indicate what the expected time is before the firm would invest in the CCS, CCU or CCUS value chain, i.e. how long it would take before this CO_2 price level is reached in the EU ETS. This numerical example led to the following insights regarding the impact of technological and market uncertainty on the investment decision in CCUS technologies.

First, the results from the real options analysis indicated that the inclusion of the market and technological uncertainty and the flexibility to choose the timing of the investment, led to an increase in the CO_2 price thresholds to invest in CCS, CCU or CCUS, compared to the thresholds from traditional NPV analysis.

Second, the anticipation of the arrival of a more attractive CCU solution in the future, does not result in a delayed investment in CCS. However, the technological uncertainty in itself, described by the

unknown time-to-market of CCU, does not influence the CO_2 price threshold to invest in CCS today. In other words, how long it takes for CCU to develop, does not affect the decision to invest in CCS.

Third, the market uncertainty, described by the unknown future CO_2 price, does affect the CO_2 price thresholds to invest in CCS and CCU. Two parameters describe the future evolution of the CO_2 price: the growth rate and the variance. When firms expect a higher growth rate for the CO_2 price, the CO_2 price threshold to invest in CCS or CCU today will already be lowered. The variance, however, has the opposite effect: when firms expect higher variance in the CO_2 price, i.e. more variations around the trend, the CO_2 price thresholds to invest in CCS or CCU will increase. In other words, higher uncertainty about the CO_2 price postpones the investment in CCS or CCU.

Fourth, the results of the real options analysis indicated that most of the parameters that are specific to CCU, such as the investment cost for the utilization plant or the conversion rate, do not affect the decision to invest in CCS. However, the fraction of CO_2 emissions that can be used in the CCU chain affects the investment decision in CCS in the current period: a higher fraction of CO_2 emissions that can be used in CCU, resulted in a decrease in the required CO_2 price threshold to invest in CCS today. This is a counterintuitive result: the more CO_2 can be used in the CCU route, the sooner CCS will be adopted already in the current period. This was explained through the shared investment cost for the capture plant. Firms that anticipate the arrival of a profitable CCU technology in the future, also anticipate that the investment cost for the capture plant will be supported by the CCU route and hence, they require a lower CO_2 price to invest in CCS already.

The real options models that were developed in this thesis can be applied in the future to other CCUS value chains, and in other industries that are also confronted with the possibility of adopting CCS, CCU or a combination of both.

7.1.5 Towards the design of a novel CO_2 conversion technology

Each of the answers to the four research questions that were defined in this dissertation contributed to defining an answer for the overall research question of this thesis:

How do variations in the design of a novel CO_2 conversion technology, i.e. plasma catalysis in a DBD reactor, translate into economic and environmental impacts for the CCU value chain as a whole?

The variations in the design of plasma catalysis, as a novel CO_2 conversion technology, were investigated systematically during the experiments performed at the University of Antwerp, in the context of the PlasMaCatDESIGN project. These technical observations were then translated into economic aspects in Chapter 3 (research question 1), in a TEA. In Chapter 4, an LCA was performed, translating the same set of technical observations into environmental impacts (research question 2). Both in the TEA and LCA, we did consider the impacts of plasma catalysis as CO_2 conversion technology alone. We evaluated its impacts within the CCU value chain in which it would fit, also considering the costs or environmental impacts of e.g. the capture of CO_2. The results of the TEA and LCA were compared in Chapter 4, to identify potential trade-offs between the economic and environmental perspectives (research question 3).

The results presented in Chapters 3 & 4 show how these variations translate into economic and environmental impacts for the CCU value chain, in which plasma catalysis is embedded as CO_2 conversion technology. The findings from these Chapters indicate that is useful to make these assessments, as it was not always the set-up with e.g. the highest CO_2 conversion rate that generated the best economic or environmental performance.

The development of the TEA- and LCA-tools not only enabled us to translate the current round of experiments into economic and environmental impacts but can also be used in the future to evaluate new rounds of experiments, with new variations in the design.

Finally, a Real Options Analysis was presented in Chapter 6, to analyse the investment decision in CCUS value chains in a broader context, considering various uncertainties that can play (research question 4). Chapter 6 was essential to understanding the complexities that can play in CCU(S) investment decisions and how to deal with these issues. While the NPV was the most convenient criterion to evaluate the profitability of the variations in the design of the plasma DBD reactor in Chapter 3, it is not always the right criterion to use in investment decisions for CCU(S) projects. The real options models that were developed in Chapter 6 can be used for future assessments of CCU(S) investment decisions. While this chapter contributed more indirectly to the overall research question of this dissertation, it has generated many useful insights for the development of future CCU value chains.

7.2 Summary of the main contributions

This dissertation holds the holistic assessment of a novel CCU route, i.e. the plasma-catalytic conversion of CO_2 in a DBD reactor. The thesis provides detailed insights into the economic and environmental performance of this novel CO_2 conversion technology at an early stage. Moreover, the effect of uncertainty and managerial flexibility on investment decisions in mature CCS projects, on the one hand, and early CCU technologies, on the other hand, is demonstrated. The implementation of both TEA, LCA and ROA in one thesis, applied to the development of CCU projects, allows us to demonstrate when each method can be used and which insights they generate.

The contributions of this thesis to the ongoing research in plasma catalysis specifically, and in CCU more generally, are now outlined in more detail.

In Chapter 1, plasma catalysis was introduced as a promising technology for the conversion of CO_2 into higher-value chemicals. As this technology is still under development, this provided an opportunity to steer the development and design of the technology to optimize its economic and environmental performance. Hence, a TEA and LCA were performed for 83 variants in the design of plasma catalysis, including variations in the *reactor configuration* (gap size, catalyst) and *process parameters* (space time, feed ratio). The major next step in the development of this novel technology was the design of tailor-made catalysts for the plasma-catalytic conversion of CO_2. Therefore, the focus in the TEA and LCA was on the selection of catalysts, based on the results from the TEA and the LCA.

Experiments in the laboratory, where the design of the plasma catalysis technology was varied systematically and the effect on technical parameters was observed, supplied the necessary data for the technical backbone of the TEA and LCA. In addition to the assessment of the technology as it performs today in the laboratory, scenarios with projections about the technology's development in the future were also assessed in the TEA and LCA. This allowed identifying the technical conditions that should be fulfilled, to make the technology economically feasible and environmentally desirable in the future.

Two important technical parameters of plasma catalysis are the CO_2 conversion rate and the energy efficiency. Up to now, the low energy efficiency of the DBD reactor was identified in the literature as the main technical barrier preventing the upscaling of the technology to a commercial scale (Snoeckx & Bogaerts, 2017a). The results from this thesis confirm that low energy efficiency is indeed an important barrier: the high electricity costs resulted in negative NPVs in the TEA and the environmental impact from the electricity supply accounted for the major part of the total

environmental impact in the LCA. However, this thesis also demonstrated that improving energy efficiency alone is not sufficient to make the technology ready to compete with other plasma or CCU technologies. Reaching a higher conversion rate, in combination with an improved selectivity towards high-value chemicals, is crucial as well: only with higher conversion rates, it was possible to reach a positive NPV and a net negative environmental impact. The selectivity of the process is important, such that the right chemical is targeted: one with a high market price and one that is currently produced in a production process with high environmental impacts.

In Chapter 4, the CO_2 conversion rates and energy efficiency levels that were needed to create both a positive NPV and a negative fossil resource scarcity were plotted in **Figure 4.13**. This illustrated that low CO_2 conversion rates need to be compensated by higher energy efficiency levels, and vice versa. The minimum conversion rate that had to be reached was approximately 25%, which is feasible in the current set-up. However, this conversion rate then would have to be accompanied by an energy efficiency level of about 65%, which is very high for DBD plasmas. The minimum energy efficiency level observed in Figure 4.13 is approximately 20%, paired with a CO_2 conversion of about 30%. While CO_2 conversion rates of 30% (and higher) were observed in the experiments, the associated energy efficiency levels only reach about 2% currently.

In sum, this thesis contributed to the ongoing research in plasma catalysis by

- evaluating how choices in the *reactor configuration* (gap size, catalyst) and *process parameters* (space time, feed ratio) affect the economic and environmental indicators;
- demonstrating in particular how the choice of catalyst affected the economic and environmental performance of plasma catalysis as CCU technology;
- and outlining the technical conditions that should be reached to make plasma catalysis a viable technology in the future.

This thesis not only contributed to the field of plasma catalysis but also to the growing body of research on CCU. Together with CCS, CCU is considered one of the key technologies to reach negative emissions, as mentioned in Chapter 1. CCU can generate revenues by selling CO_2-based products, while still offering environmental benefits by reducing the emission of CO_2 into the atmosphere and by reducing the dependency on fossil fuels. Hence, CCU is also mentioned as part of the EU's long-term vision to achieve net-zero emissions by 2050, as one of the strategies to reduce industrial emissions, particularly in the cement, steel and chemicals sectors.

The TEA, LCA and ROA that were performed in this thesis each created insights that can also be useful for the creation of a relevant policy framework for CCU. Although the policy framework for CCU in the EU is under development, the European Commission has already taken several steps to support CCU technologies. For example, since May 2023, the obligation to surrender emission allowances has been lifted for those CO_2 emissions that are captured and utilised in such a way that they are permanently chemically bound.

From the review of economic assessments for CCU projects (Chapter 2) and the TEA for plasma catalysis as an emerging CCU technology (Chapter 3), it could be observed that one of the major pitfalls for CCU technologies remains the high energy-related costs. CCU technologies typically have high energy requirements, to break the CO_2 molecule, which hampers the economic feasibility of CCU technologies. From the policymaker's perspective, the results imply that policy support is currently still needed to stimulate investments in CCU technologies.

The LCA (Chapter 4) demonstrated that CCU technologies have the potential to present a net negative fossil resource scarcity impact, meaning that these technologies can help reduce the dependency of

our society on fossil fuels. This reduction can be realized because CO_2 replaces fossil fuels as the source of carbon in conventional processes and hence, the consumption of fossil fuels is reduced. However, creating a net reduction in terms of global warming impact seemed to be more challenging. The results of the LCA revealed that the conversion of CO_2 in plasma catalysis generated additional global warming impact, even when taking into account the avoided impacts from the conventional production processes of the produced chemicals. Hence, the main environmental benefit of CCU seems to lie in reducing fossil fuel dependency, and not necessarily in reducing CO_2 emissions. This is in line with previous statements from Bruhn et al. (2016), who emphasized that the first objective of CCU is the reduction of fossil fuel consumption and not the mitigation of climate change. Bruhn et al. (2016) state that CCU can contribute mostly indirectly to the abatement of emissions, e.g. by supporting the transition away from fossil fuels to renewable energy. CCU can also be seen as part of the transition to a circular economy, as it enables the conversion of substances that are otherwise considered waste (i.e. CO_2 emissions) into valuable resources. In sum, because CCU technologies do not (necessarily) store CO_2 permanently and hence, guarantee the avoidance of CO_2 emissions, the CCU routes do not directly generate reductions in CO_2 emissions. CCU technologies can still create (indirect) environmental benefits, by using CO_2 as a substitute for fossil fuels in production processes.

The EU ETS directives currently include exemptions for CO_2 emissions that are captured and either permanently stored in underground geological formations, or utilised in such a way that the CO_2 emissions are permanently chemically bound. Based on the previous discussion, the inclusion of other CCU routes, where the CO_2 is not permanently bound in the product, in the EU ETS should be considered with much care. The LCA for the plasma-catalytic conversion of CO_2 indicated that this CCU route creates additional impacts, due to the energy used for the conversion, the capture of CO_2 and the materials used. Note that the LCA in Chapter 4 did not include a 'credit' for the CO_2 that was utilised, because this utilised CO_2 is indeed stored only temporarily in the products. Instead, the avoided impacts of the conventional production routes were taken into account. Nevertheless, the net global warming impact was still positive for the investigated CCU value chain. Hence, the findings from the LCA in Chapter 4 also do not pledge for accounting used CO_2 one-on-one as 'avoided' CO_2 in the EU ETS, without any further conditions. Instead, LCA could be used to calculate the net CO_2 emissions that are potentially avoided thanks to the CCU process. These calculated CO_2 emissions could then be exempted from paying emission allowances in the EU ETS. However, performing an LCA for every CCU project is probably not practically feasible. The results from the LCA in Chapter 4 indicated that the electricity supply is the main contributor to the environmental impact. To find a practical solution to include CO_2 used in CCU processes within the EU ETS, without risking that no CO_2 emission reduction is realized in practice, the European Commission could propose several conditions before the CO_2 used is exempted from emission allowances. For example, the CCU process should consume less than a certain amount of energy per kg of CO_2 used, and the energy that is consumed should be supplied from a renewable energy source. These two conditions would limit the impact of the energy supply in the CCU process significantly, and hence, make it more likely that the CCU process delivers a net reduction in CO_2 emissions.

The findings from the LCA in Chapter 4 did indicate potential reductions in fossil resource scarcity, conditional on some future developments in the technology. The European Commission has put forward the reduction of the EU's reliance on fossil fuels as an important goal, both to reduce GHG emissions and to improve energy security. Hence, the European Commission could consider the implementation of a policy that rewards firms who invest in CCU technologies to replace fossil fuels with CO_2 as a source of carbon, and consequently, reduce their consumption of fossil fuels. Today, most rewarding systems are more focused on the direct reduction of CO_2 emissions, while the reduction in fossil fuel dependency can also be very valuable.

Finally, with the real options analysis, the investment decisions in CCS and CCU were analysed, while taking into account the present technological and market uncertainties and the possibility of installing CCS and CCU together in a CCUS value chain. The results from the ROA indicated that CCS and CCU are not necessarily competing technologies. Even when a firm anticipates that a more profitable CCU technology will be available in the future, this firm will not delay its investment in CCS in the current period. This result also stems from the difference in scale between CCS and CCU. While CO_2 can be captured and stored on a large scale without limitations, the use of CO_2 is more limited depending on the market size of the CO_2-based product. As a result, the CCU technology will always have to be complemented with CCS to be able to capture all the CO_2 emissions. This can make the possibility to combine CCS and CCU in one CCUS value chain valuable. Moreover, the results from the ROA demonstrated that increasing the growth rate of the CO_2 price and ensuring a more stable CO_2 price is beneficial for both the investment in CCS and CCU. This means that policies can be installed that stimulate investments in both CCS and CCU.

In sum, this thesis contributed to the ongoing research in CCU by

- highlighting the need to reduce the energy consumption of CCU processes, both from the economic and environmental perspectives;
- demonstrating that CCU technologies are promising solutions to reduce our fossil fuel dependency and that policy frameworks should try to include this environmental benefit;
- analysing the investment decisions in CCS and CCU in a real options framework and demonstrating that these technologies can be complementary solutions.

This section attempted to outline the main contributions of this thesis, both for the plasma and for the CCU research field. To conclude this section, the main contribution of this thesis is two-fold:

1. the implementation of both TEA and LCA on a dataset that contained 83 variations in the design of plasma catalysis as a CCU technology, hence allowing us to translate the technical variations into economic and environmental metrics, being first to analyse the performance of plasma catalysis in a CCU value chain in such detail, and;
2. the implementation of ROA on investment decisions in CCUS value chains, being the first paper to analyse the potential complementary investment decision in CCU and CCS chains, considering both market and technological uncertainty.

7.3 Limitations

The limitations of this dissertation have to be recognized, to understand the conditions under which the results of this dissertation are valid.

An important limitation concerns the dataset that was available from the experiments in the laboratory. In the LADCA and PLASMANT research groups at the University of Antwerp, experiments were performed with a DBD *reactor configuration* with a gap size of 0.455 mm and a gap size of 4.44 mm. The work of Uytdenhouwen et al. (2021) describes the experiments with the 0.455 mm-sized DBD reactor, where either no packing material or a SiO_2 packing material was inserted. Seynnaeve et al. (n.d.) describe the experiments with the 4.44 mm-sized DBD reactor, which was filled with five different packing materials based on γ-Al_2O_3. These two experimental datasets combined result in 83 data points to be analysed. Despite the large number of different reactor configurations to be analysed, this dataset still has some limitations.

First, to isolate the effect of the gap size, the same type of packing materials should be tested in the DBD reactor with a gap size of 0.45 mm and 4.44 mm. Experiments have been performed previously for a 4.44 mm DBD reactor with a SiO_2 packing material (Michielsen et al., 2017). However, no data about the end products were gathered during these experiments and hence, this data could not be used for the TEA and the LCA. As a result, the 0.455 mm-sized DBD reactor is compared to the 4.44 mm-sized DBD reactor with different packing materials in this dissertation, which also makes it difficult to compare the performance of the SiO_2 packing to the γ-Al_2O_3 packing materials. For example, higher CO_2 conversion rates were observed for the *reactor configurations* with a gap size of 0.455 mm and the SiO_2 packing (triangular marks), than for *reactor configurations* with a gap size of 4.44 mm and the γ-Al_2O_3 packing (circular marks) in **Figure 7.2**. Because of the variation in both the gap size and type of packing, it is hard to identify the cause of the increased CO_2 conversion rates. However, since the SiO_2 packing was selected specifically because it has no catalytic properties (see Chapter 3), it is reasonable to assume that the higher conversion rates that were reached in this *reactor configuration* can be attributed to the smaller gap size (0.455 mm), instead of to a potential beneficial effect of the SiO_2 packing. Hence, we can still use both datasets to compare variations in *reactor configuration* and *process parameters*.

The second limitation of the dataset is that all experiments were performed at a lab scale with flow rates between 2 and 50 mL/min for the 0.455 mm-sized DBD reactor and between 6.9 and 110.4 mL/min for the 4.44 mm-sized DBD reactor. This lab scale is challenging because of the low throughputs that are realized in the laboratory. To estimate the economic and environmental impacts, the results of the experiments had to be converted to a pilot-scale DBD reactor installation. This was reached by arranging many DBD tubes in parallel, in a honeycomb structure, as demonstrated before for ozone synthesis (Kogelschatz, 2003). Conditions were imposed to make sure that the performance of the plasma technology should, theoretically, be the same after the scale-up: the SEI and the space time of the gas in one DBD tube were kept constant. However, it remains uncertain whether the same performance will indeed be maintained, if the technology is scaled up, in terms of conversion rate and energy efficiency. While the assessment of novel technologies at this lab stage imposes these additional uncertainties, it remains very valuable to perform TEAs or LCAs already at this early stage. Because the TEA and LCA are already performed based on the experiments from the laboratory, adjustments can still be made to the configuration of the DBD reactor and new experiments can be performed. Hence, this limitation was at the same time a great opportunity to steer the R&D process.

Besides the limitations that were present in the dataset that needed to be analysed in this dissertation, several limitations were also present in the applied methods.

First of all, the most important limitation – or rather simplification – concerns the separation of end-products at the outlet of the DBD reactor. The plasma-catalytic conversion of CO_2 in the DBD reactor results in one feed that contains a mix of end-products. If these products need to be sold separately – which is not necessarily the case – a separation step will be needed. In this dissertation, 83 variations in the design were analysed, each with varying compositions of the product mix. Because of the complexity of the separation processes, it was not possible to model or simulate the necessary separation steps for each combination in this thesis. Moreover, we expect that innovation will be needed in existing separation technologies before they can be deployed in combination with novel CCU technologies. Therefore, the separation was included in the TEA and LCA as a 'black box'. This approach meant that no economic or environmental impacts were included at first in the assessments for separation. In a second step, the 'Maximum Acceptable Cost' (MAC) and 'Maximum Acceptable Impact' (MAI) for separation were calculated, to assess how much (economic or environmental) impact for the separation steps would be acceptable, taking into account the impacts of the other

steps in the CCU value chain. This approach implies that the presented NPVs and environmental impacts in Chapters 3 and 4 do not yet include any impacts for separation, and consequently, underestimate the costs and environmental impacts of the whole CCU value chain. This has to be taken into account when interpreting the results. However, this approach allowed us to calculate the impacts of the other steps in the CCU value chain, even when we don't know yet which type of separation technology will be implemented, and it enabled us to define the feasible range of operation for the separation steps.

For the LCA, choosing the functional unit was an important methodological choice. In Chapter 4, the functional unit was defined as 1 kg of CO_2 captured. The LCA guidelines for CCU technologies, however, recommend using the mass of the end product as the basis of comparison, for products with an identical chemical structure as their conventional counterparts (Müller et al., 2020). The chemicals produced with plasma catalysis have the same structure as the chemicals produced in the fossil-based production process. If the functional unit had been defined as 1 kg of the end product, the environmental impacts would have been expressed per kg of end product. This impact could then be compared to the conventional production process of that specific end product, to assess whether the plasma catalysis performs better (i.e. lower impact) than the conventional production process or not. However, in this dissertation, the functional unit was not chosen as 1 kg of the end product. Because of the multitude of analysed combinations of *reactor configuration* and *process parameters*, there is not one end-product or end-product mix. Each DBD set-up resulted in a mix of end products, with different shares of each end product for each configuration. The objective of the LCA was to compare the different set-ups, analyse how variations in the design of the technology affect the environmental parameters and select the one with the lowest environmental impact. To allow comparison, the same functional unit had to be defined for the 48 combinations of *reactor configuration* and *process parameters* that were analysed in Chapter 4. While the composition of the end product mix was different for each of these combinations, the composition of the feed was the same: a mix of CO_2 and CH_4 in a one-to-one ratio. Therefore, the functional unit was defined as 1 kg of CO_2 captured, for the feed to the DBD reactor. This choice complied with the defined goal and scope of the LCA in Chapter 4. However, this choice of functional unit does not allow us to compare the results of this LCA against the results of other LCAs for the end-products, to evaluate whether the CCU route can create lower environmental impacts than the conventional route. To still account for the environmental benefits that the CCU route could create, the avoided impacts of the conventional production routes of the end-products in the mix were included in the Life Cycle Impact Assessment (LCIA). Hence, the comparison of the CCU route to the conventional production route was integrated into the LCIA itself. This enabled us to assess whether or not the CCU route could generate net negative environmental impacts.

In the ROA, several theoretical assumptions had to be made as well, which can limit the validity of the results in a practical setting. The most important assumption in the real options models concerns the eligibility of used CO_2 in the EU ETS. In Chapter 6, the assumption was made that the obligation to surrender emission allowances was lifted for all CO_2 emissions that were used. In practice, however, the EU ETS currently only includes provisions for CO_2 emissions that are utilised in such a way that they are permanently chemically bound (Article 12(3b)) (European Commission, 2023c). The CCU routes in the numerical example in Chapter 6 utilised the CO_2 emissions to produce ethanol, polyol and food-grade CO_2. None of these routes guarantee that the CO_2 is permanently chemically bound. Hence, under the current EU ETS regulations, the obligation to surrender emission allowances would not be lifted for the CO_2 emissions that are utilised in these routes would. Future revisions of the EU ETS could provide more scope for other CCU routes. However, it seems unlikely that all utilised CO_2 emissions will be counted one-on-one as avoided CO_2 emissions. Moreover, as mentioned above, this

may also not be desirable due to the additional impacts that a CCU value chain can generate. Taking into account the current regulation of the EU ETS for utilised CO_2, this would imply that project values of the investigated CCU routes no longer depend on the CO_2 price in the EU ETS. Hence, no CO_2 price threshold could be calculated for these projects. Although the assumption made in Chapter 6 involves an important simplification, compared to the current EU ETS regulation, this assumption allowed us to calculate CO_2 price thresholds for the CCU project as well. Hence, the ROA in Chapter 6 enabled us to illustrate what it means for the investment decisions in both CCS and CCU when they are both covered by the EU ETS regulations.

These limitations could also be tackled in future research.

7.4 Future research

This dissertation provides a detailed assessment of plasma catalysis as a novel CCU technology. Nevertheless, future research could address some of the questions that remain unanswered.

A natural progression of this work is to continue performing the TEA and LCA for new combinations of *reactor configuration* and *process parameters*. As mentioned above, the development of the tools for TEA and LCA in Excel, with a VBA script, allows us to rerun the assessments relatively quickly for new set-ups of the DBD plasma reactor. The experiments in the laboratory are still ongoing at the LADCA research group. Thanks to the TEA and LCA tools that were developed in this dissertation, the assessments can be rerun relatively quickly for newly tested combinations. Hence, the search for the optimal design of *reactor configuration* and *process parameters* can be continued in the future.

Further experimental studies are also needed to understand how upscaling the plasma catalysis technology would affect its technical performance. Once the technology is tested on a pilot plant scale, the implications on the economic and environmental level can also be analyzed once more.

Further work could usefully explore (1) the need for separation, and (2) if needed, which (innovative) separation technologies could fit into the CCU value chain. Depending on the downstream processes of the CCU value chain, separation of the product mix at the outlet of the DBD reactor may or may not be needed. If needed, the possible separation techniques to connect with the DBD reactor and separate the product mix should be identified. The first step here could be to model the separation process for one selected combination of *reactor configuration* and *process parameters* in more detail. When the separation is modelled in more detail, the associated costs and environmental impacts can also be estimated more specifically.

The effect of learning could also be interesting to explore in further research. In the TEA and LCA, future technology development scenarios were analysed, to asses how future improvements in the technology – due to R&D efforts – would affect the environmental and economic parameters. However, these assessments are still static by nature: no improvements are assumed during the lifetime of the technology. In practice, once the technology is put into operation, a learning effect may occur because of repeated actions, which can lead to further reductions in costs and environmental impacts. How the inclusion of learning effects in the TEA and LCA affects the investment decision would be an interesting area for further work.

Finally, the real options model could also be tweaked further in future studies. The assumption that all the used CO_2 emissions account for avoided emission allowance payments should be refined in future research. The real options analysis could be carried out again, with the assumption that only a fraction of the used CO_2 will be eligible in the EU ETS. Moreover, the real options analysis could be

expanded with a Life Cycle Assessment. It would be very interesting to assess the environmental impact of delaying the investment decision in CCS and CCU and find a way to integrate this environmental perspective into the investment decision. One of our findings in Chapter 6 was that the investments in CCS and CCU projects were postponed because firms delayed their investment decision to deal with the uncertainty about the CO_2 price in the EU ETS. However, this real options model only analysed the decision from the firm's perspective and did not take into account the environmental effects of delaying investments in CCS and CCU, and the associated costs for society. It would be an interesting challenge to integrate these two perspectives into one framework.

7.5 The CCUS value chain in Flanders

The results of this doctoral dissertation also have implications for the implementation of a CCUS value chain in Flanders.

The Flemish government recognizes CCUS as part of the solution to reach the climate targets in this region. Flanders has several assets that make the region uniquely positioned to implement CCUS value chains successfully (Vlaamse regering). Flanders is an innovative region, with the necessary knowledge in-house for the future development and implementation of the CCUS value chain. The port of Antwerp-Bruges, which is the largest exporting port and host to the largest chemical cluster in Europe, also entails several opportunities for CCUS. The port can become a CO_2 hub in the future, where CO_2 capture, transport, storage and utilisation can be interlinked. The chemical cluster in the port is an important source of (highly concentrated) CO_2 emissions. The fraction of CO_2 emissions that can be utilised, should be used on-site and converted into high-value chemicals, while the remaining fraction of CO_2 emissions can be shipped to Norway or the Netherlands for permanent storage. Not only the port of Antwerp-Bruges but also the presence of the steel and cement industry in Flanders turns CCUS into a very appealing solution to reduce CO_2 emissions. The IEA recognizes CCUS as a key technology to reduce CO_2 emissions in hard-to-abate industries, such as the cement and steel industry (IEA, 2019b). ArcelorMittal, the largest steel producer in Belgium, emitted an average of 9.7 Mt of CO_2 per year for the period 2005-2019 (Poortmans, 2021). In 2021, the cement industry was responsible for more than 2.6 Mt of CO_2 emissions in Belgium (Klimaat.be, 2023b). For reference, the total amount of GHG emissions in Belgium reached 110 Mt of CO_2-equivalents (Klimaat.be, 2023a). In recent years, efforts have already been made to reduce CO_2 emissions in the steel and cement industry, e.g. by reducing energy consumption and cutting material consumption. To continue the reduction of CO_2 emissions in these industries, innovative solutions will be needed. The proximity of the North Sea presents another unique opportunity in this context. The North Sea is an ideal location to build more offshore wind turbines. Together with Denmark, Germany, the Netherlands and the United Kingdom, Belgium aims to turn the North Sea into the "Green Power Plant of Europe" (FOD economie, 2023). This ambition is in line with the creation of a CCUS value chain, for which huge amounts of green power will be necessary.

Although CCUS presents many opportunities for Flanders, several challenges will have to be tackled first.

For the conversion of CO_2 in CCU routes, the high energy requirements indeed remain one of the main bottlenecks. This was also demonstrated in the results of the TEA (Chapter 3) and the LCA (Chapter 4), where the high energy consumption of the plasma-catalytic process hampered the economic profitability and the emission reduction potential of the technology. To overcome this challenge, sufficient low-carbon energy must be available to power the CCU processes. Hence, renewable energy

production should be increased further in Flanders. Renewable energy is known for its intermittent character, because of variations in windspeed and hours of sun.

In this context, one important benefit of plasma catalysis was not yet valued in this thesis: plasma catalysis is a turnkey process, which means that it can easily be switched on and off without long waiting times. This makes plasma catalysis a perfect candidate to use in combination with renewable energy sources. At moments of excess wind or solar energy, the plasma catalysis can be switched on and used to convert CO_2 into e.g. hydrogen (H_2), which can act as an energy carrier. During periods with a shortage of renewable energy, the H_2 can then again be converted into electricity. Hence, plasma catalysis as CCU technology can help to stabilize the grid. One caveat has to be made: not only the plasma catalysis itself, but the downstream processes have to be switched on and off quickly as well, in response to the fluctuations in renewable energy supply. This means that the separation of the product mix, to purify the H2, needs to be a turnkey process as well. This is an important condition for a separation technology to fit in the CCU value chain, if energy stabilization is (one of the) objective(s).

Another challenge for CCS in Flanders is the lack of potential for long-term storage in Belgium or Flanders, according to the Flemish government. Hence, long-distance transport of CO_2 will probably be necessary, to transport the captured CO_2 to the Netherlands or Norway. The Northern Lights project in Norway aims to provide CO_2 storage capacity for third parties and would offer a storage capacity of up to 5 Mt of CO_2 per year, from 2024. However, the transport of CO_2 also has a cost and contributes to the emissions over the entire CCUS value chain. Hence, it may be more profitable to use the CO_2 on-site, to avoid the transport of CO_2 overseas.

As shown in this dissertation, CCU and CCS can complement each other in a CCUS value chain (Chapter 6). CCS is already a more established solution and has virtually no limits to its scale, whereas most CCU technologies are still in development and are limited in scale depending on the market size of the CCU products. The real options analysis in this thesis showed that CCU and CCS can be complementary solutions and that they don't need to be competitive. While firms wait for the arrival of a (more profitable) CCU solution, their investment decision in CCS is not necessarily postponed. With CCS, firms can in theory capture and store all of their remaining CO_2 emissions. Nonetheless, it can be interesting to integrate both CCS and CCU in a CCUS value chain. The inclusion of CCU can help to limit the transport and storage cost, for that part of the CO_2 emissions that can be used in the CCU route, and helps to generate revenues while reducing CO_2 emissions.

Again, the port of Antwerp-Bruges seems the perfect location to develop a CCUS hub, where both CCU and CCUS can be integrated and be part of the solution to reduce CO_2 emissions and support the transition to renewable energy.

Flanders holds all the cards to develop a CCUS value chain that can contribute to the reduction of CO_2 emissions. This thesis can help to find the most optimal design of the CCU technology to fit in a future CCUS value chain in Flanders.

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