UNIVERSITÉ DU QUÉBEC À MONTRÉAL

CREATING CO_2 CAPTURE, RECOVERY AND VALORIZATION PROCESSES WHILE AVOIDING ENVIRONMENTAL BURDEN SHIFTING: HOW TO INTEGRATE LIFE CYCLE ANALYSIS FROM THE INITIAL PROCESS DESIGN PHASE

DISSERTATION
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CRÉER DES PROCÉDÉS DE CAPTATION ET DE VALORISATION DU CO_2 SANS DÉPLACER L'IMPACT AILLEURS : COMMENT INTÉGRER L'ANALYSE DU CYCLE DE VIE DÈS LA PHASE INITIALE DE CONCEPTION DES PROCÉDÉS

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LIST OF ABBRAVIATIONS

CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CDU	Carbon dioxide utilization
DALY	Disability-adjusted life year
DMC	Dimethyl carbonate
DME	Dimethyl ether
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
ISO	International Standard Organization
$kgCO_2eq$	Kilogram of carbon dioxide equivalent
LCA	Life cycle assessment
MEA	Monoethanolamine
MTO	Methanol to olefin
NRE	Non-renewable energy
$PDF.m^2.yr$	Potentially disappeared fraction of species over one square meter in one year
RE	Renewable energy

SESRG	Sorption-enhanced steam reforming of glycerol
SMR	Steam methane reforming
TRL	Technology readiness level

RÉSUMÉ

Afin d'éviter des changements climatiques catastrophiques, les industries augmentent leurs efforts pour réduire les émissions de gaz à effet de serre. Au cours des dernières décennies, de nombreuses technologies ont émergé pour capturer le CO_2 émis par les grandes entreprises. La capture et le stockage de carbone « CSC » et la capture et l'utilisation de carbone « CUC » sont deux technologies émergentes qui ont été récemment le sujet d'une attention considérable. Dans ce contexte, le projet FRQ-GES "Valorisation du CO_2 émis par les grandes industries : source de richesse et d'indépendance face aux combustibles fossiles" vise à générer des produits chimiques à partir du CO_2 capté au Québec. Le méthanol et les carbonates cycliques sont deux molécules d'importance qui peuvent être produites à partir du CO_2 capté. Cependant, même si l'impact lié au réchauffement climatique est réduit par la mise en œuvre de ces voies CUC, il est possible que les impacts environnementaux liés aux autres catégories d'impacts augmentent. Donc, dans le cadre du projet FRQ-GES, nous visons à créer un outil d'évaluation des impacts environnementaux du cycle de vie des procédés de production de ces deux produits chimiques à partir de CO_2 capté, de manière à guider en amont la conception durable des procédés en fonction de leur future de mise en œuvre. Dans ce but, la méthode d'analyse du cycle de vie « ACV » a été appliquée afin d'évaluer les impacts environnementaux de ces procédés, d'optimiser les procédés avec le moins d'impacts environnementaux et de guider la conception durable de ces procédés. Donc, dans cette étude les analyses préliminaires du cycle de vie de la production de ces deux produits chimiques à partir de CO_2 capté ont été réalisées, les points chauds et les principaux contributeurs aux impacts ont été identifiés. Les alternatives innovantes ont été également analysées. Enfin, à la suite de ces travaux de recherche, un outil simplifié de conception durable de ces procédés a été créé. Cet outil permet à partir d'un questionnaire parcimonieux à l'attention des concepteurs de procédés de prédire l'impact du cycle de vie du futur procédé et de comparer les différentes alternatives de conceptions dès l'étape du laboratoire.

Mots-clés: La capture et l'utilisation de carbone, Analyse de cycle de vie, Méthanol, Carbonates cycliques, Conception durable.

Abstract

In times of climate change concerns, focus needs to be placed on mitigating anthropogenic emissions. Carbon capture and storage (CCS) and carbon capture and utilization (CCU) are two technologies that have gained considerable attention recently. In this context, the FRQ-GES project "valorization of CO_2 emitted by large companies: source of wealth and independence from fossil fuels" aims to produce valuable chemicals from captured CO_2. Methanol and cyclic carbonates are two value-added chemicals that can be produced from captured CO_2. However, even if the global warming impact is reduced by implementing these CCU pathways, it is possible that the environmental impact of other categories increases. In this context, a holistic methodology suitable to evaluate the environmental impact of CCU at the early stage of development and to account all processes along the life cycle of CO_2-based products is Life Cycle Assessment (LCA). Thus, the main aim of this project is to integrate LCA into the process design of these two chemicals from the early stage of development. This integration will provide insights for process designer on where to set a focus in their research in order to lower the environmental impacts of their CCU processes such as improving the hydrogen source, developing a novel catalyst to lower the temperature and pressure of the reaction, etc. In this study, life cycle assessments of production of these two chemicals were carried out, hot spots and main contributors to the impacts were identified and innovative alternatives were analysed. Finally, a simplified tool was created in order to guide the sustainable design of the processes from the laboratory stage.

Keywords: Carbon capture and utilization, Life cycle assessment, Methanol, Cyclic carbonates, Sustainable design

CHAPTER I

INTRODUCTION

Global anthropogenic CO_2 emissions have increased over the last decades affecting the radiative balance of the earth, the earth's climate pattern and causing global warming (Chauvy et al., 2019, Crippa et al., 2019). The main sources of such emissions are related to energy production, industrial sectors and activities related to forestry, land use and land use changes (Edenhofer et al., 2014). According to Intergovernmental Panel on Climate Change (IPCC), human influence has warmed the atmosphere, ocean and land. The report also states that during the 21st century global warming of 2°C will be surpassed unless CO_2 and other greenhouse gas emissions decrease drastically in the coming decades (IPCC, 2021).

To address the urging challenge of climate change, focus needs to be placed on mitigating anthropogenic emissions and technical measures have to be developed along with political measures (UNFCC). Conventional mitigating efforts include decarbonization technologies and techniques such as renewable energy, fuel switching, efficiency gains and nuclear power (Fawzy et al., 2020). However, there are process-related emissions which cannot be avoided. For some industries such as cement, iron and steel, aluminum, paper, pulp and refineries CO_2 emissions are inherent due to the raw material conversion processes (regardless of the type of power supply) (Wang et al., 2016).

Alternatively, for these processes there are opportunities to capture CO_2 from the emitting point sources to prevent the increase of CO_2 concentration in the atmosphere (Styring et al., 2021). Such emerging carbon capture options include carbon capture

and storage (CCS) and carbon capture and utilization (CCU) technologies. The difference between CCS and CCU technologies is that in CCS option, the separated and captured CO_2 is transported and stored in geological reservoirs for very long periods while in CCU technology, the captured CO_2 is used as feedstock for different industrial applications and other processes, which represents a new economy based on CO_2 (Pérez-Fortes et al., 2016, Styring et al., 2021).

In recent years, the interest in replacing fossil fuels by captured CO_2 has experienced a very dynamic growth in chemical industry using fossil fuels. Both feedstock and energy supply are set to be the largest drivers of world oil consumption by 2030, which will lead to the fossil resource depletion (Kätelhön et al., 2019). Also, GHG emissions from the chemical industry need to be reduced by adapting new low-carbon production processes (Aldaco et al., 2019). In this context, CCU, also called as Carbon Dioxide Utilization (CDU) or CO_2 Recycling, has attracted more attention from industry and academia, as shown by the growth in the number of publications since 2012. It was claimed that CCU may play a role not only in mitigating climate change but also in reducing our dependency on fossil fuels by providing valuable CO_2-based products from captured CO_2 (Bruhn et al., 2016 Styring et al., 2021). Kätelhön et al. 2019 estimated that CCU technologies have the potential to reduce annual GHG emissions by up to 3.5 Gt CO_2eq (Kätelhön et al., 2019) where CO_2 stream of a sector could be a feedstock for the value chain of another industry, participating in the concept of circular economy (Artz et al., 2018).

Conventional CO_2 capture technology for both CCU and CCS pathways is based on the use of chemical amine solvents such as monoethanolamine (MEA). However, the solvent regeneration for the CO_2 capture process needs the use of high amounts of heat or steam. Moreover, this solvent suffers from other environmental issues such as generating the heat-stable salts and toxic sludges. In this context, other technologies

have also been implemented for capturing CO_2 including UNO MK3 (a participating potassium carbonate separation process) and CO_2 Solution technology. CO_2 Solution Inc (CSI) (recently bought by *Saipem*) has developed a new technology based on a non-toxic low-cost, stable salt solution as an absorption solution and the carbonic anhydrase enzyme as a catalyst with significantly lower environmental impacts than the MEA and UNO MK3 technologies (Saunier et al., 2019).

According to the International Energy Agency, chemicals, fuels, building materials and fertilizers are some of the products that can be produced from captured CO_2 (International Energy Agency, 2019). The production of chemicals from captured CO_2 consists in the conversion of CO_2 to products such as methanol, methane, dimethyl ether (DME) and dimethyl carbonate (DMC), among others (Styring et al., 2021).

1.1 Synthesis of chemicals from captured CO_2

The concept of CO_2 utilization for the synthesis of materials was investigated in chemical research for the first time in the 1970s and it began to be considered as a climate change mitigating option from the late 1980s (Aresta, 2010, Metz et al., 2005, Bruhn et al., 2016). CO_2 can be converted into a wide variety of end products such as chemicals and fuels. It has been estimated that near-term utilization potential of CO_2 for chemical production ranges from 200 Mt a^{-1} and 2 Gt a^{-1} for fuels (Quadrelli et al., 2011). According to Chauvy et al. 2019, methanol, dimethyl carbonate (DMC) and methane are the most promising CO_2-based chemicals which are suitable for short-term deployment (Chauvy et al., 2019). For methanol and methane, it is due to the maturity of their manufacturing technology, size of the market potential and the applicability of these chemicals. The interest in DMC is because of the lower toxicity of CO_2-based production route than its conventional production pathway (Chauvy et al., 2019, Styring et al., 2020). Styring et al. 2020 conducted an exhaustive literature review on the most studied CO_2 based chemicals in recent years. According to their study,

methanol represents the highest share of the literature examined for synthesis of chemicals from captured CO_2 and CO_2-based methanol synthesis has received significant attention over the past decade. The share of the widely studied chemicals produced from captured CO_2 is presented in Figure 1.1 (Styring et al., 2020).

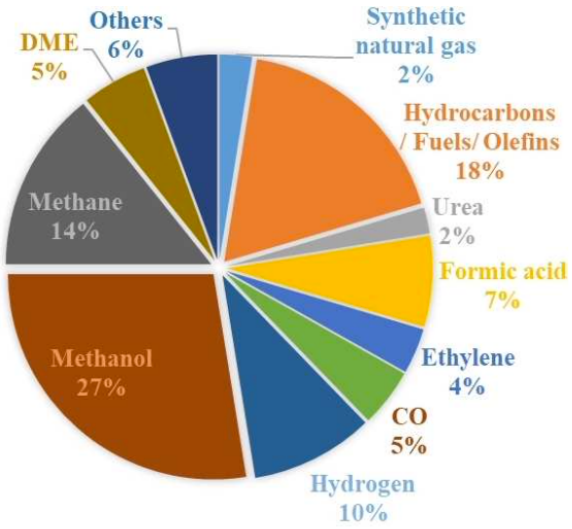

Figure 1.1. The most widely studied chemicals produced from captured CO_2 (from Styring et al., 2020).

In this context, CO_2 can be captured from specific point sources such as fossil-fuel power plant or directly from the atmosphere before being converted to energy carriers and commodity chemicals. However, the environmental benefits of CCU production pathways depend on the energy efficiency of CCU processes (Von Der Assen et al., 2014). While CO_2 utilization could be considered as an option for mitigating climate change, it has to be taken into account that both CO_2 capture and CO_2 utilization demand substantial amount of energy and materials and the environmental benefits of CCU processes cannot be taken for granted (Artz et al., 2018). Capturing CO_2 requires energy inputs, equipment and working materials such as solvents. Likewise, utilization

of CO_2 needs using highly energetic reactants such as molecular hydrogen or epoxides, or energy such as electricity to activate the chemically inert CO_2 molecule. Thus, it is questionable whether the environmental impacts of new CO_2-based products are less than their conventional counterparts (Von Der Assen et al., 2014). Also, as a key driver for CO_2 utilization is the reduction of the global warming impact, most environmental studies often focus on carbon emissions and global warming (Pérez-Fortes et al., 2016, Sternberg et al., 2017). However, even if CCU technologies can potentially reduce global warming, other questions may arise including how it may affect other environmental impacts such as human health and ecosystem quality? (Styring et al., 2021). Hence, a holistic assessment to quantify the adverse environmental impacts of CCU technologies is needed. Moreover, many alternative process schemes and options for a CCU product exist with different environmental impacts. Therefore, early-stage evaluation of CO_2-based products is necessary in order to identify the most promising CCU products and production pathways out of many candidates and predict whether a product is more environmentally friendly than another one (Von Der Assen et al., 2014, Roh et al., 2020).

1.2 Analyzing the environmental impacts of CCU products

Regarding CCU novel technologies, the supply of energy and the use of high-energetic co-reactants may cause indirect CO_2 emissions which will increase other environmental impacts. Therefore, for the new CCU products to be competitive with conventional fossil-based products, it is essential that their potential environmental impacts or benefits are fully evaluated as early as possible. Furthermore, analyzing the environmental impacts of CCU production systems is necessary in order to avoid environmental burden shifting between life cycle stages and different impact categories. However, assessing such environmental impacts is challenging due to the high required amount of data and calculations required for quantitative assessment. In this context, a holistic methodology suitable to evaluate the environmental impact of

CCU at the early stage of development and to account all processes along the life cycle of CO_2-based products is Life Cycle Assessment (LCA) (von der Assen et al., 2013, Artz et al., 2018, Styring et al., 2021).

1.3 Life cycle assessment

LCA is a standardized methodology for assessing the environmental impacts of a product or a service along its entire life cycle, including the extraction of raw materials, the production processes, the product use and the final disposal (ISO, 2006 a, ISO, 2006 b). LCA has gained wide acceptance in recent years and according to ISO 14040/14044, it is divided to four interdependent phases:

1. Goal and scope definition: in this phase the goal and the scope of the study are defined. The functional unit which is a key element in LCA studies is also defined along with the system boundary. Also, the environmental impacts categories taken into account for the study would be defined in this phase.
2. Life cycle inventory (LCI): all input and output flows and data are collected in this phase within the system boundary and the previously defined scope.
3. Impact assessment: the collected inventory date in phase 2 are translated and aggregated into environmental impacts such as global warming, human health and ecosystem quality. Also, the obtained results in terms of environmental impacts are visualized in this phase.
4. Interpretation: in this phase the obtained results in compliance with the intended goal and scope are summarized, discussed and reviewed in order to identify the crucial hot spots. The detected hot spots should be modified to improve and optimize the process (ISO, 2006 a, ISO, 2006 b).

1.4 Integrating LCA into the early-stage design of CCU processes

Conventional technologies have been optimized for production of fossil-based products over time, while most of the CCU technologies are at the early stage of development (low technology readiness level, TRL). Thus, comparative LCA studies of CCU processes at low TRL (lab-scale process) with the already optimized conventional production processes can be challenging (Styring et al., 2021). However, integrating LCA into early-stage design of CCU processes is highly recommended to quantify the potential environmental impact reduction of CCU-based products in comparison to conventional products as early as possible. These LCAs also could help to identify hot spots, guide future research by revealing valuable insights, provide performance targets and support knowledge-based decision making (Müller et al., 2020, Styring et al., 2021).

For production of chemicals from captured CO_2, performing LCA in an integrated manner and at the very early stage of development (lab scale) can provide valuable insights to guide chemists in identifying the most promising production pathways and R&D investment for the future transition by comparing the LCA results of every available options. Performing LCA at the early stage of development is extremely helpful in identifying the origin of environmental impacts of CCU process. Such assessments also help to determine the contribution of each process to the overall environmental impacts and to identify hot spots that are responsible for the overall impacts (Von Der Assen et al., 2014). The identified hot spots guide process designers by providing useful insights on where to set their focus on the process design in order to improve the process design (Kleinekorte et al., 2020). Moreover, CCU candidates with higher environmental impacts than existing traditional branch mark products can be discarded at this early-stage evaluation (Müller et al., 2020). For CO_2-based chemicals with the identical molecular structure to conventional fossil-based products,

the functional unit of "1 kg chemical production" would be considered in comparative LCA studies. Also, regarding LCAs' focus on the comparison of two products with the same molecular structure, cradle to gate LCA (Figure 1.2) will be taken into account, where all life cycle stages after the factory gate will not be considered since they are identical for CO_2-based and conventional fossil-based products (Artz et al., 2018).

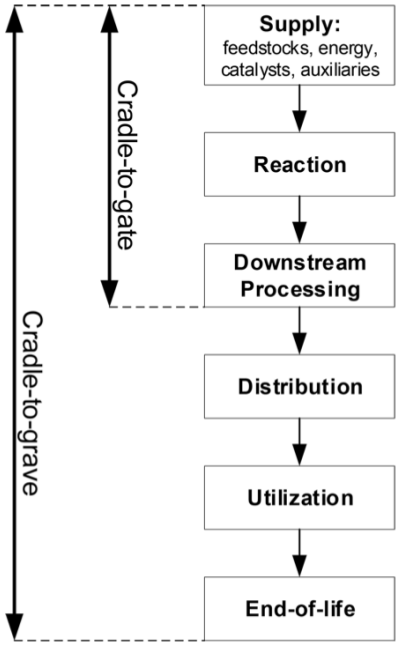

Figure 1.2. Life cycle stages of CO_2-based products (Artz et al., 2018)

Additionally, as most of the CCU processes are at the early stage of development, process data uncertainty is a major issue. For instance, performing a reliable LCA for CCU processes at lab scale is challenging due to the limited availability of data but late assessment of processes also may lead to the implementation of less sustainable ones (Von Der Assen et al., 2014, Kleinekorte et al. 2020). In order to evaluate the environmental performances of CCU processes at the early stage of development, primary and secondary data are used. Primary data will be obtained directly from the developers of the processes. However, for CCU products at lab stage the primary data

of real plant are not available and laboratory data are used as input instead for process simulations. In case of the lack of lab data, estimation methods or literature data can be used to bridge data gaps. Estimation methods include conducting second law analysis based on stoichiometric reactions, mass and energy balance (Müller et al., 2020). In addition, according to Secchi et al., 2016, in the case of a lack of inventory data for chemicals, the data can be replaced by other similar substances included in ecoinvent database (a Life Cycle Inventory database) that is called "proxy" approach. The strategy of creating a proxy inventory is based on the similarities in molecular structure, synthesis pathway, manufacturing, and refining process of the chemicals (Secchi et al., 2016). However, uncertainties resulting from assumptions and modelled data inputs need to be reported. Also, the generic and estimated data should be replaced by real values as soon as possible in order to enhance reliability and compatibility of LCA studies for CCU technologies (Müller et al., 2020, Röh et al., 2020).

1.5 Background and project objectives

Today, the chemical industry is mostly based on fossil-based feedstock which consumes large amounts of energy and materials. With this respect, the chemical industry increases its efforts to reduce the environmental impacts by transitioning toward sustainable chemical production. In recent years, the interest in carbon capture and utilization has experienced a very dynamic growth not only because of its role in mitigating climate change but also due to the fact that captured carbon dioxide can be used as a feedstock for the production of energy carriers, chemicals and materials through multiple reactions and production pathways.

In this context, the FRQ-GES project "valorization of CO_2 emitted by large companies: source of wealth and independence from fossil fuels" aims to produce valuable chemicals from captured CO_2 in Quebec. Methanol and cyclic carbonates are two chemicals that are proposed to be produced from captured CO_2 in this project.

Methanol has a wide application in the chemical industry. It can be transformed into other chemicals such as ethylene, propylene, formaldehyde, and acetic acid or can be used as a fuel for transportation (Styring et al., 2021).

Cyclic carbonates are another class of valuable chemicals that can be produced from captured CO_2. These compounds also have many applications including as a solvent replacing conventional solvents such as DMF (dimethylformamide) and DMSO (dimethyl sulfoxide) and as the electrolyte in lithium-ion batteries. Cyclic carbonates are also used as intermediates for the production of other chemicals and polymers (North et al., 2015).

The possibility of producing of these two chemicals from captured CO_2 is proposed in the efforts to mitigate carbon dioxide emission in Quebec. However, even if the global warming impact is reduced by implementing these CCU pathways, it is possible that the environmental impact of other categories increases. Thus, it is critical to integrate the life cycle assessment into the process design of these two chemicals from the early stage. It will help to optimize the environmental impact reduction and to provide insights for process designer on where to set a focus in their research. It can be by improving the hydrogen source, developing a novel catalyst to lower the temperature and pressure of the reaction, using innovative alternatives, etc.

In this context, this project (as a part of FRQ-GES project) aims to integrate the life cycle assessment into the process design of these two chemicals from the early stage of development. Along with the main objective and based on the LCA results of this integration a simplified tool to assess the environmental impacts of the life cycle of methanol and cyclic carbonates production from captured CO_2 would be created. This tool will be used by process designers to guide them from upstream steps (laboratory)

the sustainable design of the processes according to its future context of implementation.

According to the main objective, the sub-objectives consist of:

- To establish an exhaustive list of existing alternatives in terms of recovery and valorization of methanol and cyclic carbonates using captured CO_2 by an enzymatic process developed by CO_2 Solution Inc.
  Note: The technology of CO_2 Solution Inc., that has recently bought by *Saipem*, includes using low cost, nontoxic stable saline solutions in the presence of the carbon anhydrase enzyme as a catalyst for capturing CO_2. It has lower environmental impacts compared to MEA (monoethanolamine) and UNO MK3 (a participating potassium carbonate separation process) (Saunier et al., 2019).
- To carry out the life cycle analysis of the processes identified from the first sub-objective in order to determine their environmental impacts and to identify the main contributors to the impacts.
  Note: Life cycle assessment of the CO_2 capture has already been carried out by CIRAIG (Centre international de référence sur le cycle de vie des produits, procédés et services) and published (Saunier et al., 2019). It will be integrated into subsequent steps.
- To carry out the life cycle assessments of the processes identified from the first sub-objective in order to create a simplified tool for guiding the design of these processes according to their future implementation context.

The created tool, in the form of a summarized questionnaire will be used to guide the process designers to predict the environmental impacts of the life cycle of the future processes. It also allows them to effectively compare the different design alternatives from the laboratory stage as early as possible and to avoid additional potential negative

consequences associated with applying technological changes after implementation. The contribution analysis of environmental impacts will also help to identify the opportunities for improvement by focusing on "what really matters". For example, by guiding the research efforts on creating a new catalyst that allows the reaction to occur at lower pressure and temperature, improving the energy consumption of the process, finding alternative reactants, using an alternative source of hydrogen, etc.

1.6 Project outline

This study is divided as follows:

Firstly, carbon capture and utilization concept and integration of the LCA into CCU processes are discussed in Chapter one. In Chapter two, the scientific paper from this research work submitted to the "*Journal of CO_2 Utilization"* is presented. However, because this thesis has been written in a thesis by article context, it has been difficult to avoid some redundancies between the Chapter I (Introduction of the thesis) and the introduction of Chapter II. Finally, Chapter three sums up the study with the conclusions and recommendations.

CHAPTER II

CREATING CO_2 CAPTURE, RECOVERY AND VALORIZATION PROCESSES WHILE AVOIDING ENVIRONMENTAL BURDEN SHIFTING

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Abstract

Carbon capture and utilization (CCU) is a technology that has gained considerable attention recently. In this context, the FRQ-GES project "valorization of CO_2 emitted by large companies: source of wealth and independence from fossil fuels" aims to produce valuable chemicals from captured CO_2. Methanol and cyclic carbonates are two value-added chemicals that are proposed to be produced from captured CO_2. However, it is essential that the potential environmental impacts of production of these CCU chemicals are fully evaluated as early as possible. Life Cycle Assessment (LCA) is a holistic methodology suitable to evaluate the environmental impact of CCU at the early stage of development. Thus, LCA was integrated into the process design of production of methanol and cyclic carbonates from captured CO_2. For methanol production, the maximum impact reductions occur when hydroelectricity is used as a renewable energy for the entire CCU system, for capturing CO_2 from the point source and for generating H_2 by water electrolysis. Ethylene carbonate production (cyclic carbonate considered in this study) achieves the highest environmental impacts reduction for global warming and human health impact categories when CO_2 is captured by a renewable energy source and the epoxide is supplied by bioethylene oxide or from MTO pathway instead of fossil-based ethylene oxide. However, the ecosystem quality impact category increases by 10% and 16% respectively. Finally, a simplified tool was created in order to guide the sustainable design of the processes from the laboratory stage.

Keywords: Carbon capture and utilization, Life cycle assessment, Methanol, Cyclic carbonates, Sustainable design

Abbreviations

CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CDU	Carbon dioxide utilization
DALY	Disability-adjusted life year
DMC	Dimethyl carbonate
DME	Dimethyl ether
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
ISO	International Standard Organization
$kgCO_2eq$	Kilogram of carbon dioxide equivalent
LCA	Life cycle assessment
MEA	Monoethanolamine
MTO	Methanol to olefin
NRE	Non-renewable energy
$PDF.m^2.yr$	Potentially disappeared fraction of species over one square meter in one year
RE	Renewable energy
SESRG	Sorption-enhanced steam reforming of glycerol
SMR	Steam methane reforming
TRL	Technology readiness level

2.1 Introduction

Global anthropogenic CO_2 emissions have increased over the last decades affecting radiative balance of the earth, the earth's climate pattern and causing global warming (Chauvy et al., 2019, Crippa et al., 2019). The main sources of such emissions are related to energy production, industrial sectors and activities related to forestry, land use and land use changes (Edenhofer et al., 2014). According to the latest Intergovernmental Panel on Climate Change (IPCC) report released recently, global warming has been driven by human influence. The report also states that during the 21st century global warming of 1.5°C and 2°C will be surpassed in all regions unless CO_2 and other greenhouse gas emissions decrease drastically in the coming decades (IPCC, 2021).

To address the urging challenge of climate change, focus needs to be placed on mitigating anthropogenic emissions and technical measures have to be developed along with political measures (UNFCC). Conventional mitigating efforts include decarbonization technologies and techniques such as renewable energy, fuel switching, efficiency gains and nuclear power (Fawzy et al., 2020). However, there are process-related emissions which cannot be avoided. For some industries such as cement, iron and steel, aluminum, paper, pulp and refineries CO_2 emissions are inherent due to the raw material conversion processes (regardless of the type of power supply) (Wang et al., 2016).

Alternatively, for these processes there are opportunities to capture CO_2 from the emitting point sources to prevent the increase of CO_2 concentration in the atmosphere (Styring et al., 2021). Such emerging carbon capture options include carbon capture and storage (CCS) and carbon capture and utilization (CCU) technologies. The difference between CCS and CCU technologies is that in CCS option, the separated

and captured CO_2 is transported and stored in geological reservoirs for very long periods while in CCU technology, the captured CO_2 is used as feedstock for different industrial applications and other processes, which represents a new economy based on CO_2 (Pérez-Fortes et al., 2016, Styring et al., 2021).

In recent years, the interest in replacing fossil fuels by captured CO_2 has experienced a very dynamic growth as in chemical industry using fossil fuels as both feedstock and energy supply is set to be the largest driver of world oil consumption by 2030 which led to the fossil resource depletion (Kätelhön et al., 2019). Also, GHG emissions from the chemical industry are needs to be reduced by adopting new low-carbon production processes (Aldaco et al., 2019). In this overall context, CCU also called as Carbon Dioxide Utilization (CDU) or CO_2 Recycling, has attracted more attention from industry and academia (a growth in number of publications has been demonstrated since 2012) in recent years due to the claim that CCU may play the role not only in mitigating climate change but also in reducing our dependency on fossil fuels by providing valuable CO_2-based products from captured CO_2 (Bruhn et al., 2016 Styring et al., 2021). Kätelhön et al. 2019 estimated that CCU technology has the potential to reduce annual GHG emissions by up to 3.5 Gt CO_2eq (Kätelhön et al., 2019) where CO_2 stream of a sector could be a feedstock for the value chain of another industry, participating in the concept of circular economy (Artz et al., 2018).

2.1.1 Synthesis of chemicals from captured CO_2

For the first time in the 1970s, the concept of CO_2 utilization for synthesis of materials was investigated in chemical research and it began to be considered as a climate change mitigating option from the late 1980 (Aresta, 2010, Metz et al., 2005, Bruhn et al., 2016). CO_2 can be converted into a wide variety of end products such as chemicals and fuels. It has been estimated that near-term utilization potential of CO_2 for chemical production ranges from 200 Mt a^{-1} and 2 Gt a^{-1} for fuels (Quadrelli et al., 2011).

According to Chauvy et al. 2019, methanol, dimethyl carbonate (DMC) and methane are the most promising CO_2-based chemicals which are suitable for short-term deployment (Chauvy et al., 2019). For methanol and methane, it is due to the maturity of their manufacturing technology, size of the market potential and the applicability of these chemicals while, for DMC it is because of the less toxicity of CO_2-based production route than its conventional production pathway (Chauvy et al., 2019, Styring et al., 2020). Styring et al. 2020 conducted an exhaustive literature review on the most studied CO_2 based chemicals in recent years. According to their study, methanol represents the highest share of the literature examined for synthesis of chemicals from captured CO_2 and CO_2-based methanol synthesis has received significant attention over the past decade (Styring et al., 2020).

In this context, CO_2 can be captured from specific point sources such as fossil-fuel power plant or directly from the atmosphere and then it can be converted to energy carriers and commodity chemicals. However, the environmental benefits of CCU production pathways depend on the energy efficiency of CCU (Von Der Assen et al., 2014). While CO_2 utilization could be considered as an option for mitigation climate change, it has to be taken into account that both CO_2 capture and CO_2 utilization demand substantial amount of energy and materials and environmental benefits of CCU processes cannot be taken for granted (Artz et al., 2018). Capturing CO_2 requires energy inputs, equipment and working materials such as solvents. Likewise, utilization of CO_2 needs using highly energetic reactants such as hydrogen or epoxide or direct energy such as electricity to activate the chemically inert CO_2 molecule which is associated with high environmental impacts. Thus, it is questionable whether the environmental impacts of new CO_2-based products are less than their conventional counterparts (Von Der Assen et al., 2014). Also, as a key driver for CO_2 utilization is the reduction of the global warming impact most environmental studies often focus on carbon emissions and global warming (Pérez-Fortes et al., 2016, Sternberg et al., 2017).

However, another question may arise that is: while implementation of CCU technology will potentially reduce global warming impact, how it may affect other environmental impacts such as human health and ecosystem quality? (Styring et al., 2021). Hence, a holistic assessment to quantify the adverse environmental impacts of CCU technologies is needed. Moreover, many alternative process schemes and options for a CCU product exist with different environmental impacts. Therefore, early-stage evaluation of CO_2-based products is necessary in order to identify the most promising CCU products and production pathways out of many candidates and predict whether a product is more environmentally friendly than another one (Von Der Assen et al., 2014, Roh et al., 2020).

2.1.2 Analyzing the environmental impacts of CCU products

Regarding CCU novel technologies the supply of energy and using high-energetic co-reactants may cause indirect CO_2 emissions and increase other environmental impacts. Therefore, for the new CCU products to be competitive with conventional fossil-based products, it is essential that their potential environmental impacts or benefits are fully evaluated as early as possible. Furthermore, analyzing the environmental impacts of CCU production systems is necessary in order to avoid environmental burden shifting between life cycle stages and different impact categories. However, assessing such environmental impacts is challenging du to highly required amount of data and calculations. In this context, a holistic methodology suitable to evaluate the environmental impact of CCU at the early stage of development and to account all processes along the life cycle of CO_2-based product is Life Cycle Assessment (LCA) (von der Assen et al., 2013, Artz et al., 2018, Styring et al., 2021).

2.1.3 Life cycle assessment

LCA is a standardized methodology for assessing the environmental impacts of a product or a service along the entire life cycle, including the extraction of raw material, the production process, product use and final disposal (ISO, 2006 a, ISO, 2006 b) and it has gained wide acceptance in recent years. According to ISO 14040/14044, LCA is divided to four interdependent phases:

1. Goal and scope definition: in this phase the goal and the scope of the study are defined. The functional unit which is a key element in LCA studies is also defined along with the system boundary. Also, the environmental impacts categories taken into account for the study would be defined in this phase.
2. Life cycle inventory (LCI): all input and output flows and data are collected in this phase within the system boundary and previously defined scope.
3. Impact assessment: in this phase the collected inventory date in phase 2 is translated and aggregated into environmental impacts such as global warming, human health and ecosystem quality. Also, the obtained results in terms of environmental impacts are visualized in this phase.
4. Interpretation: in this phase the obtained results in compliance with the intended goal and scope are summarized, discussed and reviewed in order to identify the crucial hot spots. The detected hot spots should be modified to improve and optimize the process (ISO, 2006 a, ISO, 2006 b).

2.1.4 Integrating LCA into the early-stage design of CCU processes

Conventional technologies have been optimized for production of fossil-based products over time while, most of the CCU technologies are at the early stage of development (low technology readiness level, TRL). Thus, comparative LCA studies of CCU process at low TRL (lab-scale process) with the already optimized conventional

production processes can be challenging. However, integrating LCA into early-stage design of CCU processes is highly recommended to quantify the potential environmental impact reduction of CCU-based products in comparison to conventional products as early as possible. These LCAs also could help to identify hot spots, guide future research by revealing valuable insights, provide performance targets and support knowledge-based decision making (Müller et al., 2020, Styring et al., 2021).

For production of chemicals from captured CO_2, performing LCA in an integrated manner and at the very early stage of development (lab scale) can provide valuable insights to guide chemists in identifying the most promising production pathways and R&D investment for the future transition by comparing the LCA results of every available option. Performing LCA at the early stage of development is extremely helpful in identifying the origin of environmental impacts of CCU process. Such assessments also help to determine the contribution of each process to the overall environmental impacts and to identify hot spots that are responsible for the overall impacts (Von Der Assen et al., 2014). The identified hot spots guide process designers by providing useful insights on where to set their focus on the process design in order to improve the process (Kleinekorte et al., 2020). Moreover, CCU candidates with higher environmental impacts than existing traditional branch mark products can be discarded at this early-stage evaluation (Müller et al., 2020). For CO_2-based chemicals with the identical molecular structure to conventional fossil-based product the functional unit of "1 kg chemical" would be considered in comparative LCA studies. Also, regarding LCAs focus on the comparison of two products with the same molecular structure, cradle to gate LCA will be taken into account, where all life cycle stages after the factory gate will not be considered since they are identical for CO_2-based and conventional fossil-based products (Artz et al., 2018).

In order to evaluate the environmental performances of CCU processes at the early stage of development, primary and secondary data are used. Primary data will be obtained directly from the developers of the processes. However, for CCU products at lab stage the primary data of real plant are not available and laboratory data are used as input instead for process simulations. In case of the lack of lab data, estimation methods or literature data can be used to bridge data gaps. Estimation methods include conducting second law analysis based on stoichiometric reactions, mass and energy balance (Müller et al., 2020). In addition, according to Secchi et al., 2016, in case of lack inventory data for chemicals, the data can be replaced by other similar substances included in ecoinvent database (a Life Cycle Inventory database) that is called "proxy" approach. The strategy of creating a proxy inventory is based on similarities in molecular structure, synthesis pathway, manufacturing and refining process of the chemicals (Secchi et al., 2016). However, uncertainties resulting from assumptions and modelled data inputs need to be reported. Also, the generic and estimated data should be replaced by real values as soon as possible in order to enhance reliability and compatibility of LCA studies for CCU technologies (Müller et al., 2020, Röh et al., 2020).

2.1.5 Research objectives

Today, the chemical industry is mostly based on fossil-based feedstock which consumes large amounts of energy and materials. With this respect, the chemical industry increases the efforts to reduce their environmental impacts by transition to the sustainable chemical production.

In this context, the FRQ-GES project "valorization of CO_2 emitted by large companies: source of wealth and independence from fossil fuels" aims to produce valuable chemicals from captured CO_2 in Quebec. Methanol and cyclic carbonate are two chemicals that are proposed to be produced from captured CO_2 in this project.

Methanol has a wide application in chemical industry. It can be transformed into other chemicals such as ethylene, propylene, formaldehyde, acetic acid and other chemicals or can be used as a fuel for transportation (Styring et al., 2021).

Cyclic carbonates are another valuable chemical that can be produced from captured CO_2. These compounds also have many applications including as a solvent replacing conventional solvents such as DMF and DMSO and as the electrolyte in lithium-ion batteries, as the battery sector and electric transportation are among the priorities of Quebec government. Cyclic carbonates are also used as intermediates for the production of other chemicals and polymers (Comerford et al., 2015).

The possibility of production of these two chemicals from captured CO_2 is proposed in the effort to mitigate carbon dioxide emission in Quebec. However, even if the global warming impact is reduced by implementing these CCU pathways, it is possible that the environmental impact of other categories increases. Thus, it is critical to integrate the life cycle assessment into the process design of these two chemicals from the early stage in order to optimize the environmental impact reduction and to provide insights for process designer on where to set a focus in their research such as improving the hydrogen source, developing a novel catalyst to lower the temperature and pressure of the reaction, using innovative alternatives, etc.

In this context, this study aims to create a simplified tool to assess the environmental impacts of the life cycle of methanol and cyclic carbonates production from captured CO_2 in order to guide from upstream steps (laboratory) the sustainable design of the processes according to its future context of implementation.

According to the main objective, the sub-objectives consist of:

- To establish an exhaustive list of existing alternatives in terms of recovering and valorizing in methanol and cyclic carbonates the captured CO_2 by the enzymatic process developed by CO_2 Solution Inc.

  Note: The technology of CO_2 Solution Inc. is a technology that has recently developed and deployed. This technology includes using low cost, nontoxic stable saline solution and the carbon anhydrase enzyme as a catalyst for capturing CO_2. It has lower environmental impacts rather than MEA (monoethanolamine) and UNO MK3 (a participating potassium carbonate separation process) (Saunier et al., 2019).
- To carry out the life cycle analysis of the processes identified from the first sub-objective in order to determine their environmental impacts and to identify the main contributors to the impacts.

  Note: Life cycle assessment of the CO_2 capture has already been carried out by CIRAIG (Centre international de référence sur le cycle de vie des produits, procédés et services) and published (Saunier et al., 2019). It will be integrated into subsequent steps.
- To carry out the life cycle assessments of the processes identified from the first sub-objective in order to create a simplified tool for guiding the design of these processes according to their future implementation context.

The created tool in the form of a summarized questionnaire will be used to guide the process designers to predict the environmental impact of the life cycle of the future processes. It also allows them to effectively compare the different design alternatives from the laboratory stage as early as possible and to avoid additional potential negative consequences associated with applying technological changes after implementation. The contribution analysis of environmental impacts also helps to identify opportunities for improvement by focusing on “what really matters”. For example, by guiding the

research efforts on creating a new catalyst that allows the reaction to occur at lower pressure and temperature, improving the energy consumption of the process, finding alternative reactants, using an alternative source of hydrogen, etc.

2.2 Methodology

2.2.1 Identifying the existing alternatives in terms of recovering and valorizing CO_2

There is a wide range of possibilities and alternative options for the production of methanol and cyclic carbonates from captured CO_2. Among the parameters to be taken in account, we can include the source of the feedstock, the energy source, the distance required for the transport of the feedstock (local or imported source), amongst others. To identify the possible alternatives, data were collected directly from the experts involved in the process design of production of these two chemicals by interviews and by sending the questionnaires. Also, desk research was carried out to find out the nature of the processes that are mostly used in Quebec using keywords such as CO_2 capture technology, glycerol production, hydrogen production, epoxide production, energy sources, etc. In the case of lack of data such as the amounts of feedstocks used, stoichiometric approach was conducted to calculate these amounts based on the yield of the reaction (i.e., hydrogen production from glycerol).

2.2.2 Carrying out the life cycle assessments of different scenarios

In the light of the identified alternatives, the different scenarios for the production of methanol and cyclic carbonates were modelled. The LCIs for each scenario were built by combining the collected primary data with the data available in ecoinvent 3.4 database, along with proxy data and literature data. For instance, in the case of cyclic carbonates production process, ethylene carbonate production process from ecoinvent database was considered as a proxy data. Also, regarding CO_2 capture process, the

inventory data from the study carried out by Saunier et al 2019 were taken into account. The cradle to gate life cycle assessments were carried out where the system boundaries cover the product system from raw material acquisition to the factory gate. The software used for carrying out LCA was SimaPro 9.1.0.8 version, equipped with ecoinvent 3.4 database. The functional unit was chosen to be the production of 1 kg of chemical (the production of 1 kg of methanol and the production of 1 kg of cyclic carbonates respectively) at the factory gate. The cradle to gate approach was applied here as for both CO_2-based products (methanol and cyclic carbonate) the chemical structures and compositions are identical to their petrochemical counterparts.

In order to evaluate the environmental performances of the new CO_2-based pathways, different LCIA methods such as IMPACT 2002+, LUCAS (a Canadian-specific impact assessment method), EDIP and IMPACT World+ methods could be used. This LCIA methods are classified by the level of evaluation at midpoint or endpoint levels. In the LCIA method frameworks, the inventory data would be linked to environmental damages and the midpoint level lies on the impact pathway between the inventory results and the damages. For example, climate change is a midpoint category showing the impact of greenhouse gas emission. Then, each midpoint category will be allocated to one or more damage categories such as Human Health (HH) and ecosystems. In this regard, the EDIP method is an approach which stops at midpoint level while, the IMPACT 2002+ allows the impact assessment at midpoint and endpoint (damage) level (IMPACT 2002+ groups midpoint impacts into four damage categories: HH, ecosystem quality, climate change and resources) (Jolliet et al., 2016). However, this method has been replaced by the IMPACT World+ method (Bulle et al., 2019). The advantage of the IMPACT World+ is that this method provides factors for each continent at midpoint and damage level. Also, IMPACT World+ enables users to group certain midpoint categories associated with either climate change or water use and preventing double counting with other impact categories. With this regard, in this

study, IMPACT World+ method preferred to other impact assessment methods because it is an updated version of IMPACT 2002+, LUCAS and EDIP methods (Bulle et al., 2019). Furthermore, IMPACT World+ method offers the first globally regionalized LCIA method. A regionalized impact assessment was carried out iteratively by spatializing some inventory elementary flows when relevant (i.e., when a highly geographically variable midpoint impact category - such as water use and land use – dominated the damages on human health or ecosystem quality) as recommended by Patouillard et al. 2018. Then, the results obtained from LCIA of CCU synthesis of methanol and cyclic carbonate were interpreted and compared with the environmental impacts and benefits of the alternative processes in compliance with the intended goal and scope of the study. The key parameters and the main contributors to the impact categories of each alternative were defined. Innovative alternatives and the choice between them were also analyzed with the view of making improvements for future system designs of these processes.

2.2.3 Creating a simplified tool

Following the previous sections, a simplified tool combined the obtained LCA results of different scenarios and alternatives for the production of methanol and cyclic carbonates was created. The created tool is in the form of a summarized questionnaire that can guide the process designers to predict the environmental impact of the life cycle of the future processes and it can enable them to explore the environmental impacts of different scenarios, based on the parameters selection.

2.3 Results and discussion

2.3.1 Methanol

2.3.1.1 Identified alternatives for methanol production

2.3.1.1.1 Methanol production from syngas

Methanol is typically produced using the Fischer-Tropsch process from synthesis gas (syngas, a mixture of mainly H_2, CO and CO_2) in the presence of $Cu/ZnO/Al_2O_3$ catalyst. Syngas can be produced by two production pathways: steam reforming of light hydrocarbons such as natural gas or partial oxidation of heavy oils or solid carbonaceous materials (Pérez-Fortes et al., 2016, Styring et al., 2021). The production of methanol from syngas was considered as a reference system in this study for comparing different alternatives (Table 2.1).

2.3.1.1.2 Methanol production from captured CO_2 and H_2

CO_2-based methanol production is a mature technology that already has been implemented in Iceland by Carbon Recycling International (CRI) and in Japan by Mitsui Chemical Inc. (Quadrelli et al., 2011). The first commercial CO_2 to methanol plant has been set in Iceland since 2011, with a total production volume of 4,000 t a^{-1}. There are two catalytic routes for the production of methanol from CO_2: direct hydrogenation of CO_2 with H_2 and CO_2 conversion to CO followed by further hydrogenation of CO (Olah, 2013, Pérez-Fortes et al., 2016). With respect to the direct hydrogenation route, methanol can be produced from captured CO_2 and H_2 over a $Cu/ZnO/Al_2O_3$ commercial catalyst at 250 °C and 80 bar pressure (Equation 1) (Rosental et al., 2020). However, these catalysts are less efficient when using only CO_2 than compared when using a mixture of CO/CO_2 (Pérez-Fortes et al., 2016). For the

production of 1 kg methanol 1.441 kg of CO_2 and 0.203 kg of H_2 are needed when considering a total methanol yield of 93.4% (Meunier et al., 2020).

$$CO_2 + H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H^\circ = -50 \text{ kJ/mol}$$

Conventional methanol production	CO_2-based methanol production
From synthesis gas where synthesis gas itself is produced from: • steam reforming of light hydrocarbons such as natural gas, • partial oxidation of heavy oils or solid carbonaceous materials	Methanol production from captured CO_2 and H_2 where hydrogen is produced from: • Glycerol steam reforming • Natural gas stem reforming • Water electrolysis

Table 2.1 Alternative options identified for the production of methanol.

Methanol can be produced from a CCU pathway by the reaction of captured CO_2 and H_2 over catalysts (FRQ-GES project). In recent years, synthesis and tailoring of the catalysts for the CCU reactions have been investigated in lab scales. However, the production of these newly designed catalysts with various origins at industrial scale will lead to different environmental impacts which have to be considered for designing the new CCU process.

Note: Assessing the environmental impacts of catalysts is not within the scope of this study.

The production of methanol from captured CO_2 includes two main parts:

1. the capture of CO_2 emissions from fossil fuel point sources and the use of the captured CO_2 as feedstock.
2. the conversion of captured CO_2 to methanol using hydrogen.

2.3.1.1.2.1 CO_2 feedstock

Recently, CO_2 Solutions Inc. (CSI) (recently bought by Saipem) has developed a novel technology for capturing CO_2 from waste flue gas. In this technology, a nontoxic and

stable salt solution is employed as an absorption solution along with the carbonic anhydrase enzyme as a catalyst (Saunier et al. 2019). Generally, CO_2 is emitted to the environment as elementary flows (in- and outputs exchanged between a process and natural environment), but captured CO_2 is a product of human activity and it has to be considered as a technical flow from technosphere as so-called economic flows (Von Der Assen et al., 2014, Müller et al., 2020). Hence, the captured CO_2 is considered here as the carbon feedstock for the production of methanol.

2.3.1.1.2.2 H_2 feedstock

In the FRQ-GES project, hydrogen was proposed to be supplied from glycerol steam reforming. Glycerol or glycerine is a by-product of biodiesel manufacturing, and it is produced from the catalytic transesterification of vegetable oils or animal fats with methanol. Large volume of glycerol by-product is generated in biodiesel production, which may bring a new environmental concern (Franca et al., 2017). Therefore, the production of H_2 from glycerol steam reforming was studied for valorizing this by-product. Theoretically, 1 mole of glycerol $C_3H_5(OH)_3$, can produce 7 moles of hydrogen and 3 moles of CO_2 (Iliuta et al., 2017). However, glycerol steam reforming generates gas with a large CO_2 and CO content that may be associated with high environmental impacts. In order to address the problem, the sorption-enhanced steam reforming of glycerol (SESRG) process which consists of an *in-situ* CO_2 capture by adsorption has been investigated and developed (Iliuta M.C., Iliuta I., 2020). In Quebec, the feedstocks used for biodiesel production are mostly animal fats and used cooking oil (État de l'énergie au Québec 2020).

There are other hydrogen production routes which were also identified and considered in this study including

- hydrogen production from natural gas steam methane reforming (SMR) which is the most important and common route for H_2 production and,

- hydrogen production from water electrolysis.

SMR is representing the highest worldwide production of hydrogen. In this technology, syngas is synthesized from hydrocarbons (usually natural gas) at high temperature and pressure. Hydrogen produced from SMR is called grey hydrogen and when combined with carbon capture and storage it is referred as blue hydrogen (Delpierre et al., 2021). Electrolytic hydrogen production was also considered here, where water is split into hydrogen and oxygen through electrolysis. Both hydrogen production routes are mature technologies. However, H_2 production through water electrolysis is still costly but, overtime, its cost will be reduced, and it will be competitive with other technologies.

2.3.1.2 Life cycle assessments of methanol production

2.3.1.2.1 Inventory data and assumptions for methanol production

Data for the conventional production of methanol from natural gas is already existing in ecoinvent 3.4 database and is considered as a reference system for comparing the different production pathways.

In this research, in order to evaluate the environmental performance of CO_2-based methanol production, data for process modelling were obtained from project partners directly involved in process development by interviews. When missing data, the life cycle inventory from the study carried out by Meunier et al. 2020 was considered. For conventional production of methanol from syngas (reference system from ecoinvent database) the data for transportation and storage of feedstocks were not included in the inventory. Thus, it was assumed for the CCU production of methanol that both the CO_2 utilization process and the hydrogen production were located at the emission source in order to avoid the energy required for CO_2 transport and the need for storage. The

methanol plant for methanol production from captured CO_2 is assumed to be located in Quebec and hydroelectricity is used as an energy source for methanol production.

The life cycle assessment for the separation of 1 t of CO_2 from the flue gas stream of a coal power plant in the USA has already been carried out by Saunier et al. 2019 and the same inventory data were considered for capturing CO_2, but in the Quebec's context as an assumption in this research. It is also assumed that CO_2 was captured from a cement plant in Quebec.

Two feedstocks were considered here for production of glycerol including animal fats and used cooking oil (État de l'énergie au Québec 2020). However, the primary data for these processes were not available. To bridge the data gaps the inventory data for production of biodiesel and glycerine from beef tallow was gathered from a literature review (Dufour and Iribarren, 2012, López et al., 2010). In case of the production of biodiesel and glycerine from used cooking oil, the inventory data were used from the ecoinvent database. Both inventory data were adapted for Quebec's context as an assumption. Biodiesel and glycerine are two main products of the transesterification of beef tallow and used cooking oil. In order to deal with multifunctionality, allocation percentages were assigned to biodiesel and glycerol according to the value and mass of products (allocation is sharing the responsibility of the impact of a multifunctional process between the different function it fulfills which can be done based on different allocation principles including mass, value, etc.). For using waste cooking oil in the ecoinvent database, the inventory refers to the production of 1 kg of vegetable oil methyl ester (VOME) and glycerine from purified waste cooking oil. The economic allocation factors of 87.1% to VOME and 12.9% to glycerine were assigned for these processes. Thus, in this research the same economic allocation factors were considered (Remark: this approach will be affected by variations in market value). Also, the mass allocation factors of 88.5% and 11.5% were considered, based on the study carried out

by López et al 2010 to find out how the selection of allocation method may change the outcome of the assessment.

For the production of hydrogen by SESRG, life cycle inventory data were collected directly from the process designer by sending a questionnaire. Also, the stoichiometric estimation based on a yield of 90% was applied in order to bridge the data gaps. Spath and Mann have already assessed the environmental performance of hydrogen production via natural gas steam reforming and data from their inventory were considered in this research (Spath and Mann, 2001). For water electrolysis, the data from the ecoinvent database for alkaline electrolysis were used. The summary of sources of inventory data and assumptions for production of methanol from captured CO_2 are presented in Table 2.2. The inventory data used for production of methanol from captured CO_2 in Quebec also could be find in Table 2.3. However, the detailed inventory data for each scenario considered in this study would be available in Supplementary data.

	Assumptions	Inventory data
CO_2 feedstock	CO_2 is assumed to be captured by CO_2 Solutions Technology from a cement plant located in Quebec.	Saunier et al., 2019 (***)
H_2 feedstock	H_2 is produced by SEGSR	Project partners, État de l'énergie au Québec 2020 (***)
	H_2 is produced by SMR	Spath and Mann (***), 2001
	H_2 is produced by water electrolysis	Ecoinvent 3.4 database
Methanol production from captured CO_2 and H_2	Methanol is assumed to be produced over catalyst in Quebec. It was also assumed for the CCU production of methanol that both the CO_2 utilization process and the hydrogen production were located at the emission source.	Project partners, Meunier et al., 2020 (**)

Table 2.2 Summaries of assumptions and inventory data for methanol production from captured CO_2. (Quality of secondary data, * = poor, *** = good).

	Amount	Unit
Inputs from technosphere		
CO_2	1.375	kg
Hydrogen	0.1875	kg
Catalyst	0.00037	kg
Electricity	0.111	kWh
Methanol plant	0.0000000000372	p
Emissions to air		
Carbon dioxide	0.078	kg
Outputs to technosphere		
Treatment, sewage	0.00056	kg

Table 2.3 List of inventory data for production of 1 kg of methanol from captured CO_2 in Quebec.

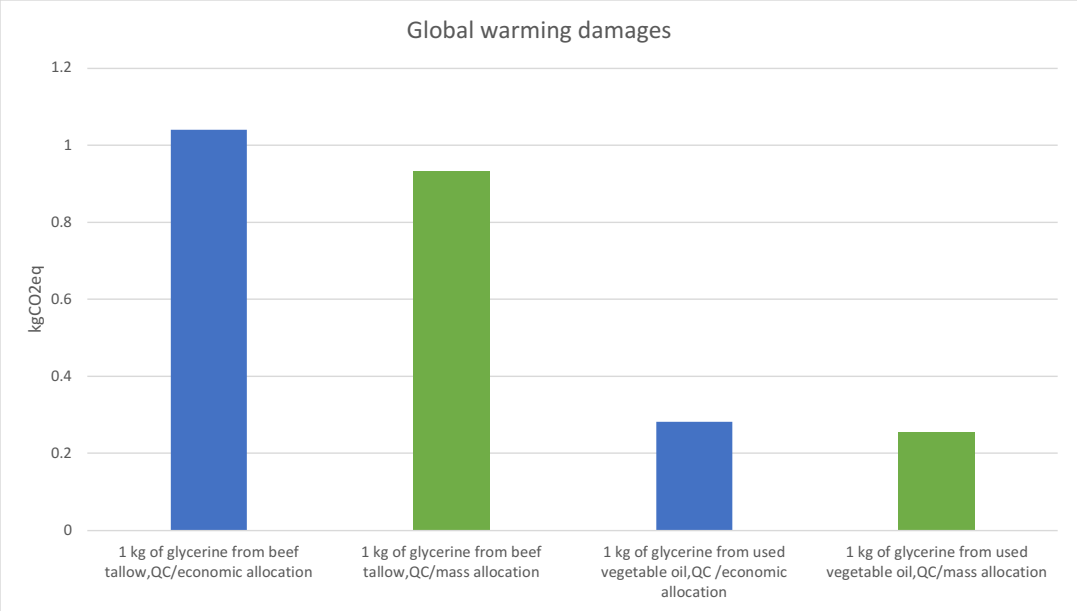
The systems studied here were the production of 1 kg methanol

- from conventional production pathway from syngas , reference system, (A),
- from CO_2, when a NRE is used for capturing CO_2 and H_2 produced from glycerol in Quebec (B),
- from CO_2, when a RE is used for capturing CO_2 and H_2 produced from glycerol in Quebec (C),
- from CO_2 when a NRE is used for both capturing CO_2 and producing H_2 by water electrolysis (D),

- from CO_2 when a RE is used for capturing CO_2 and H_2 is produced by water electrolysis with a NRE (E),
- from CO_2 when a RE is used for both capturing CO_2 and producing H_2 by water electrolysis (F),
- from CO_2, when a NRE is used for capturing CO_2 and H_2 produced from SMR (G) and,
- from CO_2, when a RE is used for capturing CO_2 and H_2 produced from SMR (H).

2.3.1.2.2 Life cycle impact assessment

For the production of glycerol from beef tallow and used cooking oil, the LCA results for the global warming, human health and ecosystem quality impact categories are presented in Figure 2.1. These results show that the glycerol production from used cooking oil feedstocks shows a better environmental performance for all impact categories (Figure 2.1).



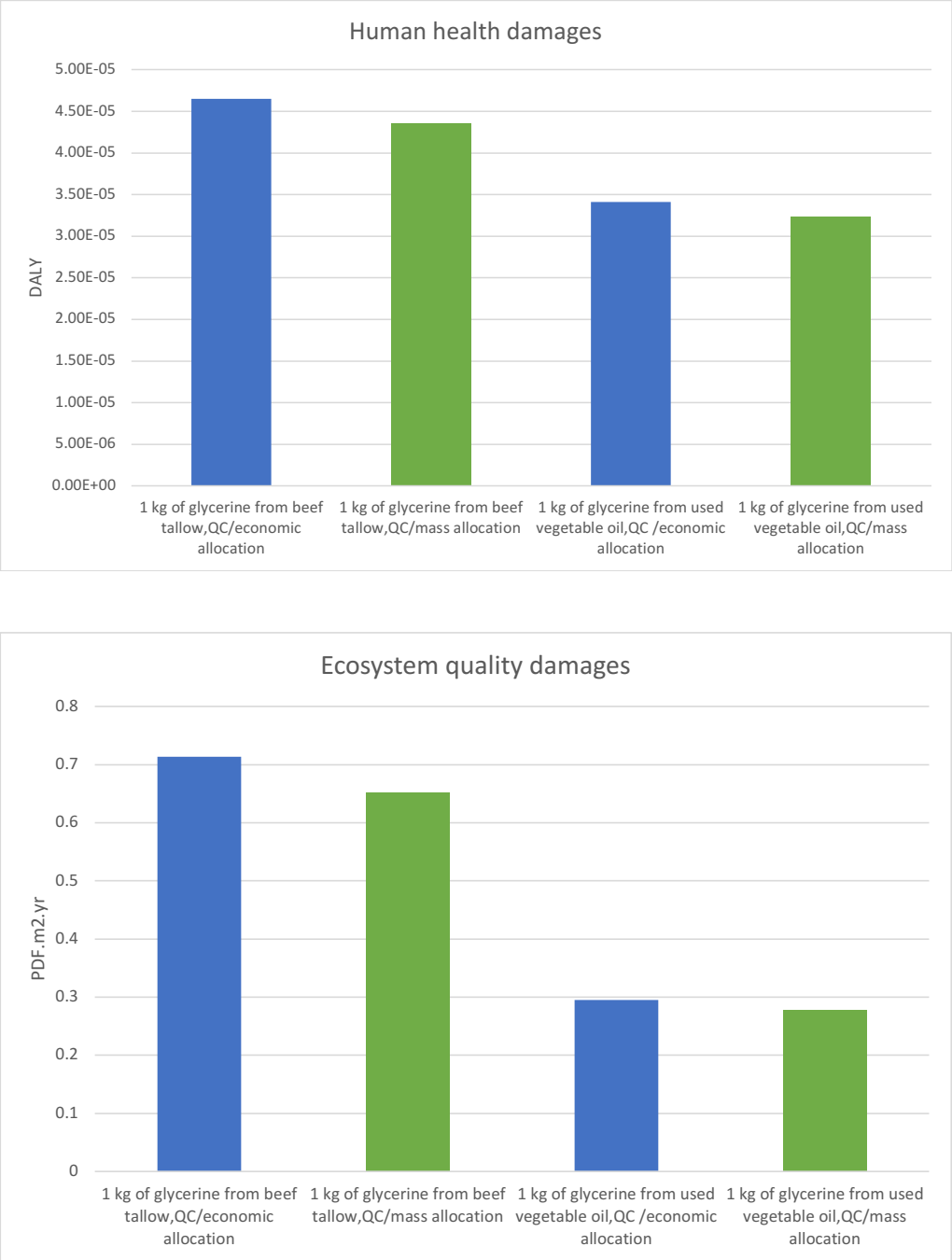
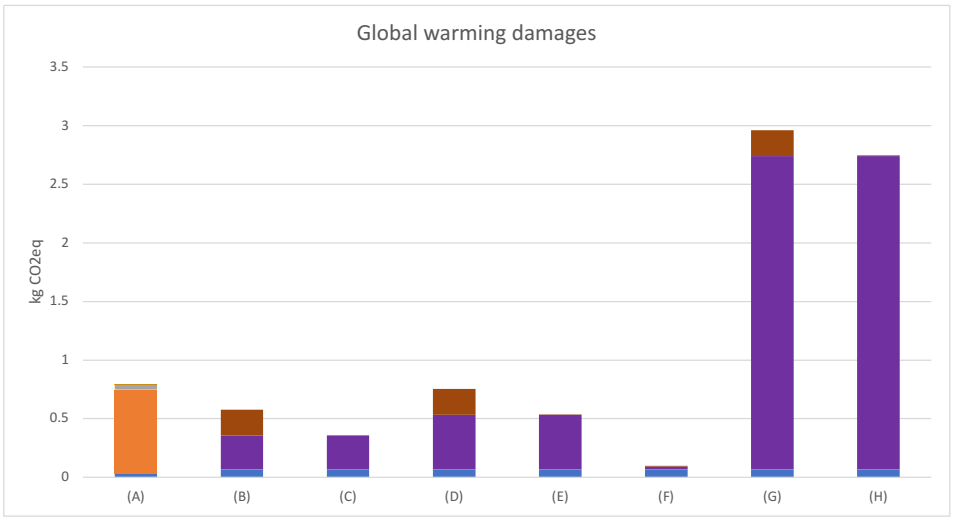
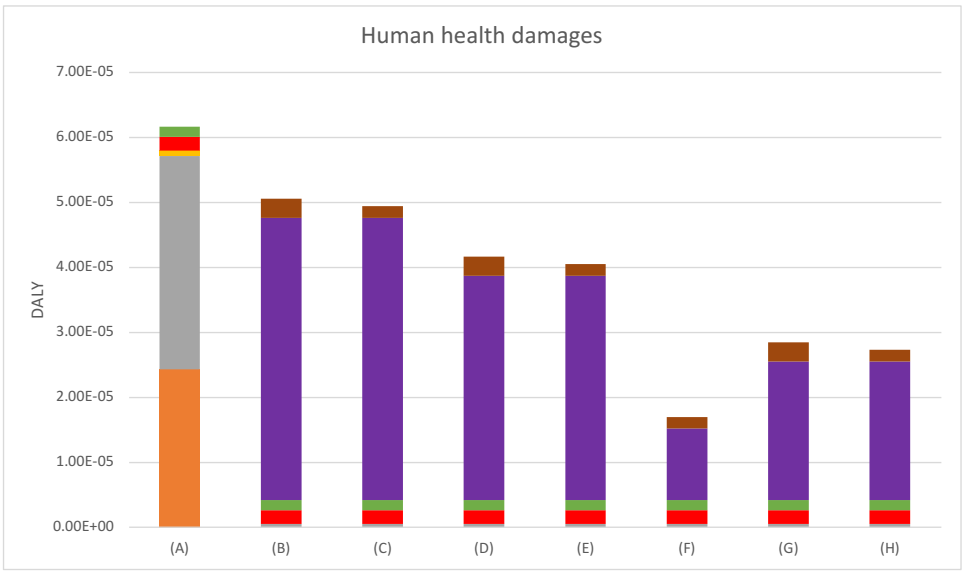


Figure 2.1. Comparison of global warming, human health and ecosystem quality damages results for the production of glycerol from beef tallow and used vegetable oils, applying mass and allocation methods (Jolliet et al., 2016).

According to these results, glycerol produced from transesterification of used vegetable oil was considered as a feedstock of choice for supplying hydrogen through SEGSR in a CCU methanol production pathway.

The LCA results for the different scenarios of methanol production from captured CO_2 and H_2 compared to the conventional methanol production from methane are presented in Figure 2.2.





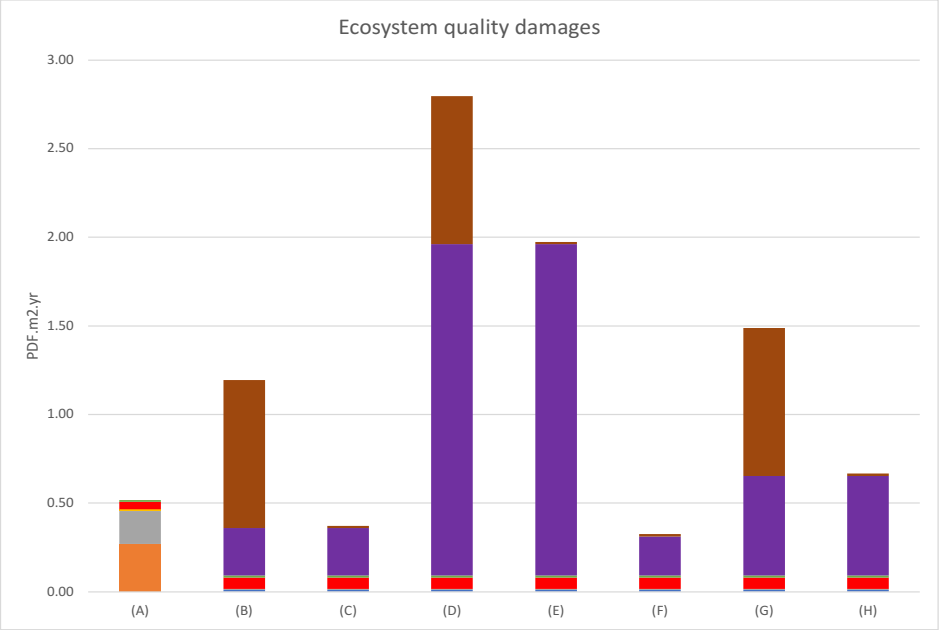


Figure 2.2. Global warming, human health and ecosystem quality damages results for eight different methanol production pathways by IMPACT World+ method. (Conventional production pathway from syngas , reference system, (A), production from CO_2, when a NRE is used for capturing CO_2 and H_2 produced from glycerol in Quebec (B), production from CO_2, when a RE is used for capturing CO_2 and H_2 produced from glycerol in Quebec (C), production from CO_2 when a NRE is used for both capturing CO_2 and producing H_2 by water electrolysis (D), production from CO_2 when a RE is used for capturing CO_2 and H_2 is produced by water electrolysis with a NRE (E), production from CO_2 when a RE is used for both capturing CO_2 and producing H_2 by water electrolysis (F), production from CO_2, when a NRE is used for capturing CO_2 and H_2 produced from SMR (G) and production from CO_2, when a RE is used for capturing CO_2 and H_2 produced from SMR (H). The colours represent the methanol production (blue), natural gas (orange), electricity (gray), water (yellow), catalyst (red), methanol plant (green), hydrogen feedstock (purple) and CO_2 feedstock (brown).

2.3.1.2.3 Interpretation

For the production of methanol from captured CO_2, the energy source used for capturing CO_2 from the waste gas stream is a key parameter since the CO_2 capture itself is an energy-intensive process (Saunier et al., 2019). Therefore, changing the energy source from coal to hydropower for capturing CO_2 affects the LCA outcomes in a large extent for all impact categories (Figure 2.2). The production of methanol from captured CO_2 and H_2 produced from glycerol outperforms conventional methanol production from syngas (global average) for global warming, human health, and ecosystem quality impact categories when hydroelectricity is the energy source for capturing CO_2.

Another key parameter for this process is the need for hydrogen. The production of H_2 is responsible for a significant share of overall impacts. In the case of the production of hydrogen from glycerol, this is due to the high requirement of glycerol per 1 kg of H_2 produced and for the methanol used for the transesterification reaction of vegetable oils. When hydrogen is generated by water electrolysis using a renewable energy (hydroelectricity in Quebec), the CO_2-based methanol shows better environmental performances than fossil-based methanol and CO_2-based methanol when H_2 is produced from glycerol. This is not only the case for the global warming impact category but also for the human health and ecosystem quality impact categories. Thus, switching the electricity source from non-renewable (coal, as a worst-case scenario) to renewable affects the environmental performance of the process in a large extent.

From an LCA perspective, it can be concluded that for methanol production, the source of energy used for capturing CO_2 from a point source and the hydrogen supply needed for converting CO_2 to methanol are the two key parameters. Replacing energy intensive feedstocks by CO_2 for methanol production via CCU pathways seems highly promising if the molecular hydrogen is supplied from water electrolysis using hydroelectricity as an energy source. However, the global warming impact is higher if the hydrogen is

supplied by steam methane reforming. The high impact in steam methane reforming is due to the consumption of natural gas as feedstock. In the electrolysis route, the highest impact is due to the use of electricity to operate the electrolyzer. Of course, the environmental impact in the electrolysis process can be minimized when renewable energy is used for producing hydrogen.

For the CCU methanol production, the commercial catalyst $Cu/ZnO/Al_2O_3$ is used. However, according to Pérez-Fortes et al., 2016 it is less efficient with only CO_2 than when used with syngas, which is a mixture of CO/CO_2 (Pérez-Fortes et al., 2016). The obtained LCA results (Figure 2.2) also show higher environmental impact for ecosystem quality impact category due to the higher load of catalysts for CO_2-based methanol production. Also, traditional metal oxide catalysts for CCU production of methanol need a high temperature. At this temperature the undesirable reverse water-gas shift (RWGS) reactions occur that produce high amount of CO by-product. Thus, research efforts on catalysts that allow the conversion of CO_2 to methanol with low energy and high efficiency is needed (Hu et al., 2021).

2.3.2 Ethylene carbonate

2.3.2.1 Identified alternatives for ethylene carbonate production

2.3.2.1.1 Conventional production pathway

Commercially, cyclic carbonates can be produced from corresponding 1,2-diols or epoxides and a one-carbon source. For the diols route, phosgene ($COCl_2$) is used as the carbon source. However, the phosgene route is phased out due to the high energy demand associated with phosgene production and legislative limitations related to the use of this highly toxic chemical (Comerford et al., 2015, Artz et al., 2018). The most important and commercial route for cyclic carbonates production is the reaction

between an epoxide and carbon dioxide, which is one of the few implemented production pathways known using CO_2 feedstock (Comerford et al., 2015). According to the ecoinvent report, carbon dioxide is a by-product generated from ammonia production and it is recovered for downstream uses (ecoinvent report No. 8, 2007). Since CO_2 affects negatively the catalysts used for ammonia synthesis, it is removed from the gas stream through scrubbing with monoethanolamine, activated diethanolamine or hot potassium carbonate. Then CO_2 captured by MEA Technology can be used for the commercial synthesis of some products such as cyclic carbonates (Table 2.4).

<table>
<tr><td>Conventional cyclic carbonates production</td><td colspan="2">CO_2-based cyclic carbonates production</td></tr>
<tr><td rowspan="2">From the reaction between 1,2-diols or epoxides and phosgene as the carbon source.</td><td colspan="2">From the reaction between CO_2 and epoxides.</td></tr>
<tr><td>Alternative CO_2 feedstocks:
CO_2 capture by MEA technology (most commercialized technology)
CO_2 capture by CO_2 Solution technology</td><td>Alternative epoxide feedstocks:
Fossil-based epoxide
Bio-based epoxide
Epoxide produced from Methanol to Olefin pathway</td></tr>
</table>

Table 2.4 Alternative options identified for the production of cyclic carbonates.

2.3.2.1.2 Ethylene carbonate production from captured CO_2 and epoxide

In the FRQ-GES project, the production of cyclic carbonates (ethylene carbonate in this study) is proposed from epoxides and CO_2 under mild conditions (80 °C and 1 bar)

over a silica catalyst produced by *Silicycle*. These CCU processes also includes two main parts:

- capturing CO_2 from point source and using the captured CO_2 as feedstock,
- converting the captured CO_2 to cyclic carbonate by using epoxide.

2.3.2.1.2.1 CO_2 feedstock

Here CO_2 is also considered to be supplied by CO_2 solutions Inc. technology (*Saipem*) as proposed by FRQ-GES project and it is used a carbon feedstock for production of ethylene carbonate.

2.3.2.1.2.2 Epoxide feedstock

Commercially, ethylene oxide is produced from fossil-based ethylene and oxygen, where ethylene is synthesized by steam cracking of naphtha from crude oil distillation. Most of the ethylene oxide used in Canada is imported from the USA to Canada (http://comtrade.un.org/data). Alternatively, the ethylene source for ethylene oxide production can be supplied by either bioethylene or by a methanol to olefin (MTO) pathway. Biomass can be transformed in bioethanol and then in ethylene through dehydration. Different biomass feedstock, such as sugar, starch rich biomass, and lignocellulose materials, can be converted to ethanol through fermentation and gasification processes (Zhao et al., 2018). Second generation ethanol or bioethanol is mostly produced from waste wood and other residual materials (État de l'énergie au Québec 2020). Another alternative method for ethylene production is through the methanol to olefin pathway where methanol itself is produced from captured CO_2. Methanol can be converted to ethylene and propylene through MTO reactions over zeolite or molecular sieves (Zhao et al., 2018, Rosental et al., 2020). Herein, we focused on MTO because of its high technology readiness level (TRL) and the fact that the production pathway could use the current infrastructure with minimum changes

(Kätelhön et al., 2019). According to data from Air liquid the oxygen supply is produced in Bramalea, Ontario (Air liquid Montreal).

Thus, three different sources of ethylene oxide were considered here including:

- Fossil-based ethylene oxide from the USA,
- Ethylene oxide made from ethylene produced from a Methanol to Olefin (MTO) pathway in Quebec,
- Ethylene oxide made from ethylene produced from wood in Quebec.

2.3.2.2 Life cycle assessments of ethylene carbonate production

2.3.2.2.1 Inventory data and assumptions

The only inventory data about cyclic carbonates production available in the ecoinvent database is for ethylene carbonate. For this process, the data set includes the reaction of ethylene oxide with CO_2 at 120 °C and 16 bars with 99.95% ethylene oxide conversion, which is considered as the reference system for comparing the commercial process with new CCU process in the FRQ-GES project. For the infrastructure, the ecoinvent dataset “chemical plant, organic” is accounted and the transportation dataset is calculated based on ecoinvent standard estimations.

In the ecoinvent database, the inventory data are represented for the production of 1 kg of liquid carbon dioxide that is considered as a feedstock for ethylene carbonate production from ethylene oxide and CO_2. The technology of this process includes the extraction of carbon dioxide out of waste gas streams from different production processes with a 15-20% MEA (monoethanolamine) solution followed by purification and liquification steps, using each electricity as an energy source.

For fossil-based ethylene oxide production, the LCI for this process was available in ecoinvent 3.4 database and was modified to the context of the USA. It is assumed the ethylene oxide is produced in the USA and is transported to Quebec. For bioethylene oxide production, bioethylene is produced from bioethanol. In Quebec, bioethanol is mostly produced from waste wood and other residual materials (État de l'énergie au Québec 2020). The primary data for this process were not available and in order to bridge the data gap, we considered secondary data from literature extended by the data from the ecoinvent database. The inventory data for bioethanol production from waste wood in the Swedish context were taken into the account. This dataset includes the transport of wood from forest, and the processing of wood to bioethanol and electricity. The economic allocation with allocation factor of 99.7% was assigned to the ethanol production. For ethylene production from bioethanol through dehydration, we used the reaction data from the study by Liptow et al. 2013 (Liptow et al., 2013). However, both series of data were modified into the Quebec's context. For production of ethylene oxide by a MTO pathway, the LCI of a commercial MTO plant operated in China using fossil-based methanol as feedstock were considered for this study (Rosental et al. 2020). In this scenario, we also assumed that the methanol is supplied by the methanol produced from captured CO_2 and H_2 from water electrolysis using Quebec's hydroelectricity. We also considered a MTO plant located in Quebec. The oxygen needed for production of ethylene oxide from ethylene is assumed to be produced in Bramalea, Ontario (Air liquid Montreal) and then transported to Montreal for ethylene oxide production. Also, oxygen is assumed to be produced in Quebec as a potential scenario considered in this study. The summary of sources of inventory data and assumptions made for ethylene carbonate production are presented in Table 2.5. The inventory data used for production of ethylene carbonate from captured CO_2 in Quebec also presented in Table 2.6. However, the detailed list of the inventory data for each assessed scenario could be find in the Supplementary data.

	Assumptions	Inventory data
CO_2 feedstock	CO_2 is assumed to be captured from a cement plant located in Quebec by MEA Technology by CO_2 Solutions	Ecoinvent database Saunier et al., 2019(***), project partners
Epoxide feedstock	Fossil-based epoxide production Bio-based epoxide production Epoxide produced from a MTO pathway	Ecoinvent database Zhao et al., 2018 (**), État de l'énergie au Québec 2020 (***), Liptow et al., 2013 (**) Zhao et al., 2018 (**), Rosental et al. 2020 (***)
Ethylene carbonate production from captured CO_2 and epoxide	Ethylene carbonate is assumed to be produced over catalyst in Quebec. It was also assumed that the CO_2 utilization process is located at the emission source and epoxide is transported by rail and lorry to CCU chemical plant.	Project partners, ecoinvent database, http://comtrade.un.org/data

Table 2.5 Summaries of assumptions and inventory data for ethylene carbonate production from captured CO_2. (Quality of secondary data * = poor, *** = good).

	Amount	Unit
Inputs from technosphere		
CO_2	0.50497	kg
Ethylene oxide	0.50053	kg
Transport, rail	0.35082	tkm
Transport, lorry	0.10055	tkm
Electricity	0.042	kWh
Chemical plant	0.0000000004	p
Emissions to air		
Carbon dioxide	0.0053021	kg
Ethylene oxide	0.00025027	kg
Heat, waste	0.0072	MJ
Outputs to technosphere		
Disposal, zeolite	0.005	kg

Table 2.6 List of inventory data for production of 1 kg ethylene carbonate from captured CO_2 in Quebec.

According to these inventory data and assumptions, the systems studied were the production of 1 kg ethylene carbonate

- from captured CO_2 (MEA Technology) with a NRE and ethylene oxide from the USA (A),
- from captured CO_2 (CO_2 Solution Technology) with a NRE and ethylene oxide from the USA (B),
- from captured CO_2 (CO_2 Solution Technology) with a RE and ethylene oxide from the USA (C),

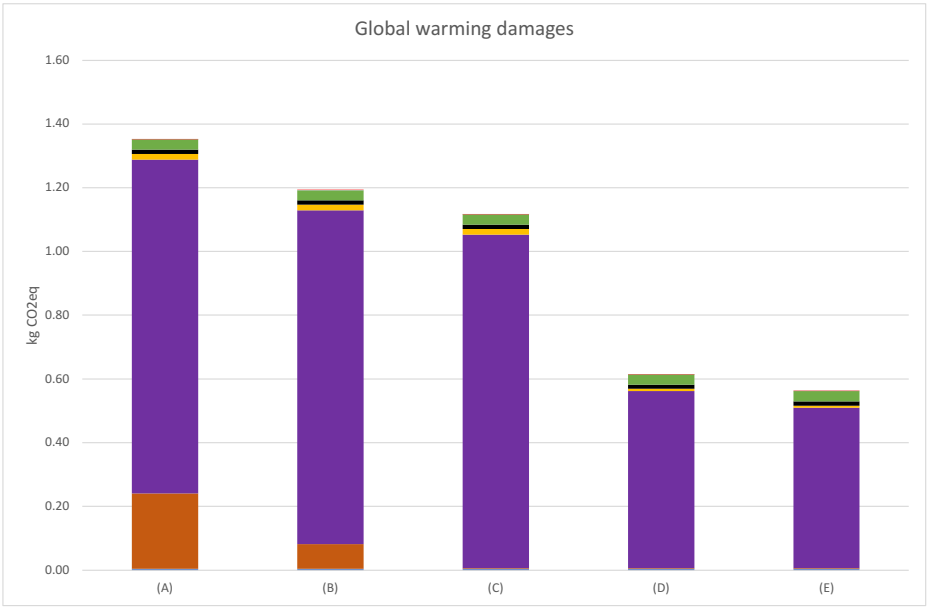
- from captured CO_2 (CO_2 Solution Technology) with a RE and bio-based epoxide (D) and,
- from captured CO_2 (CO_2 Solution Technology) with a RE and epoxide produced from a MTO pathway (E).

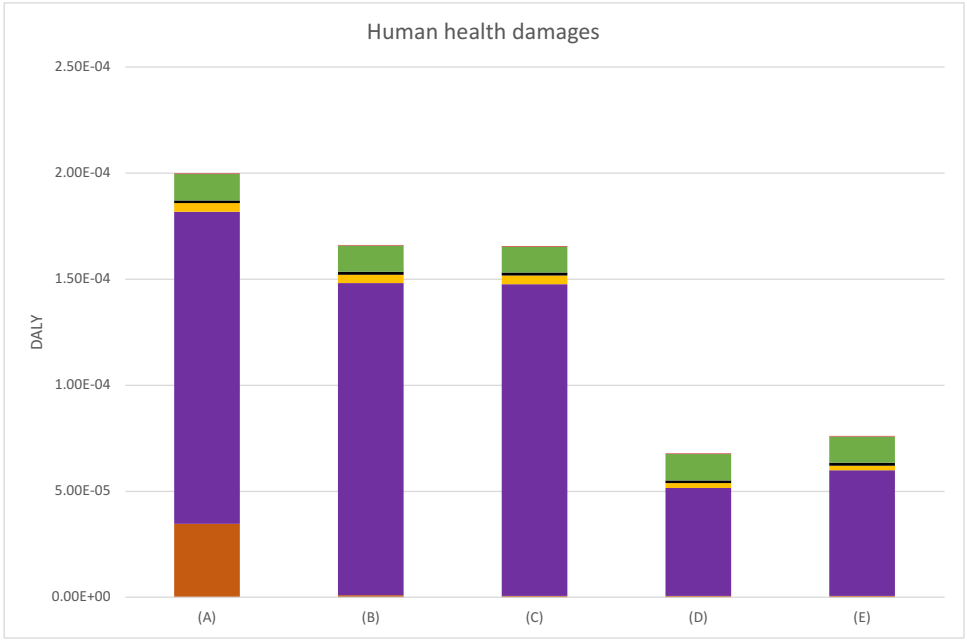
Also, different ethylene oxide production pathways using alternative ethylene feedstocks and oxygen produced in Ontario and Quebec (as a potential scenario) were considered in this study including the production of 1 kg

- fossil-based ethylene oxide in the USA (A),
- bio-based ethylene oxide production in Quebec when oxygen produced in Ontario (B),
- ethylene oxide production from a MTO pathway in Quebec when oxygen is produced in Ontario (C),
- bio-based ethylene oxide production in Quebec when oxygen produced in Quebec (D) and,
- ethylene oxide production from a MTO pathway in Quebec when oxygen is produced in Quebec (E).

2.3.2.2.2 Life cycle impact assessment

LCAs results for different scenarios of production of ethylene carbonate from captured CO_2 are presented in Figure 2.3 for global warming, human health and ecosystem quality impact categories.


Global warming damages
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
kg CO2eq
(A)
(B)
(C)
(D)
(E)


Human health damages
2.50E-04
2.00E-04
1.50E-04
1.00E-04
5.00E-05
0.00E+00
DALY
(A)
(B)
(C)
(D)
(E)

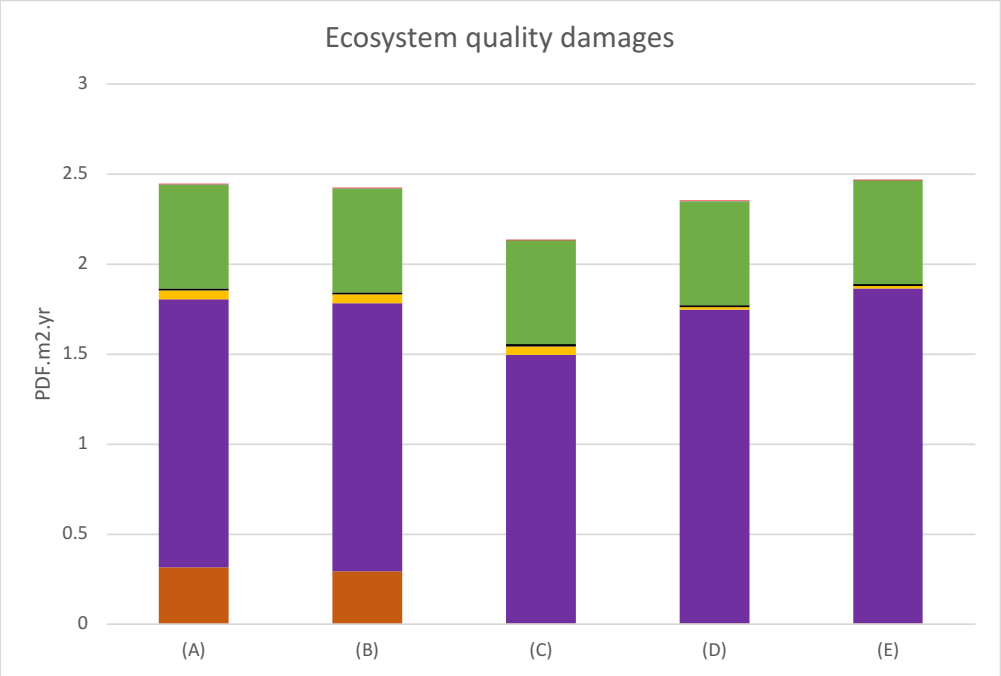
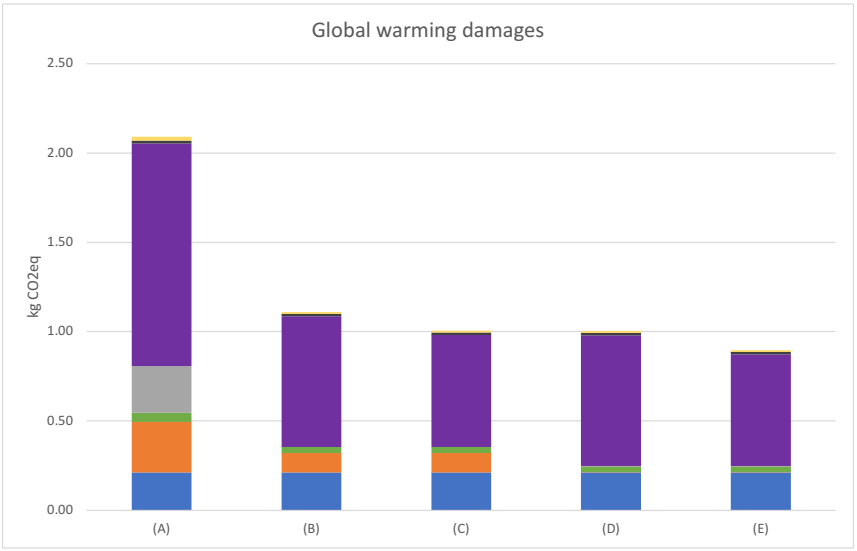
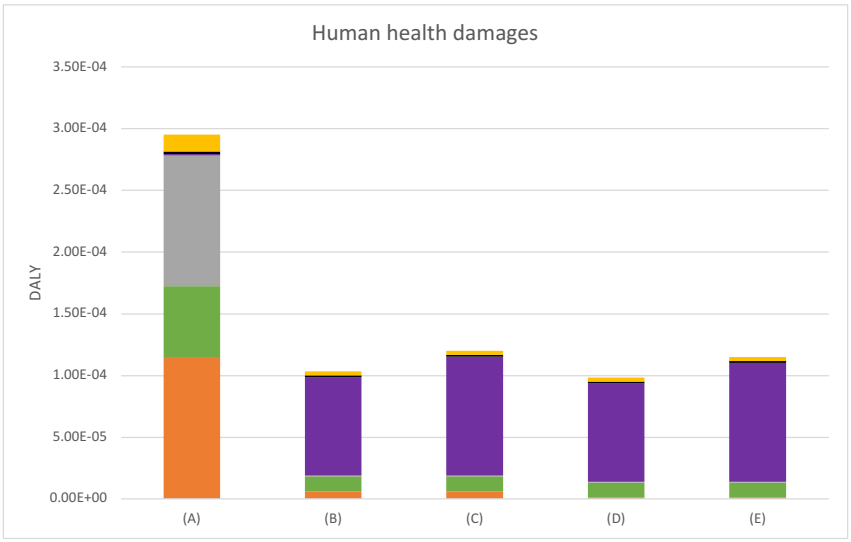


Figure 2.3. Global warming, human health and ecosystem quality damages results for five ethylene carbonate production pathways by IMPACT World+ method. (From captured CO_2 (MEA Technology) with a NRE and ethylene oxide from the USA (A), from captured CO_2 (CO_2 Solution Technology) with a NRE and ethylene oxide from the USA (B), from captured CO_2 (CO_2 Solution Technology) with a RE and ethylene oxide from the USA (C), from captured CO_2 (CO_2 Solution Technology) with a RE and bio-based epoxide (D) and, from captured CO_2 (CO_2 Solution Technology) with a RE and epoxide produced from a MTO pathway (E).The colours represent the ethylene carbonate production (blue), CO_2 feedstock (brown), ethylene oxide feedstock (purple), transport, rail (yellow), transport, lorry (black), electricity (gray), chemical plant (green), and catalyst (red).

The life cycle assessments of ethylene oxide production from different ethylene feedstocks when oxygen produced in Ontario and Quebec (potential scenarios) were also carried out. The obtained LCAs results are presented in Figure 2.4 for global warming, human health and ecosystem impact categories.


Global warming damages
kg CO2eq
2.50
2.00
1.50
1.00
0.50
0.00
(A)
(B)
(C)
(D)
(E)


Human health damages
DALY
3.50E-04
3.00E-04
2.50E-04
2.00E-04
1.50E-04
1.00E-04
5.00E-05
0.00E+00
(A)
(B)
(C)
(D)
(E)

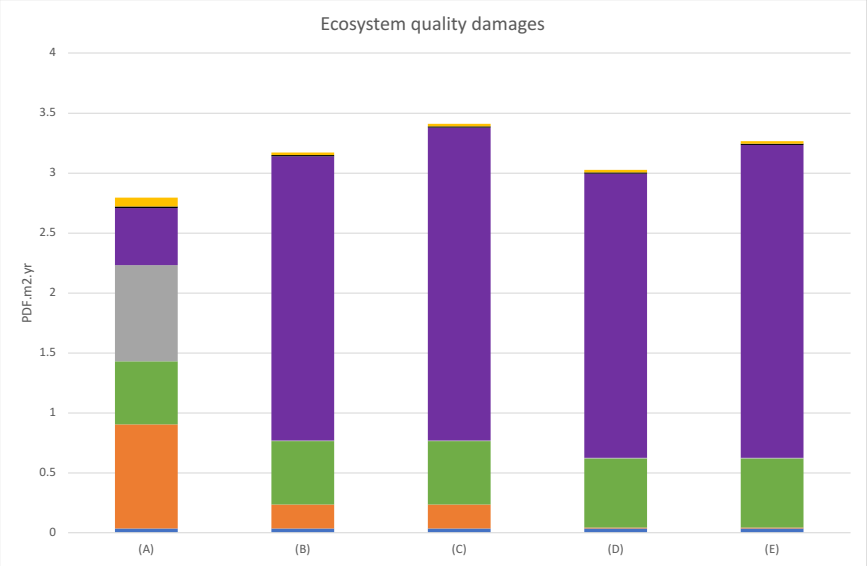


Figure 2.4. Global warming, human health and ecosystem quality damages results for five ethylene oxide production pathways by IMPACT World+ method. Fossil-based ethylene oxide production in the USA (A), bio-based ethylene oxide production in Quebec when oxygen produced in Ontario (B), ethylene oxide production from a MTO pathway in Quebec when oxygen is produced in Ontario (C), bio-based ethylene oxide production in Quebec when oxygen produced in Quebec (D) and, ethylene oxide production from a MTO pathway in Quebec when oxygen is produced in Quebec (E).The colours represent the ethylene oxide production (blue), oxygen (orange), chemical plant (green), electricity (gray), ethylene feedstock (purple), transport, lorry (black), and transport, rail (yellow).

2.3.2.2.3 Interpretation

According to the obtained results from previous section, ethylene carbonate production from captured CO_2 by CO_2 Solution technology (Saipem) and fossil-based ethylene oxide (B) shows better environmental performance than the production of the same chemical from captured CO_2 by a MEA technology (reference system considered in this study, (A)) in Quebec (Figure 2.3). Here also the energy source used for capturing CO_2 is a key parameter for environmental impacts of ethylene carbonate production

and these impacts can be minimized by changing the energy source from NRE energy (coal) to hydroelectricity.

However, ethylene oxide supply still remains a key parameter that largely affects the environmental impacts results. Therefore, ethylene oxide produced from other pathways including bioethylene oxide from wood and from methanol to olefin (MTO) (methanol produced from captured CO_2 and H_2 supplied by water electrolysis with hydroelectricity) in Quebec were also considered. The obtained LCAs results show that the global warming impact decreases respectively by 45% and 49% for the ethylene carbonate production from bioethylene or from a methanol to ethylene process. These two production routes also outperform the ethylene carbonate production from fossil-based ethylene oxide for the human health impact category by 59% for bioethanol and by 54% for the MTO process. However, the ecosystem quality impact is higher by 10% for the ethylene carbonate production from bioethylene and by 16% for the ethylene carbonate production from the MTO pathway.

Generally, the epoxide used for the production of ethylene carbonate is produced by the epoxidation of ethylene (ecoinvent). According to the LCAs results obtained for fossil-based ethylene oxide production in the USA, the oxygen supply is also a hot spot for this process (Figure 2.4). The oxygen used for the chemical synthesis of epoxides is produced from cryogenic air distillation in industrial plants, which is an energy-intensive process. Oxygen production and its compression to 35 bars consume 0.42 kWh per kg of O_2 (Van-Dal and Bouallou, 2013). Thus, energy source used for production of oxygen is another key parameter and modifying the electricity source from the Ontario energy mix to Quebec's hydropower lowers the environmental impacts of oxygen production from the cryogenic pathway. When oxygen is produced in Quebec as a potential scenario, the environmental impacts of oxygen production will

be minimized notably for global warming and ecosystem quality impact categories (Figure 2.4).

Potentially, oxygen can also be supplied by water electrolysis. In the electrolytic hydrogen production route, water splits into hydrogen and oxygen. In many production facilities, oxygen is not stored, and is vented to the atmosphere (Bhandari et al., 2014). However, oxygen is a useful co-product that can be used as a feedstock in chemical processes such as ethylene oxide production. Finally, research and development on catalysts with higher activity and selectivity will render these new processes the promising alternatives for industrial application.

2.3.3 Simplified tool

Following the LCAs results obtained in this study, the key parameters for production of methanol and ethylene carbonate from captured CO_2 were identified. For methanol production the energy source used for capturing CO_2 and the need of hydrogen are the two key parameters affecting the outcomes and for ethylene carbonate production the environmental impacts are due to the energy source for capturing CO_2, ethylene oxide supply and oxygen used for production of ethylene oxide. According to these key parameters a parametric tool was created by building mathematical linkage between identified key parameters and LCAs results. This tool is in the form of a programmed and summarized questionnaire, which allows the process designers to discover the environmental footprints of various alternative process schemes and options based on the selection of different parametric inputs. In this tool, the LCAs results are presented not only for global warming but also for human health and ecosystem quality impact categories. In this tool the LCIA data for production of these chemicals from captured CO_2 are also available (Supplementary data).

2.4 Conclusion

Integrating LCA for the production of chemicals from captured CO_2 plays an important role in the design of environmentally benign processes. In this study, different alternatives and scenarios for CO_2-based production of methanol and ethylene carbonate were analyzed based on life cycle assessment. The obtained results will help to identify promising directions for research by revealing valuable insights. Our analysis derives that the maximum impact reductions for CO_2-based methanol production occur when renewable energy is used for capturing CO_2 from the point source and H_2 is supplied by water electrolysis with renewable energy (hydroelectricity in Quebec) while hydroelectricity is also supplied to the entire CCU system. Also, our results show that the CO_2-based ethylene carbonate production achieves the highest environmental impacts reduction for global warming and human health impact categories when CO_2 is captured by renewable energy and epoxide is supplied by bioethylene oxide or from a MTO pathway instead of fossil-based ethylene oxide. However, the ecosystem quality impact category increases by 10% and 16% respectively. Although various studies have been conducted on catalyst development and improvement, but it is important that the environmental impacts of the new catalysts, their origin and rarity are also investigated. Additionally, for both CO_2-based methanol and ethylene carbonate productions, focus needs to be placed on creating novel and highly efficient catalysts in order to make these production pathways competitive with already implemented commercial routes. To achieve the specific goal of reducing environmental impacts using these CCU processes, a simplified tool was created. This tool can be used by process designers to enhance their decision making at the early stage of research and development.

CHAPTER III

CONCLUSION AND RECOMMENDATIONS

Integrating LCA into the early process design for the production of chemicals from captured CO_2 is recognized to play an important role in the design of environmentally benign processes. In this study, different alternatives and scenarios for CO_2-based production of methanol and ethylene carbonate were analyzed based on life cycle assessment. Our analysis derives that the maximum impact reductions for CO_2-based methanol production occur when renewable energy, which is hydroelectricity in Quebec, is used for capturing CO_2 from the point source and to produce H_2 by water electrolysis. Also, our results show that the CO_2-based ethylene carbonate production achieves the highest environmental impacts reduction for global warming and human health impact categories when CO_2 is captured by a renewable energy and epoxide is supplied by bioethylene oxide or from a MTO pathway instead of fossil-based ethylene oxide. However, the ecosystem quality impact category increases by 10% and 16%, respectively. Additionally, for both CO_2-based methanol and ethylene carbonate productions the focus needs to be placed on creating novel and highly efficient catalysts in order to make these production pathways competitive with already implemented commercial routes and to increase the CCU products recovery in reality.

The use of carbon dioxide as a feedstock for the production of methanol and ethylene carbonate can have an important contribution in mitigating the effects of climate change by replacing energy-intensive fossil feedstocks by chemicals made from CO_2 and green energies. Captured CO_2 could reduce oil consumption and resulting greenhouse gas emissions. However, with respect to CO_2 storage, it should be taken into account that since the product life is identical after leaving the factory gate for both

fossil-based and CO_2-based chemicals, carbon storage does not offer any more benefits once the CO_2-based product is used or consumed.

The present study has some limitations, which should be taken into account. Assumptions were made to model the new processes and some cautions needs to be applied due to the uncertainties introduced by assumptions and study limitations. Also, more research is needed to improve data quality, especially for the processes at low TRL levels (lab scale in this study).

The feasibility of producing methanol and cyclic carbonates from captured CO_2 at larger scale depends not only on environmental performances of these processes, but also on socio-economic factors. Also, the integration of life cycle assessment and techno-economic assessment (TEA) can improve decision-making for CCU implementation. Finally, fundamental research and development (e.g., on catalyst) is essential to move towards the most promising CCU-processes from the earliest stage of design to complete operational plants and to render these CCU processes the promising candidates for industrial applications (Haunschild, 2015, Pérez-Fortes et al., 2016).

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