
From Life-Cycle Assessment towards Life-Cycle Design of Carbon Dioxide Capture and Utilization

Von der Fakultät für Maschinenwesen der
Rheinisch-Westfälischen Technischen Hochschule Aachen
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From Life-Cycle Assessment towards Life-Cycle Design of Carbon Dioxide Capture and Utilization

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Aachen, im Februar 2016

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“Pollution is nothing but resources we’re not harvesting.”

Richard Buckminster Fuller

Contents

List of figures	IX
List of tables	XI
Notation	XIII
Kurzfassung	XVII
Abstract	XIX
1 Introduction	1
1.1 Structure of this thesis	2
2 CO₂ Capture and Utilization (CCU)	5
2.1 Environmental motivation for CCU	6
2.2 Definition of CCU	9
2.3 Overview of CCU processes	10
2.3.1 CO ₂ capture	10
2.3.2 CO ₂ utilization	14
2.3.3 Challenges and potential environmental benefits for CCU	23
2.4 Status of environmental assessment of CCU	24
2.4.1 General awareness and qualitative claims	24
2.4.2 Environmentally motivated metrics for CCU	25
2.4.3 Status of LCA application for CCU	28
2.4.4 Identified gaps in the environmental assessment of CCU	30
2.5 Contribution of this thesis	30
3 Life-cycle assessment (LCA) for CCU	33
3.1 General concept of LCA	34
3.2 A tutorial for LCA of CCU	37
3.2.1 Ask the right question!	37
3.2.2 Compare equally!	39

3.2.3	Consider all relevant mass and energy flows!	41
3.2.4	Account for all products in the entire life cycle!	43
3.2.5	Consider all relevant impacts!	45
3.2.6	Use existing LCA software and LCA databases!	47
3.2.7	Start early and hang in!	47
3.2.8	Are you sure?	49
3.3	Summary and conclusions	51
4	Pitfalls in LCA for CCU	53
4.1	Pitfall 1: characterization of utilized CO ₂	54
4.1.1	Flow characterization of utilized CO ₂ in LCA	55
4.1.2	Illustration for methanol synthesis from CO ₂ and H ₂	58
4.2	Pitfall 2: product-specific LCA results of CCU	61
4.2.1	Multi-functionality in LCA	62
4.2.2	Multi-functionality in CCU	63
4.2.3	Illustration for methanol synthesis from CO ₂ and H ₂	64
4.3	Pitfall 3: global warming impact of CO ₂ storage duration	69
4.3.1	A time-corrected global warming (tcGW) metric	70
4.3.2	Application of tcGW to CCU	72
4.3.3	Illustration of tcGW for polymers from CO ₂	73
4.4	Summary and conclusions	77
4.4.1	A detailed framework for LCA of CCU to avoid pitfalls	77
5	Industrial Case Study: LCA for CO₂-based Polymers	81
5.1	Introduction to CO ₂ -based polymers	82
5.2	Description of data and methodology	83
5.2.1	System boundaries and goal of LCA study	83
5.2.2	Product system for CO ₂ -based polyols	85
5.2.3	Product system for conventional polyols	87
5.2.4	Functional unit for system-wide assessment	87
5.2.5	Functional unit for product-specific assessment	89
5.3	LCA results and discussion	89
5.3.1	System-wide LCA results for polyols and electricity	89
5.3.2	Variation of propylene oxide production technologies	92
5.3.3	Product-specific global warming impacts for polyols	93
5.4	Summary and Conclusions	94
6	Selecting CO₂ Sources for CO₂ Utilization	99
6.1	Motivation	100

6.2	Description of data and methodology	101
6.2.1	The environmental-merit-order curve for CO ₂ capture	101
6.2.2	Marginal environmental impacts of CO ₂ capture	104
6.2.3	Energy demand for CO ₂ capture	105
6.2.4	Environmental impacts of energy supply	107
6.2.5	CO ₂ emissions data	107
6.2.6	Environmental impacts of CO ₂ transport	107
6.2.7	Identification of CO ₂ oases	109
6.2.8	Available CO ₂ supply	109
6.3	Selecting CO ₂ sources in Europe	110
6.3.1	Environmental-merit-order curves	110
6.3.2	Marginal fossil resource depletion for avoided CO ₂ emissions . .	112
6.3.3	Selection of CO ₂ sources	114
6.3.4	CO ₂ oases in Europe	114
6.4	Summary and conclusions	116
7	Towards Life-Cycle Design of CO₂-based Chemicals	117
7.1	From retrospective LCA towards LCA-based prospective design	118
7.1.1	Life-Cycle Design approaches for CCU	120
7.2	LCA-based process design for CO ₂ -based methanol synthesis	121
7.2.1	Goal and scope definition	122
7.2.2	Optimization formulation	124
7.2.3	Graphical targeting approach	125
7.2.4	Threshold values for optimal reaction schemes	130
7.2.5	Summary and discussion for LCA-based process design for methanol from CO ₂	133
7.3	LCA-based process and product design for CO ₂ -based polymers	134
7.3.1	Goal and scope definition	135
7.3.2	Optimization formulation	137
7.3.3	Estimation methods and constraints for polyol properties	137
7.3.4	Computational structure of allocation methods in LCA	138
7.3.5	Application of allocation methods in life-cycle design	140
7.3.6	Environmentally optimal polyols and supply chain	141
7.3.7	Recommendation for allocation methods in LCD	144
7.3.8	Summary for life-cycle design of polymers	146
8	Summary and conclusions	147

A	CO₂ capture	151
A.1	CO ₂ capture concepts for combustion processes	151
A.2	CO ₂ capture technologies	153
B	Industrial case study: LCA for CO₂-based polymers	157
B.1	Potential differences in downstream processes	157
B.2	List of data sources	158
B.3	Allocation alternatives for cyclic propylene carbonate (cPC)	160
B.4	Midpoint impact categories	161
B.5	Normalized midpoint impact categories	165
C	Selecting CO₂ sources for CO₂ utilization	167
C.1	Marginal CO ₂ emissions for CO ₂ point sources	167
C.2	Marginal CO ₂ emissions for air capture	170
C.3	Marginal fossil resource depletion	170
C.4	Emission factors	171
C.5	Energy demand	172
C.6	CO ₂ transport distances	178
D	Towards life-cycle design of CO₂-based chemicals	179
D.1	LCA-based process design for CO ₂ -based methanol synthesis	179
D.1.1	Zero lines as functions of ν_{CO_2} and ν_{H_2}	179
D.1.2	Objective functions for divided regions	180
D.1.3	Vectors pointing towards the local optimal solution	180
D.1.4	Threshold lines	181
D.2	LCA-based process and product design for CO ₂ -based polymers	182
D.2.1	Computational structure of system expansion	182
E	Student theses completed within this work	185
	Bibliography	187

List of Figures

2.1	The global carbon cycle	7
2.2	Global CO ₂ emissions by CO ₂ sources	11
2.3	Gibbs free energy diagram for CO ₂ conversion	17
2.4	Carboxylation of CO ₂	18
3.1	General concept of LCA	34
3.2	ISO structure of LCA	35
3.3	Flow classification in LCA	36
3.4	Alternative system boundaries for methanol production pathways . . .	42
3.5	Accounting approaches for co-products in LCA	44
3.6	Impact assessment in LCA	45
3.7	Fossil resource depletion of CO ₂ -based and fossil-based methanol production	51
4.1	Flow chart of entire CCU system	55
4.2	Classification of CO ₂ capture systems	56
4.3	Flow-chart and flow quantities for electricity generation and CO ₂ -based and conventional methanol production.	65
4.4	Product-specific global warming impacts for CCU products using avoided burden	66
4.5	Allocated global warming impacts for electricity and for methanol . . .	69
4.6	Time-corrected characterization factors <i>tcGWP</i>	72
4.7	Emissions time profiles for CCU and non-CCU scenarios	75
4.8	Global warming impacts (GW and <i>tcGW</i>) of polymer production . . .	76
4.9	Framework for LCA of CCU	79
5.1	Reaction scheme for polyethercarbonate polyols	82
5.2	Product systems for polyol production	84
5.3	Global warming impacts of polyols (0 and 20 wt% CO ₂) and electricity	91
5.4	Global warming impacts of polyols (0-30 wt% CO ₂) and electricity . . .	92
5.5	Global warming impact reductions of polyols per kg feedstock CO ₂ . .	93

5.6	Fossil resource depletion of polyols (0-30 wt% CO ₂) and electricity . . .	94
5.7	Global warming impact of polyols for alternative PO sources	95
5.8	Product-specific global warming impacts of polyols	96
6.1	Process flow charts for CO ₂ capture from point sources and from air . .	103
6.2	Distribution of CO ₂ point sources in Europe	108
6.3	Environmental-merit-order curves for marginal CO ₂ emissions in Europe	111
6.4	Environmental-merit-order curves for marginal fossil depletion in Europe	113
6.5	CO ₂ oases maps for Europe	115
7.1	System boundary for production of compound C _x H _y O _z	123
7.2	Solution area of MILP for methanol from CO ₂ as potential feedstock .	126
7.3	Vectors pointing towards the local optima for methanol synthesis . . .	129
7.4	Environmentally optimal reaction schemes for methanol synthesis . . .	130
7.5	Environmentally optimal reaction schemes for methanol in dependance of the global warming impact of CO ₂ and H ₂	132
7.6	Supply chain superstructure for polyol production.	136
A.1	CO ₂ capture concepts for combustion processes	152
B.1	Global warming impact for polyethercarbonate polyols with 20 wt% CO ₂ for alternative allocation options for the by-product cPC	160
B.2	Freshwater eutrophication for conventional and CO ₂ -based polyols . . .	161
B.3	Marine eutrophication for conventional and CO ₂ -based polyols	162
B.4	Ionizing radiation for conventional and CO ₂ -based polyols	162
B.5	Ozone depletion for conventional and CO ₂ -based polyols	163
B.6	Particulate matter formation for conventional and CO ₂ -based polyols .	163
B.7	Photochemical oxidant formation for conventional and CO ₂ -based polyols	164
B.8	Terrestrial acidification for conventional and CO ₂ -based polyols	164
B.9	Normalized midpoint impact categories for conventional and CO ₂ -based polyols	165
C.1	CO ₂ desert map for Europe	178

List of Tables

3.1	Recommended impact categories in the European context by EC JRC.	46
3.2	Global warming and fossil resource depletion impacts for CCU-relevant feedstocks.	48
4.1	Comparison of global warming impacts for methanol production	60
4.2	Selected allocation scenarios and allocation factors for methanol synthesis	68
4.3	Parameters and cradle-to-grave GHG emissions for CCU and non-CCU polymer production.	74
5.1	Functional units and scenarios for PO and CO ₂ sources	90
5.2	Summary of LCA results for polyol production	97
6.1	Energy demands for CO ₂ capture from alternative CO ₂ sources	106
7.1	Polyol composition and production amounts in kg of selected intermediates in the polyol supply chain.	143
B.1	List of LCA process data for polyol production. Part 1	158
B.2	List of LCA process data for polyol production. Part 2	159
C.1	Environmental impacts for electricity, heat and fuel combustion	171
C.2	Actual energy demands for CO ₂ capture from alternative CO ₂ sources.	172
C.3	References	177

Notation

Abbreviations

BFG	Blast furnace gas
CCR	Carbon (dioxide) capture and recycling
CCU	Carbon (dioxide) capture and utilization
CCUS	Carbon (dioxide) capture, utilization and storage
CDU	Carbon dioxide utilization
CDR	Carbon dioxide recycling
CCS	Carbon (dioxide) capture and storage
CED	Cumulative energy demand
CLCA	Consequential Life-Cycle Assessment
CHP	Combined heat and power
CHPO	Chlorohydrin process for propylene oxide production
DAC	Direct air capture
ELI	Energy-loss index
EMO	Environmental-merit order
eq	equivalent
EOR	Enhanced oil recovery
FD	Fossil resource depletion
FU	Functional unit
GHG	Greenhouse gas
HPPO	Production of propylene oxide from hydrogen peroxide
IGCC	Integrated gasification combined cycle
ISO	International Organization for Standardization
LCA	Life-Cycle Assessment
LCD	Life-Cycle Design
LCI	Life-Cycle Inventory (Analysis)
LCIA	Life-Cycle Impact Assessment
LP	Linear program
MILP	Mixed-integer linear program

MINLP	Mixed-integer non-linear program
NG	Natural gas
NGCC	Natural gas (fired power plant with) combined cycle
ODP	Ozone depletion potential
PO/MTBE	Production of propylene oxide with methyl tert-butyl ether
PO/SM	Production of propylene oxide with styrol monomer
PO/TBA	Production of propylene oxide with tert-butyl alcohol
PV	Photovoltaics
RNFA	Reaction network flux analysis
RWGS	Reverse water gas shift
sc	Supercritical
SETAC	Society of Environmental Toxicology and Chemistry
SMR	Steam methane reforming

Chemicals

C	Carbon
cPC	Cyclic propylene carbonate
CaO	Calcium oxide
Ca(OH) ₂	Calcium hydroxide
CaCO ₃	Calcium carbonate
CFC	chlorofluorocarbon
CH ₄	Methane
CH ₃ OH	Methanol
CH ₂ O	Formaldehyde (FA)
CO	Carbon monoxide
CO ₂	Carbon dioxide
DMC	Dimethyl carbonate
DMC	Double metal cyanide
DME	Dimethyl ether
EO	Ethylene oxide
FA	Formaldehyde (CH ₂ O)
H ₂	Hydrogen
HCOOH	Formic acid
H ₂ CO ₃	Carbonic acid
H ₂ O	Water
H ₂ O ₂	Hydrogen peroxide
H ₂ S	Hydrogen sulfite

KOH	Potassium hydroxide
MTBE	methyl tert-butyl ether
N ₂	Nitrogen
N ₂ O	Nitrous oxide
NH ₃	Ammonia
NO _x	Nitrogen oxide
O ₂	Oxygen
PC	Poly-carbonate
PE	Poly-ethylene
PO	Propylene oxide
POM	Poly-oxy-methylene
SO _x	Sulfur oxide

Greek symbols

δ	Binary variable for occurrence of compound i as reactant or product
ν	Stoichiometric coefficient / product structure variable
τ	Time variable

Latin symbols

a_i	Radiative efficiency of GHG i
$AGWP$	Absolute global warming potential
$c_i(t)$	Decay function of GHG i
f	(Objective) function
F	Functionality, number of hydroxyl groups per starter molecule
g	Gibbs free energy
GW	Global warming impact
GWP	Global warming potential
h	Enthalpy
m_i	Amount of GHG i
$m_i(t)$	Emissions time profile of GHG i
$m_{\text{zero-line}}$	Slope of zero line
M	Molar mass
OH	Hydroxyl value
p	Pressure
p	Function used for equality constraints

q	Function used for inequality constraints
R	Ideal gas constant
t	Time variable
$tcGW$	Time-corrected global warming impact
$tcGWP$	Time-corrected global warming potential
T	Temperature
T_g	Glass transition temperature
TH	Time horizon
x	Mole fraction
Y_g	Group contribution to the glass transition temperature

Matrices and vectors

A	Technology matrix
B	Intervention matrix
C	Matrix with allocation factors
f	Vector for functional unit
$\tilde{f}$	Vector for co-products
h	Vector for environmental impact indicators
I	Identity matrix
$\vec{n}$	Vector pointing towards optimal solution
Q	Matrix with characterization factors for LCIA
s	Scaling vector
T_0	Transformation matrix for the technology matrix
T_1	Transformation matrix for the intervention matrix
U	Function matrix

General subscripts and superscripts

0	Standard conditions
avo	Avoided burden
el	Electricity
exp	Expanded
f	Formation
i	Compound
P	Product
R	Reactant or reaction
th	Thermal / heat

Kurzfassung

Der vermehrte Einsatz fossiler Rohstoffe führt unweigerlich zu CO₂-Emissionen und einer steigenden CO₂-Konzentration in der Atmosphäre. Die erhöhte CO₂-Konzentration ist eine der Hauptursachen für die globale Erwärmung der Erde. Eine Möglichkeit, der Ressourcenverknappung und der globalen Erwärmung zu begegnen, ist die CO₂-Abscheidung und anschließende Nutzung von CO₂ als alternative Kohlenstoffquelle. Sowohl CO₂-Abscheidung als auch -Nutzung (CO₂ Capture and Utilization, CCU) benötigen jedoch in der Regel Energie, deren Erzeugung meist wiederum fossile Rohstoffe einsetzt und CO₂-Emissionen verursacht. Die intuitiv erwarteten ökologischen Vorteile von CCU sind daher nicht zwingend gegeben. Aus diesem Grund sollte für jeden CCU-Einzelfall eine zuverlässige ökologische Bewertung erfolgen.

Eine zuverlässige ökologische Bewertung benötigt im Allgemeinen umfangreiche Prozessdaten wie Massen- und Energiebilanzen. Die Datenverfügbarkeit ist jedoch gerade für viele CCU-Prozesse in der Entwicklungsphase beschränkt. Deshalb werden häufig einfache, so-genannte *ad-hoc* Kriterien verwendet, die jedoch keine zuverlässige ökologische Bewertung garantieren. Ökobilanzen (Life-Cycle Assessments, LCA) hingegen bewerten den gesamten Lebenszyklus einer Prozesskette hinsichtlich mehrerer Umweltwirkungen. Der ganzheitliche Ansatz von LCA vermeidet, dass Probleme zwischen Lebensphasen oder Umweltwirkungen nur verschoben werden. Die Eignung von LCA zur ökologischen Bewertung von CCU ist zwar generell anerkannt. Aufgrund der beschränkten Datenverfügbarkeit und der scheinbaren Komplexität von LCA wurde LCA bisher jedoch nur selten auf CCU angewandt. Mit dieser Dissertation werden daher zwei Ziele verfolgt: Zum einen soll die Anwendung von LCA für CCU erleichtert und veranschaulicht werden. Zum anderen soll ein Ansatz für den ökologischen Entwurf von neuen CCU-Prozessen und -Produkten entwickelt werden.

Um die Anwendung von LCA für CCU-Prozesse zu erleichtern, gibt diese Arbeit eine LCA-Einführung speziell für CCU-Prozesse. Trotz des einfach zugänglichen Konzepts von LCA werden drei besonders wichtige Probleme bei der Anwendung von LCA auf CCU im Detail beleuchtet: Zum Ersten wird das genutzte CO₂ häufig fälschlicherweise als negative Emission klassifiziert. Tatsächlich stellt das genutzte CO₂ jedoch einen Rohstoff dar, dessen Abscheidung selbst Umweltwirkungen verursacht. Zum Zweiten

wird CO₂ meist in CO₂-Quellen abgetrennt, die vornehmlich ein anderes Produkt herstellen. Dadurch liefert das gesamte CCU-System neben dem CO₂-basierten Produkt auch jenes andere Produkt der CO₂-Quelle. Für produkt-spezifische LCA-Ergebnisse müssen die Umweltwirkungen des CCU-Systems auf die einzelnen Produkte aufgeteilt werden. Die bestehenden Möglichkeiten in LCA zur Allokation von Umweltwirkungen bieten jedoch großen Spielraum. Zum Dritten wird eine lange Speicherdauer von CO₂ in Produkten häufig als wichtige Voraussetzung für einen Beitrag zum Klimaschutz angesehen. Die Berücksichtigung der CO₂-Speicherdauer in der bestehenden Bewertung von Treibhausgasemissionen zeigt jedoch, dass der Effekt der Speicherdauer in der Regel klein und somit überschätzt ist. Zur Vermeidung der drei genannten Probleme wird schließlich ein Leitfaden für LCA von CCU-Prozessen präsentiert.

Der Leitfaden wird anhand eines industriellen Beispiels zur CO₂-basierten Polyol-Herstellung für Polyurethan-Schaumstoffe verdeutlicht. Eine Pilotanlage zur CO₂-Abscheidung eines Braunkohlenkraftwerks stellt CO₂ bereit, das in einer weiteren Pilotanlage zu Polyolen mit bis zu 30 Gewichtsprozent CO₂ synthetisiert wird. Die Ökobilanz des gesamten Herstellungsprozesses veranschaulicht, dass CCU deutliche Einsparungen des fossilen Rohstoffbedarfs sowie der CO₂-Emissionen ermöglicht.

Im Gegensatz zum industriellen Beispiel bieten CCU-Prozesse in frühen Entwicklungsphasen noch viele Freiheitsgrade für die ökologische Optimierung der CO₂-Abscheidung und -Nutzung. Die CO₂-Abscheidung kann in einer Vielzahl von CO₂-Quellen erfolgen. Da der Bedarf für die CO₂-Nutzung das mögliche Angebot von CO₂-Quellen übersteigt, wird eine Methodik entwickelt, um CO₂-Quellen mit den niedrigsten Umweltwirkungen auszuwählen. Schließlich werden CO₂-Quellen und ökologisch vorteilhafte Standorte zur CO₂-Nutzung in Europa identifiziert.

Für die ökologische Optimierung der CO₂-Nutzung werden zwei Ansätze entwickelt: Der erste Ansatz identifiziert ökologisch optimale Reaktionsgleichungen für die Hydrierung von CO₂ in Abhängigkeit der Bereitstellung von Wasserstoff (H₂) und CO₂. Da der Optimierungsansatz nur wenige und verfügbare Daten benötigt, eignet er sich besonders für frühe Phasen der Prozessentwicklung. Während die Hydrierung von CO₂ typischerweise Plattformchemikalien mit identischen Eigenschaften liefert, bietet die direkte und indirekte CO₂-Nutzung für Polymere weitere Freiheitsgrade in der Lieferkette sowie im Produktdesign. Der zweite Ansatz identifiziert daher die ökologisch optimale Lieferkette und Polymerzusammensetzung für CO₂-Polymere mit definierten Eigenschaften. Im Besonderen werden dabei alternative Methoden zur Allokation von Nebenprodukten innerhalb der Lieferkette analysiert. Die präsentierten Optimierungsansätze erlauben das bedingte Potential von CCU zur Reduktion von CO₂-Emissionen und Ressourcenverknappung auszuschöpfen.

Abstract

The increasing use of fossil resources will inevitably lead to CO₂ emissions and an increasing atmospheric CO₂ concentration. The increased CO₂ concentration is one of the main reasons for the earth's global warming. To mitigate global warming and the depletion of fossil resources, CO₂ can be captured and subsequently utilized as alternative carbon source for fuels, chemicals and materials. However, both CO₂ capture and utilization (CCU) typically require energy whose provision is again associated with fossil resource use and CO₂ emissions. Thus, the intuitively expected environmental benefits of CCU are not guaranteed. Therefore, each individual CCU case requires a reliable environmental assessment.

For a reliable environmental assessment, comprehensive process data are required such as mass and energy balances. However, data availability is typically limited for many CCU process in early development stages. To overcome the limited data availability, easily accessible *ad-hoc* metrics are often used. However, they usually cannot guarantee a reliable environmental assessment. In contrast to these ad-hoc metrics, Life-Cycle Assessment (LCA) evaluates the entire life cycle of process systems with respect to multiple environmental impacts. The holistic approach of LCA avoids problem shifting between life cycle phases or environmental impact categories. Although the suitability of LCA is generally acknowledged, LCA is not yet standard practice for an environmental assessment of CCU. The goal of this thesis is twofold: The first goal is to facilitate and illustrate the application of LCA for established CCU processes. The second goal is to provide an environmental design approach for new CCU processes and products.

To facilitate the application of LCA for CCU processes, this work provides a jargon-free introduction for LCA in the context of CCU. Despite the easily accessible concept of LCA, particularly important and severe pitfalls have been identified for the application of LCA to CCU: The first pitfall is the intuitive treatment of CO₂ as negative greenhouse gas emission. An illustrative example shows that utilized CO₂ is not a negative emission but instead a feedstock with its own production emissions. The second pitfall is the choice between alternative allocation methods to still obtain environmental impacts for the individual products while the CCU system generally

provides more than one product. General implications of alternative allocation methods in CCU are discussed and illustrated by a simplified case study. The third pitfall is the overestimation of the effect of the CO₂ storage duration on the global warming impact. Whereas today the CO₂ storage duration and the global warming impact are used as two separate metrics, a method to incorporate the CO₂ storage duration into the global warming impact is presented and discussed. Finally, a framework is derived to avoid the described pitfalls in LCA of CCU.

The derived framework is then applied to an industrial case study for LCA of CO₂-based polymer production. Here, CO₂ is captured in a pilot plant of a lignite power plant and then synthesized with epoxides into polyols with up to 30 weight percent CO₂ in another pilot plant. The results of this study show that capture and utilization of CO₂ for polymers reduces not only greenhouse gas emissions and fossil resource use, but all investigated environmental impacts. Furthermore, the LCA results provide valuable insights into the origin of the environmental benefits.

In contrast to the industrial case study, many CCU processes are at early development stages and thus offer many degrees of freedom for the environmental optimization of CO₂ capture and utilization. Therefore, the second part of this thesis extends the classical, retrospective scope of LCA towards a prospective Life-Cycle Design (LCD) approach. Starting with CO₂ capture, an approach is developed for the selection of CO₂ sources that minimizes the environmental impacts associated with CO₂ capture, compression and transport. The approach is applied for CO₂ sources in Europe to identify so-called CO₂ oases: locations where CO₂ can be obtained with lowest environmental impact.

For the environmental optimization of CO₂ utilization, two approaches are presented: The first approach identifies environmentally optimal reaction schemes for the hydration of CO₂ as a function of the environmental impacts of H₂ and CO₂ supply. Since the approach requires only basic thermodynamic data, it is particularly useful for early stages of CCU process design. While the hydration of CO₂ typically yields basic commodity chemicals with identical properties, the direct and indirect utilization of CO₂ for polymers provide novel degrees of freedom to design the polymer supply chain and to modify the polymer properties. To exploit these degrees of freedom for minimization of environmental impacts, the second approach identifies environmentally optimal polymer compositions as well as optimal production processes in the polymer supply chain. In particular, the approach considers alternative methods for allocation of by-products along the supply chain. The presented optimization approaches allow fully exploiting the limited potential of CCU to reduce fossil resource use and CO₂ emissions.

CHAPTER 1

Introduction

Ever since humans have existed, they have impacted the earth in many different ways (Redman, 1999). Currently, important impacts are associated with the excessive use of non-renewable fossil fuels such as coal, oil and natural gas. Most fossil fuels are used for electricity generation, heating and mobility (eia, 2011), and as feedstock in the chemical industry (IEA et al., 2013). Moreover, the use of fossil fuels is associated with carbon dioxide emissions (CO_2) (IEA, 2014; Leimkühler, 2010). Emitting CO_2 into the atmosphere leads to global warming and disrupts the natural carbon cycle (Stocker et al., 2013). To close the disrupted carbon cycle, CO_2 can be captured and re-utilized, thereby mitigating global warming and saving fossil resources (Styring et al., 2014).

CO_2 can be captured from current anthropogenic CO_2 sources or directly from the atmosphere. Captured CO_2 can then be utilized as valuable physical product “as such” or as alternative carbon feedstock for fuels, chemicals and materials. The general concept of *CO₂ Capture and Utilization* (CCU) can be considered established: already today, CO_2 is captured and utilized in processes in the chemical industry (Aresta et al., 2014). However, the scope of CO_2 utilization is limited. Despite the existing industrial implementations as well as continuous progress and current efforts in CCU research, most CCU technologies are still in early stages of development. Besides the limited technological readiness, CCU is intrinsically challenging since both capture and utilization of CCU typically require substantial amounts of energy (Sakakura et al., 2007). If the provision of energy relies on fossil resources, indirect CO_2 emissions are caused. Therefore, the intuitively expected environmental benefits from using CO_2 are not given by default (Peters et al., 2011b). In fact, it cannot be ruled out that a tediously accomplished CCU process is finally environmentally less sustainable than a conventional fossil-based route. Therefore, it is desirable to know whether a specific CCU process is environmentally favorable. For this purpose, a reliable environmental assessment of CCU is required.

As indicators for the environmental performance of CCU, a large variety of approaches are proposed ranging from qualitative design principles (Anastas and Warner, 1998) and metrics for ‘green’ chemistry (Constable et al., 2002) to CCU-specific ad-hoc criteria (Peters et al., 2011b; Müller and Arlt, 2014). These approaches are rather intended to guide the development towards ‘sustainable’ CCU processes than to systematically quantify the actual environmental impacts. In contrast to these approaches, Life-Cycle Assessment (LCA) is a systematic and standardized methodology to analyze the actual environmental impacts of products and processes (ISO 14040, 2009). Although LCA is frequently advocated for the environmental assessment of CCU (Aresta and Dibenedetto, 2007b; Peters et al., 2011b; Quadrelli et al., 2011), it is not yet standard practice (Schäffner et al., 2014). The reasons for this are the complexity of LCA as well as the limited data availability of many CCU processes at early design stages (Quadrelli et al., 2011).

In this context, this thesis pursues two major goals: First, the thesis enables and supports the reliable environmental assessment for CCU processes using LCA. To overcome the complexity of LCA and to enable LCA novices to apply LCA to CCU, a jargon-free introduction is presented for LCA in the context of CCU. Furthermore, a framework for LCA of CCU is derived to avoid severe pitfalls in LCA of CCU. A case study for CO₂-based polymers illustrates the application of LCA as well as the size and origin of environmental benefits of CCU. The second goal of this thesis is to provide an LCA-based approach to support the design of environmentally beneficial CCU processes at early stages. In summary, the thesis is intended to facilitate the utilization of LCA for CCU from early design stages to industrial implementation.

1.1 Structure of this thesis

Chapter 2 provides an overview of CO₂ capture and utilization. The chapter starts from the global environmental motivation of CCU. Then, a clear definition of CCU is given. Current and future technologies for both capture and utilization of CO₂ are presented to understand their potential benefits and challenges from a thermodynamic and environmental point of view. A review of methods currently used for the environmental assessment of CCU shows that LCA is frequently acknowledged as important for CCU but rarely applied due to its complexity. Based on the gaps in the environmental assessment of CCU, the contribution of the thesis is highlighted.

The contribution of the thesis is divided into two parts: The first part consisting of the chapters 3-5 aims at facilitating and illustrating the use of *Life-Cycle Assessment* for CCU. The second part consisting of the chapters 6-7 presents approaches for the prospective *Life-Cycle Design* of CCU processes and products.

In chapter 3, the concept of LCA is introduced and a specific work flow is derived for the application on CCU. A detailed action list is presented in the spirit of a tutorial of LCA of CCU. The tutorial is intended to enable LCA novices to apply and understand LCA in a CCU context.

In chapter 4, three items of the tutorial are analyzed in detail since they have been identified as particularly important and commonly encountered pitfalls in LCA of CCU: The first pitfall is the intuitive treatment of CO_2 as negative greenhouse gas emission. An illustrative example shows that utilized CO_2 is not a negative emission but instead a feedstock with its own production emissions. The second pitfall is the choice between alternative allocation methods to still obtain environmental impacts for the individual products while the CCU system generally provides more than one product. General implications of alternative allocation methods in CCU are discussed and illustrated by a simplified case study. The third pitfall is the overestimation of the effect of the CO_2 storage duration on the global warming impact. Whereas today the CO_2 storage duration and the global warming impact are used as two separate metrics, a method to incorporate the CO_2 storage duration into the global warming impact is presented and discussed. Finally, a framework is derived to avoid the described pitfalls in LCA of CCU.

In chapter 5, an industrial case study for LCA of CO_2 -based polymer production is presented. The case study illustrates the methodology for LCA of CCU from chapters 3 and 4. The results of this study show that capture and utilization of CO_2 for polymers reduces not only greenhouse gas emissions and fossil resource use, but all investigated environmental impacts. Furthermore, the LCA results provide valuable insights into the origin of the environmental benefits.

Starting with chapter 6, the classical scope of retrospective *Life-Cycle Assessment* of existing CCU processes is extended to support the *Life-Cycle Design* (LCD) of novel CCU processes. In chapter 6, an approach is developed for the selection of CO_2 sources. The CO_2 source can be a decisive factor whether CCU processes are environmentally favorable. Selecting CO_2 sources with the presented approach minimizes the environmental impacts associated with CO_2 capture, compression and transport while taking into account the demand for CO_2 utilization. The approach is applied for CO_2 sources in Europe to identify so-called CO_2 oases: locations where CO_2 can be obtained with lowest environmental impact.

In chapter 7, two approaches are presented for the Life-Cycle Design of CO_2 utilization. The first approach identifies environmentally promising reaction schemes for products from hydrogenation of CO_2 . The second approach is an integrated design approach for CO_2 -based polymers that identifies environmentally optimal polymer

compositions as well as optimal production processes in the polymer supply chain.

In chapter 8, the thesis is summarized and conclusions are drawn regarding both LCA methodology and LCA results for CCU. Specifically, the capabilities and limitations of LCA and LCD for CCU are discussed. General conclusions are drawn regarding the conditions under which the presented CCU options are environmentally favorable.

CHAPTER 2

CO₂ Capture and Utilization

This chapter provides an overview of CO₂ Capture and Utilization (CCU). In section 2.1, the main environmental motivation for CCU is explained in the context of the global carbon cycle. In section 2.2, CCU is defined for the scope of this thesis. Section 2.3 contains a description of CCU technologies and their potential environmental benefits. In section 2.4, the status of the environmental assessment of CCU is reviewed and existing gaps are identified. Based on the identified gaps in environmental assessment of CCU, the contribution of this thesis is outlined in section 2.5.

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von der Assen, N., Jung, J., and Bardow, A. (2013). Life-Cycle Assessment of Carbon Dioxide Capture and Utilization: Avoiding the Pitfalls. *Energy & Environmental Science*, 6:2721-2734.

von der Assen, N., Voll, P., Peters, M., and Bardow, A. (2014). Life cycle assessment of CO₂ capture and utilization: a tutorial review. *Chemical Society Reviews*, 43:7982-7994.

2.1 Environmental motivation for CCU

The use of fossil fuels for energy supply and as feedstock for chemicals will ultimately lead to the depletion of the earth's fossil resources. Furthermore, using fossil fuels causes inherently coupled carbon dioxide (CO₂) emissions. Instead of emitting CO₂ into the atmosphere, CO₂ can be captured and subsequently be utilized as physical product or chemical carbon feedstock (Leitner, 1996; Mazzotti et al., 2005; Sakakura et al., 2007). Due to the multiple use of carbon, CO₂ capture and utilization (CCU) can partially close the carbon cycle (Styring et al., 2014). Thereby, CCU bears potential to reduce both CO₂ emissions and depletion of fossil resources (Peters et al., 2011b; Quadrelli et al., 2011; Centi et al., 2013).

To put the global reduction potential of CCU regarding CO₂ emissions and fossil depletion in perspective, CCU should be related to the global carbon cycle (Fig. 2.1). Without human activities, the natural carbon cycle was closed exchanging total carbon flows of about 169 Gt a⁻¹ of carbon (C) between the atmosphere, and the land and oceans (gray arrows in Fig. 2.1). Human activities, in particular combustion of fossil fuels and deforestation, have perturbed the natural carbon cycle by increasing the carbon flux to the atmosphere by currently 38 Gt a⁻¹ C to a total of 207 Gt a⁻¹ C (red arrows in Fig. 2.1). The carbon sinks in the oceans and on land have also increased, however, only by about 34 Gt a⁻¹ C. Thus, human activities have led to a current net carbon flux to the atmosphere of about 4 Gt a⁻¹ C. As a consequence, the carbon content in the atmosphere has increased from 589 Gt C in pre-industrial times (in about 1750) to 829 Gt C in 2011 in total amounts, or from 278 to 390 ppm in CO₂ concentration (Stocker et al., 2013).

The increased atmospheric CO₂ concentration is problematic since it is a main driver for global warming (Stocker et al., 2013): The sun radiates electromagnetic waves with a broad spectrum towards the earth. Most of the solar radiation lies within the visible spectrum which easily passes through the atmosphere towards the surface of the earth. The earth re-emits parts of the absorbed solar radiation as infrared radiation. This infrared radiation, however, is absorbed by atmospheric greenhouse gases (GHG) such as CO₂ which in turn re-emit some of that infrared radiation towards the earth. Thereby, an increased atmospheric CO₂ concentration leads to an increased greenhouse effect, and accordingly, to a temperature increase of the earth's surface and lower atmosphere, which is known as global warming. Global warming may have effects on the climate (e.g., extreme weather events), on ecosystems (e.g., distinction of species), and social systems (e.g., lower crop yields) (Field et al., 2013). In addition to an increased CO₂ concentration in the atmosphere, the carbon content in the oceans has increased by 155 Gt C in the form of solute CO₂, i.e., carbonic acid (H₂CO₃). An

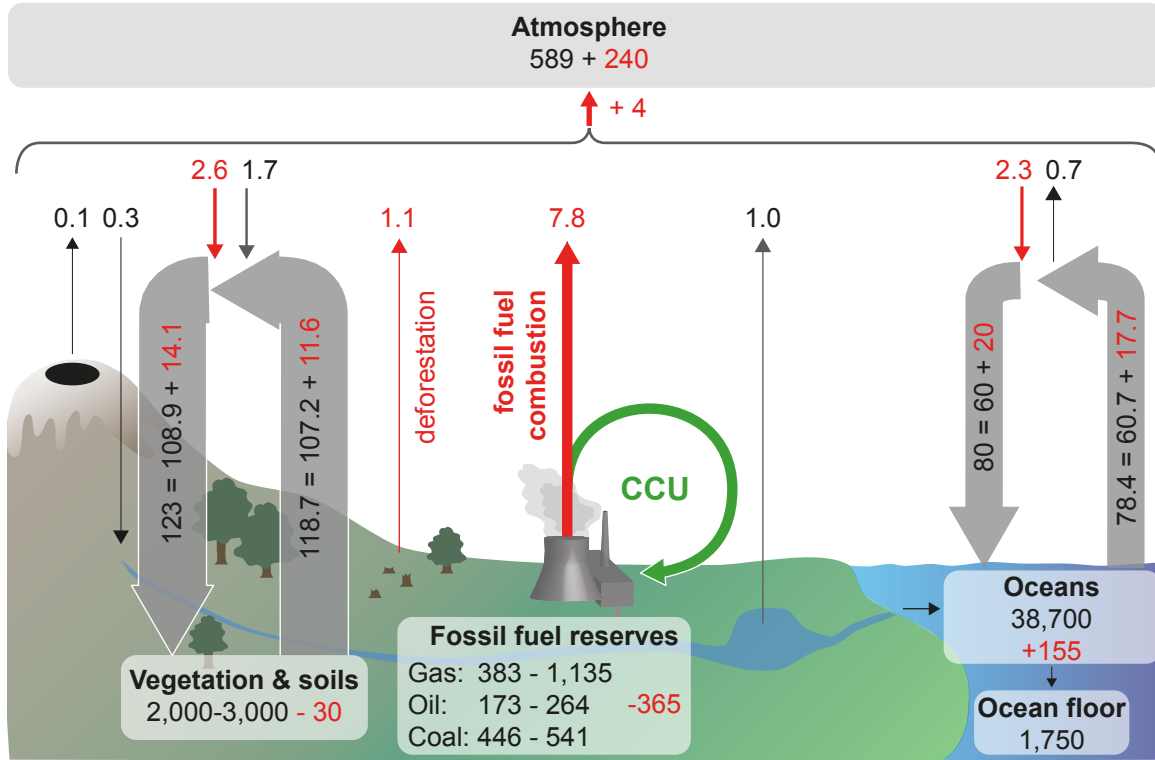


Figure 2.1: The global carbon cycle. Grey arrows indicate natural carbon flows; red arrows indicate anthropogenic carbon flows; in Gt a⁻¹ C. The carbon pools atmosphere, oceans, vegetation and soils, and fossil fuel reserves are given in Gt C. Adapted from Stocker et al. (2013).

increased concentration of carbonic acid leads to acidification of the oceans (Doney et al., 2009). Reduced pH in oceans changes calcium carbonate chemistry and impacts many shell-forming organisms such as molluscs and coral reefs. The additional carbon into the atmosphere and oceans mainly originates from fossil fuels which have been depleted for mainly combustion purposes by 365 Gt C. The rate of fossil fuel use is much larger than the replenishment. Thus, continued use of fossil fuels at the current or an even increasing rate will finally deplete the entire fossil resources.

The current anthropogenic carbon flux is a one-way street mainly from fossil resources to the atmosphere and the oceans as dead-ends. Therefore, it has been suggested to capture CO₂ emissions from CO₂ emitters and to store the CO₂ underground, where the carbon has come from, e.g., in geological reservoirs (Metz et al., 2005). An even better option to mitigate global warming, ocean acidification and fossil resource depletion appears to close the carbon cycle by recycling of CO₂ (Styring et al., 2014;

Goeppert et al., 2014). The overall recycling potential is mainly limited by the market potential of CO₂-based products. Estimates for the CO₂ utilization potential range from 0.05 Gt a⁻¹ C or 200 Mt a⁻¹ CO₂ for chemicals (Mikkelsen et al., 2010; Aresta et al., 2013) to 0.55 Gt a⁻¹ C or 2 Gt a⁻¹ CO₂ including large-scale CO₂-based methanol (DECHEMA, 2009; Centi and Perathoner, 2011). Although the amount of CO₂ utilized does not equal the amount of avoided CO₂ emissions (Aresta et al., 2014), the amounts of utilized CO₂ can serve as first estimate for the order of magnitude of avoided CO₂ emissions. The CO₂ utilization potential of 0.55 Gt a⁻¹ C has to be related to the anthropogenic CO₂ emissions¹ of 7.8 Gt a⁻¹ C or to the net carbon flux of 4 Gt a⁻¹ C: on the one hand, the potential contribution of CCU to climate mitigation is limited and thus, it definitely cannot be the only solution (Aresta and Dibenedetto, 2007a). On the other hand, the abundant CO₂ availability makes CO₂ a non-depleting, thus renewable feedstock (Sakakura et al., 2007; Mikkelsen et al., 2010; Patil et al., 2010).

Since CO₂ utilization is frequently proposed for the chemical industry, it is reasonable to narrow the perspective accordingly. The chemical industry currently uses 42 EJ a⁻¹ of fossil fuels (equivalent to about 0.9 Gt a⁻¹ C) (IEA et al., 2013), of which 27 EJ a⁻¹ are used as feedstocks (Daioglou et al., 2014), and causes 3.3 Gt a⁻¹ of CO₂ emissions (equivalent to 0.9 Gt a⁻¹ C) (Leimkühler, 2010). Comparing the fossil fuel use of 0.9 Gt a⁻¹ C to the global CO₂ utilization estimates of up to 0.55 Gt a⁻¹ C shows that CCU has the potential to significantly reduce fossil depletion within the chemical industry. For this reason, Sakakura et al. (2007) claim that the major significance of CO₂ utilization is to provide a renewable carbon feedstock for the chemical industry. In addition to fossil fuel reduction, the same claim can be made for climate mitigation since the CO₂ utilization potential of 2.0 Gt a⁻¹ CO₂ is almost as big as the 3.3 Gt a⁻¹ CO₂ emissions of the chemical industry. Therefore, for the chemical industry, a possible conclusion is that CCU has the potential to equally contribute to reduce fossil resource depletion and global warming. However, these simple comparisons do not take into account that the energy requirements of CCU might even lead to an increased fossil fuel demand and additional CO₂ emissions. Therefore, a thorough analysis is required.

¹If not stated otherwise, CO₂ emissions refer to emissions of CO₂ only. CO₂-eq emissions refer to various greenhouse gas (GHG) emissions such as CO₂, CH₄ and N₂O aggregated as CO₂ equivalent emissions. See section 3.1 for details.

2.2 Definition of CCU

Many terms are used for closing the carbon cycle by CO₂ recycling: The concept of utilizing CO₂ is known as *Carbon Dioxide Utilization (CDU)* (Styring et al., 2011; Centi and Perathoner, 2014), *Carbon Dioxide Recycling (CDR)* (Quadrelli et al., 2011; Perathoner and Centi, 2014), and, if integrated with CO₂ capture, as *CO₂ Capture and Utilization (CCU)* (Khoo et al., 2011a; Yang et al., 2012; Markewitz et al., 2012; Boot-Handford et al., 2014), *CO₂ Capture and Recycling/Re-Use (CCR)* (Centi and Perathoner, 2011; Quadrelli and Centi, 2011; Goeppert et al., 2012; Boot-Handford et al., 2014), and, if further combined with CO₂ storage, as *CO₂ Capture, Utilization and Storage (CCUS)* (Hasan et al., 2014). Moreover, the various terms are often not clearly defined. The scope of this thesis is a system analysis of both CO₂ capture and utilization. Thus, the term CO₂ Capture and Utilization (CCU) will be used here. Most CO₂ utilization technologies require concentrated CO₂. For the scope of this thesis, CCU is thus defined as follows:

CO₂ capture and utilization (CCU) comprises of
 a first step of *industrial capture* to obtain concentrated CO₂,
 and the *functional utilization* of this CO₂ in a distinct second step.

Industrial capture includes both removing CO₂ directly from the atmosphere and from stationary CO₂ point sources. Large-scale stationary CO₂ point sources include fossil-fueled power plants and industrial processes such as ammonia synthesis. An overview of CO₂ sources and capture technologies is given in section 2.3.1.

Functional utilization of concentrated CO₂ means that the utilization process fulfills a function beyond storing CO₂. This function can be direct utilization of CO₂ as product, e.g., as a solvent, or conversion of CO₂ into other products such as fuels. Processes that simply store CO₂ without further utilization are considered as *Carbon Capture and Storage (CCS)*. CCS examples include geological storage and ocean storage; furthermore, mineral carbonation can be considered as CCS if the obtained carbonates are sequestered (Metz et al., 2005). However, mineral carbonation can also be considered as CCU if the use of carbonates fulfills a function, e.g., as construction materials. Thus, the full downstream chain of the CO₂ utilization process has to be considered for classification as CCS or CCU. An overview of functional CO₂ utilization options is given in section 2.3.2.

Some processes can capture and utilize CO₂ simultaneously. For example, algae can feed on CO₂-rich flue gases and simultaneously produce useful products (Scott et al.,

2010). Since many of these integrated processes are biological conversions of CO₂ (Mikkelsen et al., 2010), they are excluded from the present definition of CCU and instead classified as bio-fixation or biomass production. Nevertheless, the methods and considerations presented in this thesis are generally also applicable for these integrated processes. However, careful considerations are required for the evaluation of biogenic carbon flows (see section 4.1.1).

2.3 Overview of CCU processes

The following sections provide an overview of CO₂ capture and utilization options. Instead of giving a thorough review, the overview highlights technological and chemical features relevant to understanding the potential environmental benefits and challenges of the CCU processes. For detailed reviews, the reader is referred to Metz et al. (2005); Mac Dowell et al. (2010); Boot-Handford et al. (2014) for CO₂ capture, and to Wells and DeSimone (2001); Mazzotti et al. (2005); Sakakura et al. (2007); Aresta and Dibenedetto (2007b); Mikkelsen et al. (2010); Quadrelli and Centi (2011); Centi et al. (2013); Aresta et al. (2014); Styring et al. (2014) for CO₂ utilization.

2.3.1 CO₂ capture

CO₂ capture generally requires energy. Providing the energy through fossil fuels causes indirect CO₂ emissions. Thus, a major challenge is to minimize the energy required for CO₂ capture. A key factor to lower the energy demand of CO₂ capture is to find CO₂ sources with high CO₂ concentrations (Farla et al., 1995). The energy demand can also be lowered by economies of scale which favors CO₂ capture from large CO₂ sources.

In addition to energy provision, environmental impacts may also be caused by chemicals involved in the capture process such as solvents. Impurities in the flue gas can affect the capture process, and may have to be removed for subsequent CO₂ utilization. The following description of CO₂ sources highlights some of the aforementioned features to enable the reader to understand the potential environmental benefits and challenges of CO₂ capture.

2.3.1.1 CO₂ sources

In 2010, the use of fossil fuels lead to CO₂ emissions of about 34 Gt a⁻¹ CO₂ (Boden et al., 2013). More than half of these CO₂ emissions origin from a large variety of CO₂ point sources (Fig. 2.2). The following part of this section presents CO₂ sources, for which CO₂ capture has been proposed in the literature. The stated CO₂ concentrations are given in volume percent (=mole fraction for ideal gases).

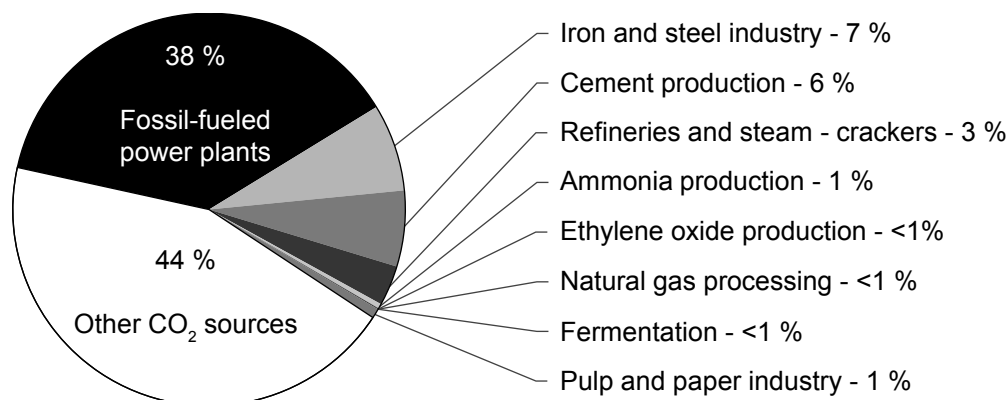


Figure 2.2: Global CO₂ emissions differentiated by CO₂ point sources. Other CO₂ sources include emissions from transport, land use change and residential heating. Data from Boden et al. (2013); Metz et al. (2005); Kuramochi et al. (2012); van Straelen et al. (2010); Farla et al. (1995); EPA (2010); Jönsson and Berntsson (2012).

Fossil-fueled power plants. The currently most discussed CO₂ point sources are fossil-fueled power plants since they emit about 12.1 Gt a⁻¹ CO₂ corresponding to 78 % of all CO₂ from large-scale point-sources greater than 0.1 Mt a⁻¹ CO₂ (Metz et al., 2005). In particular, coal- and lignite-fired power plants have the largest specific CO₂ emissions per power output among fossil-fueled power plants. Thus, they offer the largest overall CO₂ reduction potential. Furthermore, the flue gases from combustion of coal and lignite have a higher CO₂ concentration of 12-15 % than those of natural gas combustion with 3-10 % (Gale et al., 2005). However, the energy demand for CO₂ capture reduces the net output of the power plant and thus its efficiency. For current CO₂ capture technologies in coal-fired power plants, the energy demand reduces the net power plant efficiency by about 10 absolute percentage points, e.g., from 43 % to 33 % (Thambimuthu et al., 2005). In addition to CO₂, nitrogen (N₂) and remaining O₂ from air, flue gases from power plants typically contain impurities such as water (H₂O), sulfur compounds (H₂S and SO_x), carbon monoxide (CO), nitrogen oxides (NO_x) and heavy metals (Markewitz et al., 2012).

Iron and steel industry. CO₂ emissions from the iron and steel sector were about 2.3 Gt a⁻¹ CO₂ in 2007 (Kuramochi et al., 2012). The most used process for steel making is based on pig iron from blast furnaces (Kuramochi et al., 2012). The blast furnace is the process with the largest carbon throughput: iron ore sinters or pellets are reduced with coal and coke to produce metallic pig iron and so-called blast furnace gas (BFG). The BFG contains 17-25 % CO₂, 20-28 % carbon monoxide (CO), 1-5 %

hydrogen (H₂) and 50-55 % N₂ (Kuramochi et al., 2012). Currently, the BFG is mixed with other process gases and is used for on-site power generation (Gielen, 2003). Various concepts for CO₂ capture from BFG with optional CO-shift or top gas recycling have been investigated (Kuramochi et al., 2012).

Cement production. Cement production causes global CO₂ emissions of about 2.0 Gt a⁻¹ CO₂ (Kuramochi et al., 2012). About 0.8 t CO₂ per tonne of cement are emitted of which about one half is due to combustion of fossil fuels for heat supply and the other half as inherent co-product from calcination (Rodríguez et al., 2012). In calcination, the raw material limestone consisting mainly of calcium carbonate (CaCO₃) is decomposed to CO₂ and calcium oxide (CaO) at about 950 °C. Obtained CaO is then converted to cement clinker in a kiln at about 1450 °C. To provide heat for both the calcination process and the kiln, combustion of coal is typically employed (Kuramochi et al., 2012). Although using other fuels such as biomass has the potential to lower CO₂ emissions, capturing CO₂ from the cement plant flue gases (15-30 % CO₂ concentration, from combustion and calcination) has been identified as most effective measure for reducing absolute CO₂ emissions in cement plants (Rodríguez et al., 2012).

Refineries and steam crackers. Refineries emit about 0.8 Gt a⁻¹ CO₂ (Gale et al., 2005) of which more than 65 % are generated in furnaces and boilers (van Straelen et al., 2010). In conventional boilers, the CO₂ concentration of the flue gas is 12 %; for combined heat and power (CHP), the CO₂ concentration is only 4 % (van Straelen et al., 2010). Although refineries could basically provide large amounts of CO₂, a single refinery usually has multiple exhaust stacks and thus, CO₂ capture would probably require a complex gas gathering system (Gale et al., 2005).

Steam crackers cause worldwide CO₂ emissions of about 0.26 Gt a⁻¹ CO₂ (Gale et al., 2005). Steam crackers mainly produce the bulk chemicals ethylene and propylene with a couple of by-products such as hydrogen, methane or pygas. Cracking the feed is an endothermic process and requires heating in furnaces and steam for reaction control. Combustion emissions for heat and steam supply are the major sources for CO₂ emissions in steam crackers (Kuramochi et al., 2012). The CO₂ concentration in the steam crackers' flue gases is about 12 % (Gale et al., 2005).

Methane steam reforming and ammonia production. In methane steam reforming, methane and steam are converted to synthetic gas, or short syngas. Syngas is a mix of mainly hydrogen and carbon monoxide but raw syngas can contain up to 15 % CO₂ (Collodi and Wheeler, 2010). Syngas is an important feedstock for many chemical processes. Usually, the downstream processes require a CO₂-free syngas which requires CO₂ capture and thus yields CO₂ as co-product.

Instead of using syngas directly, the contained CO can be shifted with H₂O to CO₂

and H_2 , thus increasing the H_2 yield. Pure H_2 is separated from the shifted syngas leaving a tail gas with a high CO_2 concentration (Collodi and Wheeler, 2010).

For ammonia production in the Haber-Bosch process, ammonia (NH_3) is produced from N_2 and H_2 . H_2 is produced via methane steam reforming similarly as described above. Thereby, 127 Mt a^{-1} of high-purity CO_2 are currently provided as co-product in NH_3 production (Gale et al., 2005). Most of the CO_2 that is sold as pure product today is recovered from syngas, H_2 and NH_3 production (Ebner and Ritter, 2009).

Ethylene oxide production. Production of ethylene oxide (EO) accounts for 3 Mt a^{-1} CO_2 (Gale et al., 2005). Ethylene is directly oxidized to EO with a fraction of ethylene and EO being completely oxidized to CO_2 and H_2O . The gaseous products are finally separated and, in addition to the main product EO, highly concentrated CO_2 with only traces of impurities is obtained (Farla et al., 1995).

Natural gas processing. Specifications for natural gas require removal of acid gas impurities such as H_2S and CO_2 (Ebner and Ritter, 2009). The CO_2 concentration in the raw natural gas varies largely between 2 and 65 % (Gale et al., 2005). Gale et al. (2005) estimate that 5 Mt a^{-1} of high-purity CO_2 are currently produced in natural gas processing worldwide.

Fermentation. Fermentation of biomass in ethanol plants and distilleries provides about 17.6 Mt a^{-1} CO_2 at almost 100 % CO_2 concentration (Gale et al., 2005). The CO_2 stream can be treated in a simple water wash to remove sulfur compounds and odor (Ebner and Ritter, 2009).

Pulp and paper industry. The pulp and paper industry is responsible for about 171 Mt a^{-1} CO_2 in the United States (EPA, 2010), and about 83 Mt a^{-1} CO_2 in Europe (Jönsson and Berntsson, 2012). About 50-80 % of these emissions is from combustion of biomass waste to produce steam, which is required to digest wood chips into paper pulp (EPA, 2010; Jönsson and Berntsson, 2012). The CO_2 concentration of combustion flue gases can vary between 13-25 % (Möllersten et al., 2004; Hasan et al., 2014). The fuel for combustion is a biomass waste product from the pulp process. The biomass has taken up CO_2 from the atmosphere during tree growth. With integrated CO_2 capture, production of pulp and paper thus has the potential to serve as net CO_2 sink (Möllersten et al., 2004). Furthermore, integrated pulp and paper mills and in particular market pulp mills offer promising options for process and heat integration with CO_2 capture (Hektor and Berntsson, 2007, 2009).

CO_2 from the atmosphere. The atmosphere contains about 829 Gt C (Fig. 2.1) or 3000 Gt CO_2 , corresponding to 390 ppm (ESRL, 2012). Industrial capture of CO_2 directly from the atmosphere, so-called air capture, has been proposed (Keith

et al., 2006; Goeppert et al., 2012; Lackner, 2013). CO₂ capture from the atmosphere allows to indirectly capture CO₂ emissions from mobile CO₂ sources such as vehicles, ships and planes (Mazzotti et al., 2013; Goeppert et al., 2012). However, due to the low atmospheric CO₂ concentration of 0.039 %, the theoretical minimal energy requirement for air-capture is about 3.4 times higher compared to point-sources with 10 % CO₂ concentration (Keith et al., 2006).

The presented CO₂ sources feature very different characteristics: whereas power plants, iron and steel plants and cement plants cause the largest share of CO₂ emissions among CO₂ point sources, their flue gases have relatively low CO₂ concentrations of about 3-30 %. Highly concentrated CO₂ can be obtained from production of ammonia and ethylene oxide, from gas processing and from fermentation processes. However, these CO₂ sources could only provide limited amounts of CO₂ of about 150 Mt a⁻¹.

2.3.1.2 CO₂ capture concepts for combustion processes

Most of the CO₂ emissions from the described CO₂ sources are due to combustion processes. For combustion processes, CO₂ capture concepts are classified according to where and how the combustion takes place in post-combustion, pre-combustion, oxy-fuel combustion, and chemical looping combustion. For the alternative CO₂ capture concepts, individual environmental benefits are discussed in Appendix A.1.

2.3.1.3 CO₂ capture technologies

For the presented CO₂ point sources, CO₂ is typically emitted in gaseous waste streams, e.g., combustion flue gases. Thus, CO₂ capture means to separate CO₂ from other gases. For gas separation, four main unit operations are frequently used: membranes, cryogenic distillation, adsorption, and physical and chemical absorption (Ebner and Ritter, 2009). For the alternative separation technologies, individual environmental benefits are discussed in Appendix A.2.

Except for a few, limited cases where pure CO₂ is already available, provision of CO₂ by capture from diluted gas streams requires substantial amounts of energy. Supplying the energy for CO₂ capture by fossil fuels leads to additional CO₂ emissions and fossil fuel depletion. In addition to energy, capital goods for CO₂ capture cause further economic and environmental burdens.

2.3.2 CO₂ utilization

Technologies for CO₂ utilization can be divided into direct utilization of CO₂ as product and conversion of CO₂ into products.

2.3.2.1 Direct CO₂ utilization

The unique physico-chemical properties of CO₂ make it a useful product for a variety of applications. Since CO₂ is inert, non-flammable and non-toxic, it is used as protecting gas, e.g., in fire extinguishers, welding and for conservation of food products (Peters et al., 2011b). In enhanced oil recovery (EOR)², CO₂ is pressed into oil fields to reduce oil viscosity and to enhance oil extraction. Furthermore, CO₂ that is not dissolved in the extracted oil can be stored in the oil reservoirs (Jaramillo et al., 2009). In the textile, paper and steel industry, the ability of CO₂ to dissolve in water and form the weak carbonic acid (H₂CO₃) is exploited to adjust pH in H₂O₂ production (Peters et al., 2011b; Wells and DeSimone, 2001). Beverages are also carbonized with CO₂/carbonic acid. Some properties of CO₂ such as density, viscosity, miscibility, solubility or polarity can be changed largely by only small changes in pressure and temperature (Wells and DeSimone, 2001; Peters et al., 2011b). Thereby, CO₂ can trigger property switches of solutions and allow for energy-efficient separation processes (Jessop et al., 2012).

In addition to gaseous CO₂, utilization of CO₂ is particularly interesting in its supercritical state. The supercritical state of CO₂ can be achieved under moderate conditions (31.3 °C and 7.39 MPa) (Hintermair et al., 2010). Supercritical CO₂ (scCO₂) has the density of a fluid and the viscosity of a gas (Wells and DeSimone, 2001). Supercritical CO₂ is used as cleaning and extracting agent, e.g., for decaffeinating coffee, (Leitner, 2002) and in the reverse process of extraction, namely impregnation (Peters et al., 2011b). ScCO₂ is a promising solvent due to its low heat of vaporization and thus energy efficient recovery compared to water (Darensbourg et al., 1995; Leitner, 1999; Wells and DeSimone, 2001). Furthermore, scCO₂ can substitute conventional, harmful solvents such as chlorofluorocarbon (CFC) (Mikkelsen et al., 2010). In cooling cycles, CO₂ can substitute currently used refrigerants which are flammable, toxic and more potent greenhouse gases (Pearson, 2005). Due to fugitive emissions of today's refrigerants, about 3.9 Mt a⁻¹ CO₂ equivalent emissions are caused by air conditioners in cars in Germany (UBA, 2013).

CO₂ in its solid state, so-called “dry ice”, can also be used for refrigeration where technical cooling is not possible (Mikkelsen et al., 2010).

The main environmental motivation for direct utilization of CO₂ is to exploit the unique properties of CO₂ which allow for better process efficiency compared to a process without using CO₂. Thereby, GHG emissions and fossil fuel use can be reduced indirectly (Jessop et al., 2012). For most applications of direct CO₂ utilization, CO₂

²EOR is considered as CCU according to the definition in section 2.2 since extracting more oil due to CO₂ utilization can be considered as functional CO₂ utilization beyond geological CO₂ storage.

is released shortly after its use. Thus, a direct climate benefit cannot be expected.

2.3.2.2 CO₂ Conversion

This section gives an overview of the options to convert CO₂ into useful products. To understand the environmental benefits and challenges of CO₂ conversion, it is useful to start with a close look on the thermodynamics of CO₂ conversion.

Conversion of CO₂ is thermodynamically challenging since CO₂ is the most oxidized state of carbon. Thus, CO₂ is relatively unreactive due to its low energy level (Mikkelsen et al., 2010; Sakakura et al., 2007). More precisely, the Gibbs free energy of formation $\Delta g_{\text{CO}_2}^{f,0} = -394$ kJ/mol of CO₂ is low, thus impeding the driving force for CO₂ conversion (Fig. 2.3a). The major driving force for reactions is the Gibbs free energy of reaction Δg_0^R , which is defined as difference in Gibbs free energy of formation³ $\Delta g_i^{f,0}$ of the products and reactants i , where ν_i are the stoichiometric coefficients of products ($\nu_i > 0$) and reactants ($\nu_i < 0$):

$$\Delta g_0^R = \sum_i \nu_i \Delta g_i^{f,0}. \quad (2.1)$$

The Gibbs free energy of reaction Δg_0^R determines the equilibrium composition x_i , e.g., for ideal gases:

$$e^{\left(\frac{\Delta g_0^R}{RT}\right)} = \prod_i x_i^{\nu_i} \left(\frac{p}{p_0}\right)^{\sum_i \nu_i}, \quad (2.2)$$

and for ideal liquids:

$$e^{\left(\frac{\Delta g_0^R}{RT}\right)} = \prod_i x_i^{\nu_i}, \quad (2.3)$$

where x_i is the mole fraction of compound i . In Fig. 2.3a, Δg_0^R sets a fixed inclination of the scales. For $\Delta g_0^R < 0$, the reaction has a driving force and the equilibrium of the reaction is on the product side: a large fraction of the supplied reactants is reacted to the products. For $\Delta g_0^R \geq 0$, the reaction can still take place (Müller et al., 2014) due to the free energy of mixing as additional driving force. However, the equilibrium is mainly on the reactant side and only minor, often negligible fractions of products are formed. Furthermore, separation of the highly diluted products is energy intensive. Therefore, the thermodynamic challenge for CO₂ conversion is to find reaction conditions for which $\Delta g_0^R < 0$. Negative Δg_0^R and/or high yields of the wanted product can be achieved in the following ways (Havran et al., 2011; Kim et al., 2011; Romero and Steinfeld, 2012; Sakakura et al., 2007; Mikkelsen et al., 2010):

³The Gibbs free energy of formation $\Delta g_i^{f,0}$ of compound i is given relative to its constituent elements in their standard state.

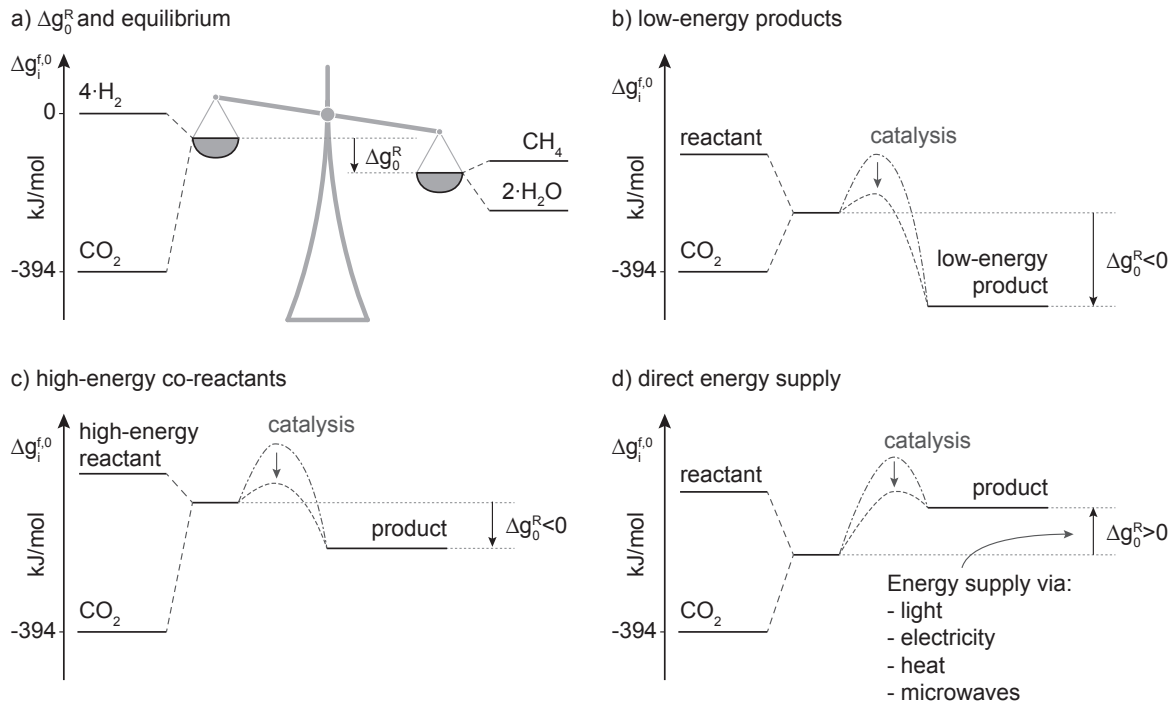


Figure 2.3: a) The effect of the Gibbs free energy of reaction Δg_0^R on the equilibrium composition for CO_2 conversion. Illustration of Δg_0^R and catalysis for b) low-energy products, c) high-energy co-reactants, and d) supply for direct energy for exergonic reactions ($\Delta g_0^R > 0$).

- Choosing low-energy products,
- Using high-energy co-reactants such as hydrogen and epoxides,
- Providing energy as light, electricity, heat or microwaves,
- Removing by-products such as water to shift the equilibrium to the product side,
- Adjusting temperature and pressure.

The first three options are illustrated in Fig. 2.3b-d. Removing a by-product j means decreasing x_j in Eqs. (2.2) or (2.3) and consequently, the reaction continues to proceed giving a higher concentration x_k of another product k . In other words, removing a by-product from the right cup of the scales in Fig. 2.3a must lead to an increase of another product given the fixed inclination by Δg_0^R . The equilibrium composition x_i in Eqs. (2.2)-(2.3) is a function of temperature and pressure. Furthermore, $\Delta g_i^{f,0}$ and thus Δg_0^R depend on the temperature. However, adjusting the equilibrium composition by temperature and pressure in general also requires energy.

In addition to Δg_0^R as reaction driving force, catalysis plays a vital role in CO₂ conversion. The Gibbs free energy of reaction describes only the free energy difference of the overall reaction and does not consider any intermediate reactions. In particular, many reactions require an activation energy: an energy input to kick off the reaction (Fig. 2.3b). The activation energy can be lowered by the presence of a catalyst. Furthermore, catalysts can selectively favor the wanted products over unwanted by-products (Centi et al., 2013).

In the following description of CO₂ conversion into products, the reactions are divided in carboxylation and CO₂ reduction reactions (Quadrelli et al., 2011; Aresta and Dibenedetto, 2007a).

Carboxylation reactions

In carboxylation reactions, the entire CO₂ molecule is built into products without entirely splitting the C=O bonds. CO₂ condenses onto a substrate that often brings in the required energy for the reaction (Fig. 2.3b+c) (Havran et al., 2011). Thus, carboxylation reactions typically do not require much additional energy and can proceed at low temperatures (Havran et al., 2011; Quadrelli et al., 2011). Carboxylation products can be inorganic or organic (poly) carbonates, carbamates, carboxylic acids and lactones (Fig. 2.4) (Mazzotti et al., 2005; Quadrelli et al., 2011; Peters et al., 2011b).

Inorganic carbonates. Inorganic carbonates can be obtained from magnesium- and calcium-rich brines (Quadrelli et al., 2011), and naturally occurring minerals such as olivine, serpentine and wollastonite (Mazzotti et al., 2005). Mineral carbonation is frequently discussed as storage option in CCS. However, the mineral end-products can also be used as cement-like building materials (Quadrelli et al., 2011). According to

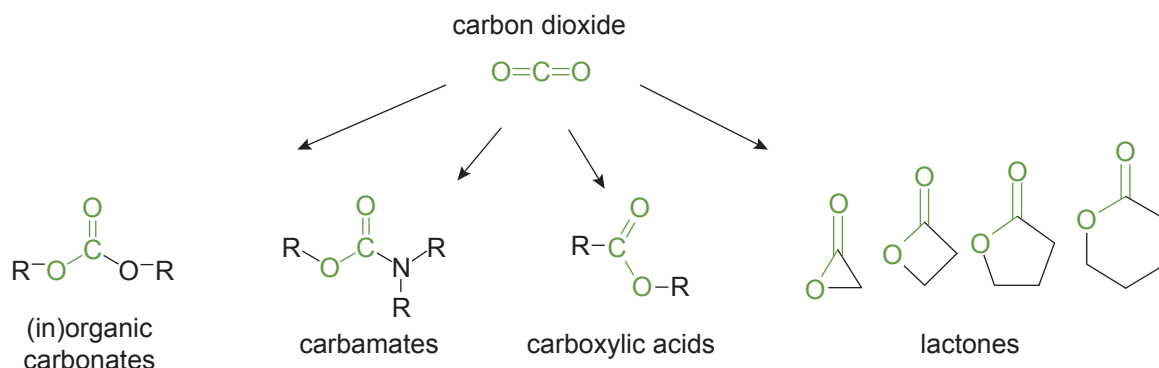


Figure 2.4: Carboxylation of CO₂ to carbonates, carbamates, carboxylic acids and lactones.

the definition of CCU in section 2.2, mineral carbonation is only considered as CCU if the use of minerals fulfills a function, e.g., in construction. The typical low-energy products do not require additional energy or high-energy reactants (Fig. 2.3b). Mineral carbonation is an exothermic reaction but the exploitation of the heat of reaction is challenging (Mazzotti et al., 2005). A further limitations is the energy-intensive mining and grinding of the solid reactants (Mazzotti et al., 2005; Sanna et al., 2014).

Organic carbonates. Organic carbonates include cyclic carbonates, dimethyl carbonate and polycarbonates. Cyclic carbonates can be synthesized from CO₂ and epoxides as high-energy reactant. Epoxides have a high Gibbs free energy due to the epoxides' highly strained three atoms ring (Sun et al., 2005; Lu and Darensbourg, 2012). Cyclic carbonates can be used in a wide spectrum of applications (see section 5.2.4). CO₂ and methanol can be converted to dimethyl carbonate (DMC), which can replace phosgene in polycarbonate synthesis (Sakakura et al., 2007). Polycarbonates can also be directly synthesized from polymerization of CO₂ and epoxides (Darensbourg, 2007). Suitable properties of polycarbonates allow for substitution of many other conventional, entirely fossil-based plastics. The polymerization of epoxides with CO₂ can also be exploited in the synthesis of polyols which are currently produced from epoxides only. The environmental impacts of conventional and CO₂-based polyols are compared in chapter 5.

Carbamates. Ammonium carbamate is a CO₂-based intermediate in the production of urea. Urea is an important agricultural fertilizer (Peters et al., 2011b). The synthesis of urea is currently the largest CO₂ user in the chemical industry with about 100 Mt a⁻¹ CO₂ (Mikkelsen et al., 2010). Carbamic acids can be dehydrated to isocyanates, which are currently produced via amines and phosgene (Sakakura et al., 2007).

Carboxylic acids. A prominent *carboxylic acid* is salicylic acid which is produced from sodium phenolate and CO₂ in the Kolbe-Schmitt reaction since 1874 (Mikkelsen et al., 2010). Salicylic acid is a direct precursor to acetyl salicylic acid (aspirin). Other possibly CO₂-based carboxylic acids of industrial importance are acrylic and acetic acid (Sakakura et al., 2007; Havran et al., 2011).

Lactones. Lactones are cyclic esters and have successfully been synthesized from CO₂ with unsaturated compounds such as dienes and alkynes (Sakakura et al., 2007; Peters et al., 2011b; Quadrelli et al., 2011). As fine chemicals, they are typically used as flavors, fragrances or plastics (Quadrelli et al., 2011).

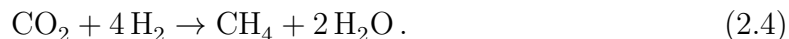
For all described carboxylation reactions, the potential environmental benefits are manifold: CO₂ is used instead of being emitted. Furthermore, CO₂ can replace fossil

fuels as carbon feedstock. In particular, CO₂ can substitute energy- and emission-intensive fossil-based reactants such as epoxides (Aresta and Dibenedetto, 2007a). Many of the carboxylation products have a long product lifetime and can thus store CO₂ at least temporary (Peters et al., 2011b). With CO₂ as additional feedstock, completely new products with superior properties can be manufactured (Peters et al., 2011b). Many carboxylation reactions do not require much energy since CO₂ can be inserted as entire molecule. Nevertheless, some reactions are limited by the Gibbs free energy of the reaction. The resulting yields are low leading to diluted products and energy-intensive separation. The Gibbs free energy of the reaction can be lowered, i.e., the driving force is increased, if alternative co-reactants with higher energy are used, e.g., epoxides instead of diols for cyclic carbonates.

CO₂ reduction and hydrogenation

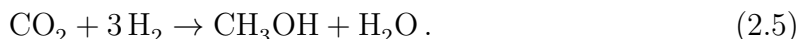
In CO₂ reduction reactions, one or both C=O bonds are fully broken. Due to the cleavage of C=O bonds, reduction reactions are inherently energy intensive (Quadrelli et al., 2011; Havran et al., 2011). The required energy for CO₂ reduction is frequently provided by H₂ as reactant (Fig. (2.3)c) (Wang et al., 2011). The environmental relevance of H₂ provision is discussed separately at the end of this section. The most discussed candidate products from CO₂ reduction are methane, methanol, carbon monoxide, formic acid⁴ and synthetic gas.

Methane. Methane can be produced by complete hydrogenation of CO₂ in the “Sabatier” reaction:



CO₂-based methane production is frequently discussed in the context of using surplus power from renewable sources for H₂ electrolysis (Sternberg and Bardow, 2015). In this so-called power-to-gas concept, the obtained methane can be used as chemical feedstock or it can be stored in existing gas grids and converted back to electricity when electricity demand is high.

Methanol. Methanol can be produced from CO₂ in the following reaction:



An economy based on methanol has already been proposed by Asinger (1986) since methanol can serve as “drop-in” solution to our existing energy and chemical infrastructure. Methanol can serve as platform chemical for current bulk olefins, can be

⁴Although no C=O bond is broken in the formation of formic acid, it is included in reduction reactions because of identical reduction methods in this transformation.

converted to gasoline fuel or used directly in internal combustion engines and methanol fuel cells (Goeppert et al., 2014). Given the wide application range for methanol, it has the potential to utilize large amounts of CO₂ (Quadrelli et al., 2011).

Formic acid. CO₂ can be hydrogenated to formic acid with equimolar amounts of CO₂ and H₂:

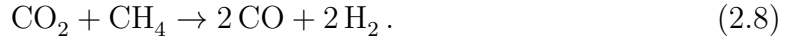


Similar to the methanol economy, a formic acid economy has been proposed (Leitner, 1995; Jessop et al., 1995). Synthesis (2.6) can efficiently store H₂ and thus energy since no H₂ has to be sacrificed for water formation (Agarwal et al., 2011; Federsel et al., 2010). Furthermore, supercritical CO₂ can be used as both reactant and solvent, thus exploiting additional benefits of direct physical CO₂ utilization (section 2.3.2.1) (Wesselbaum et al., 2012).

Carbon monoxide and syngas. CO₂ is hydrogenated to carbon monoxide (CO) in the so-called reverse water gas shift (RWGS) reaction:



To obtain a syngas with a typical H₂/CO ratio of at least 2:1 (Havran et al., 2011), CO from RWGS (2.7) can be mixed with syngas from conventional steam reforming or with pure H₂. Syngas and CO can also be obtained from reactions based on CO₂ and fossil fuels in the dry reforming of methane:



and the “Boudouard” reaction:



The benefit of CO₂-based syngas is that syngas can be converted to a huge variety of products such as methanol, ethylene or higher hydrocarbons via the Fischer-Tropsch process (Dry, 2002). Thus, large amounts of CO₂ could be easily introduced into the chemical supply chain (Peters et al., 2011b).

Photo-chemical reduction and photo-catalysis. For synthesis of hydrocarbons from CO₂, water can also be used directly as H₂ source:



Using water as reactant for CO₂ conversion means that only fully oxidized reactants are employed. The large energy requirement for this conversion poses an extreme thermodynamic challenge (Fig. 2.3d). In photo-catalysis and photochemical reductions,

sunlight serves as renewable energy source (Kondratenko et al., 2013; Usubharatana et al., 2006). The environmental potential originates from using only renewable energy and raw material sources.

Hydrogenation and H₂ source. In hydrogenation of CO₂, H₂ provides the required energy for splitting the C=O bonds. For high-energy products such as methane or CO, up to half of the H₂ is not incorporated into the desired products but instead sacrificed for oxidation to water as by-product to make the forward reaction thermodynamically feasible (Mikkelsen et al., 2010). From an environmental viewpoint, sacrificing H₂ is unfavorable since the provision of H₂ is generally associated with CO₂ emissions and other environmental impacts. The ‘clean’ provision of H₂ has already been identified as key pre-requisite for environmentally favorable CO₂ hydrogenation (Quadrelli et al., 2011).

The current large-scale production technology for H₂ is steam reforming of natural gas, which causes considerable CO₂ emissions. An alternative fossil-based technology is thermal decomposition of methane into H₂ and solid carbon (Steinberg, 1999). A non-fossil-based alternative for H₂ production is splitting of water into O₂ and H₂. Water splitting is again energy-intensive. The use of solar irradiation as direct energy source in photo-catalytic or photo-electrochemical water splitting remains a long-term vision (Hisatomi et al., 2014). An already viable technology for water splitting is electrolysis (Ursua et al., 2012). Here, the use of electricity from renewable energy sources is advocated to avoid indirect CO₂ emissions from electricity generation (Peters et al., 2011b).

Utilization and storage of renewable energy for H₂ production. The chemical industry currently relies mostly on fossil fuels as chemical feedstock and as source for process energy (IEA et al., 2013). The required process energy is typically provided as heat from combustion of fossil fuels (Centi et al., 2013). Switching to biomass fuels for heat generation in the chemical industry has the potential to lower associated CO₂ emissions. To reduce also the use of fossil fuels as chemical feedstock, CO₂ and H₂ can be converted to important platform chemicals, which can be easily introduced as drop-in solutions into upstream stages of the chemical supply chain (Centi and Perathoner, 2011). If H₂ is produced by electrolysis, CO₂ hydrogenation allows to introduce renewable electricity technologies in the chemical industry.

The introduction of renewable electricity technologies in the chemical industry is particularly interesting if so-called surplus power is used. Surplus power is electricity that cannot be used since electricity supply exceeds the demand. The amount of surplus power is estimated to increase due to an increasing integration of fluctuating renewable energy sources into the electricity grid (Sternberg and Bardow, 2015). Thus,

products from CO₂ hydrogenation can serve as chemical storage for surplus power from renewable energies (Centi and Perathoner, 2011). The obtained products can be used as chemical feedstock and fuel for electricity generation, heating and mobility (Centi and Perathoner, 2011; Sternberg and Bardow, 2015). If the energy for CO₂ conversion to fuels originates from the sun, these so-called *solar fuels* offer a completely fossil-free alternative to current fossil fuels (Haije and Geerlings, 2011; Centi and Perathoner, 2014; van der Giesen et al., 2014). However, since fuels are burned soon after production, CO₂ storage duration is short (Mazzotti et al., 2005).

In summary, all CO₂ reduction reactions are inherently energy intensive. The provision of energy generally causes indirect GHG emissions, thus rendering reduction reactions environmentally challenging. However, large market sizes for products from CO₂ reduction offer the potential to utilize CO₂ in large quantities.

2.3.3 Challenges and potential environmental benefits for CCU

In the previous sections, the environmental challenges and potential benefits of CO₂ capture as well as CO₂ utilization have been discussed separately. The following lists summarize the environmental challenges and benefits for combined CO₂ capture and utilization (CCU).

Environmental challenges of CCU. The low concentration of CO₂ in many flue gases as well as the low energetic state of CO₂ render CCU processes environmentally challenging. In particular, the following challenges have been identified:

- Reducing the energy demand for CO₂ capture,
- identifying concentrated, impurity-free CO₂ sources,
- identifying environmentally promising and thermodynamically reasonable CO₂ reactions,
- developing selective catalysts to enable new CO₂ reaction routes,
- providing “clean” energy and co-reactants for CO₂ conversion, and
- increasing the short CO₂ storage duration for direct CO₂ utilization and fuels.

Potential environmental benefits of CCU. Despite the challenges, utilization of CO₂ can still be environmentally beneficial over currently employed processes by:

- Replacing fossil fuels by CO₂ as alternative source of carbon,
- re-utilizing CO₂ as feedstock instead of emitting it as greenhouse gas (multiple use of carbon),

- creating more environmentally friendly processes for existing products due to unique properties of CO₂,
- synthesizing entirely new CO₂-based products with superior properties⁵,
- storing CO₂ in products, at least temporarily, and
- integrating renewable energy in the chemical industry via CO₂-based products.

2.4 Status of environmental assessment of CCU

In the previous section, environmental challenges and potential benefits of CCU have been presented. Whether the benefits outweigh the challenges or vice versa, requires a detailed environmental assessment of a specific CCU process. This section contains an overview of current practice in the environmental assessment of CCU. The overview focuses on methods that have been applied until 2010 when the present thesis project was initiated. Nonetheless, recent methods from the literature are also presented.

2.4.1 General awareness and qualitative claims

The energy requirements for both CO₂ capture and CO₂ transformation are well known (Mac Dowell et al., 2010; Sakakura et al., 2007). The indirect CO₂ emissions from energy provision have been widely recognized as well as the emissions from final disposal of CO₂-based products (Havran et al., 2011). It has been repeated for more than 15 years that the amount of avoided CO₂ emissions does therefore not equal the amount of utilized CO₂ (Aresta and Galatola, 1999; Aresta et al., 2014). In particular, Quadrelli et al. (2011) warn that the additional CO₂ emissions should not be larger than the amount of CO₂ utilized. Thus, CCU does not automatically contribute to climate mitigation (Sakakura et al., 2007). The largest benefits for climate mitigation are often proclaimed for CCU in combination with renewable energy technologies (Mikkelsen et al., 2010). Some even claim that CCU processes are inherently *carbon neutral* as long as renewable energies are used (Olah et al., 2009).

Famous qualitative principles for designing environmentally more sustainable chemical processes are the *Twelve Principles of Green Chemistry* by Anastas and Warner (1998). For example, principle 7 suggest the “use of renewable feedstocks”. For CCU, CO₂ is frequently considered as renewable and inexhaustible carbon source (Sakakura et al., 2007; Patil et al., 2010; Mikkelsen et al., 2010; Lu and Darensbourg, 2012). However, following the Twelve Principles does not lead to environmentally favorable

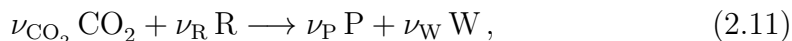
⁵Superior properties can be environmentally beneficial, e.g., if enhanced mechanical properties prolong the product lifetime and thus reduce the replacement rate.

processes or products by itself. Furthermore, the qualitative principles do not allow to rank alternative chemical routes.

2.4.2 Environmentally motivated metrics for CCU

To enable a ranking of alternatives, a variety of environmentally motivated metrics are currently used in chemistry (Constable et al., 2002; Jiménez-González et al., 2012). These metrics are readily available and easily computable. However, they have only limited significance as environmental impact indicators as is discussed in this section for some of the proposed metrics.

- The **atom economy** is intended as very simply metric to quantify how many atoms of the reactants end up in the final product (Trost, 1991). Considering a generic CO₂ reaction



the atom economy for main product P is calculated as follows:

$$\text{atom economy} = \frac{\nu_{\text{P}} M_{\text{P}}}{\nu_{\text{CO}_2} M_{\text{CO}_2} + \nu_{\text{R}} M_{\text{R}}} , \quad (2.12)$$

where M_i denotes the molar mass of compound i . As CCU example, organic carbonates from CO₂ are favored due to their 100 % atom economy, i.e., no atoms are wasted for by-products (Styring et al., 2014; Song, 2006). Ranking alternatives by atom economy favors by-product-free reactions. However, an integrated synthesis of multiple products can be environmentally favorable over the corresponding separate processes without by-products.

- The **yield** is the ratio of actually obtained amount and stoichiometric amount of the product:

$$\text{yield} = \frac{\text{actual amount of product P}}{\text{stoichiometric amount of product P}} . \quad (2.13)$$

Although not in a direct environmental context, Swapnesh et al. (2014) propose to compare alternative CO₂ utilization processes based on yield, among other criteria. Generally, an increased yield for a given reaction is desirable. A high yield is often achieved by utilizing high-energy, thus emission intensive co-reactants. However, the environmental impacts of co-reactant supply are not reflected in the yield.

- The **E-factor** quantifies the mass of waste per mass of product where wastes include everything produced but the product (Sheldon, 2000). However, the

hazardousness of wastes are not considered:

$$\text{E factor} = \frac{m_{\text{waste}}}{m_{\text{P}}} . \quad (2.14)$$

Ad-hoc metrics for CCU. In addition to these general metrics, additional environmentally motivated *ad-hoc metrics* have been developed for the specific context of CCU. Many of them are entirely based on the masses of reactants and products:

- The **product-specific amount of CO₂ utilized** is the amount of CO₂ per amount of product and intends to serve primarily as indicator for utilization of non-fossil based carbon resources (Peters et al., 2011b):

$$\text{specific amount of CO}_2 \text{ utilized} = \frac{m_{\text{CO}_2}}{m_{\text{P}}} . \quad (2.15)$$

- The **total CO₂ utilization volume** of a product takes into account the product-specific amount of CO₂ utilized and the product's market potential (Styring, 2012; Mikkelsen et al., 2010).
- The **mass ratio of CO₂-based product and CO₂** is the reciprocal metric of the product-specific amount of CO₂ utilized (Müller and Arlt, 2014):

$$\text{mass ratio}_{\text{product based}} = \frac{m_{\text{P}}}{m_{\text{CO}_2}} = \frac{M_{\text{P}}}{\nu_{\text{CO}_2} M_{\text{CO}_2}} . \quad (2.16)$$

The metric indicates whether a large molecule can only incorporate a small amount of CO₂. The metric is intended as short-cut indicator for the carbon fixation. However, it does not take into account direct process CO₂ emissions nor CO₂ emissions from reactant supply.

- The **mass ratio of all reactants except CO₂, and utilized CO₂** indicates whether large amounts of co-reactants are required to react small amounts of CO₂ (Müller and Arlt, 2014):

$$\text{mass ratio}_{\text{reactant based}} = \frac{m_{\text{R}}}{m_{\text{CO}_2}} = \frac{\sum_i \nu_{\text{R},i} M_{\text{R},i}}{\nu_{\text{CO}_2} M_{\text{CO}_2}} . \quad (2.17)$$

Müller and Arlt (2014) advocate that both mass ratios in Eqs. (2.16) and (2.17) “*should have small values to constitute a substantial negative contribution to the CO₂ balance.*” However, the authors admit that the reactant-based mass ratio does not properly account for light-weighted, but highly energetic H₂.

In addition to the above described mass-based metrics, the following metrics aim at assessing the global warming impacts either by CO₂ balances, by simple regression analyses for net CO₂ emissions or by qualitative assertions for CO₂ storage effects:

- The **net amount of CO₂ fixed** is the product-specific amount of CO₂ utilized minus product-specific CO₂ emissions in the utilization or upstream processes (Peters et al., 2011b):

$$m_{\text{CO}_2,\text{fixed}} = m_{\text{CO}_2,\text{utilized}} - m_{\text{CO}_2,\text{emitted}} \quad (2.18)$$

In principle, this metric accounts for indirect CO₂ emissions from provision of reactants such as H₂. However, Peters et al. (2011b) have limited the CO₂ balance to the CO₂ utilization process. Thus, any emissions occurring from CO₂ capture are not considered. Instead, utilized CO₂ is treated as negative GHG emission.

- The **C/H ratio of CO₂-based product** has been fitted to the net CO₂ fixation by Audus and Oonk (1997) for screening purposes. The authors expect a net CO₂ fixation for a CO₂-based reaction if the C/H ratio of the CO₂-based product is greater than the C/H ratio of the original CO₂ source. The metric aims at a general assessment of CCU routes. However, it does not account for the specific CO₂ and H₂ sources.
- The **enthalpy of reaction** Δh_0^R has also been fitted to the net CO₂ fixation by Audus and Oonk (1997) for screening purposes. The authors expect a net fixation of CO₂ for most CO₂-based hydrocarbons if the enthalpy of reaction is smaller than 1.25 times the heat of combustion of the reference fossil fuel. At best, Δh_0^R can serve as estimate for direct process emissions. However, it does not take into account the specific source of reactants.
- A negative or slightly positive **Gibbs free energy of reaction** Δg_0^R is frequently advocated as indicator for the chemical feasibility of the considered reaction and as constraint to avoid energy-intensive separation of a diluted product (Audus and Oonk, 1997; Müller et al., 2014). As for Δh_0^R , the use of Δg_0^R as environmental impact indicator does not account for the environmental impacts from reactant supply.
- The **number of process steps** is used as indicator for process efficiency and thus for direct process emissions. In an example for CO₂-based methanol production, an increase in net CO₂ emissions is expected compared to conventional methanol production due to an increased number of process steps (Audus and Oonk, 1997). Whereas a reduced number of process steps is generally desirable, an environmental ranking of processes based on the number of process steps is not reasonable.
- The **CO₂ storage duration** is the time period between CO₂ utilization and product degradation back to CO₂ (Peters et al., 2011b; Mazzotti et al., 2005) and

corresponds to the product lifetime (Audus and Oonk, 1997). The CO₂ storage duration has been identified as crucial factor for climate mitigation (Mazzotti et al., 2005; Markewitz et al., 2012; Mikkelsen et al., 2010; Peters et al., 2011b). As additional metric for climate mitigation, the global warming impact, also known as carbon footprint, is used to balance greenhouse gas emissions. Hence, two separate metrics exist for climate mitigation. The question arises which of the two metrics has a larger effect on climate mitigation. Thus, the metrics should be weighted and/or combined into a single metric.

The presented metrics are intended to be easily accessible (“the more/less, the better”) and computable to enable their use at early development stages. However, the named metrics are incapable of assessing the actual environmental impacts of CCU processes. Therefore, they can be misleading if used as indicator for environmental impacts. Furthermore, many of these metrics focus only on the CO₂ utilization process while ignoring any environmental impact occurring in up- or downstream processes. In particular, the CO₂ source is often not considered. In contrast, Life-Cycle Assessment (LCA) is a holistic environmental assessment tool that takes into account all up- and downstream processes and that establishes a direct link to actual environmental impacts.

2.4.3 Status of LCA application for CCU

Life-Cycle Assessment (LCA) is a standardized methodology to analyze the environmental impacts of products and processes along the entire life cycle from cradle to grave (ISO 14040, 2009). The life cycle spans from the extraction of raw materials, transport, production and packaging over use of the product to reuse, recycling and final disposal of wastes. LCA evaluates the life cycle with respect to environmental impacts such as fossil resource depletion and global warming, among others (Curran, 2012). This section presents the status of LCA application in the context CCU.

CO₂ capture is a common feature of CCU and Carbon Capture and Storage (CCS). In the context of CCS, LCA is already frequently applied to CO₂ capture from power plants (Marx et al., 2011; Schreiber et al., 2012). Here, CCS can effectively reduce CO₂ emissions; however, at the expense of increasing all other investigated environmental impacts (Marx et al., 2011). In addition to various case studies, detailed frameworks for LCA of CCS have been developed (Sathre et al., 2012).

In contrast to CCS, LCA is not yet standard practice for the environmental assessment of CCU. Although LCA is frequently advocated (Aresta and Dibenedetto, 2007a,b; Quadrelli et al., 2011; Peters et al., 2011b; Centi and Perathoner, 2011; Markewitz et al., 2012), only a few LCA studies have been published for CCU (Schäff-

ner et al., 2014): Aresta and Galatola (1999) conducted a preliminary LCA for the cradle-to-gate process of dimethyl carbonate (DMC) production from CO₂. Khoo et al. (2011b) used an LCA approach to determine the preliminary environmental impacts of CO₂ capture from an NGCC power plant with subsequent mineralization. Jaramillo et al. (2009) analyzed the life-cycle GHG emissions for CO₂ capture from power plants and utilization of CO₂ in enhanced oil recovery (EOR). Until recently, no LCA studies existed for promising CCU products such as CO₂-based fuels or polymers. In particular, Centi and Perathoner (2014) explicitly state: “*For the production of CO₂-based polymers, correct LCA assessments [also] do not exist [...].*”

First LCA studies for CO₂-based fuels and polymers have been published very recently: Schäffner et al. (2014) presented an LCA for a biomass- and CO₂-based carbonated fatty acid ester plasticizer. For production of synthetic hydrocarbon fuels from CO₂, van der Giesen et al. (2014) investigated the life-cycle GHG emissions and cumulative energy demand using LCA. Cuéllar-Franca and Azapagic (2015) reviewed 16 LCA studies on CCU options including mineralization (3 studies, including the above mentioned), DMC (1 study, including the above mentioned), EOR (2 studies, including the above mentioned) and diesel production from micro-algae (10 studies, not within the scope of this thesis).

As reason for the restricted use of LCA for CCU, Quadrelli et al. (2011) identified the limited data availability. In addition to the literature view, the restricted use and related challenges of LCA for CCU are confirmed by the personal experience made by the author of this thesis at conferences and project meetings. Quadrelli et al. (2011) and Schäffner et al. (2014) recommend to strengthen the efforts for LCA and to develop new approaches for the environmental assessment based on LCA. Furthermore, both groups underline the necessity to include LCA in CCU discussions and recommend using LCA in early stages of CCU research.

To overcome limited availability of data and process models at early stages, a couple of approaches have already been made to estimate the environmental impacts of chemical production (Patel et al., 2007; Wernet et al., 2008; Sugiyama et al., 2008; Wernet et al., 2009; Bumann et al., 2010; Huijbregts et al., 2010; Wernet et al., 2012; Patel et al., 2012). However, none of these approaches has been applied to CCU. Thus, their suitability for the environmental assessment of CCU processes at early stages is unknown.

2.4.4 Identified gaps in the environmental assessment of CCU

Based on status of environmental assessment for CCU presented in sections 2.4.2-2.4.3, the following gaps are identified.

Complexity of LCA for CCU. Due to the complexity and terminology of LCA, only a few LCA studies for CCU have been published. Instead, easily accessible ad-hoc metrics are typically used as estimates for the environmental impacts of CCU. Since LCA is acknowledged as suitable tool for the environmental assessment of LCA, the application of LCA for CCU should be facilitated, especially for LCA novices.

System boundaries limited to the CO₂ utilization process. The system boundaries for CO₂ balances are often limited to the CO₂ utilization process, thereby neglecting impacts from CO₂ capture. Thus, the system boundaries should be thoroughly extended to include the CO₂ source and capture process.

Power plants as only assessed CO₂ source. LCA studies for CO₂ capture are mainly limited to power plants whereas many CO₂ sources are generally considered for CO₂ utilization. To identify environmentally favorable CO₂ sources, an environmental comparison across all proposed CO₂ sources for CO₂ utilization should be drawn.

CO₂ storage duration as separate metric for climate mitigation. The relevance of the CO₂ storage duration for climate mitigation has not been analyzed systematically. For this purpose, a single metric for global warming impacts should be developed that integrates the CO₂ balance and the CO₂ storage duration.

Limited data availability at early stages. Many CCU processes are still at lab-scale and thus, comprehensive mass and energy balances are not available. Thus, design approaches with low data requirements are desirable to support an environmentally motivated CCU development at early stages.

2.5 Contribution of this thesis

The previous sections highlight the environmental challenges for CO₂ Capture and Utilization (CCU) and reveal the restricted use of Life-Cycle Assessment (LCA) for the environmental assessment of CCU. The goal of this thesis is to facilitate the application of LCA for CCU by providing a sound LCA framework for CCU. Furthermore, the LCA framework for CCU is exploited to support the design of environmentally favorable CCU processes at early stages. In particular, the thesis aims to make the following contributions.

Sound LCA framework for CCU. A major barrier for the application of LCA to CCU is the apparent complexity of LCA to novices. However, the general concept of LCA is easily accessible. Thus, chapter 3 provides a jargon-free introduction for LCA of CCU directed at LCA novices. In the spirit of an intended tutorial, the chapter enables LCA novices to apply and understand LCA in a CCU context.

Three particularly important pitfalls in LCA of CCU have been identified: environmental impacts from CO₂ capture are frequently neglected; product-specific environmental impacts requires an ambiguous but important choice between alternative allocation methods, and the CO₂ storage duration is used as separate metric for climate mitigation. The existence of the pitfalls is not always recognized and a common approach to their solution does not exist. Therefore, chapter 4 provides an explanation and illustration of the pitfalls. To avoid the pitfalls, a framework for LCA of CCU is derived.

Insights from an industrial case study. An LCA for an industrial case study of CO₂-based polymers is presented to illustrate the applicability of the previously described framework for LCA of CCU. The CO₂ is obtained from a lignite-fired power plant with CO₂ capture. The captured CO₂ is converted to poly-ether-carbonate polyols. The LCA results provide valuable insights into the origin of the environmental benefits of CCU.

Selection of CO₂ sources. All CO₂ sources considered for CCU are compared in terms of GHG emissions and fossil resource use. A methodology is presented to select the environmentally most favorable CO₂ sources in Europe that are required for expected demands of CO₂ utilization. Based on the presented methodology, preferable CO₂ utilization locations are identified where large amounts of CO₂ can be captured with lowest environmental impacts

LCA-based targeting for CCU processes at early design stages. Due to the limited data availability for many CCU processes at lab-scale, LCA studies can often only be performed retrospectively for already implemented technologies. However, an assessment at early design stages is desirable to guide the development. Therefore, in section 7.2, a methodology is presented to identify environmentally promising reaction schemes for CO₂-based products. The underlying optimization is based on thermodynamics and available LCA data. The resulting reaction schemes serve as environmental target for chemical synthesis and catalyst development.

Environmental product and process design. The utilization of CO₂ has the potential to provide new synthesis routes, to produce new products with superior properties, and to lower environmental impacts. To account for all effects simultaneously, an integrated approach is required. Therefore, an environmental product and

process design approach is presented that allows to identify environmentally optimal products along with an optimal supply chain.

CHAPTER 3

Life-Cycle Assessment for CO₂ Capture and Utilization

This chapter provides an introduction to Life-Cycle Assessment (LCA) of CCU directed at LCA novices. The experienced LCA practitioner might want to continue with chapter 4. In section 3.1, the general concept of LCA is introduced. In section 3.2, LCA is specified for the application on CCU. In the spirit of a how-to manual, nine action items are described and illustrated in a CCU context. Finally, in section 3.3, the chapter is summarized and conclusions are drawn for a sound environmental assessment of CCU.

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von der Assen, N., Lorente Lafuente, A.M., Peters, M., and Bardow, A. (2014). Environmental Assessment of CO₂ Capture and Utilisation. In *Carbon Dioxide Utilisation. Closing the Carbon Cycle*, Styring, P., Quadrelli, E.A., and Armstrong, K. (Eds.), Elsevier, Amsterdam, pp. 45-56.

3.1 General concept of LCA

Life cycle assessment (LCA) is a methodology to analyze the environmental impacts of products and processes along the entire life cycle. The life cycle spans from the extraction of raw materials, transport, production and packaging over use of the product to reuse, recycling and final disposal of wastes. (left part of Fig. 3.1). Along the life cycle, material and energy flows are exchanged and interact with the natural environment (center part of Fig. 3.1). The interactions are evaluated across the entire life cycle with respect to a variety of potential environmental impacts such as global warming, fossil resource depletion, acidification and many other impacts (right part of Fig. 3.1) (Curran, 2012).

The main feature of LCA is its holistic perspective that avoids problem shifting in two ways: First, when improving one life cycle stage, LCA can identify whether impacts are only shifted towards other life cycle stages. Second, LCA can avoid problem shifting between environmental impacts (Bauman and Tillman, 2004).

The first LCA-like studies were already conducted in the late 1960s and early 1970s due to growing concerns about resource depletion and other environmental issues (ICCA, 2013). Until the 1990s, LCA was frequently applied, however, without a common and obligatory methodology (Curran, 2012). Therefore, the Society of Environmental Toxicology and Chemistry (SETAC) published a first guideline for LCA in

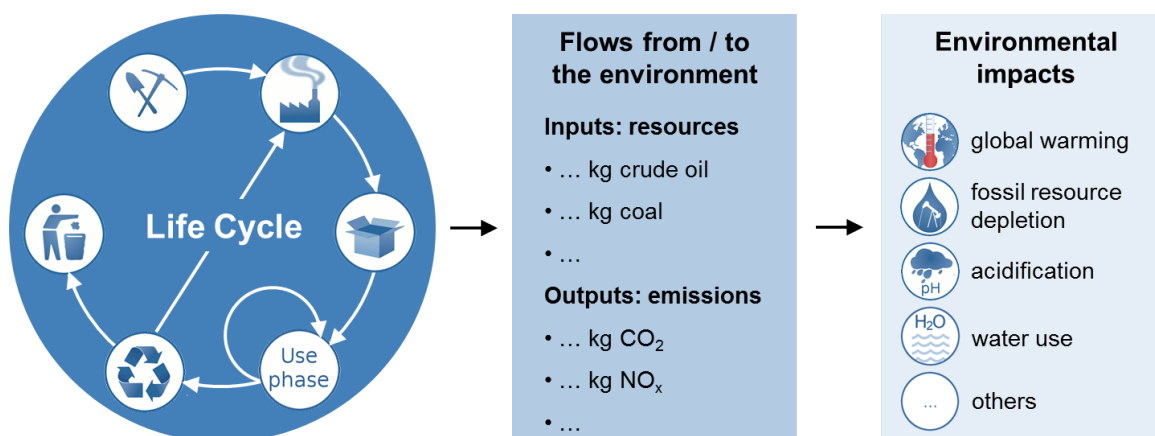


Figure 3.1: General concept of LCA: LCA takes into account the entire life cycle (left) from cradle (raw material extraction; first icon) to grave (final disposal; last icon). For this life cycle, all flows exchanged with the natural environment are cumulated (center). These flows are then translated into environmental impact categories (right).

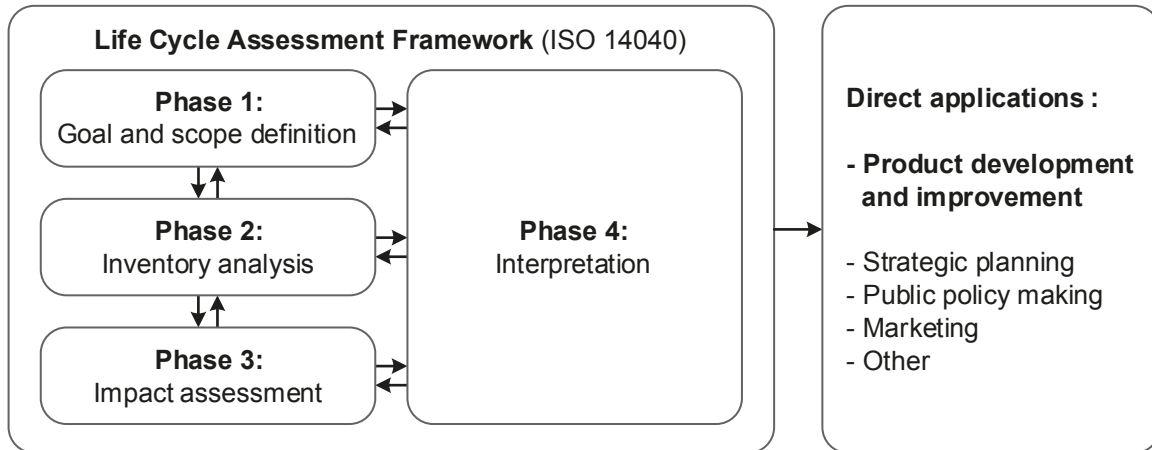


Figure 3.2: Stages of an LCA according to the corresponding ISO standards (ISO 14040, 2009; ISO 14044, 2006).

1993 (Consoli et al., 1993). In 1996, LCA was standardized by the International Organization for Standardization (ISO) and updated in 2006. The current LCA standards divide LCA into four major phases (Fig. 3.2) (ISO 14040, 2009; ISO 14044, 2006) .

Although LCA is a quantitative methodology, Phase 1 is completely data-free and question-oriented: it clearly defines the goal of an LCA study (why?), and the conditions and assumptions under which the study results are valid, i.e., the scope (what and how?). Therefore, Phase 1 of LCA is called *goal and scope definition*.

Phase 2 comprises data collection for the previously defined scope: all in- and outputs of the considered processes in the life cycle are quantified (Fig. 3.3). In LCA, two kinds of flows are distinguished: elementary and economic flows (ISO 14040, 2009; ISO 14044, 2006; Heijungs and Frischknecht, 1998). Elementary flows enter and leave “*the system being studied without either previous or subsequent human transformations*” (ISO 14040, 2009; ISO 14044, 2006), i.e., they are flows between the technosphere and the environment. The technosphere is the counterpart to the natural environment and embraces all human-built products and technologies. In contrast to elementary flows, economic flows occur between processes within the technosphere and undergo both previous and subsequent human transformations. Economic flows are further divided into valuable products and unwanted wastes (Guinée et al., 2009).

Usually, data are first gathered for each individual process. Based on these process data, an inventory list for the complete life cycle is calculated. Thus, Phase 2 is called *life cycle inventory (LCI)*. The resulting inventory contains all elementary flows, i.e., emissions and resources exchanged with the natural environment (cf. center part of

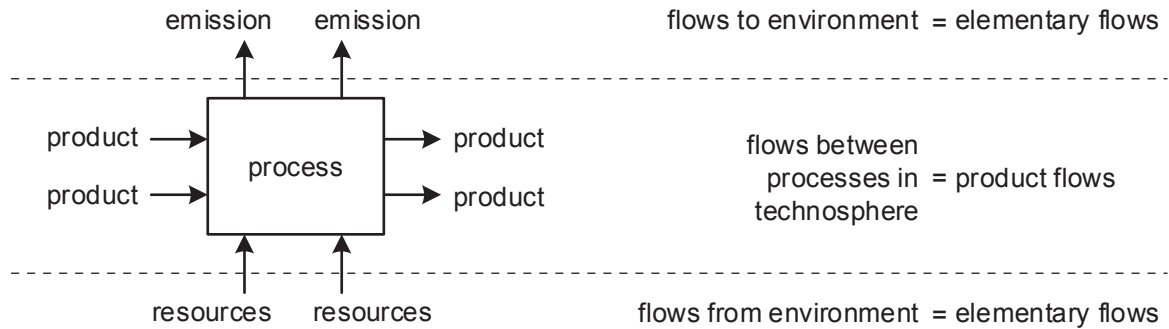


Figure 3.3: Flow classification in LCA.

Fig. 3.1). The list of elementary flows is very long; for example, the LCA database ecoinvent v3 considers 4,661 different elementary flows (ecoinvent, 2010). The data are usually collected for the nominal state of the system where everything works normally, and failures and accidents are not included.

In Phase 3, the inventory is translated and aggregated into environmental impact categories. For example, all greenhouse gas (GHG) emissions (such as CO_2 , CH_4 and N_2O) are translated into a single metric for global warming. Each gas is weighted according to its strength to absorb radiation. The weighting factors for global warming are therefore called global warming potential (GWP) (Forster et al., 2007). In the general LCA methodology, the weighting factors are called characterization factors. The final score for an environmental impact is calculated by multiplying each elementary flow in the inventory list with the corresponding characterization factor. In order to avoid problem shifting from one environmental impact to another, LCA takes into account a large, yet not complete, set of impacts such as global warming, fossil resource depletion and acidification (Fig. 3.1). Phase 3 of calculating the environmental impacts is called *life cycle impact assessment (LCIA)*.

In Phase 4, called *interpretation*, the LCI and/or LCIA results are interpreted to “reach conclusions, explain limitations and provide recommendations.” (ISO 14040, 2009) The first element of Phase 4 is the identification of “significant issues” (ISO 14044, 2006). Significant issues can be processes or substances that contribute significantly to the overall results. The next element is the evaluation of results in terms of uncertainty. Uncertainty arises from assumptions made in the scope definition, from uncertainty in the data gathered or from lack of data in the inventory phase, and from uncertainty in characterization factors in the impact assessment phase (Björklund, 2002). This uncertainty propagates into final LCA results and should therefore be analyzed. With the uncertainty of results in mind, conclusions and recommendations are given while their limitations should be discussed. The type and detail

of conclusions given depend on the LCA application such as ecological product development, policy-making, or marketing (ISO 14040, 2009; ISO 14044, 2006). Since many CCU technologies are still being developed, the following sections focus on the application of LCA to *product development and improvement* of CCU (Fig. 3.2).

3.2 A tutorial for LCA of CCU

The overview of CCU in section 2.3 already shows that the environmental performance of CCU is affected by features such as energy demand, total CO₂ utilization potential, and CO₂ storage duration. To consider all these features simultaneously, a holistic environmental assessment using LCA is mandatory. Even though the general concept of LCA from section 3.1 is easily understandable, actually conducting an LCA for CCU can be difficult due to the LCA jargon and open choices in the ISO standards. To provide more detailed guidance, excellent handbooks on LCA are available (Curran, 2012; Bauman and Tillman, 2004; Guinée et al., 2002). However, specific guidance for conducting an LCA in the context of CCU is missing. This might be one of the reasons why only a few LCA for CCU exist (cf. section 2.4). Therefore, this section contains a comprehensive tutorial for LCA of CCU directed towards LCA novices. In the spirit of an how-to manual, each step is formulated as an action item. In the following, each action item is introduced and then illustrated by CCU examples.

3.2.1 Ask the right question!

The very first step of an LCA is to define the goal of the LCA, or in other words, the question that LCA is supposed to answer. As Bauman and Tillman (2004) humorously demonstrate by referring to the Hitch Hiker’s Guide to the Galaxy, LCA could always yield a numeric answer (such as ‘42’) but without a previously defined question, this number remains meaningless. Although it might seem like common sense, a precise definition of the question is essential. Furthermore, one must ask the right question: not all questions are reasonable within the LCA context for CCU as the following discussion of potential questions illustrates.

CCU example (1): *Is methanol production from CO₂ and H₂ environmentally sustainable?* Independent from the actual performance of the methanol production process, this is not a valid question that LCA can answer. LCA cannot give threshold values below which a process is environmentally sustainable. LCA can determine the contribution of different life cycle stages to the overall environmental impact (CCU example (2) below). LCA can also identify whether a product or process is environmentally more sustainable than another (CCU example (3) below).

CCU example (2): *What are the environmental impacts in the production of methanol from CO_2 and H_2 and where do they come from?* A frequent and valid goal of LCA is to determine the environmental impacts that can be attributed to a product. This type of goal is answered by a so-called *stand-alone, attributional LCA*. It is also used to determine the contributions of individual processes or elementary flows to the overall environmental impact. Such an assessment is extremely helpful in identifying so-called hot spots, i.e., processes or elementary flows that are responsible for a significant share of the overall impact. In CCU example (2), the production process of H_2 could be such a hot spot process which causes most of the overall life-cycle GHG emissions. In this case, LCA leads to the conclusions to switch to or to develop an environmentally more sustainable H_2 production alternative, and to make efficient use of H_2 in the methanol process.

CCU example (3): *Can lower environmental impacts be achieved by producing methanol from CO_2 and H_2 than from natural gas?* Comparative studies are probably the most common type of LCA studies since the choice between alternatives is a frequent problem. LCA results for all alternatives are computed. A comparative LCA can then identify the alternative with the lowest environmental impact. This type of goal is called *comparative LCA*.

CCU example (4): *What are the environmental consequences of switching from today's fossil-based to CO_2 -based methanol production?* Determining the environmental consequences compared to the status quo is the idea of so-called *consequential LCA (CLCA)*. CLCA goes beyond the physical interactions within the life cycle and also accounts for market and behavioral effects (Earles and Halog, 2011). For example, a change from fossil-based feedstocks to CO_2 might decrease direct environmental impacts and also the price of the final product. A decreased price might lead to an increased demand of the product and eventually to a total increase of environmental impacts, the so-called *rebound effect* (Girod et al., 2011).

Comparative studies are often intended to support the choice between alternatives. Instead of comparing alternative production processes, a reasonable goal can also be to compare alternative utilization processes for a common product. In the latter case, one should analyze whether the choice between alternative utilization options is a *real choice*, i.e., whether the commonly used product is a limited resource or not. If the commonly used product is limited, the alternative(s) with the greatest environmental benefits should be chosen (Sternberg and Bardow, 2015). If the commonly used product is not limited, all alternatives with environmental benefits should be chosen.

CCU example (5): *Is it environmentally favorable to utilize CO_2 for methanol or for mineral production?* The global CO_2 emissions and CO_2 utilization potentials

presented in section 2.1 indicate that CO_2 is not a limited feedstock (see section 4.2.2 and chapter 6). Therefore, all CO_2 utilization options should be realized that allow for a reduction of environmental impacts compared to the currently employed alternatives. Instead of comparing alternative utilization options for CO_2 , it is reasonable to compare alternative sources of CO_2 (see chapter 6).

CCU example (6): *Is it environmentally favorable to utilize H_2 for CO_2 -based methanol or for CO_2 -based methane production?* The production of H_2 with low environmental impacts requires the availability of renewable energy, which however, is typically limited (Sternberg and Bardow, 2015). Thus, H_2 availability might also be limited and one has to choose how to use H_2 . The comparison of alternative H_2 utilization options then allows to identify the option that uses H_2 environmentally most efficiently.

For any comparative LCA, whether attributional or consequential, and whether for production or utilization processes, a fair comparison must be guaranteed.

3.2.2 Compare equally!

To compare products or processes, the products or processes under study must be comparable. The comparability also holds for the scopes of the studies.

3.2.2.1 Consider product function and technical performance!

LCA usually analyzes the environmental impacts of *products*. However, the assessment of *processes* in LCA is equivalent to an assessment of their products, as shown at the end of this section. Thus, for a comparison of either products or processes, products must be comparable.

In LCA, products are considered comparable if both their *function* and their *technical performance* are identical. The function refers to the application of the product while the technical performance is a quantitative measure how well the function is fulfilled. The following CCU examples illustrate the meaning of function and technical performance.

CCU example (7): *Comparison of CO_2 -based methanol with CO_2 -based minerals.* Methanol and minerals are not comparable in LCA since these products have different primary functions: methanol can serve as fuel or chemical feedstock whereas minerals can be used as construction material. A comparison of products with different functions can be reasonable if they require identical and limited feedstocks (CCU example (6) above).

CCU example (8): *Comparison of CO_2 -based methanol with fossil-based methanol.* Assuming that the production technologies yield methanol of equal quality, the

products are identical. Even if methanol can be used in various ways (cf. section 3.2.2.2), their function and performance within each utilization pathway is identical. The comparison is straightforward and can for example be based on a mass basis, i.e., to compare the environmental impacts per kg of methanol.

CCU example (9): *Comparison of CO₂-based polymers with petrochemical polymers.* The different polymers can be very similar products. For example, both polymers could be used as packaging material and thus fulfill the same function. However, the technical performance could be different due to different material properties such as density, mechanical and gas barrier properties. These properties might cause a higher material demand per packaging unit for one polymer. Since LCA is based on a comparison of products with the same quality, the higher material demand might finally render one polymer environmentally less sustainable even though it might be environmentally preferable on a kg basis. Since the polymers do not perform equally, it is better to change the basis of comparison from kg of polymer towards packaging unit. For the example, one could compare a packaging unit made of 1 kg of petrochemical polymer with an equally performing packaging unit made of 1.2 kg of CO₂-based polymer.

The last example shows how to define a valid basis for comparison that reflects function and performance. In LCA, the basis for comparison is called *functional unit* and is a quantitative measure for providing a function with a certain performance. All results in LCA are presented with respect to the functional unit. The following example illustrates the definition of the functional unit in more detail.

CCU example (10): *Comparison of CO₂-based polyurethane insulation with mineral wool.* Both polyurethanes and mineral wool can be used as thermal insulation materials in buildings. The function of both materials is the same: to thermally isolate the building. However, (CO₂-based) polyurethanes have a much lower density and much better insulation properties (lower thermal conductivity) than mineral wool. A reasonable functional unit could be a defined thermal insulation for a wall. It is not unusual to have a long sentence for the definition of a functional unit such as: ‘to limit the heat loss of a 20 m² wall to 4 Watt for each °C temperature difference between the wall sides.’ To fulfill the same functional unit, different masses of polyurethanes and mineral wool would be required.

The concept of the functional unit shows that LCA analyzes the function and performance of a product. Likewise, LCA of a process analyzes the function of this process. Often, the function of a chemical process is to produce a certain chemical product with a defined quality. In this case, LCA for product and process are directly related. However, chemical processes often provide more than one product and thus

more than one function. For comparative LCA of processes, one has to make sure that the processes under study provide the same functions, e.g., the same products with equal quality in equal quantities. Jung et al. (2013) recently presented a framework to conduct sound comparative LCA of processes based on equal functions.

3.2.2.2 Define the system boundaries!

The definition of the system boundaries is an utmost important part of the scope definition in LCA. The system boundaries describe which processes of the entire life cycle are included in the assessment. Ideally, the system boundaries should include the entire life cycle from cradle to grave. However, taking this approach seriously generally leads to an explosion of the system boundaries and ultimately to a ‘world model’. Therefore, simplifications are required which should be systematic, i.e., intentional and justified as opposed to inherently implicit and unconscious (Rebitzer, 2005).

For comparative studies, the easiest simplification is to focus on differing life cycle stages. Identical life cycle stages can then be omitted, as illustrated next.

CCU example (11): *System boundary selection for a comparison of CO₂-based and fossil-based methanol.* Methanol can be used in various ways, e.g., for production of formaldehyde, dimethyl ether (DME) or methyl tert-butyl ether (MTBE) (Fig. 3.4). If the goal of the LCA is to compare the alternative methanol production technologies, it is sufficient to limit the system boundaries to the methanol production processes and the corresponding upstream processes. The downstream processes of methanol utilization can be excluded. This scope is called a *cradle-to-gate* boundary in LCA terms (Fig. 3.4).

This simplification to the cradle-to-gate scope is very convenient for commodity producers who do not even know in which way their commodity will be used after sale. For example, methanol can be used in various ways (Fig. 3.4). However, if processes are omitted in the definition of the system boundaries, one must be careful when interpreting results: omitted processes obviously do not show up in any contribution analysis but they can still cause significant environmental impacts.

Another systematic simplification regarding system boundaries is to focus only on relevant flows, which is discussed in the following section.

3.2.3 Consider all relevant mass and energy flows!

In practice, it is often not possible to quantify all flows in LCA due to monetary and time constraints. Therefore, irrelevant flows are ‘cut off’ and are not considered. However, how can relevant flows be distinguished from irrelevant ones in advance, especially if the very goal of a study is to determine which flows and processes are

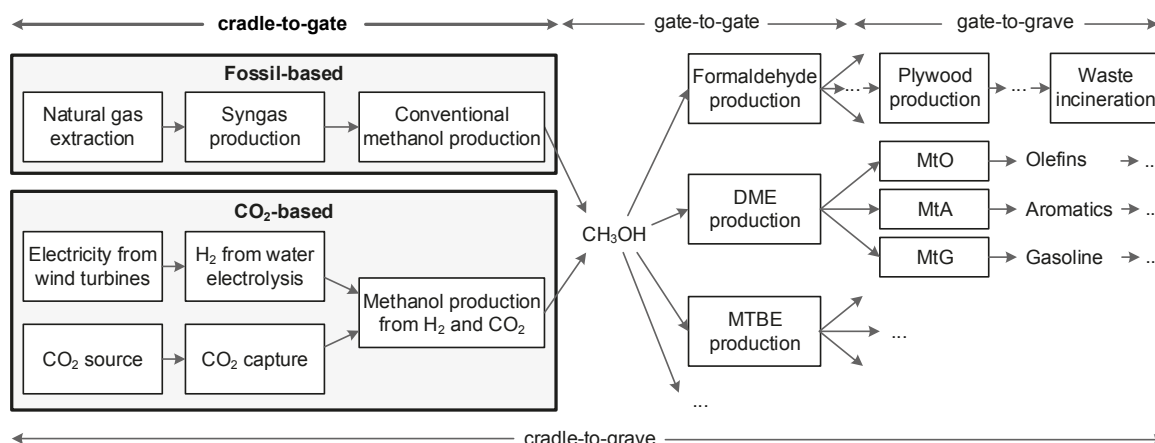


Figure 3.4: Alternative scopes for the definition of system boundaries for fossil-based and (hypothetical) CO_2 -based methanol production pathways. The various potential downstream processes (gate-to-grave) of methanol for production of formaldehyde, DME or MTBE are indicated. In a comparative assessment of methanol production technologies, a cradle-to-gate scope (bold, left part) is often sufficient.

most relevant to the overall environmental impact? A first and frequent attempt is to mark a flow as relevant when its relative mass, energy content and price is more than e.g. 1 % of all flows in the analyzed system (Büchel, 1996).

CCU example (12): *Mass - Feedstock CO_2 is a relevant flow.* In most, if not all CO_2 reactions, CO_2 is used as feedstock in significant amounts greater than 1 %. Therefore, feedstock CO_2 is a relevant flow. All upstream processes of feedstock CO_2 should be included in the system boundaries. The upstream processes for feedstock CO_2 include CO_2 transport, CO_2 capture and the CO_2 source. How to include the CO_2 source in LCA is explained in detail in section 4.1.

CCU example (13): *Energy - Hydrogen is light weighted but highly energetic.* H_2 is a frequently used co-reactant for CO_2 reductions reactions (section 2.3.2.2). In the case of CO_2 -based production of formic acid ($\text{CO}_2 + \text{H}_2 \rightarrow \text{HCOOH}$), H_2 accounts for only 4 % of total mass for a stoichiometric reaction, which might be seen close to a potential cut-off. However, H_2 is the energetic driver of the reaction and therefore needs to be considered. Therefore, a flow should only be considered for cut-off, if mass, energy content *and* price are below 1 %.

Considering the relative mass, energy and price to identify relevant flows works quite well for economic flows such as feedstocks and wastes. However, many environmentally relevant emissions might still be overlooked, as they are low-concentrated

or not-tracked, low energetic and unpriced. Büchel (1996) discusses pragmatic suggestions for identifying relevant emissions: An emission must be classified as relevant when specified in the goal of the study. If, for example, the global warming impact of a product is of interest, all greenhouse gas emissions must be taken into account. Flows can also be considered as relevant when they are an issue in scientific, politic or public debate. If flows are regulated by a legal framework such as REACH (2006), they should be included in the analysis. Finally, a less objective but still useful approach is to ask for experience of chemists and process engineers.

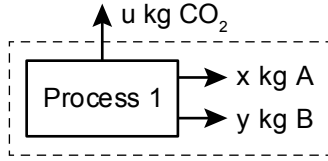
3.2.4 Account for all products in the entire life cycle!

Even in a single chemical reaction, usually more than one product is formed. While some of the co-products are unwanted, many co-products are useful and valuable. Integrated production of many chemicals in a single process can be both economically and environmentally favorable compared to individual production. This integrative character is therefore already well-established in the chemical industry. CCU has the potential to advance the integration of the chemical industry with the energy sector: the chemical industry can make use of CO₂ from power plants, and CO₂ can even act as basis for chemical storage of fluctuating renewable energies (section 2.3.2.2). The upstream processes in a CCU life cycle usually provide many co-products that should be accounted for in LCA.

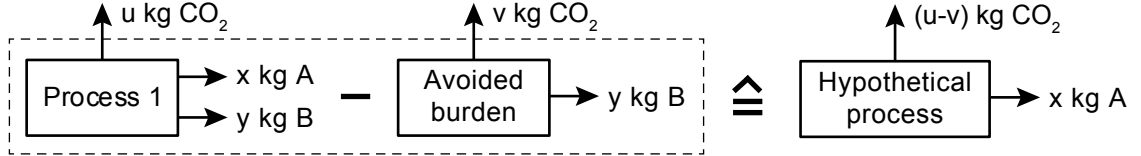
Various approaches to account for co-products exist in the LCA literature. The ISO standards for LCA recommend to include co-products in the system boundaries and in the functional unit (ISO 14040, 2009; ISO 14044, 2006). The environmental impacts are then calculated for the entire system and related to all products, e.g., u kg CO₂-eq emissions per x kg of product A and y kg of product B (Fig. 3.5). This procedure is called *system expansion* in LCA (Heijungs, 2014). System expansion avoids ambiguous choices in allocating inputs and emissions (Jung et al., 2013).

For a typical CCU system, including all products along the life cycle in the functional unit, as required in the system expansion approach, is practically impossible since the system boundaries would include nearly the entire chemical industry. This can be avoided by assigning environmental impacts to individual products, i.e., to calculate product-specific impacts. A first approach for product-specific impacts is to credit the by-products with a so-called avoided burden (Curran, 2012). The avoided burden refers to the environmental impacts v of an alternative production process for the by-products, which is now avoided (Fig. 3.5). By subtracting the avoided burden v from the impacts u of the overall system, product-specific results ($u - v$) for the main products can be obtained.

a) system expansion



b) avoided burden



c) allocation

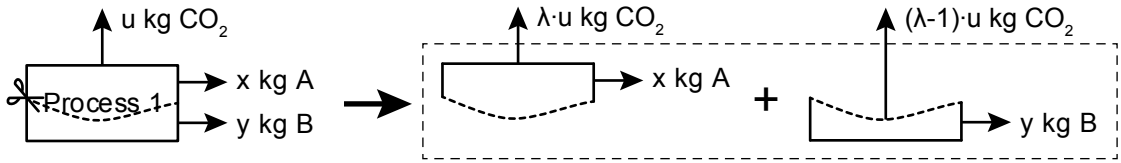


Figure 3.5: Accounting approaches for co-products in LCA: a) system expansion, b) avoided burden and c) allocation; illustrated for CO₂ emissions.

A second approach for product-specific impacts allocates the impacts to individual products based on product properties such as mass or price. This approach is called (*proportional*) *allocation*⁶ (Heijungs and Guinée, 2007; Guinée et al., 2009). For example, for mass-proportional allocation, the allocation factors λ for product A corresponds to the mass ratio of product A and all products, i.e., $\lambda = x/(x + y)$.

When applying avoided burden or proportional allocation to obtain product-specific LCA results, ISO 14044 (2006) state: “*The sum of the allocated inputs and outputs of a unit process shall be equal to the inputs and outputs of the unit process before allocation.*” This so-called *100 %-rule* prevents double-counting of impacts or benefits.

Since allocation can become quite complicated, allocation approaches are specified in the context of CCU separately in section 4.2.

⁶Allocation often refers to obtaining product-specific results in general. In contrast to this *broad* sense of allocation, the term allocation in this thesis is used in the *narrow* sense of assigning emissions based on allocation criteria such as mass or economic value. This narrow understanding of allocation is sometimes also referred to as *partitioning* (Heijungs and Guinée, 2007).

3.2.5 Consider all relevant impacts!

Assessing impacts on the environment is not straightforward as complex cause-and-effect chains are involved. In LCA, environmental impacts are usually assessed at the so-called midpoint level (Fig. 3.6). For example, for the emission of greenhouse gases, the midpoint indicators quantifies their contribution to global warming by absorbed radiation. In contrast, an endpoint indicator would consider the effects of global warming on ecosystems, human health and resources (Hauschild et al., 2013), e.g., the extinction of a species which could not adapt to increased global temperatures. Since uncertainty increases towards endpoint indicators, the standard practice in LCA is to evaluate impacts at the midpoint level. Besides global warming, other examples for midpoint indicators are (fossil) resource depletion, water use, acidification, toxicities, eutrophication, and land transformation, among many others (Table 3.1).

The assessment of the large number of environmental impacts at the midpoint level can render conducting a LCA very complex. Moreover, there are several models to assess these impacts. An overview of impact assessment (LCIA) models is given by Curran (2012). It is often too costly and time consuming to assess all of these impacts and models. Therefore, the European Commission's Joint Research Centre (Hauschild et al., 2013) analyzed available impacts categories and models with regard to completeness, relevance, robustness, transparency, applicability as well as acceptance and

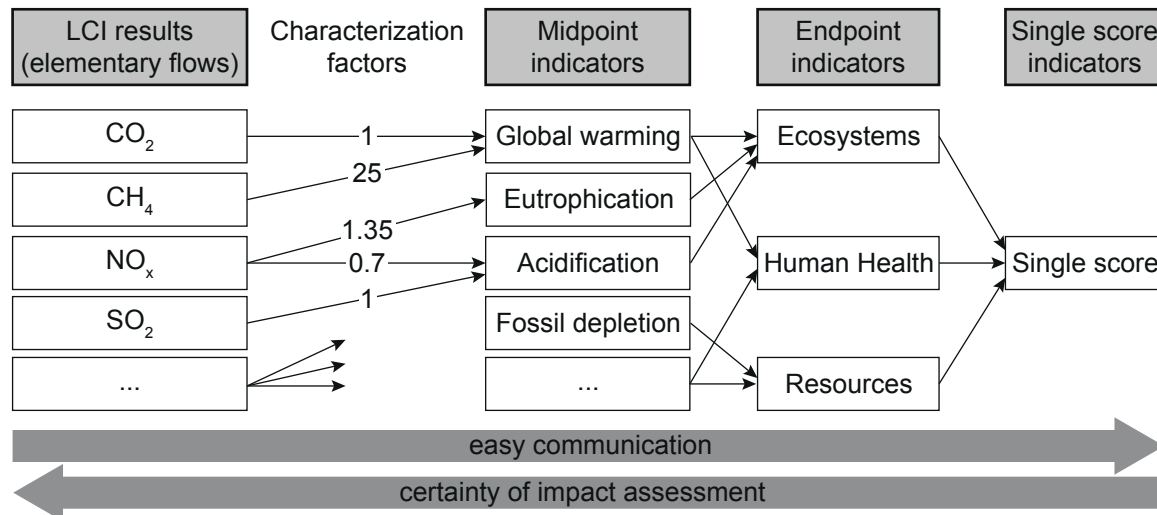


Figure 3.6: Impact assessment in LCA using midpoint, endpoint and single score indicators. Usually, the uncertainty increases towards single score indicators. However, they are often easier to communicate.

suitability for communication. The impact categories are classified in three quality levels in order to facilitate their selection (Table 3.1). These quality levels should be considered when interpreting the indicator results in the last phase of an LCA.

As already briefly mentioned in section 3.2.3, the selection of impact categories has to be in line with the goal and scope definition: if the goal of the LCA study is to determine the global warming impact of a product, then the impact category ‘global warming’ must obviously be included.

CCU often aims at reducing CO₂ emissions and uses CO₂ as an alternative source of carbon. Thus, in the author’s view, the assessment of impacts on global warming and on fossil resource depletion should always be included in the scope of LCA for CCU.

Table 3.1: Impact categories recommended by European Commission’s Joint Research Centre in the European context. For the corresponding LCIA models, please refer to Hauschild et al. (2013) and references therein. Quality levels: I: recommended and satisfactory, II: recommended but in need of some improvement, III: recommended but to use with caution.

Quality level I	Quality level II	Quality level III
Global warming ^a	Ionizing radiation, human health	Land use
Ozone depletion	Photochemical ozone formation	Resource depletion, water
Particulate matter/respiratory inorganics (I/II)	Acidification	
	Eutrophication, terrestrial and aquatic	
	Resource depletion, mineral and fossil	
	Human toxicity, cancer and non-cancer effects (II/III)	
	Ecotoxicity, freshwater (II/III)	
^a In LCA, the impact category ‘global warming’ is often called ‘climate change’ (Curran, 2012).		

3.2.6 Use existing LCA software and LCA databases!

LCA computations can become very involved and rely on many data. Therefore, using LCA software and LCA databases can save a lot of time and effort. Commercial software such as GaBi (PE International, 2012), SimaPro (Consultants, 2014) and Umberto (ifu, 2014) as well as freeware tools such as openLCA (GreenDelta, 2012), CMLCA (Heijungs, 2012) and brightway (Mutel, 2014) are available (cf. pp. 143 in Curran (2012)). Using a software tool is recommended as it does not only facilitate the computation but usually also guides the user through LCA methodology, e.g., defining a functional unit, setting allocation criteria, and illustrating results.

LCA databases provide data for single processes, partial life cycle stages or complete life cycles. For an overview of LCA databases, the reader is referred to Table 5.1 in Curran (2012). Particularly relevant databases for production of chemicals are ecoinvent v3 (ecoinvent, 2010) and Eco-profiles (PlasticsEurope, 2014). The ecoinvent v3 database contains more than 9,000 datasets that cover all sorts of products from electricity to chemicals, food, transport, recycling and disposal (ecoinvent, 2010). A major advantage of the datasets in ecoinvent is the transparency as usually data for each process can be accessed in detail. The freely available Eco-profiles by PlasticsEurope offer aggregate cradle-to-gate life cycle inventories for plastics, basic precursors and on-site energy such as electricity and steam (PlasticsEurope, 2014). When using data from LCA databases or other sources, the suitability of data for the present LCA study should be checked: for example, data can be specific for one technology or averaged across production technologies.

CCU example (14): *LCA data for feedstocks relevant to CCU.* In Table 3.2, impact assessment results for global warming and fossil resource depletion are given for feedstocks relevant to CCU. The fossil resource depletion (FD) measured in kg oil-eq can also be expressed by the cumulative fossil energy demand (CED) measured in MJ ($1 \text{ kg oil-eq} \hat{=} 42 \text{ MJ}$).

3.2.7 Start early and hang in!

Many CO₂ utilization reactions are still in early stages of research where little data are available. Since LCA is data-driven, a reliable assessment might be difficult but is still accessible. Depending on the research stage, different approaches can be applied.

Prior to any experiments, a simplified LCA can estimate “best-case” results as screening indicator for promising CO₂ utilization reactions. For this approach, stoichiometric amounts can be used as optimal mass balance (Sugiyama et al., 2008). The obtained feedstock masses are multiplied with the corresponding impact data,

e.g., data from Table 3.2. If the overall impacts of this “best-case” estimation are lower than impacts from conventional production, potential impact reductions exist and experiments should be started. If the best-case results are already worse, there is no environmental incentive under the assumed conditions.

CCU example (15): *Environmental potential for CO₂-based production of formic acid.* Formic acid can be produced from CO₂ and H₂ according to the reaction:



Assuming stoichiometric amounts of 957 kg CO₂ and 43 kg H₂ for the formation of 1000 kg of formic acid (HCOOH), the lowest possible impacts for this reaction can be computed. For CO₂ from a coal fired power plant (using lowest values from Table 3.2) and H₂ from electrolysis using wind power, the lowest possible impacts on global

Table 3.2: Overview of global warming (GW) and fossil resource depletion (FD) impacts caused by production of feedstocks frequently used in CO₂ chemistry per kg of feedstock. Results that are particularly sensitive to the choice of allocation criteria are marked with an asterisk (*).

Chemical	Global warming GW / (kg CO ₂ -eq / kg)	Fossil resource depletion FD / (kg oil-eq / kg)
CO ₂ from coal power plant	(−0.7) – (+0.1) ^{a*}	0.1 ^a
CO ₂ from air-capture	−0.4 ^a	0.3 ^a
H ₂ from electrolysis & wind	1.0 ^a	0.2 ^a
H ₂ from chlorine electrolysis	1.0 ^{c*}	0.2 ^{c*}
H ₂ from cracking	1.7 ^{c*}	1.7 ^{c*}
H ₂ from electrolysis & photovoltaics	2.4 ^d – 6.0 ^a	0.8 ^d
H ₂ from steam reforming	7.5 ^c – 11.9 ^a	1.7 ^c
Natural gas	0.5 ^c	1.3 ^c
Methanol (CH ₃ OH)	0.7 ^b	0.9 ^b
Ethylene oxide (C ₂ H ₄ O)	1.8 ^b	1.4 ^b
Propylene oxide (CH ₃ CHCH ₂ O)	4.5 ^b	2.2 ^b

^a cf. sections 4.2.3, 5.3.3 and 6.3, ^b ecoinvent (2010), ^c PlasticsEurope (2014), ^d Cetinkaya et al. (2012)

warming (GW) and fossil resource depletion (FD) are:

$$GW_{\text{HCOOH}} = -0.7 \cdot 957 + 1.0 \cdot 43 = -627 \text{ kg CO}_2\text{-eq} \quad \text{per 1000 kg HCOOH} \quad (3.2)$$

$$FD_{\text{HCOOH}} = 0.1 \cdot 957 + 0.2 \cdot 43 = 104 \text{ kg oil-eq} \quad \text{per 1000 kg HCOOH} \quad (3.3)$$

Compared to the classical production of 1000 kg formic acid from methyl formate with 3067 kg CO₂-eq and 1500 kg oil-eq (ecoinvent, 2010), the CO₂-based production of formic acid has an enormous potential to reduce global warming impacts and fossil resource depletion by up to 120 % and 93 %, respectively.

While and after experiments, LCA results should continuously be updated with experimental data, e.g., replace stoichiometric data with mass balance from experiments (Sugiyama et al., 2008). LCA results can be further refined with estimations tools, e.g., for the process energy demand. As indicator for the process energy demand, the energy-loss index (ELI) has been proposed (Sugiyama et al., 2008): The ELI index has a value between 0 and 1 depending on the water concentration, product concentration, minimum difference of boiling point, inherent waste amount, and reaction energy (Sugiyama et al., 2008). ELI was recently extended by the number of co-products and the (non-) existence of feedstock pre-treatment (Patel et al., 2012). Based on the ELI values, the gate-to-gate process energy consumption can be estimated with a relative error between 30 % and 35 % (Bumann et al., 2010). By also taking into account the cumulative energy demand (CED) of feedstock production, the entire cradle-to-gate CED can be estimated. For 146 organic chemicals and 33 plastics (among others), Huijbregts et al. (2010) showed that CED correlates with other environmental indicators and can thus be used as screening indicator for environmental impacts. However, the interpretation of CED as screening indicator results should be done with caution: correlation among environmental indicators cannot be taken for granted (Guillén-Gosálbez, 2011) and results can change drastically from research stage to industrial implementation due to scale-up challenges or improvements, and process design optimization such as heat integration.

3.2.8 Are you sure?

LCA results always contain uncertainty, e.g., due to uncertain or missing data. Data uncertainty is particularly high when assessing products at early development stages. Since uncertainties of all kinds cannot be resolved completely, one has to find a way to deal with them. Elaborating uncertainties in the interpretation phase of LCA is therefore explicitly mentioned in the ISO standards in order to make LCA studies

as reliable and transparent as possible (ISO 14040, 2009; ISO 14044, 2006). Since the author is not aware of a systematic uncertainty assessment for processes at early development stages, the following procedure for an uncertainty assessment of LCA for CCU is suggested.

As a first step after having computed initial LCA results based on reaction stoichiometry, experimental data used as input for LCA as well as the LCA results should be checked against corresponding data from the literature or from LCA databases (cf. Section 3.2.6). In a second step, the most important parameters for the LCA results are identified. During reaction design, parameters such as amount and type of catalyst, temperature and pressure are typically varied for reaction optimization. The most important parameters in reaction optimization are not necessarily equally important for LCA. Each set of experimental data should therefore be fed into the LCA calculations to determine the effects of reaction parameters on LCA results. Thereby, the most sensitive and most resilient parameters in LCA can be determined. As third step, different technologies for feedstock production should be considered to evaluate the influence of potential technology changes. Finally, LCA-related assumptions such as allocation criteria should be analyzed.

CCU example (16): *Alternative feedstock supply for CO₂-based methanol production.* Methanol production from stoichiometric amounts of CO₂ and H₂ is considered. In Fig. 3.7, the fossil resource depletion of CO₂-based methanol production is shown for alternative feedstock production technologies from Table 3.2. The fossil resource depletion of fossil-based methanol production is also included as benchmark. In the example, CO₂-based methanol has the potential to reduce the use fossil resource depletion compared to fossil-based methanol regardless of the technologies for H₂ and CO₂ supply.

Typical methods for assessing uncertainty include scenario analysis, sensitivity analysis and uncertainty analysis (Björklund, 2002). In scenario analysis, defined scenarios are evaluated and compared. Scenario analysis is easily accessible, both in terms of performing the analysis and understanding the results (cf. example 16). In sensitivity analysis, the change in results due to a small change of input data is analyzed. In contrast, uncertainty analysis investigates the change in results due to actual variations in input data. Uncertainty analysis is often performed statistically as Monte-Carlo simulation, or alternatively analytically. Recently, a unified analytical framework for uncertainty assessment of uncertainties in data and allocation criteria has been published (Jung et al., 2014).

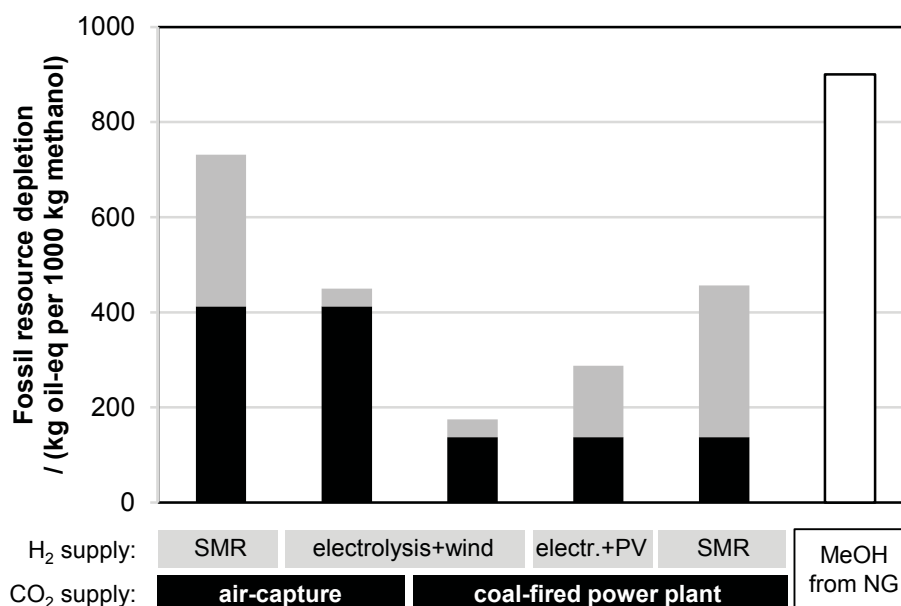


Figure 3.7: Fossil resource depletion of CO₂-and fossil-based methanol production. SMR: steam methane reforming, PV: photovoltaics, NG: natural gas.

3.3 Summary and conclusions

In this chapter, the concept of LCA has been introduced. Due to the holistic perspective of LCA, problem shifting between life-cycle stages or between environmental impacts can be avoided. Thus, LCA should be used for environmental assessment of CCU.

To enable LCA novices to apply and understand LCA of CCU, a jargon-free tutorial for LCA of CCU has been presented. Nine particularly important aspects have been identified for conducting an LCA of CCU. With the intention of a how-to manual, each aspect has been explained and illustrated by CCU examples.

The examples suggest that CCU has an enormous potential to reduce environmental impacts when compared to the classical fossil-based alternative. Furthermore, the examples show that LCA of CCU is accessible and possible even in early stages of process development. In early stages, the environmental impacts of a CO₂-based product or process can be estimated by the impacts of the feedstocks. For the impacts of feedstock CO₂, the CO₂ source must always be included in the analysis since CO₂ capture from a typically diluted CO₂ source requires significant amounts of energy and causes indirect environmental impacts. The environmental friendly production of highly energetic feedstocks such as H₂ is often a crucial prerequisite for CCU be-

ing environmentally more sustainable than the traditional fossil-based route. The application of LCA should allow for identifying environmentally promising routes for CCU.

Pitfalls in LCA for CO₂ Capture and Utilization

In this chapter, three particularly important pitfalls for the application of Life-Cycle Assessment (LCA) for CO₂ Capture and Utilization (CCU) are identified. The first pitfall is to intuitively treat the utilized CO₂ as negative greenhouse gas (GHG) emission (section 4.1). The second pitfall is how to allocate environmental impacts to individual CCU products since co-products are inherently present for CO₂ capture from CO₂ point sources (section 4.2). The third pitfall is the overestimation of the effect of the CO₂ storage duration on the global warming impact (section 4.3). In sections 4.1-4.3, each pitfall is first described. Second, a general methodology is presented for LCA of CCU avoiding the described pitfalls. Third, this methodology is detailed for the specific case of CCU and finally illustrated by simplified CCU examples. In section 4.4, the chapter is summarized and conclusions are drawn from the illustrative examples. Furthermore, a detailed framework is derived for LCA of CCU to avoid the described pitfalls.

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von der Assen, N., Jung, J., and Bardow, A. (2013). Life-Cycle Assessment of Carbon Dioxide Capture and Utilization: Avoiding the Pitfalls. *Energy & Environmental Science*, 6:2721-2734.

The general concept of Life-Cycle Assessment (LCA) as well as the application to CCU have been presented in chapter 3. While the intention of chapter 3 has been to encourage the use of LCA for CCU, the application of LCA to CCU bears three particularly important methodological pitfalls:

1. Utilized CO₂ is often intuitively considered as negative greenhouse gas (GHG) emission.
2. Since CCU usually generates products in both the capture and utilization processes, choices exist how to allocate emissions to the individual products.
3. Since the CO₂ storage duration is not reflected in traditional LCA, the CO₂ storage duration is frequently used as separate, overestimated metric for global warming impacts.

The goal of this section is to provide a more detailed framework for LCA of CCU processes avoiding these existing pitfalls. Since these pitfalls become particularly obvious in the impact category global warming, the following illustrating examples discuss global warming impacts only. However, the presented methods are also valid for any other impact category (cf. section 3.2.5).

The so-called global warming potential (GWP_i) of GHG emission i measures its relative global warming strength in terms of its absorbed radiation in comparison to a CO₂ emission (Forster et al., 2007). To obtain a global warming impact score GW for all GHG emissions m_i along a life cycle, the amounts m_i of all GHG emissions i are multiplied by their characterization factors GWP_i and added (Curran, 2012):

$$GW = \sum_i m_i GWP_i. \quad (4.1)$$

The global warming impact GW is also known as Carbon Footprint. The distinction between GWP_i and GW is essential: GW describes the actual global warming impact of a product's life cycle by weighting multiple GHG emissions i with their GWP_i , whereas GWP_i is a molecular property and characterizes the radiation absorption of a single GHG emission independently from any product life cycle.

4.1 Pitfall 1: characterization of utilized CO₂

For a CO₂ utilization process, the utilized CO₂ could be intuitively treated as negative GHG emissions, i.e., the global warming impact of utilizing 1 kg CO₂ would be (Aresta and Dibenedetto, 2007a; Kim et al., 2011):

$$GW = -GWP = -1 \frac{\text{kg CO}_2\text{-eq}}{\text{kg CO}_2}. \quad (4.2)$$

However, this assumption neglects relevant emissions in the upstream CO₂ capture process caused by energy requirements for CO₂ capture. This neglect can lead to qualitatively wrong results. Still, a common ad-hoc metric is the ‘net amount of CO₂ fixed’ (cf. section 2.4.2) where the amount of utilized CO₂ is often simply balanced with the emissions of the utilization process. Thereby, the utilized CO₂ is treated as negative GHG emission (cf. Eq. (2.18)).

4.1.1 Flow characterization of utilized CO₂ in LCA

In section 3.1, process in- and outputs have been divided into elementary and economic flows. To characterize the utilized CO₂, the origin and destiny of utilized CO₂ have to be analyzed.

According to the definition of CCU in section 2.2, the first step of CCU is industrial capture of CO₂ to obtain concentrated CO₂ as feedstock. Concentrated CO₂ is thus the product of a human transformation (capture), and it undergoes a subsequent human transformation (utilization). Concentrated CO₂ for utilization is therefore clearly an economic flow: it remains within the technosphere; the atmosphere is not directly affected by the concentrated CO₂ as illustrated in Fig. 4.1. Whether a flow represents an elementary or economic flow is not a matter of the name of the molecule, but depends only on how this flow occurs in the system. CCU can turn CO₂ from emission to feedstock. Accordingly, in LCA, concentrated CO₂ has to be treated just like any other feedstock with its own upstream emissions. Therefore, in the following, concentrated CO₂ for utilization is called *feedstock CO₂* (for CO₂ utilization) or *product CO₂* (for CO₂ capture) to distinguish it from *CO₂ emissions*.

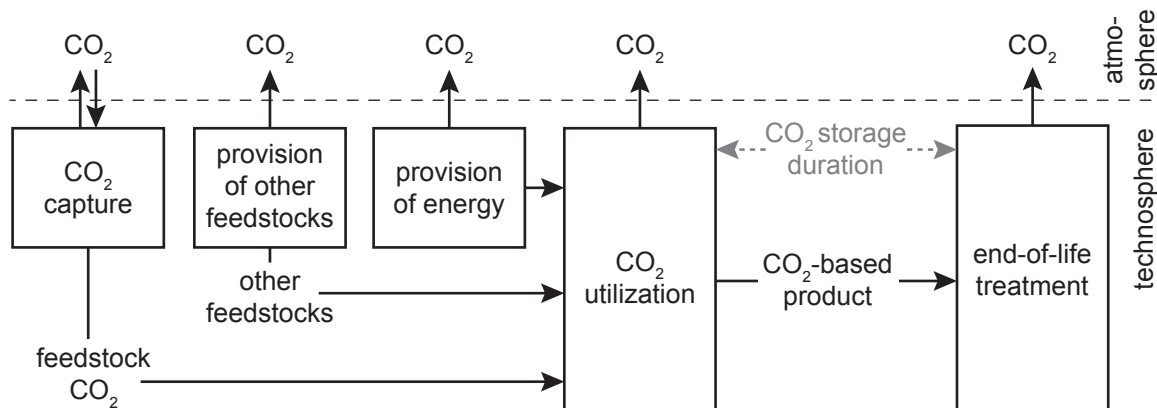
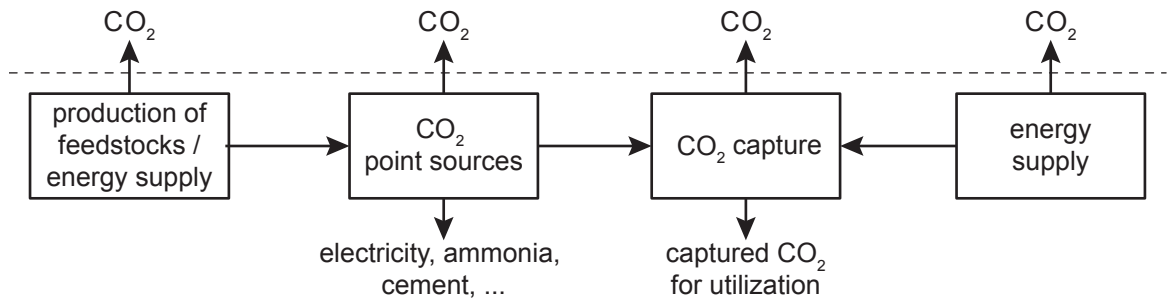
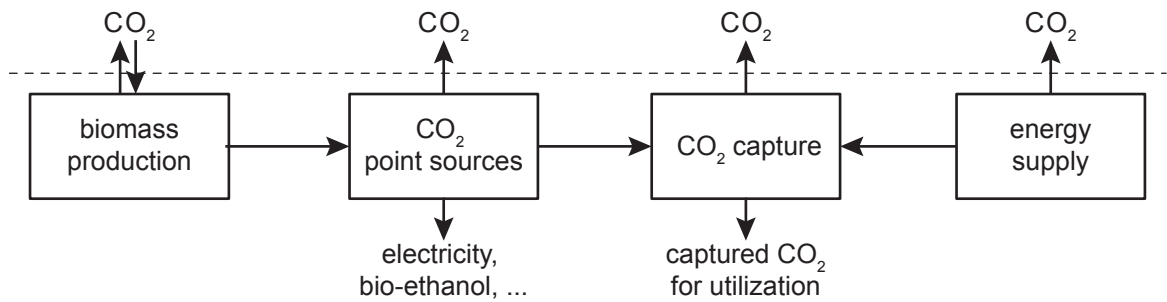


Figure 4.1: The flow chart of the entire CCU system emphasizing the two subsystems of CO₂ capture and CO₂ utilization and classifies the feedstock CO₂ (in bold circle) as economic flow, not as negative emission.

a) non-biogenic point sources



b) biogenic point sources



c) air-capture

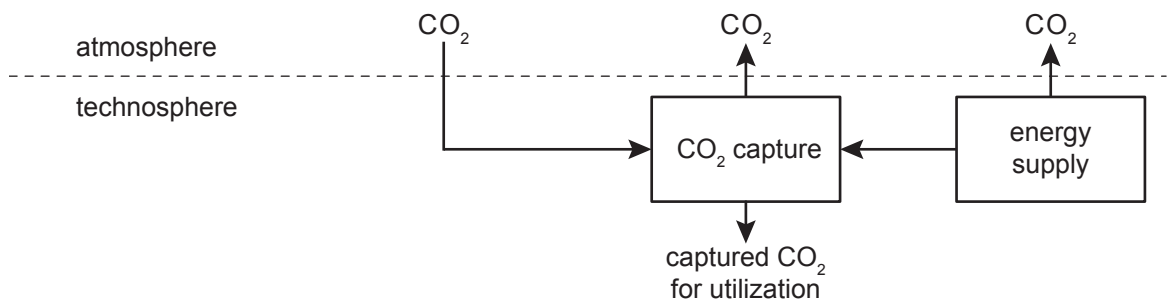


Figure 4.2: Classification of CO₂ capture systems according to carbon origin: a) CO₂ capture from non-biogenic point sources includes capture from power plants and industrial processes; b) CO₂ capture from biomass combustion or conversion processes; c) CO₂ capture from ambient air. In case a) and b), a valuable product besides feedstock CO₂ is always co-produced. Only case b) and c) can potentially act as negative emission technologies.

As identified in section 3.2.3, CO₂ used as feedstock is obviously a relevant input flow. Therefore, the system boundaries should comprise all upstream processes of feedstock CO₂ including CO₂ transport, CO₂ capture and the CO₂ source. The CO₂ source can be classified in three general categories depending on the carbon source: a) CO₂ capture from non-biogenic point sources, b) CO₂ capture from biogenic point sources, and c) CO₂ air-capture (Fig. 4.2).

Systems with CO₂ capture from non-biogenic point sources (Fig. 4.2a) include power plants and industrial processes. Together with feedstock CO₂, a main valuable product, e.g., electricity or ammonia, is always co-produced. Due to usual capture rates below 100 %, part of the produced CO₂ is emitted to the atmosphere. Fig. 4.2a thus already shows that non-biogenic point sources necessarily have positive CO₂ emissions.

In biogenic point sources, the carbon from the captured CO₂ ultimately originates from a biomass source as in the production of pulp and paper, in fermentation (see section 2.3.1.1) or in biomass-fired power plant with CO₂ capture (Akgul et al., 2014). When using biomass (Fig. 4.2b), negative CO₂ emissions can occur since CO₂ from the atmosphere is fixed. Whether biogenic point sources lead to negative CO₂ emissions depends on how much CO₂ can be fixed and how much is released during the capture process. For the uptake of atmospheric/biogenic CO₂ in air-capture and biomass production and re-release to the atmosphere, it currently is an open issue in LCA whether and how fossil and biogenic GHG emissions should be treated differently (Guinée et al., 2009; Cherubini et al., 2011). Biogenic CO₂ is sometimes completely left out in LCA inventories due to the claim that CO₂ is first taken up by plants and the same amount is re-emitted in downstream process (Rabl et al., 2007). However, the biogenic carbon is not necessarily re-emitted completely (maybe the biogenic-CO₂-based product does not degrade) or it is not re-emitted as CO₂ but as the more potent GHG methane (CH₄). Therefore, the recommendations by Rabl et al. (2007) should be followed “that emission and removal of CO₂ be counted explicitly at each stage of the life cycle”. For biogenic point sources, a valuable product is again co-produced besides feedstock CO₂.

In contrast to the cases considered in Fig. 4.2a+b, the sole reason for operating air-capture (Fig. 4.2c) is provision of feedstock CO₂ without any co-products. As in the biomass case, the balance of air-captured and emitted CO₂ determines whether the entire air-capture system releases or captures net CO₂ emissions.

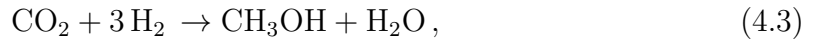
A large spectrum of CO₂ sources exists differing in properties such as CO₂ concentration or impurities (section 2.3.1.1). Depending on these properties and the required specifications for subsequent CO₂ utilization, CO₂ capture requires more or less energy. In addition to energy, CO₂ capture requires equipment and working materials such as capture solvents. Furthermore, the captured CO₂ is usually compressed and transported. Providing energy, equipment and working materials, as well as compression and transport cause indirect CO₂ emissions and other environmental impacts. Due to these indirect CO₂ emissions, the amount of captured CO₂ does not equal the amount of avoided CO₂ emissions at the source, i.e., the global warming impact (*GW*) of providing 1 kg of feedstock CO_{2,feed} is $GW(\text{CO}_{2,\text{feed}}) > -1 \text{ kg CO}_{2\text{-eq per kg CO}_{2,\text{feed}}$ (Aresta and Galatola, 1999; Aresta et al., 2014).

Few CO₂ sources already offer almost pure CO₂ so that concentrating CO₂ becomes dispensable. Similarly, concentrating CO₂ is not required if diluted CO₂ streams can be used directly. For example, algae can directly feed on diluted CO₂ from power plant flue gases (Scott et al., 2010). Nevertheless, even these cases usually require energy, e.g., to power fans that ventilate high volumes of CO₂ containing flue gas to algae ponds (Scott et al., 2010). Only for the very rare (if not impossible) case where no additional energy is required and no indirect emissions occur, it can be assumed that capturing of 1 kg of feedstock CO₂ leads to a reduction of 1 kg of CO₂ emissions at the source, i.e., $GW(\text{CO}_{2,\text{feed}}) = -1 \text{ kg CO}_2\text{-eq per kg CO}_{2,\text{feed}}$.

In summary, LCA clearly defines feedstock CO₂ from CO₂ capture as economic flow and not as negative GHG emission. Provision of feedstock CO₂ cannot be treated as net CO₂ sink or source by default. Instead, a detailed evaluation is required for the entire CCU system.

4.1.2 Illustration for methanol synthesis from CO₂ and H₂

To analyze the consequences of flow characterization of utilized CO₂ on the global warming impacts, an illustrative example for methanol (CH₃OH) synthesis from CO₂ and hydrogen (H₂) is presented. Methanol is produced according to the reaction



which means that stoichiometrically 1,375 kg CO₂ and 187.5 kg H₂ are necessary to produce 1,000 kg CH₃OH. Reaction conditions of 500 K and 5 MPa require 1.27 kWh/kg CH₃OH of electricity (Rihko-Struckmann et al., 2010). With a grid emission factor of 0.55 kg CO₂-eq/kWh for the USA (EPA, 2012), electricity demand causes indirect GHG emissions of 0.70 kg CO₂-eq/kg CH₃OH.

For supply of CO₂, two cases are considered in this example: direct utilization of atmospheric CO₂ and capture of CO₂ from air. In the first case, direct utilization of atmospheric CO₂ can be employed if the CO₂ utilization process can directly utilize dilute CO₂ from ambient air rather than requiring concentrated CO₂. Industrial capture of CO₂ as first step of CCU is then not required. In this hypothetical case, feedstock CO₂ can be treated as negative GHG gas emissions with a global warming impact of $GW(\text{CO}_{2,\text{feed}}) = -1 \text{ kg CO}_2\text{-eq/kg CO}_2$. In the second case, concentrated CO₂ is obtained by capturing CO₂ from ambient air (air-capture). The CO₂ capture process requires energy whose provision is associated with indirect CO₂ emissions (details are given in section 6.2.2). These indirect CO₂ emissions of 0.59 kg CO₂-eq/kg CO₂ reduce the credit of capturing CO₂ ($-1 \text{ kg CO}_2\text{-eq/kg CO}_2$) leading to a net global warming impact of $GW(\text{CO}_{2,\text{feed}}) = -0.41 \text{ kg CO}_2\text{-eq/kg CO}_2$.

The goal of this illustrative example is to compare the global warming impacts of methanol production for five scenarios:

- (i) methanol from CO₂ and H₂; production of H₂ via electrolysis using power from photovoltaics and direct utilization of atmospheric CO₂
- (ii) methanol from CO₂ and H₂; production of H₂ via electrolysis and photovoltaics but with provision of CO₂ by air-capture
- (iii) methanol from CO₂ and H₂; production of H₂ via electrolysis and wind power and provision of CO₂ by air-capture
- (iv) methanol from CO₂ and H₂; production of H₂ via steam reforming of natural gas and provision of CO₂ by air-capture
- (v) methanol via steam reforming of natural gas (=non-CCU benchmark)

The global warming impact GW for methanol is calculated for a cradle-to-gate boundary, i.e., usage and end-of-life treatment are not included since methanol can be used in various ways. For this illustrative example, all plants are assumed to be located close together and thus transport of H₂ and CO₂ can be neglected for simplicity. However, relevant emissions from transportation especially over long distances should be considered in LCA for real technologies as already discussed in the CCS context (Marx et al., 2011). GW values for the feedstocks H₂ and CO₂ (scenario i-iv) and for the product CH₃OH as well as the ‘net amount of CO₂ fixed’ are shown in Table 4.1.

In scenario (i), CO₂-based methanol synthesis does not act as GHG sink but has much lower GHG emissions than the non-CCU benchmark. Scenario (ii) is even worse than the benchmark due to indirect GHG emissions induced by the energy demand of air-capture. The indirect GHG emissions of air capture are not reflected in the ‘net amount of CO₂ fixed’. If H₂ can be produced by electrolysis using wind power in scenario (iii), the CCU system achieves minimal, though still positive GHG emissions. However, ‘net amount of CO₂ fixed’ misleadingly classifies scenario (iii) as GHG sink. For H₂ production via steam reforming of natural gas (scenario iv), the GHG emissions of the CCU system are more than three times larger than the GHG emissions of the non-CCU benchmark (v).

The example shows that none of the CCU scenarios acts as GHG sink since $GW(\text{CH}_3\text{OH}) > 0$. It also shows that CCU is not necessarily better than the traditional, non-CCU benchmark (scenarios ii and iv).

From an LCA perspective, a CO₂ balance of the utilization process alone as used for the ‘net amount of CO₂ fixed’ would only be correct for the unlikely case of directly

Table 4.1: Comparison of global warming impact GW and the net amount of CO_2 fixed (see section 2.4.2) for methanol synthesis from CO_2 and H_2 and for traditional methanol synthesis via steam reforming of natural gas. CO_2 is either supplied directly from the atmosphere (CO_2 as negative emission, scenario i) or via air-capture (feedstock CO_2 as economic flow, scenarios ii to iv). H_2 is produced via electrolysis powered by different renewable energy technologies. For the CCU scenarios i to iv, indirect GHG emission of 0.70 kg $\text{CO}_2\text{-eq/kg}$ CH_3OH due to feed gas compression are included (Rihko-Struckmann et al., 2010).

Scenario	$GW(\text{H}_2)$ [kg $\text{CO}_2\text{-eq/kg}$]	$GW(\text{CO}_2, \text{feed})$ [kg $\text{CO}_2\text{-eq/kg}$]	$GW(\text{CH}_3\text{OH})$ [kg $\text{CO}_2\text{-eq/kg}$]	net amount of CO_2 fixed [kg $\text{CO}_2/\text{kg CH}_3\text{OH}$]
(i) H_2 via electrolysis and photo-voltaics and direct utilization of atmospheric CO_2	6.0 ^a	-1	0.45	0.45
(ii) H_2 via electrolysis and photo-voltaics and CO_2 air-capture	6.0 ^a	-0.41 ^c	1.26	0.45
(iii) H_2 via electrolysis and wind power and CO_2 air-capture	1.0 ^b	-0.41 ^c	0.32	-0.49
(iv) H_2 via steam reforming of natural gas and CO_2 air-capture	11.9 ^d	-0.41 ^c	2.37	1.55
(v) benchmark: traditional methanol synthesis via steam reforming of natural gas	—	—	0.75 ^e	—

^aKoroneos et al. (2004), ^bSpath and Mann (2004), ^cown LCA calculation based on an air-capture technology described by Keith et al. (2006), see chapter 6, ^dSpath and Mann (2001), ^eecoinvent (2010)

utilizing atmospheric CO₂ (scenario i). For industrial CO₂ capture, however, a CO₂ balance of the utilization CO₂ process alone is not only quantitatively wrong, but it can be even qualitatively wrong and therefore misleading (scenario iii). Therefore, CO₂ capture at the CO₂ source, associated energy requirements and indirect GHG emissions must be included in the CO₂ balance.

4.2 Pitfall 2: product-specific LCA results of CCU

A CCU system with CO₂ capture from point sources delivers two products: the original main product of the point source (Fig. 4.2), and the CO₂-based product or service from the utilization process (Fig. 4.1). In an industrial context, often two different companies are involved in the capture and utilization processes. Both companies are usually interested in LCA results for their individual products, so-called product-specific LCA results or footprints. The total emissions of the system have then to be allocated to the individual products.

For example, the operator of a power plant with CO₂ capture is interested in the global warming impact *GW* of electricity generated in the power plant. At the same time, a chemical company has to report on the *GW* of a chemical produced from the power plant's feedstock CO₂. As shown in section 4.1, *GW* of the CO₂-based product depends on *GW* of the feedstocks including feedstock CO₂. To obtain *GW* of feedstock CO₂, GHG emissions from the power plant have to be allocated to the two economic flows electricity and feedstock CO₂.

Product-specific LCA results might also be required if the CO₂-based product falls under a regulatory legislation. For example, CO₂-based fuels might in future be included in a renewable fuel directive such as the European Renewables Directive (European Parliament and Council, 2009). Here, eligible bio-fuels must reduce GHG by at least 35 % compared to a fossil fuel reference based on product-specific GHG emissions (g CO₂-eq/MJ). Furthermore, LCA databases typically contain product-specific LCA results. These cases require a single absolute value for each product and each environmental impact category. For this purpose, emissions of the total CCU system must be allocated to the individual products.

However, allocation of emissions to co-products requires subjective choices among different allocation approaches. In section 3.2.4, the allocation approaches have been explained briefly. Jaramillo et al. (2009) showed for enhanced oil recovery that product-specific LCA results for CCU strongly depend on the allocation procedure. Therefore, the following sections provides detailed guidance how to address choices in allocation for CCU. This purpose requires a deeper look into the LCA methodology.

4.2.1 Multi-functionality in LCA

The allocation problem in LCA is directly linked to multi-functionality. Multi-functionality occurs when a system or process has two or more functions. A *function* in LCA can be producing a valuable product output or disposing an unwanted waste input (Guinée et al., 2009). Multi-functionality can occur for any combination of these functions (Guinée et al., 2009):

- co-production of multiple valuable products
- combined processing of multiple unwanted wastes
- recycling of unwanted wastes into valuable products

The distinction between valuable products and unwanted wastes is usually based on the economic value (Guinée et al., 2009). Valuable product output flows and unwanted waste input flows are called *functional flows*. For co-production processes with multiple products, alternative allocation approaches have already been presented in section 3.2.4. In the following, the allocation approaches are extended for combined waste processing and recycling.

All functions of a system can be evaluated jointly or separately. Whether functions are studied jointly or separately, is defined in the *functional unit* (section 3.2.2.1): either one functional unit contains all functions or multiple functional units contain one function each. The joint evaluation of all functions is called *system expansion*, since the functional unit is expanded to contain all functions (Jung et al., 2013). Although this approach is recommended by ISO 14040 (2009); ISO 14044 (2006), a joint evaluation is often practically inappropriate since product-specific or, more general, function-specific results are required.

For function-specific LCA results, multiple functional units contain only one individual function each. Two different procedures for obtaining product-specific results are possible: avoided burden and allocation (see section 3.2.4). In the avoided burden procedure, one has to choose which function is the main reason of operation. For the remaining functions, processes that fulfill equivalent functions are chosen. Emissions of these processes are subtracted from the emissions of the system under study assuming these processes are substituted and hence their environmental burdens are avoided. In allocation, emissions are allocated to individual functions based on functional-flow properties such as carbon-content, mass, energy or economic value.

For details on computation and on the comparison of procedures for product-specific results, the reader is referred to recent literature on multi-functionality in LCA (Heijungs and Frischknecht, 1998; Heijungs and Guinée, 2007; Reap et al., 2008; Jung et al., 2013; Pelletier et al., 2015). Only issues relevant for CCU are addressed in the

following.

4.2.2 Multi-functionality in CCU

First, it is identified which processes in CCU are potentially multi-functional. Then, CCU-specific solutions to the multi-functionality problem are elaborated. For simplicity, the utilization process is assumed to produce only one valuable CO₂-based product (Fig. 4.1).

Occurrence of multi-functionality in CCU. For air-capture (Fig. 4.2c), captured CO₂ is the only functional flow. Captured CO₂ can be assumed to be a valuable product since it is the reason of operating air-capture. Thus, air capture is always mono-functional. The entire CCU system produces only the CO₂-based product and is therefore also mono-functional.

CO₂ capture from point sources (Fig. 4.2a+b) is coupled to production of the original main product. The capture process delivers two economic output flows: the original main product and feedstock CO₂. Whether the capture process for point sources is multi-functional depends on the classification of feedstock CO₂ as valuable product or unwanted waste: in case feedstock CO₂ is considered as valuable product, the capture process delivers two valuable products and is therefore multi-functional. The utilization process is mono-functional. In contrast, with feedstock CO₂ being considered as waste, the capture process is mono-functional but the utilization process becomes multi-functional by recycling a waste into a valuable product.

Feedstock CO₂ is usually classified as valuable product or waste according to its economic value. Quadrelli et al. (2011) give a positive price range for concentrated CO₂ of 60-450 € per ton CO₂, whereas the future price for concentrated CO₂ might become zero or even negative (Centi and Perathoner, 2011; Quadrelli and Centi, 2011). Today, it seems unclear how the price for feedstock CO₂ will develop if it becomes abundantly available.

Functional-unit choice and multi-functionality treatment. The functional unit defines which functions are evaluated and whether they are evaluated either jointly or separately. The functional unit is determined by the scope of the study. Reasonable scopes in the context of CCU have been discussed in sections 3.2.1 and 3.2.2. In the following, alternative scopes and thus, alternative definitions of the functional unit are considered. Resulting implications are illustrated and discussed for the alternative approaches to treat multi-functionality in LCA of CCU.

For mono-functional CCU systems using air-capture, the functional unit is easily defined as production of the CO₂-based product and the subsequent evaluation is unambiguous. In contrast, capturing CO₂ from point sources results in a multi-functional system with two functions: provision of the original main product at the CO₂ point source, and provision of a CO₂-based product in the utilization process.

These functions can be evaluated jointly or separately. The joint evaluation using the system expansion approach is also straightforward as choices are avoided. Following ISO 14040 (2009); ISO 14044 (2006), system expansion should be used if the scope allows a joint evaluation.

However, separate evaluation for the individual functions can become necessary. In CCU, usually different companies are involved whose individual scopes are: “how many emissions are caused by my (individual) product or function?” In this case, choices regarding multi-functionality are inevitable. In the following section, the consequences of system expansion, avoided burden and allocation procedures are analyzed for a CCU system with methanol synthesis from CO₂.

4.2.3 Illustration for methanol synthesis from CO₂ and H₂

As illustrative example for obtaining product-specific GW values, methanol synthesis from CO₂ and H₂ is again used. Hydrogen is provided by electrolysis using wind power. In contrast to the example in section 4.1.2, CO₂ is now captured from a sub-critical, pulverized coal power plant using post-combustion CO₂ capture (DoE case 10: net power 550 MW_e, chemical absorption with monoethanolamine, 90 % CO₂ capture rate (NETL, 2010a)). Since CO₂ is already pressurized to 15.3 MPa in the capture process, electricity demand for compression in the methanol process can be reduced to 0.76 kWh/kg CH₃OH (Rihko-Struckmann et al., 2010) and corresponding GHG emissions are 0.42 kg CO₂-eq/kg CH₃OH (with US grid emission factor of 0.55 kg CO₂-eq/kWh) (EPA, 2012). All plants are assumed to be located close together and emissions from transportation of feedstock CO₂ and H₂ are neglected. Fig. 4.3a shows the flow-chart including flow quantities of the considered CCU system. A non-CCU reference system consists of the equivalent pulverized coal plant without CO₂ capture (same net power, DoE case 9 (NETL, 2010a)), and of methanol synthesis via steam reforming of natural gas (Fig. 4.3b). The goal of this section is to determine and compare GHG emissions for the CCU system and the non-CCU reference system for alternative functional unit definitions.

System expansion. For system expansion, the functional unit includes both the production of 1,000 kg CH₃OH and 1,273 kWh of electricity from the power plant (FU_{system}). The global warming impact of the entire CCU system is $GW_{CCU} =$

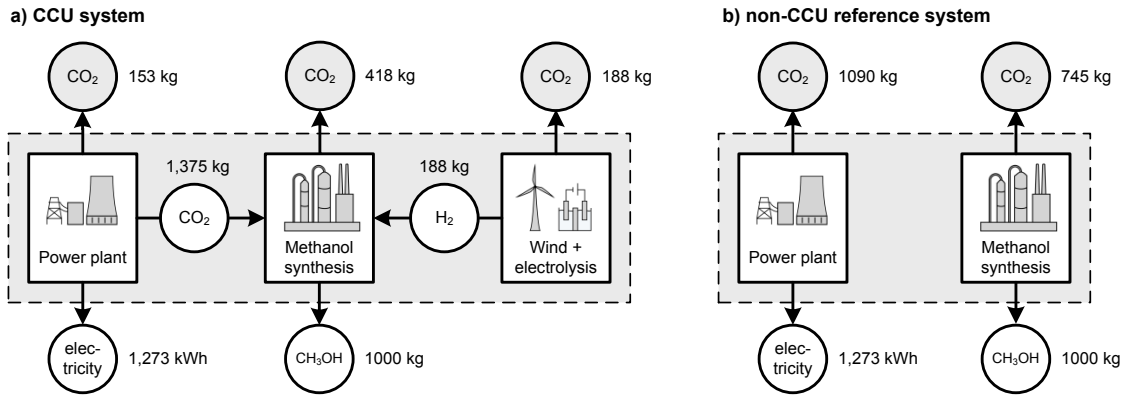


Figure 4.3: Flow-chart and flow quantities a) for CCU system producing electricity and methanol from CO₂, and b) for non-CCU reference system with traditional, non CO₂-based technologies.

$153+418+188= 759 \text{ kg CO}_2\text{-eq/FU}_{\text{system}}$, and of the non-CCU system $GW_{\text{non-CCU}}= 1,090+745= 1,835 \text{ kg CO}_2\text{-eq/FU}_{\text{system}}$ (Fig. 4.3). The CCU system is clearly favored over the non-CCU system as GHG emissions are reduced by $1076 \text{ kg CO}_2\text{-eq/ FU}_{\text{system}}$ (-59%). However, the CCU system still leads to CO₂ emissions and thus, cannot be considered as net GHG sink. The example shows that system expansion allows for a sound environmental evaluation and comparison of CCU and non-CCU avoiding ambiguous choices regarding multi-functionality.

However, such choices become inevitable when product-specific LCA results are required. For product-specific LCA results, functional units are defined for the two individual products: $\text{FU}_{\text{el}} = 1,273 \text{ kWh}$ electricity from the power plant, and $\text{FU}_{\text{CH}_3\text{OH}} = 1,000 \text{ kg}$ methanol. Product-specific LCA results are obtained by applying the avoided burden or the allocation procedure.

Avoided burden. In the avoided burden approach, a main function of the system must be defined: this can be *either* electricity *or* methanol synthesis. For the methanol producer, methanol synthesis is the main function. The total CCU system has a surplus of electricity. This surplus avoids electricity production by a power plant without CO₂ capture (Fig. 4.4a). The same procedure can be applied for defining electricity generation as main function (Fig. 4.4b). For methanol synthesis as main function, the avoided burden approach yields $GW_{\text{el}}=1,090 \text{ kg CO}_2\text{-eq/FU}_{\text{el}}$ and $GW_{\text{CH}_3\text{OH}}=-331 \text{ kg CO}_2\text{-eq/FU}_{\text{CH}_3\text{OH}}$. For electricity generation as main function, the approach yields $GW_{\text{el}}=14 \text{ kg CO}_2\text{-eq/FU}_{\text{el}}$ and $GW_{\text{CH}_3\text{OH}}=745 \text{ kg CO}_2\text{-eq/FU}_{\text{CH}_3\text{OH}}$.

A comparison of the product-specific results for the products from the CCU system and the conventional system reveals a reduction of $1076 \text{ kg CO}_2\text{-eq/FU}$, both for

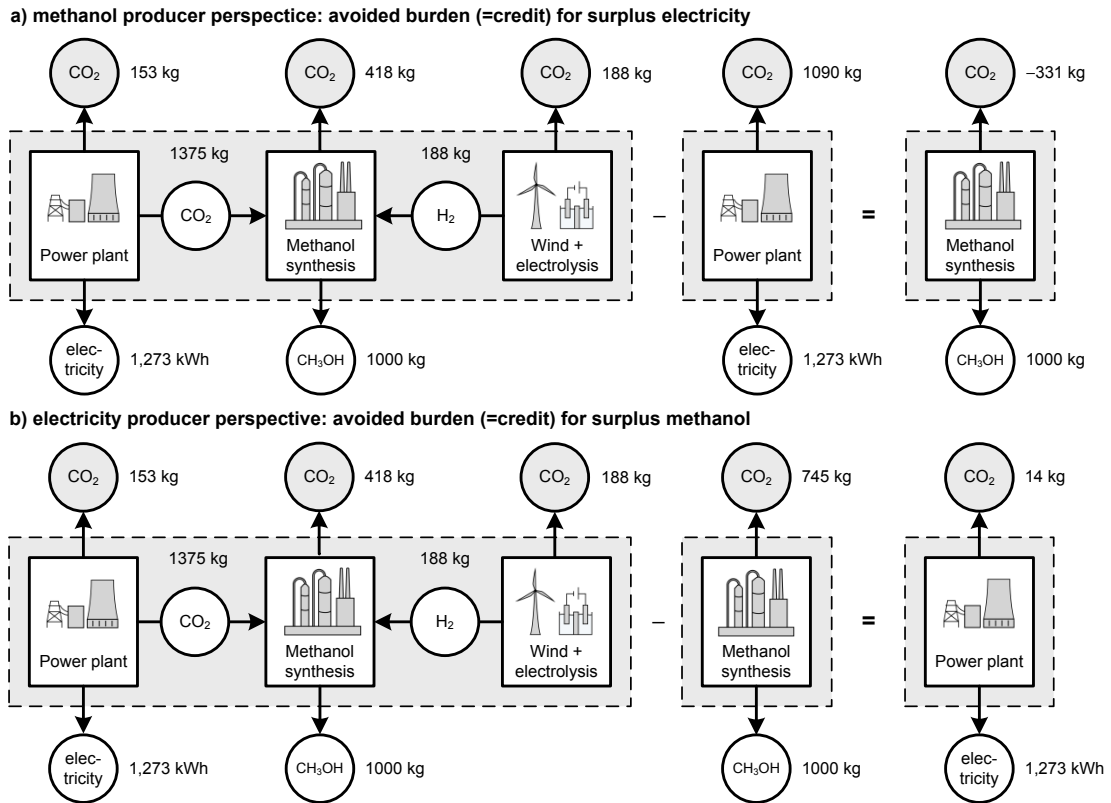


Figure 4.4: Product-specific global warming impacts GW for the CCU system's products using avoided burden processes for a surplus of a) electricity and b) methanol.

electricity and methanol. This reduction is identical to the one obtained from the comparison in the system expansion approach. For comparative LCA studies, the approaches system expansion and avoided burden are conceptually equivalent and lead to the same impact reduction (or increase). However, the avoided burden can only be applied to one of the products to avoid double-counting of the reduction. The avoided burden approach implies comparison. Thus, the avoided burden approach is recommended for product-specific LCA results in a comparative assessment (Jung et al., 2013).

In a stand-alone, attributional LCA of individual CCU products (section 3.2.1), a single absolute value is desired for each product and each impact category. The absolute value can also be understood as footprint of the product. For these footprints, the avoided burden approach can be practically and also conceptually inappropriate for several reasons. A mono-functional avoided burden process is not always available.

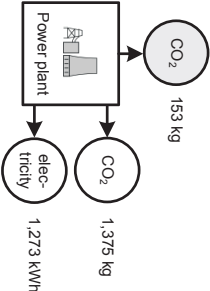
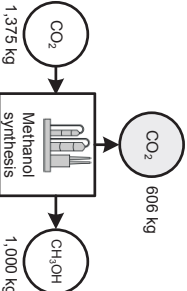
If various avoided burden processes exist, the selection of one of these processes as avoided burden is ambiguous. Furthermore, the avoided burden approach does not distribute environmental benefits among all functions, but assigns it always fully to one function only. When different companies are responsible for the functions, the avoided burden approach thus does not create incentives for both companies simultaneously since they have to agree on a common main function. It is inconsistent if each company selects a different main function to obtain its beneficial carbon footprint GW , e.g., $GW_{\text{CH}_3\text{OH}} = -331 \text{ kg CO}_2\text{-eq/FU}_{\text{CH}_3\text{OH}}$ and $GW_{\text{el}} = 14 \text{ kg CO}_2\text{-eq/FU}_{\text{el}}$, since the total environmental impacts are not conserved (see 100 % rule in section 3.2.4). Most importantly, the avoided burden approach implies a comparison and offsets the LCA results by assigning credits. Due to the credits, negative LCA results are possible. A negative product-specific GW can lead to the wrong interpretation that the CCU product acts as GHG sink or is carbon-negative although the entire system releases GHG emissions, cf. Fig. 4.4. In summary, the avoided burden approach requires very careful interpretation and a clear statement of the underlying assumptions if applied to obtain absolute product-specific footprints in a stand-alone LCA for multi-functional CCU processes, e.g., if the scope is to analyze whether a product is carbon-positive or -negative. To avoid possible misinterpretations and misleading incentives, the author recommends to not use the avoided burden approach for absolute product-specific footprints.

Allocation. For illustration of allocation, four scenarios are selected. The corresponding allocation factors are shown in Table 4.2. In the first three scenarios, the feedstock CO_2 has a non-negative economic value. In this case, emissions of the power plant are allocated among the two functions ‘*electricity generation*’ and ‘*provision of feedstock CO_2* ’. Chosen allocation criteria are the products’ exergy (scenario a) and economic value (scenario b and c). In scenario d, a negative economic value for feedstock CO_2 is assumed declaring feedstock CO_2 as waste. Emissions of the utilization (recycling) process are allocated to the functions ‘*waste processing of feedstock CO_2* ’ and ‘*production of methanol*’. In this case, the power plant pays for the waste processing of feedstock CO_2 not only in terms of economic but also ecological costs: the electricity is also assigned with part (in this case 6 %) of the GHG emissions from the utilization process.

The allocation factors in Table 4.2 are used to calculate product-specific GW values (Fig. 4.5). For electricity, GW ranges from 66-187 $\text{kg CO}_2\text{-eq/FU}_{\text{el}}$. For methanol, GW ranges from 572-693 $\text{kg CO}_2\text{-eq/FU}_{\text{CH}_3\text{OH}}$.

Allocation is theoretically capable of a fair assignment of the benefit to all func-

Table 4.2: Overview of selected allocation scenarios and allocation factors for the CCU system for methanol synthesis in Fig. 4.3a

allocation criterion	flow	flow property (specific)	flow property (total)	allocation factor		
Feedstock CO ₂ as product: allocation of emissions from capture process (co-production) between electricity and feedstock CO ₂						
	a) exergy	electricity	3600 MJ/MWh ^a	4583 MJ	88 %	
	b) economic value 1: CO ₂ for free	electricity	feedstock CO ₂	450 MJ/ton ^b	619 MJ	12 %
	c) economic value 2: positive CO ₂ price	electricity	feedstock CO ₂	50 €/MWh ^c 60 €/ton ^d	63.65 € 82.50 €	100 % 0 %
Feedstock CO ₂ as waste: allocation of emissions from utilization process (recycling process) between methanol and CO ₂ waste treatment						
	d) economic value 2: negative CO ₂ price	methanol	350 €/ton ^e	350.00 €	94 %	
		feedstock CO ₂	-15 €/ton ^f	20.63 €	6 %	

^aElectricity is treated as pure exergy, ^bchemical exergy with atmosphere as reference state, as described in Sankaranarayanan et al. (2010), ^crounded average electricity price according to the European Electricity Index (ELIX) by EEX (2012a), ^dLow end of feedstock CO₂ price range given in Quadrelli et al. (2011), ^erounded average price for methanol according to Methanex (2012), ^fprice for waste treatment of CO₂ was approximated by the price for EU Emission Allowances in 2010, see EEX (2012b).

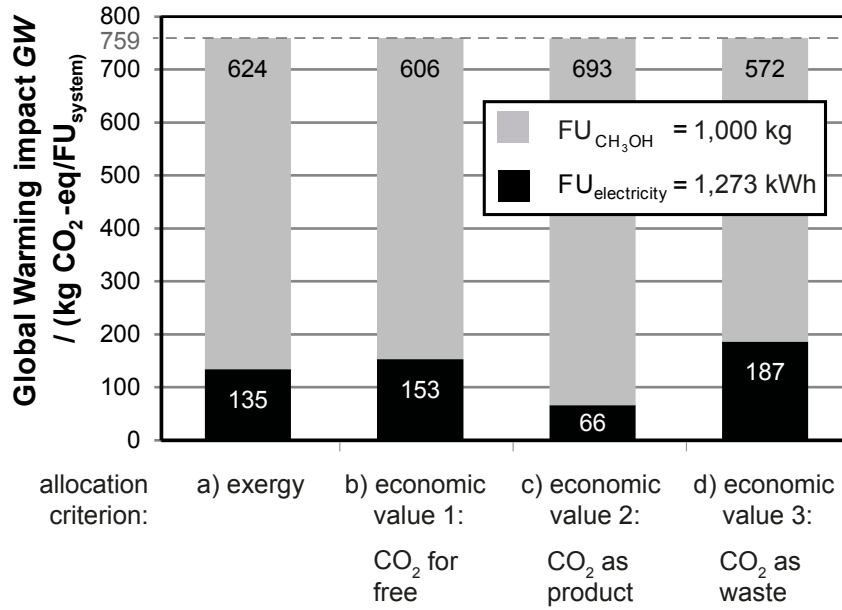


Figure 4.5: Allocated *GW* values for electricity and for methanol as products from the CCU system in Fig. 4.3a.

tions. Choices remain in selecting an allocation criterion. The common criteria mass and energy content do not seem applicable in all cases, e.g., for allocation between electricity (no mass) and feedstock CO₂ (no energy). Exergy and economic value are the only generally applicable criteria for CCU. Exergy, however, always depends on an ambiguous reference state. Therefore, the economic value is recommended as generally applicable allocation criterion for CCU if product-specific LCA results are desired for all products of the CCU system.

4.3 Pitfall 3: global warming impact of CO₂ storage duration

Beyond reducing the total amount of GHG emissions, CCU can mitigate climate change by temporarily storing CO₂ in products. Delayed GHG emissions are beneficial compared to early GHG emissions for two reasons: first, early GHG emissions might cause irreversible impacts if large amounts are released in a short period of time (Schwietzke et al., 2011). Second, early GHG emissions remain longer in the atmosphere within a given time horizon than later ones, thus absorb more radiation and have a higher contribution to global warming (Brandão et al., 2012; Schwietzke et al., 2011). This temporal effect of early GHG emissions has already been recognized for

bio-fuels (Schwietzke et al., 2011; Levasseur et al., 2010). Accordingly, GHG emissions delayed by CCU should also be accounted for in LCA. However, the emissions' point of time and thus the CO₂ storage duration are not reflected in current LCA practice.

Instead, the CO₂ storage duration is frequently used as separate metric alongside the carbon footprint. However, both metrics assess impacts on global warming. The third pitfalls is that often too much emphasis is attributed to the CO₂ storage duration. In the following, a metric for global warming impacts is presented that combines the conventional carbon footprint with the CO₂ storage duration.

4.3.1 A time-corrected global warming metric

The current standard for GHG accounting is the global warming impact GW where different GHGs i are weighted with their characterization factors GWP_i (Eq. (4.1)). The characterization factor GWP_i compares the cumulative absorbed radiation of GHG i to CO₂. The cumulative absorbed radiation of a pulse emission⁷ of a GHG i over a time horizon TH is called absolute global warming potential $AGWP_i$ (Levasseur et al., 2010; Forster et al., 2007):

$$AGWP_i(TH) = \int_{t=0}^{TH} a_i c_i(t) dt, \quad (4.4)$$

and depends on the time horizon TH , for which the absorbed radiation is considered, on the radiative efficiency a_i , i.e., the strength of GHG i to absorb radiation, and on the decay function $c_i(t)$ for the pulse emission of GHG i (for values of a_i and $c_i(t)$ see Forster et al. (2007)). The characterization factor GWP_i is then defined as $AGWP$ ratio of GHG i and CO₂:

$$GWP_i(TH) := \frac{AGWP_i(TH)}{AGWP_{CO_2}(TH)}. \quad (4.5)$$

For CO₂ emissions, GWP_{CO_2} is by definition fixed to 1, independently from the time horizon TH . For other GHGs, $GWP_i(TH)$ depend strongly on the time horizon due to different decay functions $c_i(t)$ for different GHGs (Brandão et al., 2012).

While the time horizon TH is clearly recognized as crucial parameter for GWP_i (Brandão et al., 2012), the emissions' point of time is not reflected in traditional LCA. To account for the emissions' point of time, alternative characterization factors for global warming have recently been developed (Schwietzke et al., 2011; Levasseur et al., 2010; Forster et al., 2007; Peters et al., 2011a; Brandão et al., 2012). Since all metrics build upon radiative forcing and are conceptually very similar, the approach by Levasseur et al. (2010) is briefly described.

⁷A pulse emission is a single, instantaneous emission at time $t = 0$.

The traditional characterization factors GWP_i neglect any absorbed radiation beyond the chosen time horizon. The choice of an adequate time horizon is difficult: A too-short time horizon disregards climate impacts for future generations; a too-long time-horizon ignores the urgency of climate mitigation. The usual time horizon of $TH = 100$ years in current LCA practice is “*a subjective, policy-driven choice*” (Brandão et al., 2012).

To be consistent with the neglect of impacts beyond the time horizon, delayed GHG emissions should only be evaluated within the chosen time horizon. For example, for $TH = 100$ years, a GHG emission released today is considered to absorb radiation for the entire duration of 100 years, whereas a delayed GHG emission released 30 years later should be considered to absorb radiation only for the following 70 years. The global warming impacts should therefore be measured not only in equivalents of CO₂ emissions, but in equivalents of CO₂ emissions *released at time $t = 0$* (CO₂-eq _{$t=0$}) (Levasseur et al., 2010). The corresponding characterization factor for CO₂-eq _{$t=0$} is called time-corrected global warming potential $tcGWP_i$ in this work⁸ and defined as:

$$tcGWP_i(TH, t_s) = \frac{AGWP_i(TH - t_s)}{AGWP_{CO_2}(TH)}, \quad (4.6)$$

where t_s is the time delay of the pulse emission of GHG i . Fig. 4.6 shows $tcGWP_{CO_2}$ for delayed CO₂ emissions with time horizons TH of 50, 100 and 500 years in dependence of the delay t_s . The $tcGWP_{CO_2}$ curve is non-linear due to the non-linear CO₂ decay function (Forster et al., 2007). The $tcGWP_{CO_2}(TH)$ factor for CO₂ depends on the time-horizon, whereas the conventional GWP_{CO_2} is fixed to 1 for all TH . Hence, $tcGWP$ is even more sensitive to the time horizon than GWP .

Application of $tcGWP$ requires a time-resolved emissions profile $m_i(t)$, here assumed as discrete time series $m_{i,\tau}$. Equivalent to Eq. (4.1), a time-corrected global warming impact score $tcGW$ can be obtained by multiplying the amounts $m_{i,\tau}$ of GHG emission i at time τ with the corresponding $tcGWP_i(TH, \tau)$ and finally summing over time and all GHGs i :

$$tcGW = \sum_i \sum_{\tau=0}^{TH} m_{i,\tau} tcGWP_i(TH, \tau). \quad (4.7)$$

⁸To the best of the author’s knowledge, there is no name for time-corrected characterization factors for global warming yet: Brandão et al. (2012) refer to it as “*relative impact of an emission occurring at year t* .” Levasseur et al. (2010) do not explicitly mention this factor, however it is similar to the “*relative global warming impact GWI_{rel}* ” in dynCO₂ by Levasseur et al. (2011). The British Standard PAS2050:2011 contains an approximation for Eq. (4.6) and simply calls the factor “weighting factor FW ” (BSI, 2011).

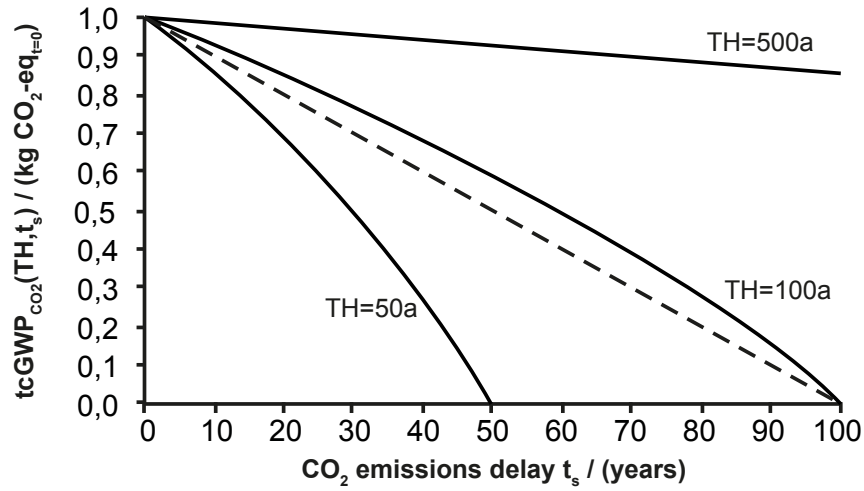


Figure 4.6: Time-corrected characterization factors $tcGWP$ for delayed CO_2 pulse emissions using time horizons TH of 50, 100 and 500 years. The dashed-line represents a linear approximation to $tcGWP(TH = 100a)$.

4.3.2 Application of $tcGW$ to CCU

A time-dependent global warming assessment becomes necessary when comparing systems with qualitatively different emissions time profiles $m_i(t)$. Differences in emissions time profiles are caused by differences in emissions during:

- (i) construction of plants,
- (ii) manufacture of products,
- (iii) product use phase,
- (iv) end-of-life treatment, and by
- (v) different product lifetimes.

In the context of CCU, all these differences can apply:

- (i) CO_2 reduction reactions are often connected to renewable energy systems, which cause emissions mainly during construction.
- (ii) Emissions during production can be reduced if CO_2 substitutes emission-intensive feedstocks such as epoxides (Aresta and Dibenedetto, 2007a) .
- (iii) CO_2 as solvent promises higher process efficiencies and can thus lower the emissions during the use phase.
- (iv) CO_2 -based polyurethanes can have better flame retardation properties than conventional polyurethanes (Quadrelli et al., 2011). Changes in these properties

might affect the end-of-life treatment such as waste incineration.

- (v) CO₂-based products could have different lifetimes compared to a non-CO₂-based product.

The lifetime of the CO₂-based products is equivalent to the CO₂ storage duration. A different CO₂ storage duration changes the emissions time profile by shifting the end-of-life emissions. Thus, applying the *tcGWP* factors to the emissions time profile can incorporate the CO₂ storage duration into the global warming metric.

4.3.3 Illustration of *tcGW* for polymers from CO₂

Because data for real technologies are yet unavailable, purely fictitious CCU and non-CCU systems for producing polymers are created. The results do not allow a technology assessment; instead they should only exemplify the different global warming metrics *GW* and *tcGW*. The CCU technology comprises polymer synthesis from feedstock CO₂ delivered by an air-capture system (mono-functional CCU system). The non-CCU technology uses traditional petrochemical feedstocks to produce polymers with the same function as CO₂-based polymers.

Three CCU scenarios and one non-CCU scenario are considered (Table 4.3). For all CCU scenarios, the GHG emissions for plant construction are higher than for the non-CCU plant due to the additional air-capture unit. Production capacity and the years of production are the same for the CCU and non-CCU plant. GHG emissions for the production of polymers are lower for CCU than for non-CCU due to CO₂ substituting other high-energetic feedstocks. The three CCU scenarios are characterized by:

- (i) equal polymer lifetime (=CO₂ storage duration) and equal end-of-life GHG emissions as in the non-CCU system,
- (ii) longer polymer lifetime (+100%),
- (iii) longer polymer lifetime (+100%), lower production emissions (−1 t CO₂-eq/t polymer) but higher emissions from end-of-life treatment (+1 t CO₂-eq/t polymer).

The parameters in Table 4.3 are chosen in such way that total life-cycle GHG emissions are equal in all scenarios. However, the chosen parameters lead to different shapes of the emission time profiles (Fig. 4.7). The emissions time profile is the time-resolved series of GHG emissions for a single polymer plant including plant construction ($t=0$), polymer production ($1 \leq t \leq 40$), and polymer end-of-life treatment ($31 \leq t \leq 70$ for non-CCU and CCU (i), and $61 \leq t \leq 100$ for CCU (ii) and (iii)).

Table 4.3: Parameters and cradle-to-grave GHG emissions for CCU and non-CCU polymer production. All values are purely fictitious to illustrate the effect of the time-corrected *tcGWP* metric. Changes between scenarios are highlighted in italics.

life-cycle stage	unit	non-CCU	CCU		
			scenario (i)	scenario (ii)	scenario (iii)
<i>plant construction</i>	t CO ₂ -eq/plant	500,000	<i>800,000</i>	<i>800,000</i>	<i>800,000</i>
production capacity	t polymers/(year*plant)	15,000	15,000	15,000	15,000
years of production	year	40	40	40	40
<i>polymer production</i>	t CO ₂ -eq/t polymer	4	<i>3.5</i>	<i>3.5</i>	<i>2.5</i>
use phase	t CO ₂ -eq/t polymer	0	0	0	0
<i>polymer lifetime</i>	year	30	30	<i>60</i>	<i>60</i>
<i>end-of-life treatment</i>	t CO ₂ -eq/t polymer	1.5	1.5	1.5	<i>2.5</i>

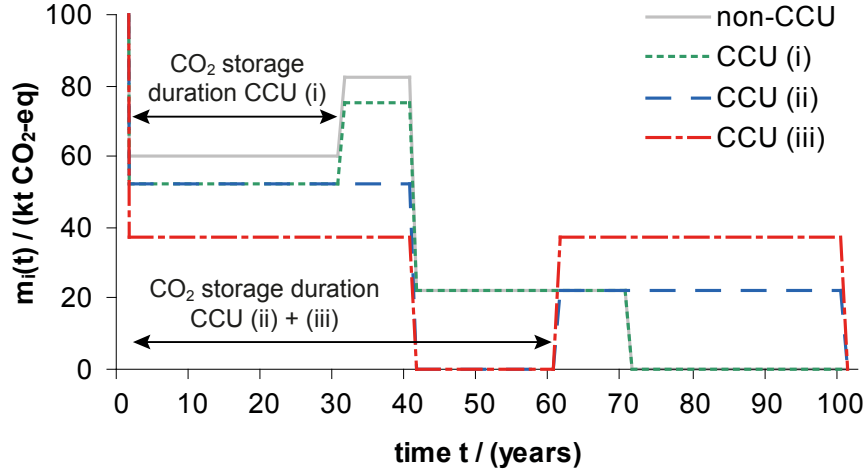


Figure 4.7: Emissions time profiles for CCU and non-CCU scenarios as described in Table 4.3. Emissions from plant-construction (500 and 800 kt CO₂-eq/plant for non-CCU and CCU scenarios, respectively) are capped for better visualization.

The traditional metric GW shows equal total life-cycle GHG emissions for all scenarios (Fig. 4.8). In contrast, the time-corrected global warming impact $tcGW$ varies between scenarios due to different emissions time profiles $m_i(t)$: CCU scenario (i) has slightly higher $tcGW$ than the non-CCU scenario due to early higher plant-construction emissions. An extended polymer lifetime by 30 years in scenario (ii) delays end-of-life emissions and $tcGW$ is lower compared to the non-CCU scenario. In scenario (iii), emissions from polymer production are shifted to the later end-of-life treatment allowing for further reduction in $tcGW$.

Although the CO₂ storage duration in scenario CCU (i) is 30 years, comparison of non-CCU and CCU (i) shows that $tcGW$ is higher for CCU (i) due to higher production emissions. Thus, the CO₂ storage duration alone does not lead to an advantage for the CCU system in terms of global warming impacts. Only extending the lifetime and thus the CO₂ storage duration shifts emissions and leads to a reduced global warming impact: the polymer lifetime in CCU (ii) is extended by 30 years to 60 years and therefore, CCU (ii) exhibits lower $tcGW$ values. As rule of thumb, shifting a CO₂ emission by one year decreases the corresponding global warming impact by 1% for $TH = 100a$ (cf. dashed-line in Fig. 4.6). However, extending the CO₂ storage duration usually shifts only end-of-life emissions. Therefore, even for a quite large extension of the CO₂ storage duration by 30 years in CCU scenario (ii), the overall reduction of global warming impacts is rather small. Since only minor extensions of

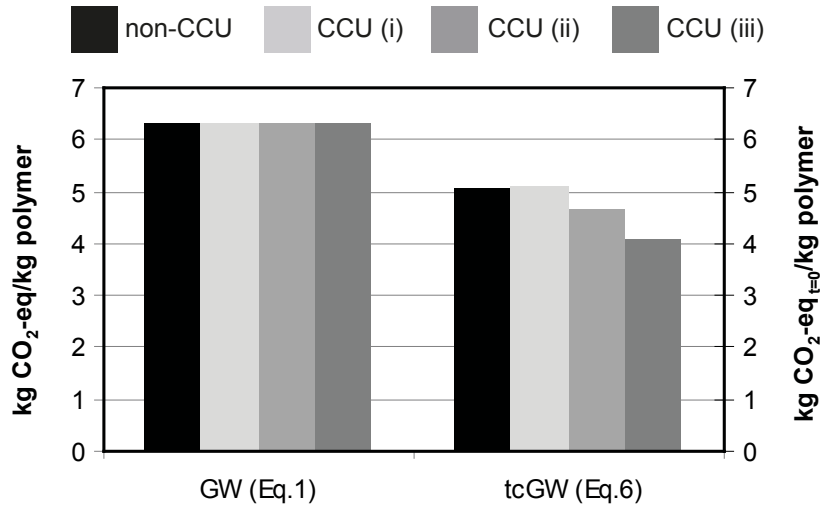


Figure 4.8: Evaluation of global warming impacts of polymer production by non-CCU and CCU technologies with variable polymer lifetimes and end-of-life CO₂ emissions (cf. Table 4.3) using GW (left axis) and $tcGW$ (right axis).

CO₂ storage durations are expected in practice, the climate benefit of CO₂ storage duration is usually small. In the literature, however, the CO₂ storage duration has frequently be proclaimed as crucial factor for climate mitigation by CCU (Mazzotti et al., 2005; Mikkelsen et al., 2010; Peters et al., 2011b; Markewitz et al., 2012). Thus, the third pitfall is that the effect of the CO₂ storage duration for climate mitigation is overrated.

The $tcGW$ metric should not be used to report footprints or as basis for labels since $tcGW$ strongly depend on the CO₂ emissions profiles for which no guidelines exist. Furthermore, $tcGW$ is always smaller than the corresponding GW . Therefore, application of $tcGW$ could be mis-used in communication of carbon footprints to the public. The metric should rather be used to compare alternatives which are known to have similar total GHG emissions but qualitatively very different emission time profiles.

The author of this thesis made the experience at conferences and presentations that some LCA researchers are skeptical towards the $tcGW$ metric. In their opinion, later GHG emissions are cut-off which is irresponsible towards future generations. However, this also holds for the conventional GW metric. This issue is not a matter of $tcGW$ vs. GW but rather the question of a reasonable time-horizon TH . Thus, the discussion of the time horizon should be repeated in the context of $tcGW$. An infinite time horizon, as used for toxicities (Goedkoop et al., 2013; Huijbregts et al., 2001),

is not reasonable for the currently used metrics to obtain CO₂ *equivalents*: according to the decay function of CO₂ (Forster et al., 2007), about 20 % of emitted CO₂ remains permanently in the atmosphere whereas other GHG gases are considered to decay completely at some point in the future. Thus, for $TH = \infty$, one gets $GWP_{CO_2} = tcGWP_{CO_2} = 1$ for CO₂ emissions and $GWP_i = tcGWP_i = 0$ for all other GHGs i . Another possibility would be to express global warming impacts in absolute terms, e.g., as radiative forcing by $AGWP$ in W/m² as in Eq. (4.4) (Peters et al., 2011a). However, the issue with TH also remains with $AGWP$.

4.4 Summary and conclusions

The illustrative examples have clearly shown that CCU does often not act as greenhouse gas sink, not even when renewable energies are employed and the scope excludes the end-of-life emissions (section 4.1.2). The examples have also shown that CCU is not necessarily better than the traditional, non-CCU benchmark. Thus, the environmental benefits of CCU are not guaranteed and require a detailed quantitative environmental assessment by LCA. To assess the environmental benefits for typically multi-functional CCU systems compared to the conventional production, the system expansion approach should be applied since ambiguous choices can be avoided. The illustrative examples have shown that methanol production from CO₂ and H₂ bears potential to reduce global warming impacts compared to the conventional fossil-based production if renewable energies are used for H₂ production. In addition to the conventional carbon footprint, the CO₂ storage duration is often used as second, separate metric for global warming impacts. In section 4.3, the CO₂ storage duration has been integrated into a single, time-corrected global warming metric. The hypothetical example for CO₂-based polymers has shown that only an extension of the CO₂ storage duration leads to a climate mitigation benefit. However, this benefit is small in the example. Thus, if the CO₂ storage duration is still used as separate metric, not too much emphasis should be attributed to its climate mitigation benefit.

4.4.1 A detailed framework for LCA of CCU to avoid pitfalls

The pitfalls in LCA for CCU discussed in sections 4.1-4.3 can lead to wrong decisions whether or which CCU technologies should be employed. To avoid these misleading pitfalls, a detailed framework for LCA of CCU is presented here (Fig. 4.9).

The framework starts with the definition of CCU from section 2.2. In this work, CCU is defined as industrial CO₂ capture and separate functional CO₂ utilization. This definition excludes utilization processes with the only function CO₂ storage (CCS), and it excludes bio-fixation where CO₂ capture and utilization occur simulta-

neously.

LCA flow classification clearly distinguishes elementary flows from economic flows (section 4.1). Feedstock CO₂ is classified as economic flow since it undergoes a previous (capture) and subsequent (utilization) human transformation. As for all economic flows, the upstream process of CO₂ capture must be included in the system boundaries and its emissions must be considered.

The occurrence of multi-functionality depends on whether the capture process delivers co-products (section 4.2). In the case of air-capture, providing feedstock CO₂ is the only function and evaluation for such mono-functional systems is unambiguous. In most other cases, CO₂ is co-produced with other products such as electricity in power plants making the total CCU system inherently multi-functional. If the goal of the study is to determine emission *reductions*, the author recommends to treat the multi-functionality according to the guidelines for comparative LCA by Jung et al. (2013). If the goal of the study is to determine *absolute* emissions, the author recommends the following procedure for multi-functionality treatment: If a system-wide scope is possible, the use of system expansion is recommended to avoid any ambiguous choices in selecting avoided burden processes or allocation criteria. If, however, the scope requires absolute product-specific LCA results for all products of the CCU system, individual functional units have to be defined for the individual products. Since, in this case, the avoided burden approach is conceptually inappropriate due to the implied comparison and offsetting through credits, the author recommends to apply allocation using the economic value as allocation criterion to obtain absolute product-specific LCA results for all products of the CCU system.

The presented time-corrected global warming metric *tcGW* can be used to incorporate the effects of temporary CO₂ storage in materials (section 4.3). To support the practical application of *tcGW*, emissions time profiles and compatible software should be developed. Furthermore, the discussion of the subjective time horizon should be repeated in the context of increased sensitivity of *tcGWP* and *tcGW* toward the time horizon. While the examples have focused on global warming impacts, CCU is also motivated by a reduced use of fossil fuels. Therefore, resource use should be assessed using a suitable metric such as abiotic resource depletion potential (Guinée et al., 2002; Schneider et al., 2011). Further environmental impacts should also be analyzed.

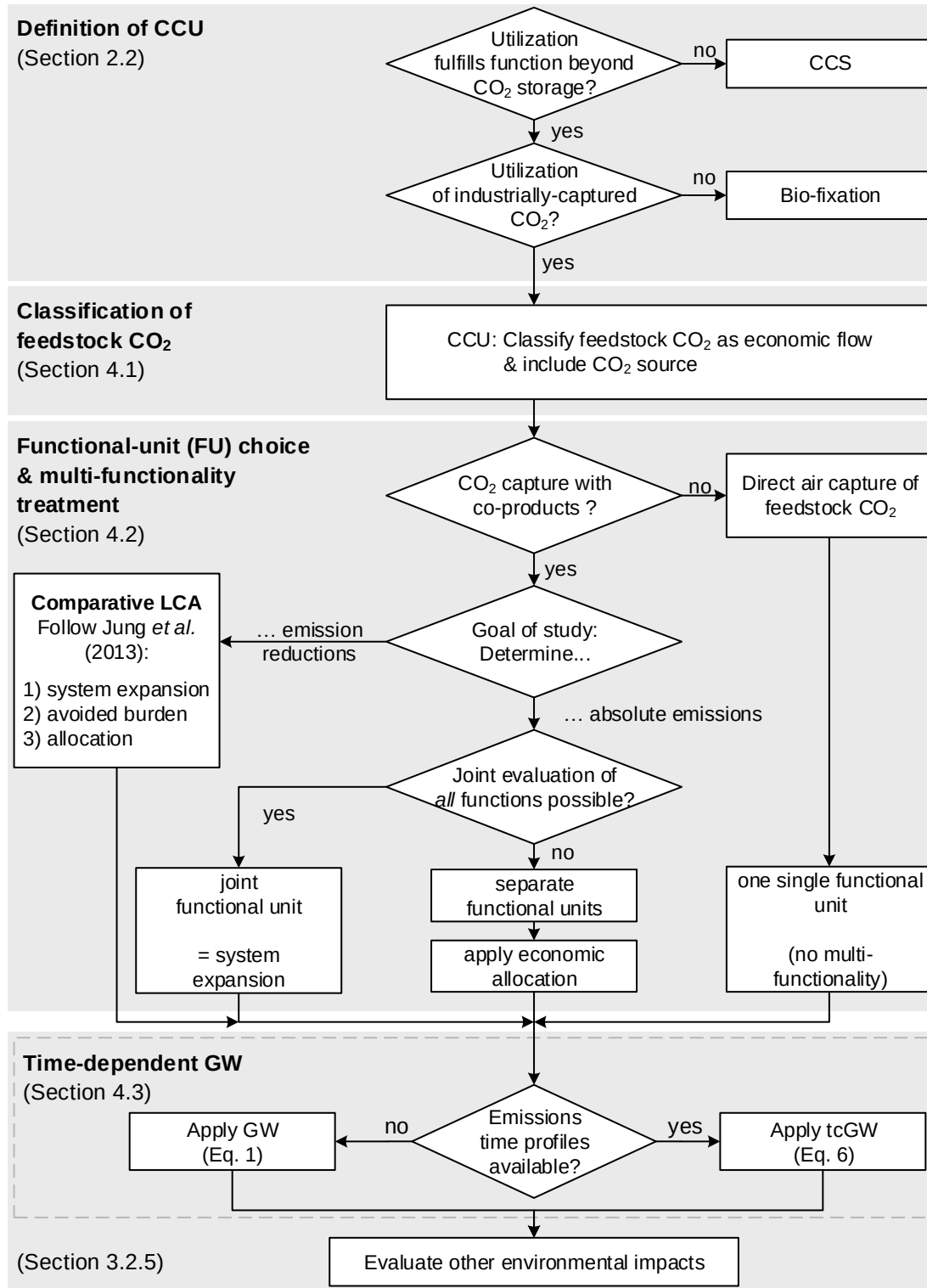


Figure 4.9: Framework for LCA of CCU.

Industrial Case Study: LCA for CO₂-based Polymers

In this chapter, a Life-Cycle Assessment (LCA) case study for the production of polymers from CO₂ is presented. CO₂-based polymer production serves as example for a CO₂ carboxylation reaction (see section 2.3.2.2). In this chapter, the previously presented framework for LCA of CCU (section 4.4.1) is applied for an industrial case study. In section 5.1, the production of CO₂-based polymers and polyols in particular is introduced. Section 5.2 contains a description of the defined scope and the collected process data for the industrial case. The results in section 5.3 show that polyols produced from CO₂ allow for significant savings in all considered environmental impacts. Moreover, the origin of the savings are analyzed. Finally, in section 5.4, the LCA study and results are summarized and conclusions are drawn regarding the overall environmental potential of CO₂-based polyol production.

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von der Assen, N., and Bardow, A. (2014). Life cycle assessment of polyols for polyurethane production using CO₂ as feedstock: insights from an industrial case study. *Green Chemistry*, 16:3272-3280.

5.1 Introduction to CO₂-based polymers

Many CCU technologies are still in early development phases (see section 2.3). An already viable CCU technologically is the utilization of CO₂ for polymers (Lu and Darensbourg, 2012; Langanke et al., 2014a). The synthesis of alternating polypropylene carbonates (PPC) from propylene oxide (PO) and CO₂ has already been commercialized (Darensbourg and Wilson, 2012). However, the glass transition temperature of PPC is about 37 °C which limits its application to specialty polymers (Darensbourg and Wilson, 2012; Langanke et al., 2014b). Recently, the successful synthesis of polyethercarbonate polyols by copolymerization of CO₂ and epoxides has been reported (Fig. 5.1) (Langanke et al., 2014b). Due to a favorable glass transition temperature and low viscosity, the polyethercarbonate polyols can readily be processed to polyurethane (PU) foams (Langanke et al., 2014b). Thus, polyethercarbonate polyols can substitute conventional polyether polyols, of which the global production was 8 Mt a⁻¹ in 2012 (BMS, 2014). Assuming an average CO₂ content of 20 wt%, production of polyethercarbonate polyols could theoretically utilize up to 1.6 Mt a⁻¹ CO₂ as feedstock.

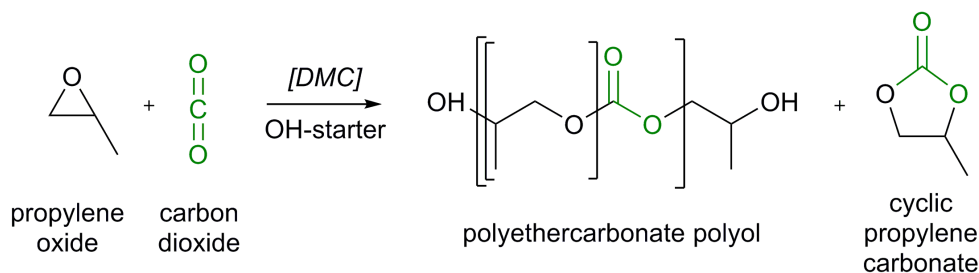


Figure 5.1: Polymerization of propylene oxide (PO) and carbon dioxide (CO₂) to polyethercarbonate polyols using a DMC catalyst and a multifunctional alcohol (e.g., glycerol) as starter. Adapted from Darensbourg and Wilson (2012) and Langanke et al. (2014b).

In section 2.3.2.2, it is discussed that CO₂ is a promising feedstock for some polymers since CO₂ can be inserted as monomeric C1 building block without the energy-intensive cleavage of C=O bonds (Quadrelli et al., 2011). Furthermore, CO₂ partially substitutes energy- and emission-intensive epoxides. However, provision of epoxides required as co-reactants as well as provision of CO₂ itself still require energy and thus cause GHG emissions and other environmental impacts (section 3.2.3). Therefore, the environmental impacts of CO₂-based polyol production should be determined in a detailed environmental assessment using Life-Cycle Assessment (LCA).

The following part of this chapter presents an LCA study for production of polyethercarbonate polyols from PO and CO₂. For this purpose, a cradle-to-gate LCA scope is employed: the analyzed product system comprises production and purification of CO₂-based polyethercarbonate polyols as well as all processes for provision of energy and feedstocks. In particular, provision of the feedstock CO₂ is included: CO₂ is captured from a lignite-fired power plant, compressed and transported to the polyol production plant. The major environmental impacts considered are global warming (CO₂ equivalents) and fossil resource depletion (oil equivalents). Regarding these impacts, the product system for CO₂-based polyethercarbonate polyols is compared to an equivalent product system consisting of conventional polyols production and a lignite-fired power plant without CO₂ capture.

5.2 Description of data and methodology

5.2.1 System boundaries and goal of LCA study

The primary goal of this LCA is to determine whether it is environmentally favorable to utilize CO₂ as feedstock for polyols. For this purpose, the system-wide effects of CO₂ utilization compared to conventional polyol production are considered (Fig. 5.2). The product system for CO₂-based polyethercarbonate polyols is compared to an equivalent product system for conventional polyether polyols. It is sufficient to consider the production of polyols only (cradle to gate) since product properties are similar for CO₂-based and conventional polyols, as well as for the subsequent polyurethanes (Langanke et al., 2014b). The downstream processes of polyurethane foaming, foam use and foam disposal are similar for CO₂-based and conventional polyols and therefore neglected. Potential differences in downstream processes are discussed in Appendix B.1. In addition to the comparative assessment, the goal is to analyze the absolute environmental impacts of the CCU and conventional system, and of the CO₂-based polyols. Sections 5.2.2 and 5.2.3 contain descriptions for the cradle-to-gate product systems for CO₂-based and for conventional polyols.

Since the main environmental motivations for CCU are reducing CO₂ emissions and establishing an alternative carbon source, this study compares the product systems for CO₂-based and conventional polyols with respect to global warming and fossil resource depletion (cf. section 2.1 and 3.2.5). The global warming impacts (GW) are calculated as cumulative GHG emissions in CO₂-equivalents using 100-year global warming potentials (GWP_{100a}). Fossil resource depletion (FD) is calculated as the energy content of used fossil resources in oil-equivalents. Results are computed using GaBi LCA software and ReCiPe 1.08 Midpoint (Hierarchist) impact categories (Goedkoop et al.,

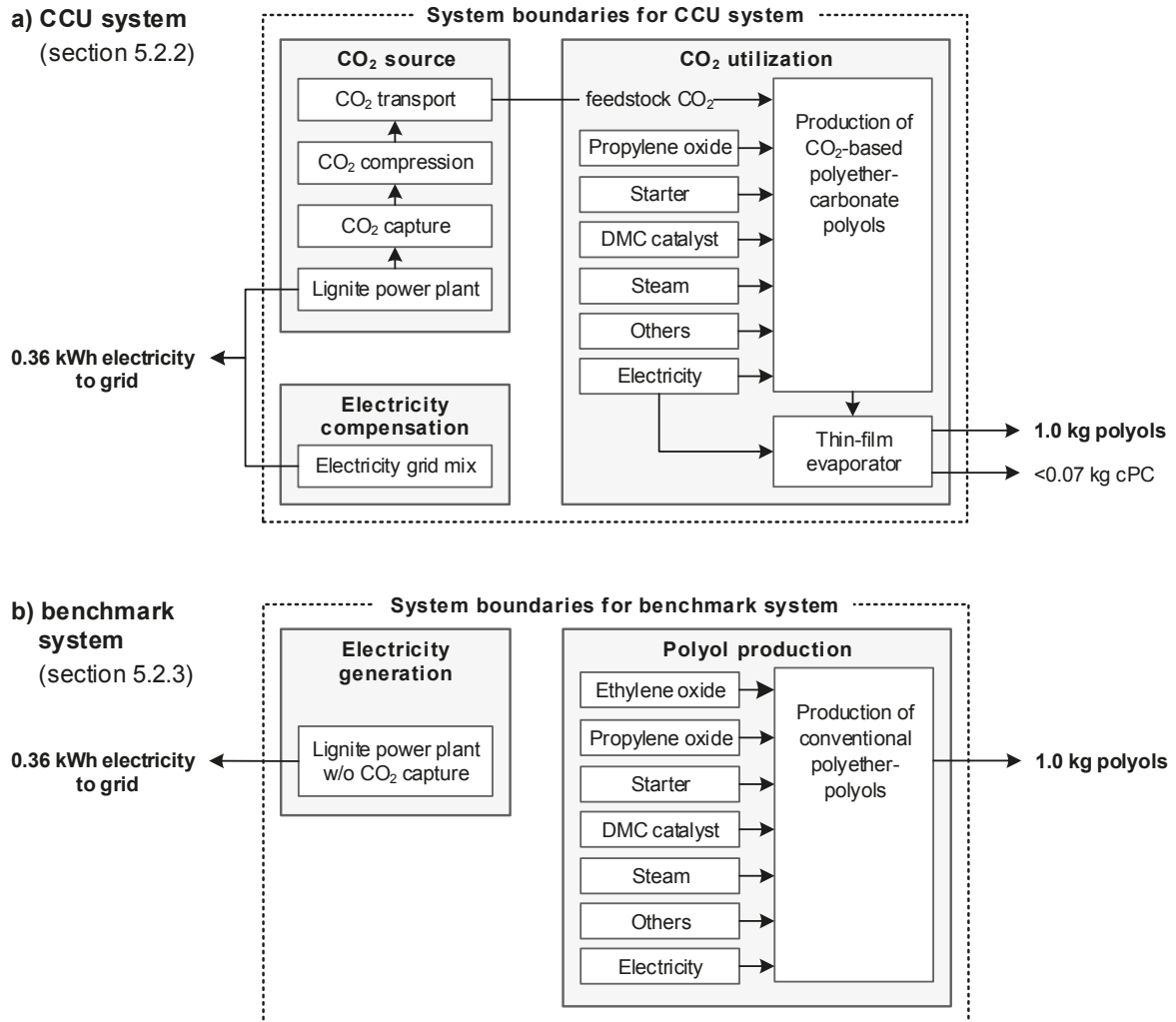


Figure 5.2: a) Product systems for CO₂-based polyethercarbonate polyols. CO₂ utilization (right gray box) comprises production of polyethercarbonate polyols and separation of the by-product cyclic propylene carbonate (cPC) as well as provision of all feedstocks and energy. Feedstock CO₂ is provided by a lignite-fired power plant with CO₂ capture (CO₂ source, top left gray box). Additional electricity from the grid mix compensates for the energy penalty of CO₂ capture (Electricity compensation, bottom left gray box). b) Product system for conventional polyether polyols from fossil-based feedstocks. Polyol production (right gray box) comprises the production process itself as well as provision of all feedstocks and energy. Electricity generation (left gray box) from a lignite-fired power plant without CO₂ capture is added to the product system to enable a sound comparison to the CCU system (a) with identical product outputs (functional unit).

2013; PE International, 2012). Results for the midpoint impact categories eutrophication, ionizing radiation, ozone depletion, particulate matter formation, photochemical oxidant formation, and terrestrial acidification as well as corresponding normalized values have also been analyzed and are given in Appendix B.4.

5.2.2 Product system for CO₂-based polyols

The product system for CO₂-based polyols includes the production of polyethercarbonate polyols as well as provision of required energy and feedstocks. In section 3.2.3, the importance of including all upstream processes for feedstock production in LCA has been highlighted. In particular, the provision of feedstock CO₂ should be included in the product system (section 4.1). The present LCA case study is conducted within the publicly funded research project “Dream Production”. In this project, CO₂ is obtained from a lignite-fired power plant with a pilot plant for CO₂ capture. Due to a significant energy penalty from CO₂ capture, the nominal net electricity output of the lignite-fired power plant is reduced and must be compensated (Sathre et al., 2012). Therefore, the product system for CO₂-based polyols consists of the following three stages: CO₂ source including CO₂ capture, electricity compensation, and CO₂ utilization for polyols production (Fig. 5.2a). The author refers to this entire product system as CCU system. LCA data for the CCU system are taken from GaBi LCA database (PE International, 2012) if not stated otherwise. A complete list of LCA data sources is given in Appendix B.2.

The CO₂ source in the project “Dream Production” is a lignite-fired power plant in Niederaussem, Germany, operated by electricity supplier RWE (RWE, 2014). The plant unit provides a net power of 950 MW with an efficiency of 43 %. The unit is equipped with a pilot plant for post-combustion CO₂ capture, which separates 300 kg h⁻¹ of CO₂ from a flue gas bypass with a capture rate of 90 % (Moser et al., 2009). An amine-based solvent is considered with a regeneration heat demand of 2760 MJ_{th} per ton CO₂ captured which corresponds to an equivalent work loss of 123 kWh_{el} per ton CO₂ captured (Moser et al., 2009; Boot-Handford et al., 2014; Moser et al., 2011). After CO₂ capture, the CO₂ stream is fed into a pilot plant for CO₂ cleaning, compression and filling in cylinders. Cleaning, compression to 17.5 bar and filling requires 142 kWh of electricity per ton CO₂. Cleaned CO₂ achieves EIGA standard (European Industrial Gases Association, complies with food grade quality (EIGA, 2008) and proved suitable for polyols synthesis. CO₂ cylinder rags are transported to the 40 km distant polyol production plant by truck. Construction of the lignite-fired power plant and facilities for CO₂ capture and filling was shown to have a minor contribution to total life cycle impacts (Schreiber et al., 2012) and is therefore

not considered in this LCA.

Due to the electricity demand for CO₂ cleaning, compression and filling, and the work loss from solvent regeneration, the power plant's electricity output to the grid is reduced by 265 kWh per ton CO₂ captured. The power plant is limited by its boiler for steam generation and cannot compensate for the reduced electricity. Consequently, the remaining electricity producers at the grid have to compensate for the reduced electricity with an increased electricity supply. Sathre et al. (2012) recommend accounting for electricity compensation in LCA. Following a simplified approach used by NETL (2010b), the compensated electricity is based on average grid characteristics in Germany in 2010 (0.60 kg CO₂-eq and 0.16 kg oil-eq per kWh).

The main process of the CO₂ utilization stage is the production of polyethercarbonate polyols from PO and CO₂ using a multi-functional alcohol starter and a double metal cyanide (DMC) catalyst (Fig. 5.1). For production of polyethercarbonate polyols within "Dream Production", the chemical manufacturer Bayer set up a kg-scale pilot plant in Leverkusen, Germany. From this pilot plant, primary input data for feedstocks, catalyst and energy demand such as steam or electricity as well as output data for (by-) products were collected. By using a DMC catalyst, the formation of the by-product cyclic propylene carbonate (cPC) can be limited to 0.02-0.07 kg cPC per kg polyol, depending on the CO₂ content in the final polyethercarbonate polyols. Suitable product properties are obtained for CO₂ contents of up to 30 wt% in the polymer chains (Langanke et al., 2014b). In this study, three different CO₂ contents in the polymer chains are evaluated: 10 wt%, 20 wt% and 30 wt%. Absolute mass fractions of CO₂ in the entire polyol are between 10 and 29 wt% due to the weight of the starter. In the following, 'wt% CO₂' always refers to the CO₂ content in the polymer chains. The by-product cPC is separated from the polyols by passing the reactor output through a thin-film evaporator.

A cradle-to-gate LCA considers all upstream processes such as provision of feedstocks, catalyst and energy. The major feedstock PO can be obtained by alternative production technologies. The goal of this LCA is not to assess a particular PO technology for feedstock supply, but rather to assess CO₂-based polyol production in general. Therefore, a PO production mix with the following composition is used in the default scenario (ChemSystems, 2009): 43 % chlorohydrin process (CHPO), 33 % PO/SM process with styrene monomer as co-product, 16 % PO/TBA with t-butyl alcohol as co-product (also called PO/MTBE), 5 % hydrogen peroxide process (HPPO), and 4 % Sumitomo process with cumene hydro peroxide as oxidant. The impact of replacing this mix by the individual PO technologies is assessed in a scenario analysis (section 5.3.2). LCA data for CHPO and PO/TBA are taken from

GaBi LCA database (PE International, 2012). LCA data for PO/SM and HPPO processes were modeled according to material and energy flows from HIS Chemical PEP Yearbook (IHS Chemical, 2010). The Sumitomo process is not considered due to missing LCA data and the other PO processes are rescaled accordingly. Glycerol is used as starter. A detailed sub-LCA for the production of DMC catalyst (Hofmann et al., 2001) was performed using data on material and energy flows provided by Bayer. Construction of the pilot plant or of any other components is not included for two reasons: first, production plants for CO₂-based and conventional polyols are similar and largely cancel each other out in a comparison; second, the share of environmental impacts from plant construction is typically found to be small in the chemical industry (Frischknecht, 2007).

5.2.3 Product system for conventional polyols

The product system for conventional polyols serves as benchmark and is divided into electricity generation and conventional polyol production (Fig. 5.2b). For production of conventional polyether polyols, only fossil-based feedstocks PO and ethylene oxide (EO) are consumed. The same PO, starter, and DMC catalyst as in the CCU system are used in the LCA inventory. Since no by-products are formed, purification of polyols is not required. Conventional polyol production does not utilize CO₂ and is therefore not linked to a CO₂ source. However, electricity generation is added to the product system to account for the electricity generated in the CCU system (Fig. 5.2 and section 5.2.4). Electricity in the benchmark system is generated in an equivalent lignite-fired power plant without CO₂ capture and a net efficiency of 43 % (0.96 kg CO₂-eq and 0.26 kg oil-eq per kWh).

LCA data sources for the benchmark system are identical to the CCU system for all energy sources and feedstocks except EO. EO is mainly produced by direct oxidation of ethylene with oxygen (Rebsdatt and Mayer, 2001). For this process, LCA data are taken from GaBi (appendix B.2).

5.2.4 Functional unit for system-wide assessment

The functional unit in LCA quantifies the functions of the investigated product systems and serves as basis for comparison (section 3.2.2.1). The main functions of the CCU system (Fig. 5.2a) and the benchmark system (Fig. 5.2b) are production of polyols for polyurethane production, *and* supply of electricity to the German electricity grid. Production of cPC is not considered as main function (see below).

To quantify the main functions, 1.0 kg of polyol is chosen as reference for the function ‘polyol production’. The second function ‘electricity supply’ can be quantified

through the amount of CO₂ that is captured to produce 1.0 kg of polyol. However, the CO₂ content and thus the amount of captured CO₂ are varied in this study. Since the amount of CO₂ captured determines the energy need for CO₂ capture, the second function ‘electricity supply’ would be different for each case. To still use one functional unit for all cases studied, the function ‘electricity supply’ is quantified as follows:

The maximum amount of 30 wt% CO₂ is considered for production of polyether-carbonate polyol. For 1.0 kg of polyol with 30 wt% CO₂ content, 0.31 kg CO₂ is captured from the flue gas. The difference of 0.01 kg between captured CO₂ and CO₂ incorporated into in the polyol is due to unused CO₂ deposits in the CO₂ cylinders. While capturing 0.31 kg CO₂, the lignite-fired power plant with CO₂ capture generates net electricity of 0.28 kWh. Using the same lignite input, net electricity of 0.36 kWh would be produced by an equivalent conventional lignite-fired power plant without CO₂ capture since it does suffer from the energy penalty from CO₂ capture. The lower electricity supply of 0.08 kWh of the power plant with CO₂ capture, i.e., the energy demand of CO₂ capture, is assumed to be compensated by the grid mix (bottom left box in Fig. 5.2a). This approach to account for the so-called make-up power is commonly applied for LCA of retrofit CCS systems (Sathre et al., 2012; NETL, 2010b).

Thus, for each 1.0 kg polyols with 30 wt% CO₂, a total generation of 0.36 kWh of electricity (0.28 kWh from the lignite-fired power plant and 0.08 kWh make-up power) is supplied to the grid. For production of 1.0 kg of conventional polyether polyols (0 wt% CO₂), no CO₂ is captured from the flue gas and the conventional lignite-fired power plant directly supplies 0.36 kWh electricity to the grid. For production of 1.0 kg polyols with CO₂ contents between 0 and 30 wt%, the make-up power is between 0 and 0.08 kWh; the electricity by the lignite-fired power plant is between 0.28 and 0.36 kWh, whereby both always total to 0.36 kWh.

Thus, the functional unit is defined as production of 1.0 kg polyols for polyurethane production, and supply of 0.36 kWh electricity to the electricity grid (short: 1.0 kg polyols and 0.36 kWh grid electricity).

The formation of by-product cPC should be considered in LCA since cPC is a valuable chemical. CPC is used as aprotic polar solvent, electrolyte for batteries, cleaning solvent, plasticizer, precursor for linear (poly-) carbonates and additive for cosmetics and adhesives (Lu and Darensbourg, 2012; Shaikh and Sivaram, 1996; Sun et al., 2005). Since only small amounts of less than 7 wt% cPC are formed, environmental impacts from CO₂ utilization processes (Fig. 5.2a) are allocated to polyols and cPC. Feedstocks (PO, CO₂ and glycerin) are allocated according to the feedstock masses incorporated in polyols and cPC, respectively. The catalyst is fully assigned to the

polyols. Other inputs are allocated according to polyol and cPC masses. The minor influence of alternative allocation options for cPC is illustrated in Appendix B.3.

5.2.5 Functional unit for product-specific assessment

A second functional unit is defined as solely 1.0 kg polyols to obtain product-specific LCA results for polyols. However, this approach requires ambiguous choices for allocation of impacts to polyol production and grid electricity supply as discussed in detail in section 4.2. To illustrate the effect of alternative allocation options, two options are considered:

The first allocation option assigns all impacts of the entire CCU system fully to polyols whereas grid electricity is not assigned with any impacts at all. This option represents a *worst-case allocation* scenario for polyols. In the second allocation option, the avoided burden method is used to illustrate the full range of allocation effects. For avoided burden, polyethercarbonate polyols in the CCU system are assigned with a credit for the supply of grid electricity. Grid electricity supplied in the CCU system is assumed to substitute electricity from the conventional power plant without CO₂ capture. This option assigns environmental benefits fully to CO₂-based polyol production and represents a *best-case allocation* scenario for CO₂ supply from lignite-fired power plants.

In addition to these extreme allocation options, an alternative ideal CO₂ source is assessed. The ideal, though hypothetical CO₂ source requires no energy for CO₂ capture and does not cause any indirect GHG emissions. Therefore, the ideal CO₂ source has a global warming impact of $GW(\text{CO}_{2,\text{feed,ideal}}) = -1 \text{ kg CO}_2\text{-eq/kg CO}_2$ and no other environmental impacts (section 6.2.2).

The alternative definitions for the functional unit as well as the investigated scenarios are summarized in Table 5.1.

5.3 LCA results and discussion

5.3.1 System-wide LCA results for polyols and electricity

The cradle-to-gate impacts on global warming and fossil resource depletion are assessed for the functional unit (FU) of 1.0 kg polyols and 0.36 kWh of grid electricity. Fig. 5.3 shows the global warming impacts for the benchmark system with conventional polyether polyols, and for the CCU system with polyethercarbonate polyols containing 20 wt% CO₂. In both systems, the largest contributor to total GHG emis-

Table 5.1: Overview of functional units and scenarios for PO and CO₂ sources.

	Functional unit	PO sources	CO ₂ sources
system-wide assessment	1 kg polyol & 0.36 kWh electricity	i) production mix ii) CHPO iii) PO/SM iv) PO/TBA v) HPPO	power plant
midrule product-specific assessment	1 kg polyol	production mix	i) power plant ii) ideal CO ₂ source

sions is the production of epoxides (80-81 %). By utilizing CO₂ as feedstock for polyols, the system-wide GHG emissions can be reduced by 15 % (−0.54 kg CO₂-eq per FU). About 28 % of the total GHG emission reductions originate from CO₂ capture effects (−0.15 kg CO₂-eq per FU) as result from emission reductions at the CO₂ source and additional emissions for electricity compensation. Major GHG emission reductions of about 72 % originate from CO₂ utilization in the polyol production (−0.39 kg CO₂-eq per FU) which can be explained by substitution of emission-intensive epoxides with CO₂. The contributions in Fig. 5.3 only show in which processes emissions (reductions) occur. These emissions cannot directly be assigned to the processes' functions and products. For example, emissions from electricity compensation (0.04 kg CO₂-eq for the CCU system) cannot be assigned to either 0.36 kWh grid electricity or 1.0 kg polyols. Instead, product-specific impacts require a more detailed allocation approach (section 5.3.3). The global warming impacts for all considered CO₂ contents of 0, 10, 20 and 30 wt% are shown in Fig. 5.4.

Recent CCU literature clearly distinguishes the amount of CO₂ used from the avoided CO₂-eq emissions (Aresta et al., 2014). Fig. 5.5 illustrates the amount of avoided CO₂-eq emissions per amount of CO₂ incorporated into polyethercarbonate polyols for CO₂ contents of 10, 20 and 30 wt%. For all CO₂ contents, the amount of avoided CO₂-eq emissions is greater than the amount of CO₂ incorporated into polyols. The main reason for this effect is the much larger global warming impact of the epoxides PO (1.74 - 4.5 kg CO₂-eq/kg) and EO (1.6 kg CO₂-eq/kg) compared to CO₂ (below 0.2 kg CO₂-eq/kg, see section 5.3.3). For 10 wt% CO₂ content, mainly EO is replaced. For higher CO₂ contents, the additional CO₂ incorporated substitutes PO allowing for larger reductions than EO substitution.

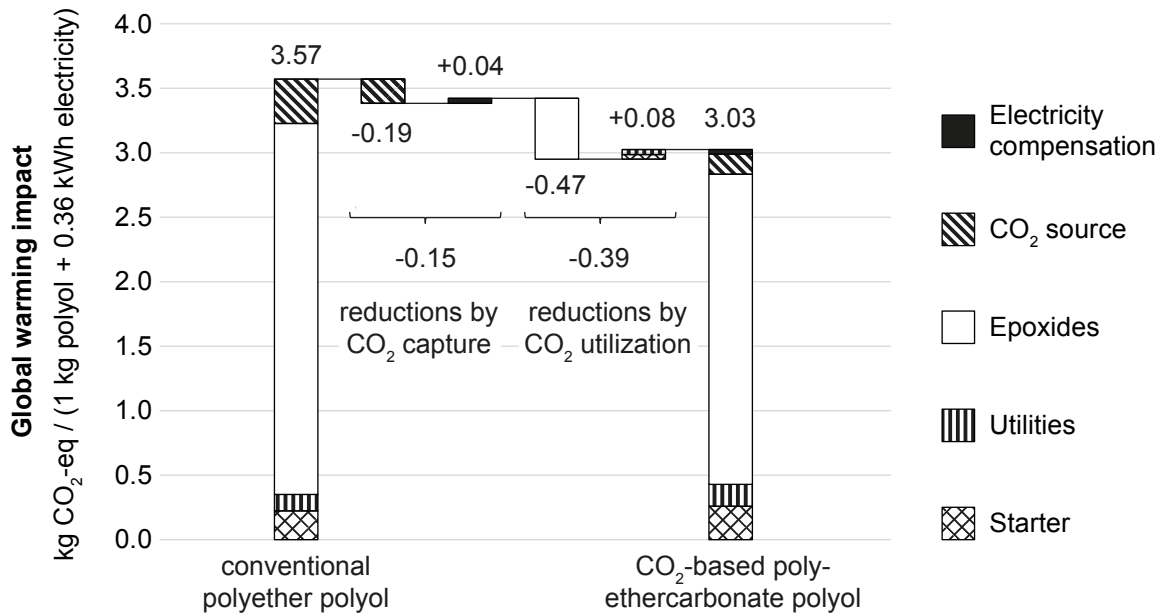


Figure 5.3: Global warming impacts in kg CO₂-equivalents for product system of conventional polyether polyols (left) and CO₂-based polyethercarbonate polyols (right, 20 wt% CO₂ content). The CO₂ source includes the lignite-fired power plant, CO₂ capture, CO₂ compression and CO₂ transport, if applicable. Utilities include DMC catalyst, steam, electricity, thin-film evaporator and others; see Fig. 5.2. Major reductions of GHG emissions originate from CO₂ capture (−0.15 kg CO₂-eq) and substitution of epoxides with CO₂ (−0.47 kg CO₂-eq). Changes in the polyol process do not add significantly to overall GHG emissions (+0.08 kg CO₂-eq).

Fig. 5.6 shows the fossil resource depletion caused by the benchmark system with polyether polyols, and by the CCU system with polyethercarbonate polyols containing 10, 20 and 30 wt% CO₂. For fossil resource depletion, the utilization of CO₂ for polyols shows a similar behavior as for global warming impacts. The main impact source is epoxide production and a substitution of these fossil-based epoxides reduces overall fossil resource depletion. It is well known from LCA for CCS that the fossil resource demand of power plants increases due to the energy required for CO₂ capture (Schreiber et al., 2012). However, the increased fossil resource demand from CO₂ capture is much smaller than the fossil resource reduction due to epoxide substitution. Therefore, the CCU system reduces overall fossil resource depletion by up to 22 % for a 30 wt% CO₂ content compared to the benchmark system.

In addition to impact reductions for global warming and fossil resource depletion,

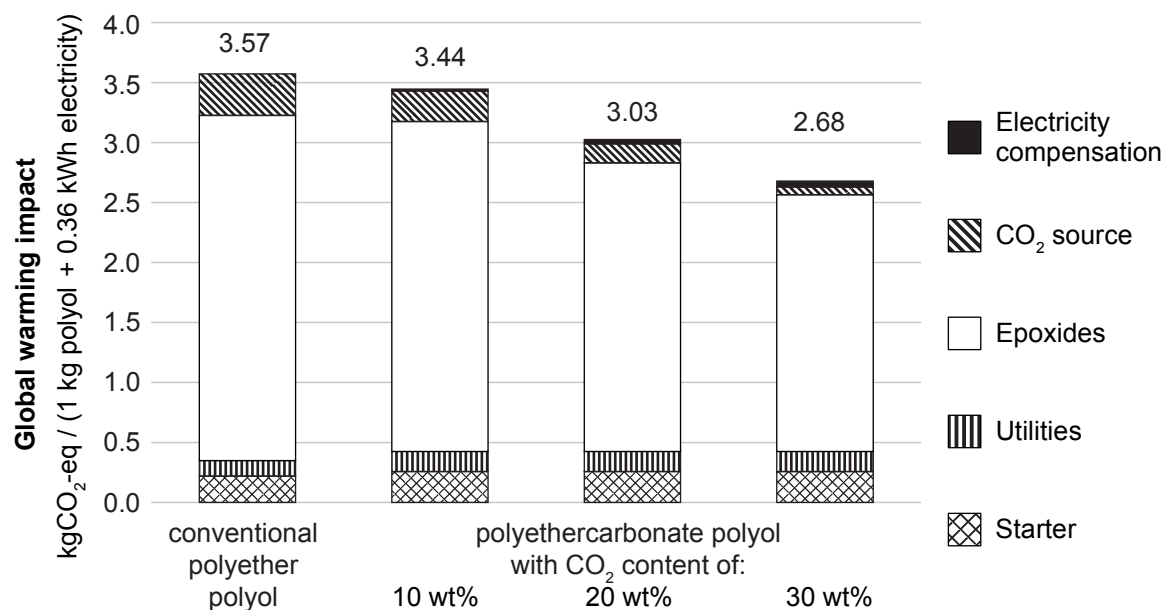


Figure 5.4: Global warming impacts in kg CO₂-equivalents for product system of conventional polyether polyols (left) and CO₂-based polyethercarbonate polyols with 10, 20 and 30 wt% CO₂ content (second left to right).

the CCU system also lowers impacts for eutrophication, ionizing radiation, ozone depletion, particulate matter formation, photochemical oxidant formation, and terrestrial acidification as shown in Appendix B.4. To compare these different impact categories, one approach is so-called normalization. Normalization can be achieved by dividing the environmental impacts (e.g., in kg CO₂-eq, kg oil-eq etc. per functional unit) by average per-capita emissions (e.g., in kg CO₂-eq/(person-eq · year)) to obtain impact results in a common unit ((person-eq · year) per functional unit). Normalized values for all impact categories are shown in Appendix B.4: normalized values for fossil resource depletion are much larger than other environmental impacts indicating the importance of fossil resource depletion for polyol production.

5.3.2 Variation of propylene oxide production technologies

The results for the system-wide LCA illustrated in Fig. 5.3 and Fig. 5.6 show that the main source of impacts on global warming and fossil resource depletion is production of PO. This also holds for other environmental impact categories as shown in Appendix B.3. Thus, alternative production technologies for PO can significantly affect LCA results. Fig. 5.7 therefore shows the global warming impact for the benchmark and the CCU system using alternative PO production technologies. The global

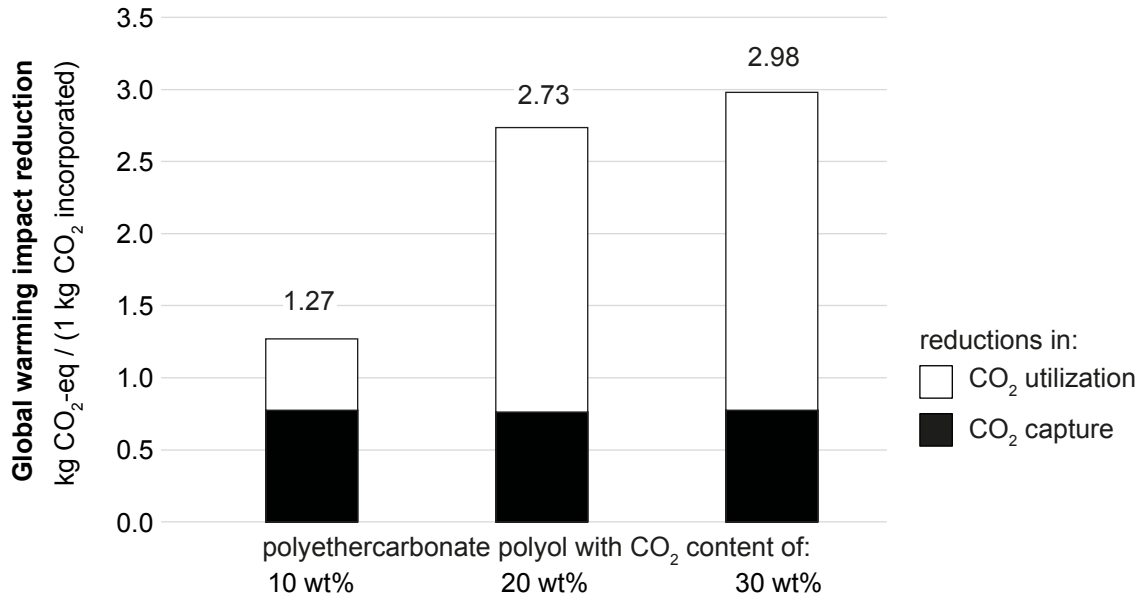


Figure 5.5: Global warming impact reductions in kg CO₂-equivalents per kg feedstock CO₂ incorporated into polyols. Due to substitution of GHG emission intensive epoxides, the amount of avoided GHG emissions is higher than the amount of CO₂ used as feedstock. For 30 wt% CO₂, about three times as many CO₂-eq emissions are avoided as CO₂ is utilized as feedstock.

warming impact varies substantially between PO production technologies, from 2.40 to 4.88 kg CO₂-eq per FU for the benchmark system, and from 1.95 to 4.18 kg CO₂-eq per FU for the CCU system. However, when comparing the CCU system to the benchmark based on the same PO production technology, the CCU system always leads to reduced GHG emissions regardless of the considered PO production technology. These GHG emission reductions vary only between 14 and 19 %.

5.3.3 Product-specific global warming impacts for polyols

Sections 5.3.3 and 5.3.2 show global warming impacts of the entire CCU system including supply of grid electricity. In Fig. 5.8, product-specific global warming impacts are shown for 1.0 kg of polyols. Conventional polyether polyols cause GHG emissions of 3.22 kg CO₂-eq/kg. For polyethercarbonate polyols with 20 wt% CO₂ content, the global warming impact is between 2.65 and 2.86 kg CO₂-eq/kg depending on the allocation approach. Thus, the global warming impact of CO₂-based polyols is between 11 and 18 % lower than for conventional polyols. For an ideal CO₂ source with no energy demand for CO₂ capture (right bar in Fig. 5.8), the maximum global warming impact reduction is 18 % compared to conventional polyols. This implies that switching to

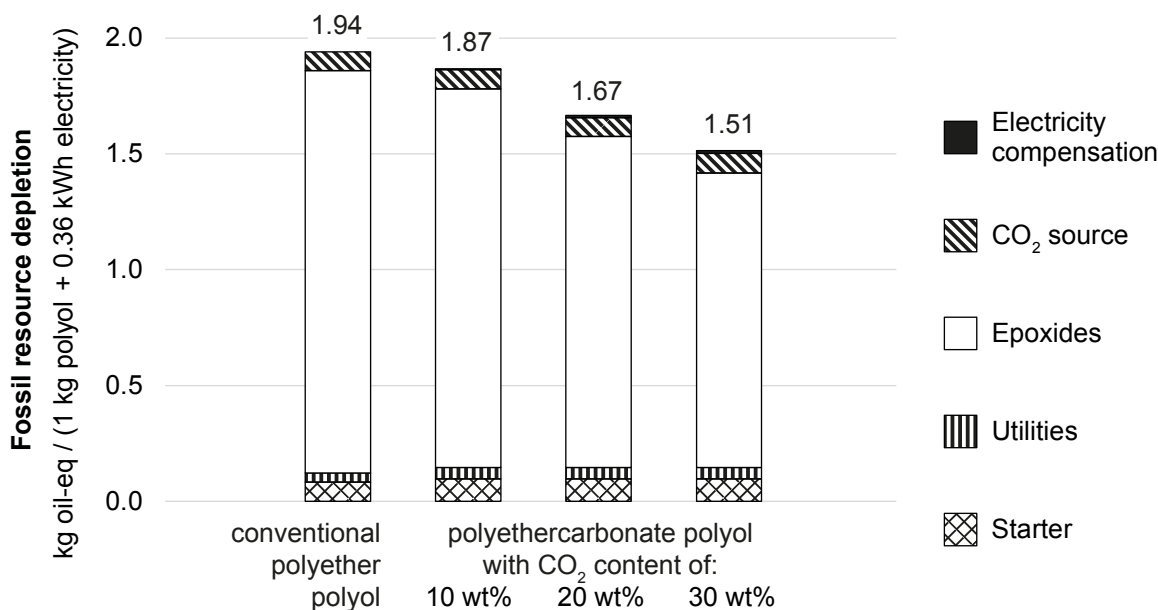


Figure 5.6: Fossil resource depletion in kg oil-equivalents for product system of conventional polyether polyols (left) and CO₂-based polyethercarbonate polyols with 10, 20 and 30 wt% CO₂ content (second left to right). Major reductions of fossil resource depletion originate from substitution of epoxides with CO₂ (−0.10, −0.31, and −0.47 kg oil-eq for 10, 20, and 30 wt% CO₂ content, respectively). Additional impacts from the CO₂ source, electricity compensation, and changes in the polyol process are small (between 0.03 and 0.04 kg oil-eq).

environmentally favorable CO₂ sources does not lead to major additional reductions in the total global warming impact for CO₂-based polyols.

For the different functional units and product systems, the results for the global warming impact and fossil resource depletion are summarized in Table 5.2.

5.4 Summary and Conclusions

LCA results show that the environmental impacts caused by polyol production mainly originate from propylene oxide (PO) production. Therefore, an environmentally favorable PO source should be chosen for PO supply. For further reductions of the environmental impacts of polyols, PO should be substituted by CO₂ as carbon feedstock. The resulting CO₂-based polyols cannot be considered as net GHG sink, i.e.,

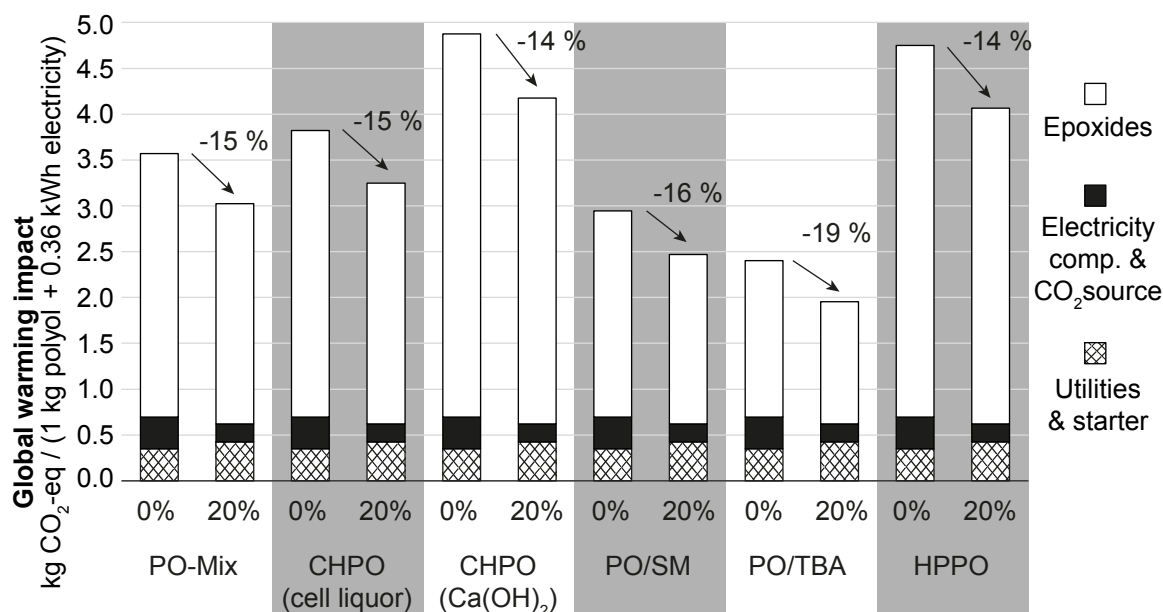


Figure 5.7: Global warming impact considering alternative PO production technologies for product system of conventional polyether polyols (left bar for each PO technology) and CO₂-based polyethercarbonate polyols with 20 wt% CO₂ (right bar for each PO technology). Despite large variations between alternative PO production technologies, the global warming impact reduction for the CCU system varies only between 14 and 19 %.

it is still better for climate protection not to produce polyols in the first place. However, if polyol production is desirable, the utilization of CO₂ allows for significant impact reductions: compared to conventional polyether polyols, polyethercarbonate polyols with 20 wt% CO₂ reduce GHG emissions by 11-19 %, and save fossil resources by 13-16 %. CO₂-based polyols can also lower impacts on eutrophication, ionizing radiation, ozone depletion, particulate matter formation, photochemical oxidant formation, and terrestrial acidification. Overall, CO₂-based polyols are an excellent option for CO₂ utilization: up to three kg CO₂-eq GHG emissions can be reduced per kg CO₂ incorporated. Furthermore, CO₂-based polyols can be readily processed to polyurethanes enabling utilization of large amounts of CO₂ and significant reductions of environmental impacts.

The industrial case study for CO₂-based polyol production allows the following conclusions from a methodological perspective. The overall CCU system is inherently multi-functional due to the generation of electricity as main-product in the power plant as CO₂ source. To avoid ambiguous choices regarding the multi-functionality

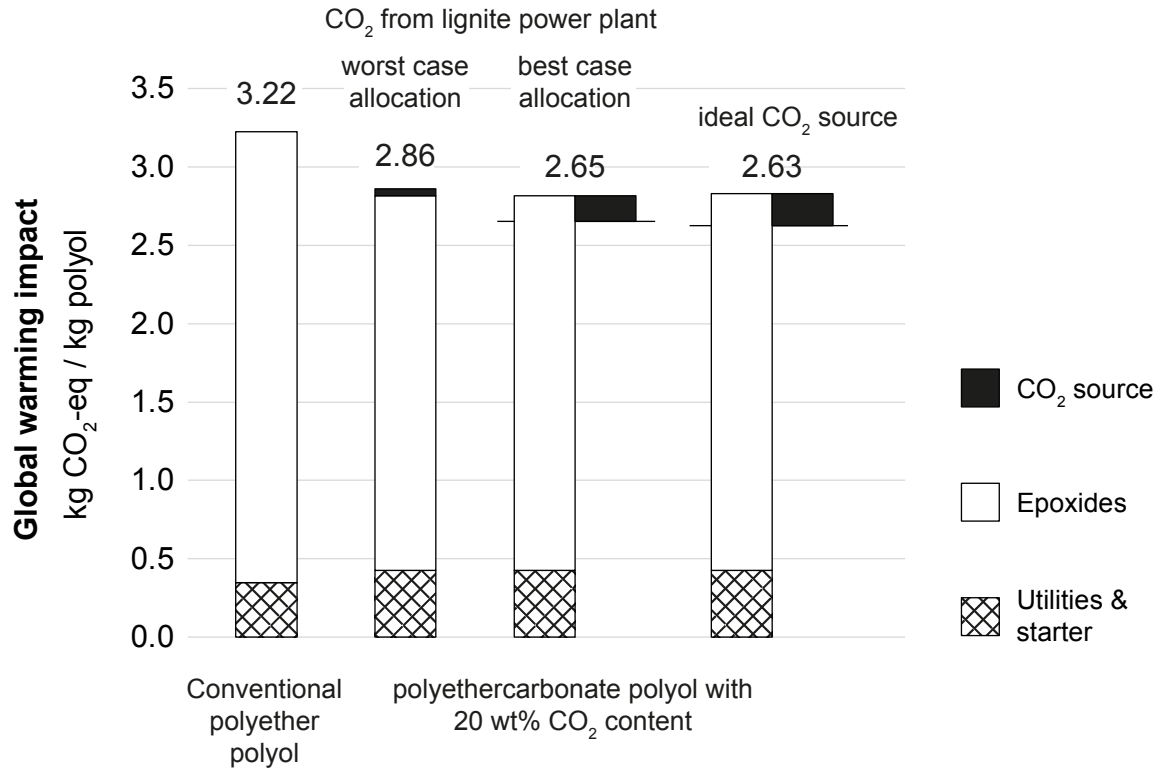


Figure 5.8: Product-specific global warming impacts in kg CO₂-equivalents per kg of polyols. For polyethercarbonate polyols, impacts were obtained by 100 % allocation to polyols (worst case allocation, second from left, $GW(\text{CO}_{2,\text{feed}})=0.2 \text{ kg CO}_2\text{-eq/kg}$) and by crediting an avoided burden for supply of grid electricity in the CCU system (best case allocation, third from left, $GW(\text{CO}_{2,\text{feed}})= -0.8 \text{ kg CO}_2\text{-eq/kg}$). An ideal CO₂ source is added to illustrate the theoretically minimal global warming impact for CO₂ supply ($GW(\text{CO}_{2,\text{feed}})= -1.0 \text{ kg CO}_2\text{-eq/kg}$).

treatment, a system expansion approach has been used successfully to account for the system-wide environmental impacts. Results for the system-wide scope have been proven to be communicable. Nevertheless, a product-specific scope has also been employed to account for the environmental impacts of polyols only. Due to the dominance of PO production on all considered environmental impacts, the effect of alternative allocation approaches for the multi-functional CO₂ source (electricity and product CO₂) is small (less than 8 % for global warming impacts). This also means that the impacts cannot be further reduced significantly by selecting an environmentally favorable CO₂ source. However, the negligible effect of the CO₂ source has only been shown for the particular case of polyol production. In other cases, e.g., if H₂ as co-reactant is pro-

Table 5.2: Summary of LCA results for the product systems of conventional and CO₂-based polyols with respect to impact on global warming (GW; in kg CO₂-equivalents) and fossil resource depletion (FD; in kg oil-equivalents). For the polyols with 20 wt% CO₂, the percentages in italics show the highest and lowest impact reductions for each impact category which are used in the conclusions.

		Conventional polyether polyol	CO ₂ -based polyethercarbonate polyol					
			10 wt% CO ₂	20 wt% CO ₂	30 wt% CO ₂			
Functional unit: 1 kg polyols and 0.36 kWh grid electricity								
GW	PO-Mix	3.57	3.45 (-3 %)	3.03 (-15 %)	2.68 (-25 %)			
GW	Lowest PO ^a	2.40	2.22 (-6 %)	1.95 (-19 %)	1.72 (-27 %)			
GW	Highest PO ^b	4.88	4.76 (-2 %)	4.18 (-14 %)	3.70 (-24 %)			
FD	PO-Mix	1.94	1.87 (-4 %)	1.67 (-14 %)	1.51 (-22 %)			
FD	Lowest PO ^a	1.43	1.35 (-6 %)	1.22 (-15 %)	1.11 (-22 %)			
FD	Highest PO ^c	2.53	2.46 (-2 %)	2.19 (-13 %)	1.98 (-22 %)			
Functional unit: 1 kg polyols								
GW	Lower bound ^d	3.22	3.07 (-5 %)	2.63 (-18 %)	2.26 (-30 %)			
GW	Upper bound ^e	3.22	3.20 (-1 %)	2.86 (-11 %)	2.63 (-18 %)			
FD	Lower bound ^d	1.87	1.78 (-5 %)	1.58 (-16 %)	1.42 (-24 %)			
FD	Upper bound ^e	1.87	1.81 (-1 %)	1.63 (-13 %)	1.50 (-20 %)			

^a Lowest PO for GW and FD is PO/TBA. ^b Highest PO for GW is CHPO (Ca(OH)₂).

^c Highest PO for FD is HPPO. ^d Lower bound obtained with ideal CO₂ source. ^e Upper bound obtained with 100 % allocation to polyols (worst case allocation).

duced with little environmental impacts, the source of feedstock CO₂ can be crucial for the environmental performance of the entire CCU system (Sternberg and Bardow, 2015). Therefore, the following chapter analyzes CO₂ sources for CO₂ utilization from an environmental point of view.

Selecting CO₂ Sources for CO₂ Utilization

In this chapter, an approach for the selection of CO₂ sources is presented. In section 6.1, the approach is motivated by the fact that only a few CO₂ sources are required to satisfy the global near-term CO₂ demand. Therefore, CO₂ sources with lowest environmental impacts should be selected. For this purpose, the environmental-merit-order (EMO) curve is introduced as suitable approach. In section 6.2, the methodology of the EMO curve as well as required data are presented. In section 6.3, environmentally favorable CO₂ sources in Europe are identified using the EMO curve approach. Finally, in section 6.4, the results are summarized and conclusions are drawn regarding the selection of CO₂ sources.

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6.1 Motivation

For supply of CO₂, a large variety of potentially promising CO₂ sources is available (section 2.3.1.1). Since they emit much more CO₂ than the expected demand for CO₂ utilization, the environmentally most favorable CO₂ sources should be selected. The selection of CO₂ sources for CO₂ utilization is a complex task since it depends on a number of important factors (Middleton et al., 2014; Hasan et al., 2014). In this chapter, the focus is on the energy demand for CO₂ capture, on the spatial distribution of CO₂ sources, and on the potential amounts of CO₂ supply. The energy demand for CO₂ capture is the key parameter for associated costs and environmental impacts (Farla et al., 1995; Kuramochi et al., 2012; Zapp et al., 2012). The spatial distribution and supply amounts of CO₂ sources is important to determine transport distances to CO₂ utilization sites (Middleton et al., 2014; Hasan et al., 2014). Transport distances from high-purity CO₂ sources in the United States have recently been illustrated in a so-called map of ‘CO₂ deserts’ (Middleton et al., 2014). However, the ‘CO₂ deserts’ maps consider only transport distances and do not reflect the environmental impacts associated with CO₂ capture, compression and transport. Furthermore, the scope in Middleton et al. (2014) is limited to high-purity CO₂ sources in the US. For Europe, IEA GHG (2005) evaluated a large variety of CO₂ sources with respect to CO₂ capture costs. What is still missing is:

1. an *integrated* assessment of CO₂ capture
2. from *all* proposed types of CO₂ sources
3. in a *European* context
4. with respect to *environmental impacts*.

The goal of this chapter is to identify and rank all proposed CO₂ sources for CO₂ utilization in Europe from a climate-mitigation and fossil-resource-preservation point of view. For this purpose, an environmental-merit-order (EMO) curve is introduced that allows selecting CO₂ sources while minimizing the overall environmental impacts on global warming and fossil resource depletion. A comprehensive literature research has been conducted for energy demands of CO₂ capture from a variety of CO₂ sources. Furthermore, a database has been constructed for potential CO₂ sources from a CO₂ emissions database for individual facilities in Europe (EEA, 2014). An analysis of the spatial distribution of CO₂ sources shows that CO₂ transport distances are generally small. First, EMO curves for Europe are presented where impacts from CO₂ transport are neglected. The EMO curves allow identifying environmentally most favorable CO₂ sources in Europe in dependence of unknown demands for CO₂ utilization. Second, the European-wide perspective is refined: For a 0.1×0.1° latitude-longitude grid

(about 10×10 km), local EMO curves are determined for each grid point considering actual transport distances and country-specific impact factors for energy supply. For variable CO₂ demands, the obtained environmental impacts for CO₂ supply are mapped for each grid point to identify so-called ‘*CO₂ oases*’: favorable locations for CO₂ utilization with lowest environmental impacts of CO₂ supply.

6.2 Description of data and methodology

6.2.1 The environmental-merit-order curve for CO₂ capture

The concept of the *environmental-merit-order (EMO)* is derived from the classical merit order, which is often used in electricity generation: the classical merit-order curve ranks electricity sources according to their marginal production costs in ascending order over their available supply (Pehnt et al., 2008; Sensfuss et al., 2008). Using the electricity sources with lowest marginal production costs minimizes overall production costs for electricity supply (Pehnt et al., 2008). In close analogy to the merit-order curve for electricity generation, an EMO curve ranks CO₂ sources according to their marginal *environmental impacts* due to CO₂ capture in ascending order over the available CO₂ supply. Consequently, selecting sources for CO₂ capture according to the EMO curve minimizes the overall environmental impact.

The CO₂ demand for CO₂ utilization is difficult to predict. Existing estimates for the CO₂ utilization potential of 300 Mt a⁻¹ in 2016 (Aresta et al., 2013) and 1.5-2.0 Gt a⁻¹ in the long-term (DECHEMA, 2009; Centi and Perathoner, 2011) can at best serve as upper bound potentials for the actual CO₂ demand. Since the EMO curves are a function of the CO₂ supply, they represent a convenient approach for unknown amounts of CO₂ supply and thus CO₂ demand.

The main motivation for CO₂ capture and utilization (CCU) is reducing greenhouse gas (GHG) emissions and substituting fossil resources with CO₂ (section 2.1). Thus, impacts on global warming and fossil resource depletion are considered. Certainly, other environmental impacts are also very important in the context of CCU and should be assessed. However, detailed emission data are usually not available and many potential environmental effects of CO₂ capture are not yet fully understood such as the degradation of unintentional amine solvent losses (Mac Dowell et al., 2010; Nielsen et al., 2012).

The considered environmental impacts are determined using comparative Life-Cycle Assessment (LCA) (Jung et al., 2013). Comparative environmental impacts are obtained by comparing the cradle-to-gate impacts of the CO₂ source with retro-fitted

CO₂ capture to the status quo of the CO₂ source without CO₂ capture. In order to emphasize that typical consequential LCA elements such as market effects (Earles and Halog, 2011) are not considered, this approach is called comparative LCA instead of consequential LCA in this work. According to the framework for LCA of CCU in section 4.4.1, product-specific LCA results for captured CO₂ are obtained by applying the avoided burden approach.

For CO₂ point sources, the status quo is the CO₂ source without CO₂ capture, i.e., the CO₂ emissions from the point source are completely emitted to the atmosphere (Fig. 6.1a). For CO₂ capture from the atmosphere, the status quo is no capture at all and thus the comparative environmental impacts are the impacts of the direct-air-capture (DAC) system (Fig. 6.1b).

The cradle-to-gate system boundaries comprise the CO₂ source, the retro-fitted capture process including CO₂ compression and corresponding energy supply, and CO₂ transport. The subsequent CO₂ utilization option is not included since the goal of this study is to compare alternative CO₂ sources for a given CO₂ utilization option. To separate CO₂ from the flue gas ($m_{\text{CO}_2, \text{fluegas}}$) or atmospheric air ($m_{\text{CO}_2, \text{air}}$), the CO₂ capture process requires different forms of energy: electricity (W_{el}) is needed for fans, pumps, compressors etc. For sorption-based CO₂ capture, desorption requires heat (Q_{th}), which is typically supplied by steam. For post-combustion capture in power plants, the steam required for solvent regeneration is then no longer available for power generation in the turbines. Power plants with retro-fitted CO₂ capture are typically limited by the boiler. Thus, it is not possible to produce additional steam for solvent regeneration and consequently, the electricity output of the power plant is reduced. For post-combustion capture at power plants, the steam demand for CO₂ capture can therefore be expressed as electricity loss (Boot-Handford et al., 2014). The method in this chapter follows a common approach for system-wide LCA for CO₂ capture from power plants where the electricity loss is interpreted as electricity demand (section 5.2.2). For other CO₂ sources with heat demand, it is assumed that heat is provided by steam generated through combustion of natural gas. For cement plants (Rodríguez et al., 2008, 2012) and DAC (Keith et al., 2006; Baciocchi et al., 2006), heating is provided directly through oxy-fuel combustion Q_{fuel} where CO₂ emissions from fuel combustion ($m_{\text{CO}_2, \text{fuel}}$) are also captured.

Compression of CO₂ is typically required for the subsequent transport from point sources to CO₂ utilization sites. Most data for CO₂ capture are obtained from CCS studies, which consider pipeline transport and include compression of CO₂ to at least 10 MPa. Thus, the compression of CO₂ to 10 MPa is included in the system boundaries to be able to compare across alternative CO₂ sources.

1 tonne of product CO₂ changes CO₂ emissions and fossil resource depletion.

The following subsections describe how to obtain marginal environmental impacts for global warming and fossil resource depletion, the available CO₂ supply and present the required data.

6.2.2 Marginal environmental impacts of CO₂ capture

CO₂ point sources produce a main product such as electricity and provide CO₂ as co-product. As shown in Fig. 6.1a, the marginal CO₂ emissions (in t CO₂-eq (t CO_{2,product})⁻¹) are obtained by comparing CO₂ emissions of the point source retro-fitted with CO₂ capture to the status quo (no CO₂ capture), divided by the amount of product CO₂. For both cases (CO₂ capture and status quo), it is assumed that the same amount of main-product ($m_{\text{main-product}}$) is produced, e.g., electricity in power plants or ammonia in ammonia plants (section 4.1.1). For post-combustion capture at power plants, the electricity output is actually reduced. However, a constant electricity output is assumed and the electricity loss is modeled as electricity demand. This allows to evaluate all CO₂ point sources with a common approach. The marginal CO₂ emissions ($m_{\text{CO}_2\text{-eq,marginal}}$) are determined by:

$$m_{\text{CO}_2\text{-eq,marginal}} = (m_{\text{CO}_2,\text{el}} + m_{\text{CO}_2,\text{th}} + m_{\text{CO}_2,\text{fuel-supply}} + m_{\text{CO}_2,\text{offgas}} + m_{\text{CO}_2,\text{transport}} - m_{\text{CO}_2,\text{fluegas}}) / m_{\text{CO}_2,\text{product}} , \quad (6.1)$$

where $m_{\text{CO}_2,i}$ are the CO₂ flows i as illustrated in Fig. 6.1. Eq. (6.1) can be re-written as (see appendix C.1):

$$m_{\text{CO}_2\text{-eq,marginal}} = -1 + W_{\text{el}} GW_{\text{el}} + Q_{\text{th}} GW_{\text{th}} + Q_{\text{fuel}} GW_{\text{fuel}} + GW_{\text{transport}} , \quad (6.2)$$

where W_{el} , Q_{th} , and Q_{fuel} are the energy demands of electricity, heat and fuel per tonne of product CO₂, respectively; GW_{el} , GW_{th} , and GW_{fuel} are the GHG emission factors for generation of electricity and heat, and for supply and combustion of fuels, respectively; and $GW_{\text{transport}}$ are the GHG emissions for CO₂ transport per tonne of product CO₂.

The ‘minus one’ in Eq. (6.2) comes from the comparison with the status quo (no CO₂ capture) and corresponds to a credit for the ‘CO₂ otherwise emitted’. The following, positive terms in Eq. (6.2) correspond to indirect CO₂ emissions: CO₂ emissions for electricity, heat supply and transport are directly added. CO₂ emissions from construction of the capture equipment or working materials such as solvents are not considered in this work but would have to be added in Eq. (6.2) as well. Indirect CO₂ emissions from heat supplied by fuel combustion include both the CO₂ emissions from

supply of the fuel and from fuel combustion. Interestingly, the marginal CO₂ emissions do not change whether or not capturing CO₂ emissions from fuel combustion: If these CO₂ emissions are captured, they reduce the share of flue gas CO₂ in the product CO₂. Thus, less flue-gas CO₂ is captured per product CO₂. For example, in some proposed air-capture systems only 50-70 % of the total captured CO₂ origins from the atmosphere and the remaining 30-50 % from combustion of natural gas (Mazzotti et al., 2013; Zeman, 2007). For DAC, the marginal CO₂ emissions are the impacts of the DAC system: balancing the CO₂ input from ambient air and the direct and indirect CO₂ emissions from the capture process also yields Eq. (6.2) (see appendix C.2). DAC units are assumed to be located next to the CO₂ utilization plants making CO₂ transport dispensable, i.e., $GW_{\text{transport}} = 0$ for DAC.

Eq. (6.2) allows to identify the pitfalls described in chapter 4: Only if no energy is required and no indirect emissions occur, capturing 1 kg of product CO₂ avoids CO₂ emissions of 1 kg at the CO₂ source (cf. pitfall 1 in section 4.1). Using the marginal CO₂ emissions from Eq. (6.2) as product-specific carbon footprint for CO₂ implies the avoided burden approach for multi-functionality treatment (cf. pitfall 2 in section 4.2). Thus, the marginal CO₂ emissions from Eq. (6.2) should be used with caution when calculating product-specific carbon footprints of the final CO₂-based products. However, for comparing alternative CO₂ sources, it is reasonable to use the marginal CO₂ emissions in Eq. (6.2) which quantify the system-wide global warming impact due to CO₂ capture.

The marginal fossil resource depletion can be calculated in the same way as the marginal CO₂ emissions, where again no impacts from transport are considered for air-capture:

$$m_{\text{resources,marginal}} = W_{\text{el}} FD_{\text{el}} + Q_{\text{th}} FD_{\text{th}} + Q_{\text{fuel}} FD_{\text{fuel}} (+FD_{\text{transport}}) , \quad (6.3)$$

For fossil depletion, there is no credit; instead an increased fossil demand is expected due to CO₂ capture. In the following sections, the collected data are presented for energy demands (W_{el} , $Q_{\text{th/fuel}}$) and environmental impact factors (GW_j , FD_j).

6.2.3 Energy demand for CO₂ capture

Equations (6.2) and (6.3) require various energy demands for CO₂ capture. A comprehensive literature research for current energy demands for CO₂ capture from alternative CO₂ sources has been performed. In this work, the type of energy demands is divided into electricity, heat, natural gas and coal. The CO₂ sources considered in this work include the atmosphere, NGCC, IGCC and coal power plants, refineries

Table 6.1: Current energy demands for CO₂ capture from alternative CO₂ (point) sources in Europe including CO₂ compression to at least 10 MPa (up to 15 MPa). A table with resolved values for the energy demands from the individual literature references is provided in Appendix C.5.

Type of CO ₂ source	CO ₂ concentration	Current energy demand / (GJ (t CO _{2,product}) ⁻¹)			
		Electricity	Heat	Natural gas	Coal
Air	400 ppm	1.29		4.19	
NGCC power plant	3-4 %	1.60			
Refineries and steam cracker	3-13 %	0.91	3.16		
Coal power plant	12-15 %	1.22			
Integrated pulp and paper mills	7-20%	0.04		1.57	
Market pulp mills	7-20 %	1.03			
Iron and steel plants	17-35 %	0.87	0.95		
Cement plants	14-33 %	0.09			3.35
IGCC power plant	≈100 %	0.40	0.01		
Ammonia plants	100 %	0.40	0.01		
Ethylene oxide plants	100 %	0.40	0.01		
Gas processing	100 %	0.40	0.01		
Hydrogen reforming	100 %	0.35			

and steam crackers, (pulp and) paper mills, production of iron and steel, cement, ammonia, ethylene oxide, natural gas and hydrogen.

Table 6.1 lists the average current energy demand for CO₂ capture for each CO₂ source. A detailed table with resolved values for the energy demands from the individual literature references is provided in Appendix C.5. For details of the considered CO₂ sources and CO₂ capture technologies, the reader is referred to section 2.3.1 and to several comprehensive descriptions in the literature (Peters et al., 2011b; Farla et al., 1995; Hunt et al., 2010; Kuramochi et al., 2012; Mac Dowell et al., 2010; Boot-Handford et al., 2014).

6.2.4 Environmental impacts of energy supply

The marginal environmental impacts of CO₂ capture ($m_{\text{CO}_2\text{-eq,marginal}}$, $m_{\text{resources,marginal}}$) should ideally be determined using *marginal* environmental impact factors for energy supply (GW_j , FD_j). For supply of heat and fuels, marginal environmental impact factors are assumed to correspond well to the *average* environmental impact factors. Marginal environmental impact factors for electricity supply, however, are difficult to obtain since a detailed energy systems analysis would be required including a model for the electricity market (Pehnt et al., 2008; Lund et al., 2010). Such detailed assessment of the electricity supply is beyond the scope of this study. Therefore, average impacts factors are also used for the electricity grid mix. Two scenarios are considered: First, EU-average impact factors are used assuming a common European electricity grid (values given in the SI). Second, country-specific impact factors are used. Comparing the two scenarios also allows to analyze the sensitivity of the environmental impacts towards the electricity impact factor. For both scenarios, environmental impact factors are obtained from the GaBi LCA database (PE International, 2012).

6.2.5 CO₂ emissions data

A database for potential CO₂ sources has been constructed from the E-PRTR v5.1 database for CO₂ emissions of individual facilities in Europe (EEA, 2014). The emissions database contains facilities emitting >0.1 Mt a⁻¹ CO₂. In total, 1,149 facilities could have been classified into the types of CO₂ sources shown in Table 6.1. Fig. 6.2 shows the resulting CO₂ emissions by type of CO₂ source. The obtained database for potential CO₂ sources is in good agreement with a CO₂ emissions database from IEA GHG (2005).

6.2.6 Environmental impacts of CO₂ transport

For CO₂ point sources, the environmental impact of CO₂ transport depends on the transport distance and the mode of transport. Suggested modes of CO₂ transport are pipeline, ship or truck (Doctor et al., 2005). CO₂ transport by truck causes GHG emissions of 0.05-0.10 kg CO₂-eq/tkm, by ship 0.01-0.10 kg CO₂-eq/tkm, and by pipeline 0.01-0.02 kg CO₂-eq/tkm (Boot-Handford et al., 2014; Doctor et al., 2005; PE International, 2012).

Determining CO₂ transport distances requires the locations of the CO₂ sources and of the CO₂ utilization plants. The locations of the CO₂ sources are known from the constructed database of potential CO₂ sources. However, locations of future CO₂ utilization sites are typically unknown. Therefore, the maximum distances have been calculated for transport from the known CO₂ sources to each location in

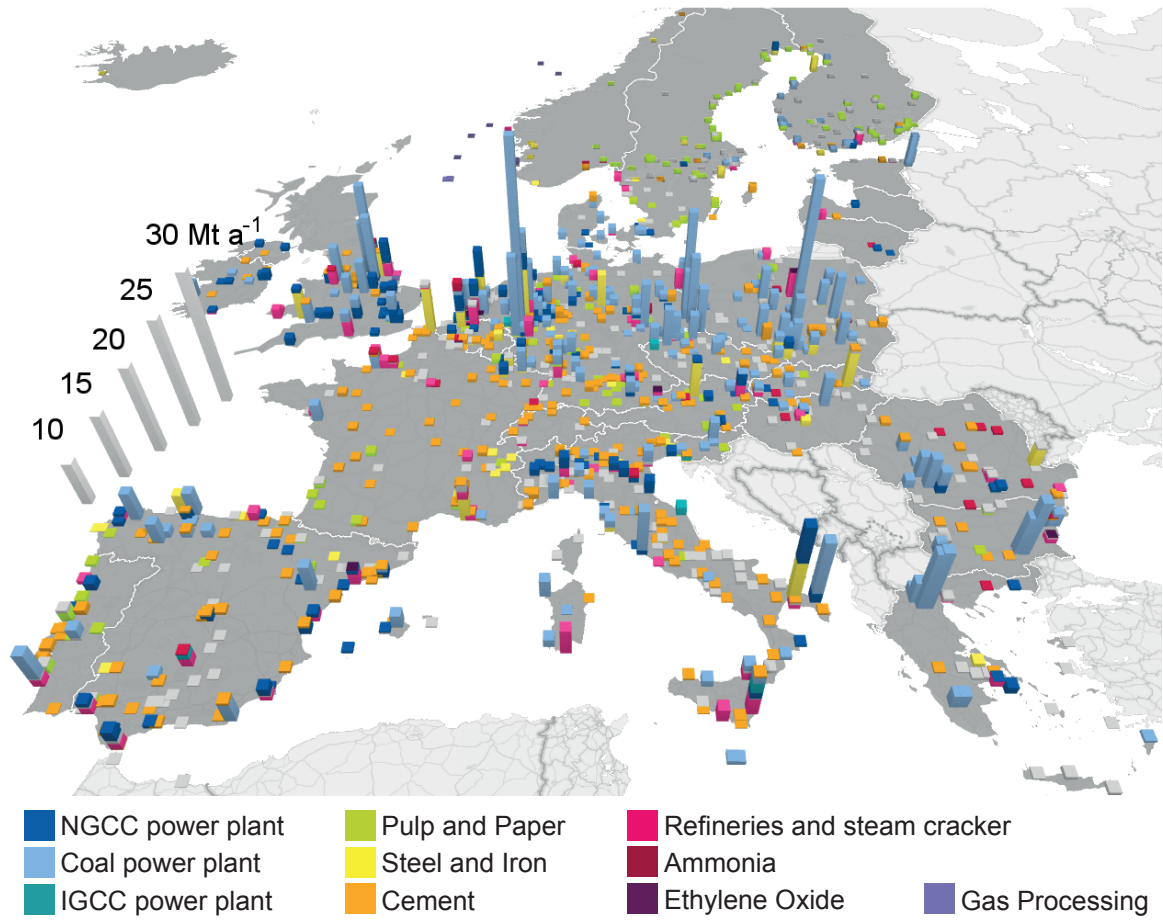


Figure 6.2: Distribution of CO₂ point sources ($>0.1 \text{ Mt a}^{-1}$) in Europe in 2011. The CO₂ emissions map has been created using the PowerMap Preview Plugin for Microsoft Excel 2013 (Microsoft, 2014).

Europe as potential CO₂ utilization site. For this purpose, the recently presented approach of ‘CO₂ desert’ maps by Middleton et al. (2014) has been employed (see Appendix C.6). For individual locations demanding CO₂ of up to 5 Mt a^{-1} , the transport distances for the central part of Europe are mostly below 200 km (see Fig. C.1 in Appendix C.6). The associated CO₂ emissions from transport are thus below $0.02 \text{ t CO}_2\text{-eq (t CO}_{2,\text{product}})^{-1}$. Therefore, in a first European-wide analysis, impacts from transport are neglected in the comparison of CO₂ sources. A second regionally-refined assessment then takes into account actual transport distances.

6.2.7 Identification of CO₂ oases

Since future locations for CO₂ utilization are unknown, it is desirable to know which CO₂ utilization locations would be environmentally favorable. The ‘CO₂ deserts’ approach can identify locations with nearby CO₂ sources. Thereby, transport distances and associated impacts are minimized. However, relevant impacts from CO₂ capture from alternative CO₂ sources are not considered. In fact, it might be environmentally favorable to obtain CO₂ from farther but ‘cleaner’ CO₂ sources. Therefore, an approach is presented to identify environmentally favorable locations for CO₂ utilization with minimal environmental impacts of CO₂ supply, so-called *CO₂ oases*.

The procedure for CO₂ oases is similar to the CO₂ deserts. Instead of selecting the closest CO₂ sources, CO₂ sources are selected according to a local EMO curve. Precisely, the following steps are performed for each point within a 0.1×0.1° latitude-longitude grid (about 10×10 km) in Europe: Actual distances are computed from the considered grid point to all CO₂ sources. For all CO₂ sources, the transport-associated environmental impacts are computed and added to the environmental impacts of CO₂ capture and compression. Together with the potential amounts of CO₂ supply, a local EMO curve is obtained. The CO₂ sources are selected according to the local EMO curves until a pre-defined CO₂ demand is fulfilled. For the selected CO₂ sources, the average environmental impact for the considered grid point is calculated and is illustrated in the CO₂ oases map.

6.2.8 Available CO₂ supply

The EMO curve ranks CO₂ sources according to their environmental impacts over the available CO₂ supply. The available supply $m_{\text{CO}_2, \text{supply}}$ of each CO₂ point source is estimated from its total annual CO₂ emissions $m_{\text{CO}_2, \text{emissions}}$, from additional CO₂ emissions from fuel combustion for CO₂ capture ($m_{\text{CO}_2, \text{supply}} \cdot Q_{\text{fuel}} \cdot e_{\text{CO}_2, \text{fuel}}$), and the capture ratio CR :

$$m_{\text{CO}_2, \text{supply}} = CR \frac{m_{\text{CO}_2, \text{emissions}}}{1 - CR \cdot Q_{\text{fuel}} \cdot e_{\text{CO}_2, \text{fuel}}}, \quad (6.4)$$

where $e_{\text{CO}_2, \text{fuel}}$ are the CO₂ emissions from fuel combustion in kg CO₂/GJ and CR is the ratio of obtained product CO₂ and total CO₂ in the waste stream ($m_{\text{CO}_2, \text{fluegas}} + m_{\text{CO}_2, \text{fuel}}$, see Appendix C.1).

6.3 Selecting CO₂ sources in Europe

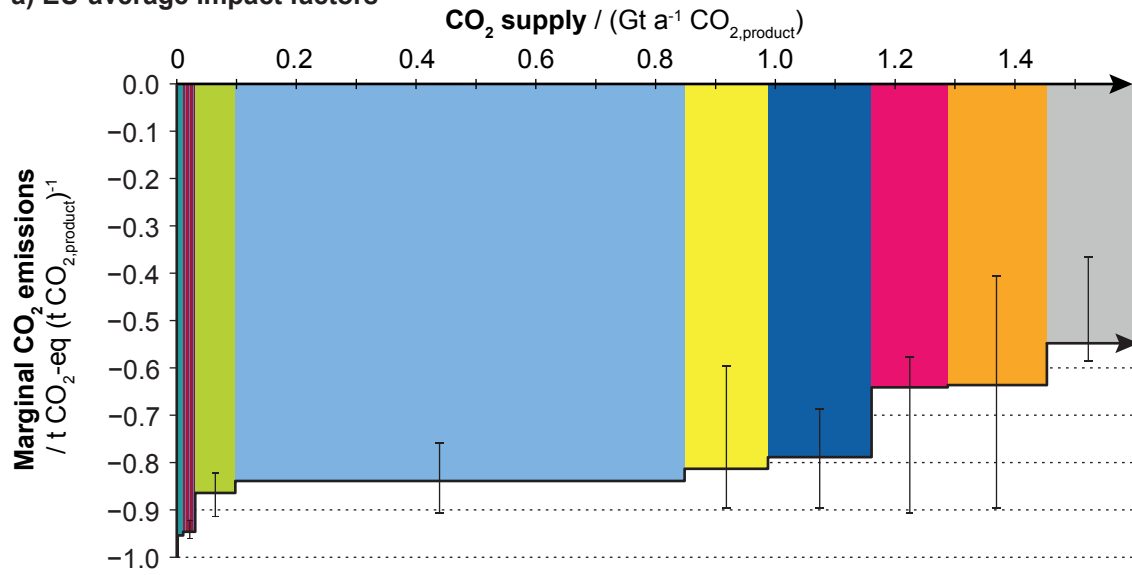
6.3.1 Environmental-merit-order curves

First, environmental-merit-order curves are presented for a European-wide perspective without impacts from CO₂ transport. Two scenarios are considered for the environmental impact factors of electricity generation: EU-average and country-specific impact factors. For EU-average impact factors, the EMO curve for impacts on global warming are shown in Fig. 6.3a: the y-axis shows the marginal CO₂ emissions for CO₂ capture from alternative CO₂ sources, whereas the x-axis shows the sources' available amounts of CO₂ supply. According to Eq. (6.2), the marginal CO₂ emissions have a baseline at '−1' from the credit for the CO₂ otherwise emitted; any other indirect GHG emissions from energy supply are added. The negative values for all cases prove that CO₂ capture from all considered sources can avoid GHG emissions. However, the CO₂ emissions avoided by CO₂ capture vary. Using EU-average impact factors can give a general ranking for CO₂ reductions from alternative CO₂ sources: the largest reductions arise for CO₂ capture from the almost pure sources in hydrogen¹⁰, ammonia and ethylene oxide production as well as in natural gas processing and IGCC power plants ($0.94 \text{ t CO}_2\text{-eq (t CO}_{2,\text{product}})^{-1}$). These CO₂ savings are in very good agreement with the reported CO₂ intensities in Middleton et al. (2014). CO₂ capture in the paper industry reduces CO₂ emissions slightly less ($0.86 \text{ t CO}_2\text{-eq (t CO}_{2,\text{product}})^{-1}$). Capturing CO₂ from coal and natural gas power plants and from iron and steel plants leads to CO₂ reductions between 0.79 and 0.83 t CO₂-eq (t CO_{2,product})^{−1}. CO₂ capture from refineries and steam crackers is very site-specific and thus, CO₂ reductions vary largely between 0.57 and 0.91 t CO₂-eq (t CO_{2,product})^{−1}. Average CO₂ reductions for CO₂ capture from refineries and steam crackers ($0.64 \text{ t CO}_2\text{-eq (t CO}_{2,\text{product}})^{-1}$) are similar to those in cement production ($0.63 \text{ t CO}_2\text{-eq (t CO}_{2,\text{product}})^{-1}$). Lowest CO₂ reductions results from CO₂ capture from ambient air (DAC) with $0.54 \text{ t CO}_2\text{-eq (t CO}_{2,\text{product}})^{-1}$.

Fig. 6.3b shows the EMO curve for impacts on global warming based on country-specific impact factors for electricity generation. In this case, CO₂ capture leads to CO₂ reductions from 0.42 to 0.99 t CO₂-eq (t CO_{2,product})^{−1}. Due to the country-specific impact factors, the CO₂ reductions can vary for identical types of CO₂ sources in different countries. Nevertheless, the order of CO₂ sources in Fig. 6.3b is similar to Fig. 6.3a (Spearman's rank correlation coefficient of 0.80). In the follow-

¹⁰In general, CO₂ capture from hydrogen production allows for large CO₂ reductions. Hydrogen production is not shown in the EMO curves since hydrogen production sites could not have been identified in the CO₂ emissions database.

a) EU-average impact factors



b) country-specific impact factors

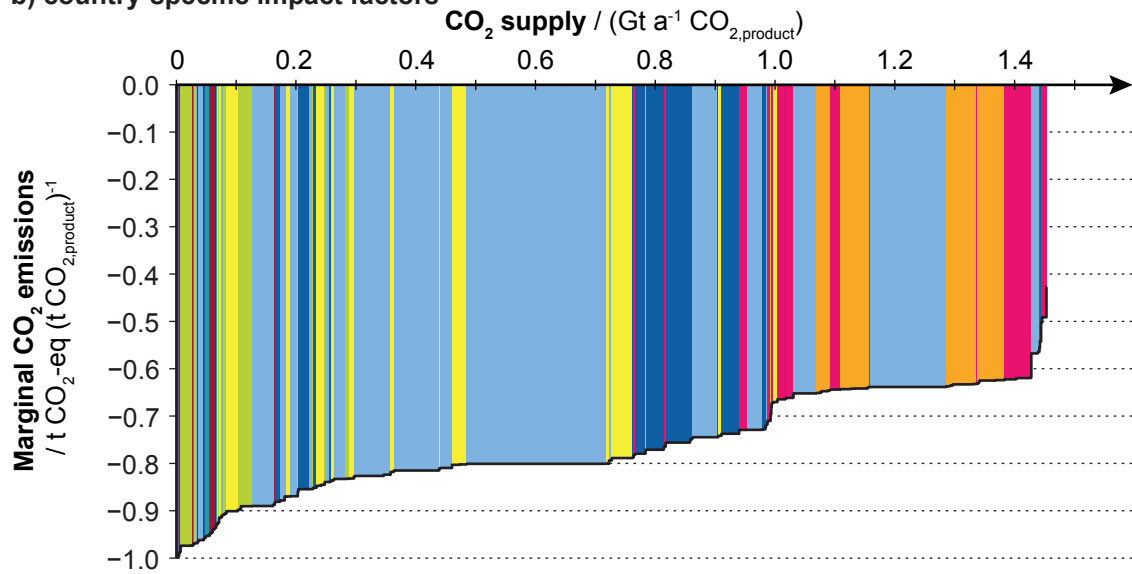


Figure 6.3: Environmental-merit-order curve for marginal CO₂ emissions over the available CO₂ supply in Europe using a) EU-average and b) country-specific GHG emission factors for electricity supply. The energy demands for CO₂ capture vary between literature sources for each CO₂ source (see appendix C.5 for detailed table) and lead to the shown error bars.

ing, results are given for country-specific impact factors. For country-specific impact factors, DAC is not included in the EMO curves for better visualization since the potential amounts of CO₂ supply for DAC are generally very large.

In total, CO₂ capture from CO₂ point sources has a potential climate-mitigation benefit of up to 1.10 Gt a⁻¹ CO₂-eq. This amount of avoided CO₂ emissions does not include downstream CO₂ emissions from CO₂ utilization. Most importantly, CO₂ will usually be released at the end of the product life cycle and thus, CO₂ utilization is not an overall CO₂ sink (section 5.3).

For impacts on fossil resource depletion, the EMO curve in Fig. 6.4a) illustrates the marginal fossil resources for CO₂ capture from alternative CO₂ sources over their available CO₂ supply amounts. CO₂ capture from alternative CO₂ sources leads to an increase of fossil resource depletion between 0.00 and 0.19 t oil-eq (t CO_{2,product})⁻¹. The EMO for fossil depletion impacts (Fig. 6.4a) is very similar to the order regarding impacts on global warming (Fig. 6.3b, Spearman's rank correlation coefficient of 0.94). Taking into account the shown uncertainties due to the energy demand, the EMO for impacts on global warming and fossil resource depletion can be considered as practically non-conflicting.

6.3.2 Marginal fossil resource depletion for avoided CO₂ emissions

Providing CO₂ by CO₂ capture can avoid CO₂ emissions for all considered CO₂ sources (Fig. 6.3). Avoiding CO₂ emissions can also be considered as valuable function from a climate-mitigation point of view. Hence, an alternative functional unit is defined as 'CO₂ capture avoiding 1 tonne of CO₂ emissions'.

The marginal impacts on fossil resource depletion per CO₂ avoided (y-axis) as well as the total amount of avoided CO₂ emissions (x-axis) are shown in Fig. 6.4b). The shown marginal impacts correspond to the marginal fossil resource depletion per product CO₂ (Fig. 6.4a) divided by the negative marginal CO₂ emissions (=CO₂ avoided) per product CO₂ (Fig. 6.3). Since usually less CO₂ is avoided than produced, the marginal fossil resource depletion is larger per avoided CO₂ than per product CO₂. Moreover, since the EMOs in Figs. 6.3b) and 6.4a) are similar, the EMO curve in Fig. 6.4b) increases even more drastically than the EMO curve in Fig. 6.4a).

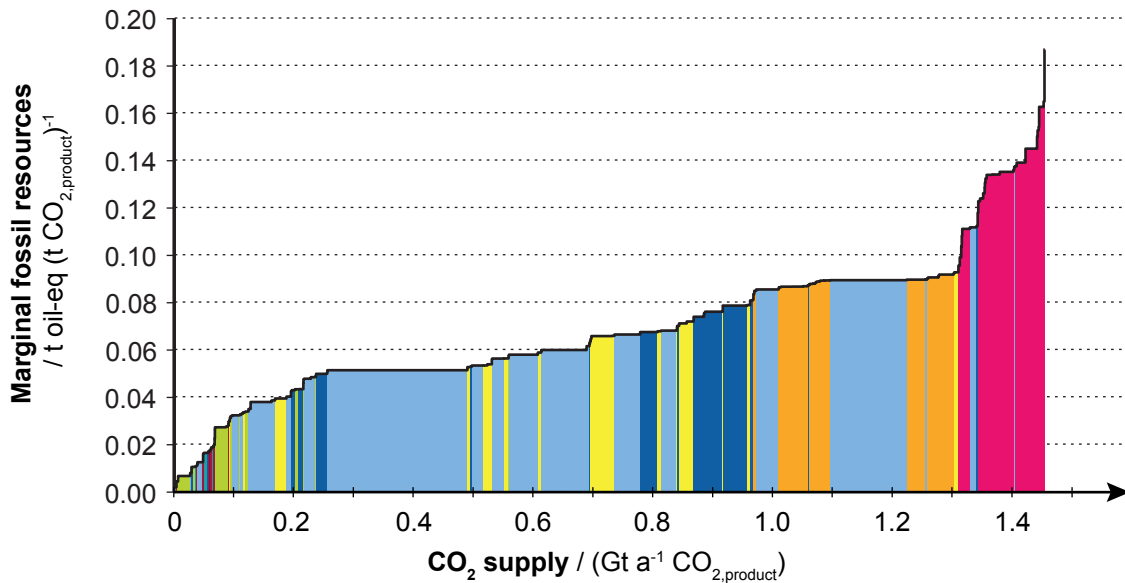
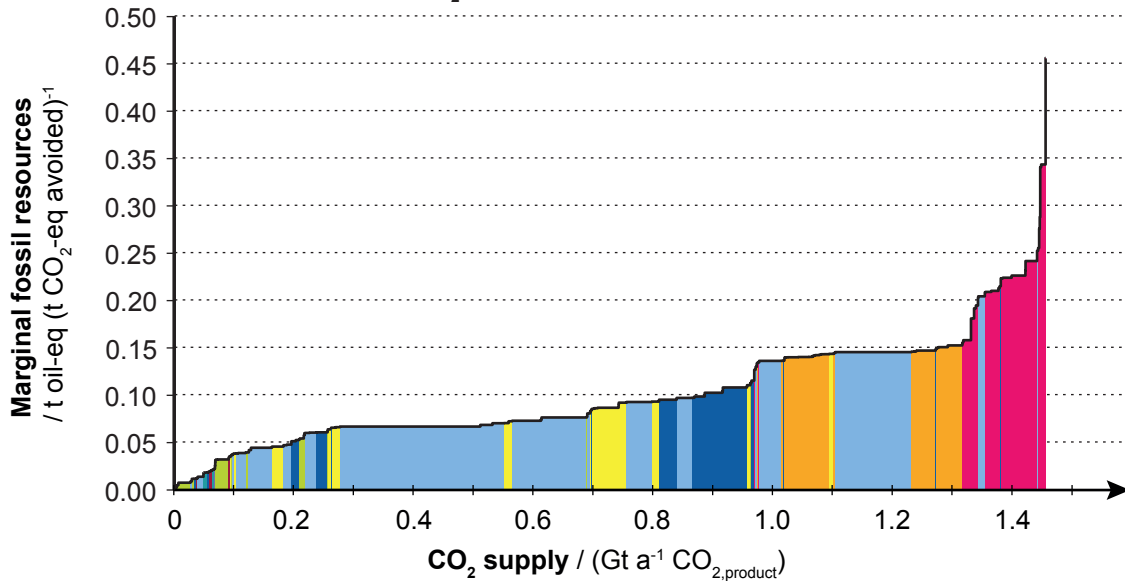
a) marginal fossil resources per CO₂ productb) marginal fossil resources per CO₂ avoided

Figure 6.4: Environmental-merit-order curve for marginal fossil resource depletion a) per amount of product CO₂ and b) per amount of CO₂ avoided. The marginal fossil resource depletion is shown over the available CO₂ supply in Europe using country-specific impact factors for electricity supply.

6.3.3 Selection of CO₂ sources

The selection of CO₂ sources according to Figs. 6.3-6.4 depends on the CO₂ demand. Currently, about 200 Mt a⁻¹ CO₂ are being used (Aresta et al., 2013). Estimates for the future demand range from 300 Mt a⁻¹ in 2016 to 2 Gt a⁻¹ in the long-term including CO₂-based fuels such as methanol (Aresta et al., 2013; DECHEMA, 2009; Centi and Perathoner, 2011). Assuming that about 25 % of global CO₂ utilization takes place in Europe (Europe's share of global GDP is 23 % and its share of chemical shipments is 29 % (The World Bank, 2014; ACC, 2014)), an optimistic CO₂ utilization potential for Europe can be estimated at about 75 Mt a⁻¹ in the near-term and about 500 Mt a⁻¹ in the long-term.

Even for the long-term optimistic CO₂ utilization potentials, only a few CO₂ sources are needed to satisfy the demand. Based on average environmental impacts and EU-average impact factors, CO₂ should be captured only from the almost pure CO₂ sources (hydrogen, gas processing, ethylene oxide, ammonia, IGCC power plants), and then from the paper industry, power plants and iron and steel plants. These CO₂ sources can already supply enough CO₂. In the long term, however, the CO₂ supply amounts and thus the EMOs might change. On the one hand, renewable energies are expected to substitute a large share of fossil-fueled power plants. Thereby, the CO₂ supply by power plants is expected to decrease to about 230 Mt a⁻¹ according to ECF (2010). On the other hand, new large-scale concentrated CO₂ point sources such as ethanol plants and biogas fermentation will probably emerge (Kheshgi and Prince, 2005; Gollakota and McDonald, 2012; Privalova et al., 2013).

Using air as CO₂ source is not needed to satisfy the expected CO₂ demand: DAC will only be beneficial compared to cement plants ('worst' CO₂ source in Fig. 6.3a) if CO₂ is transported for more than 1,000 km by truck or ship or 4,000 km by pipeline. Thus, DAC can be environmentally favorable in locations far away from large-scale point sources. Whether and where DAC should be implemented can be analyzed by the CO₂ oases approach.

6.3.4 CO₂ oases in Europe

The European-wide analysis in Figs. 6.3-6.4 can be refined to provide a regional perspective for the selection of CO₂ sources for individual CO₂ utilization sites. For this purpose, a local EMO considering CO₂ capture, compression and transport is calculated for each location. Locations with minimal environmental impacts are called CO₂ oases and are shown in Fig. 6.5 for global warming impacts and CO₂ demands from 0.1 to 200 Mt a⁻¹. CO₂ oases are generally located in the center of Europe.

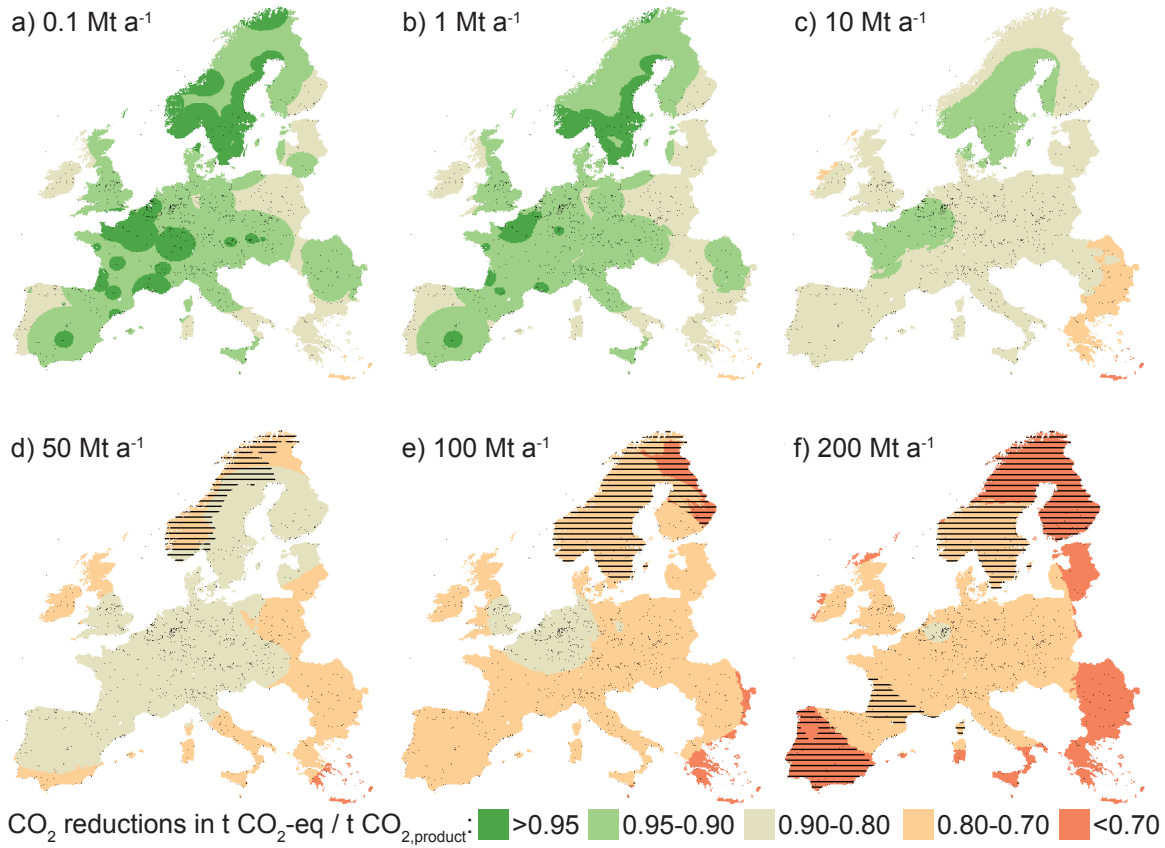


Figure 6.5: CO₂ oases maps for Europe showing the maximum average CO₂ emission reductions in t CO₂-eq (t CO_{2,product})⁻¹ for CO₂ demands of a) 0.1, b) 1, c) 10, d) 50, e) 100, and f) 200 Mt a⁻¹. The shaded areas in Scandinavia, France, Spain and Portugal are regions where direct air capture (DAC) is (partially) employed.

The presented approach for identifying CO₂ oases does not account for competition of CO₂: computing the CO₂ reductions for one potential CO₂ utilization location is independent from all other CO₂ utilization sites. However, even if 50 Mt a⁻¹ CO₂ (25 % of today's demand) are used in a single location, CO₂ can still be provided with quite large average CO₂ reductions of 0.70-0.90 t CO₂-eq (t CO_{2,product})⁻¹ including emissions from transport. Furthermore, capture and transport from CO₂ point sources is still favorable over DAC. Only for large CO₂ demands above 100 Mt a⁻¹ in a single location, DAC should be implemented in countries with few CO₂ sources and low-impact electricity generation (Sweden, Norway, Finland, Spain, Portugal and France; shaded areas in Fig. 6.5e-f).

6.4 Summary and conclusions

In industrialized regions like Europe, CO₂ could be captured from a large variety of well-distributed CO₂ sources. The potential CO₂ supply of the considered CO₂ sources is much larger than the estimated long-term CO₂ demand in Europe. Thus, only a few CO₂ sources should be selected. So far, the mainly considered CO₂ source for CO₂ utilization has been power plants. In this chapter, an environmental comparison across all considered CO₂ source for CO₂ utilization is presented. For this purpose, a comprehensive literature research has been conducted for energy demands of CO₂ capture from a variety of CO₂ sources. Furthermore, a database for CO₂ sources in Europe has been constructed.

The presented environmental-merit-order (EMO) curves rank these CO₂ sources according to the environmental impacts due to CO₂ capture. Regarding impacts on global warming, the environmental-merit-order (EMO) curve proves that CO₂ capture from any CO₂ source can avoid CO₂ emissions. However, avoiding CO₂ by CO₂ capture from CO₂ sources comes along with an increased depletion of fossil resources.

Selecting CO₂ sources according to the presented environmental-merit-order (EMO) curves minimizes environmental impacts. EMO curves for a European-wide perspective show that highest CO₂ emission reductions and lowest fossil resource depletion are obtained by CO₂ capture from almost pure CO₂ sources such as in production of hydrogen, ammonia and ethylene oxide, in natural gas processing, and in IGCC power plants, followed by pulp and paper plants, power plants and iron and steel plants. The integration of cement plants, refineries and steam crackers as CO₂ sources for CO₂ utilization depends on the site-specific conditions. Capture of CO₂ from air, however, causes highest fossil resource depletion at lowest CO₂ emission reductions. Thus, air-capture should only be implemented if CO₂ point sources cannot fully satisfy the overall CO₂ demand and/or if they are located very far away from the CO₂ utilization site. Based on local EMO curves reflecting actual transport distances, locations where large amounts of CO₂ can be obtained with lowest environmental impact have been identified. The resulting ‘CO₂ oases’ are located in the center of Europe. However, large amounts of CO₂ with low environmental impacts can be obtained anywhere in Europe.

The presented EMO curves for impacts on global warming and fossil resource depletion provide a simple, yet effective way of selecting CO₂ sources for CO₂ utilization.

Towards Life-Cycle Design of CO₂-based Chemicals

In this chapter, the classical Life-Cycle Assessment (LCA) approach is exploited for the conceptual design of CCU processes at early development stages. In section 7.1, the life-cycle design approach for CCU is motivated by a brief review of existing approaches for the environmental assessment and process design at early development stages. In section 7.2, an LCA-based process design approach for CO₂ hydrogenation reactions is presented to identify optimal reaction schemes under different conditions for reactant supply. The presented approach is illustrated for production of methanol. In section 7.3, an integrated product and process design approach based on LCA is developed for polymer production to identify a polymer composition and corresponding supply chain with minimal environmental impacts. Summary and conclusions for the two design approaches are given at the end of the corresponding sections.

Parts of section 7.2 have been published in:

Dumont, M.-N., von der Assen, N., Sternberg, A., and Bardow, A. (2012). Assessing the environmental potential of carbon dioxide utilization: A graphical targeting approach. Volume 31 of *Computer Aided Chemical Engineering*, pages 1407–1411. Elsevier.

Parts of section 7.3 have been published in:

Von der Assen, N., Lampe, M., Müller, L., Bardow, A. (2015). Life-Cycle Assessment Principles for the Integrated Product and Process Design of Polymers from CO₂. Volume 37 of *Computer Aided Chemical Engineering*, pages 1235–1240. Elsevier.

7.1 From retrospective LCA towards LCA-based prospective design

The classical, “retrospective” Life-Cycle Assessment (LCA) approach is to analyze existing products or implemented processes (Earles and Halog, 2011). In this case, data of material and energy in- and outputs are available or can be collected. The LCA results of the studied product or process can be compared to existing and feasible alternatives to identify the option with lowest environmental impact. This type of LCA approach is employed in chapter 5 for a comparison of fossil- and CO₂-based polyols.

In the design of products and processes, LCA results are also desirable even at early stages. At these stages, however, data availability is typically very limited and detailed process models do often not exist. To overcome data limitations and to avoid detailed process models, Wernet et al. (2008, 2009, 2012) developed approaches to estimate environmental impacts from production of fine chemicals solely based on the chemical’s molecular structure. The approach is extremely helpful to estimate environmental impacts of chemicals if the process routes are unknown. However, it is incapable of comparing alternative process routes for one chemical. Thus, the approach is not suitable for a comparison of conventional and CO₂-based process routes.

Several approaches have been developed for the evaluation of alternative process routes with limited available data at early stages: Sugiyama et al. (2008) present a stage-gate decision framework where alternative process routes are evaluated against multiple criteria including environmental indicators. Regarding environmental indicators at the very first stages, the raw materials’ CED (cf. section 3.2.8) and indicators for the process energy demand are used to obtain a 0 (low) to 1 (high) score for life-cycle environmental impacts. As indicator for the process energy demand, the mass-loss index (similar to the E factor, cf. section 2.4.2 or Heinzle et al. (1998)) and the energy-loss index (ELI) are used. The ELI index has a value between 0 and 1 depending on the water concentration, product concentration, minimum difference of boiling point, inherent waste amount, and reaction energy (Sugiyama et al., 2008). ELI was recently extended by the number of co-products and the (non-) existence of feedstock pre-treatment (Patel et al., 2012). Furthermore, Bumann et al. (2010) fitted ELI to the gate-to-gate energy consumption. Together with the raw materials’ CED, a complete cradle-to-gate CED can be estimated using simple reaction data. Since CED correlates well with other environmental indicators (Huijbregts et al., 2010), the combination of the above described approaches provides an LCA-based screening in-

indicator to compare alternative process routes. However, the generation of alternative process routes remains a challenge. Manual generation generally leads to a limited number of alternatives which might exclude optimal solutions.

The generation of alternative process routes is a known problem in process design. In process design for example, alternative process routes can be systematically generated and analyzed by reaction network flux analysis (RNFA) (Hechinger et al., 2010; Voll and Marquardt, 2012). A reaction network is constructed based on stoichiometric coefficients of known reactions. In general, the generation of all possible process routes is prohibitive due to the combinatorial character of the problem. Thus, a single optimal process route is obtained by mathematical programming. Mathematical programming is frequently applied in all areas of chemical process design (Biegler et al., 1997). Typically, process design optimizes costs or efficiencies while considering environmental impacts as constraints. In contrast, a *design for sustainability* has been proposed with the objective to minimize environmental impacts (Bakshi and Fiksel, 2003). For this purpose, process design has been coupled with LCA (Azapagic and Clift, 1999; Guillén-Gosálbez et al., 2008).

When coupling process design with LCA, typical LCA principles should be considered such as the functional unit and allocation methods. The functional unit reflects function and performance of a product (cf. section 3.2.2.1). Products with indistinguishable performance and quality are commodities, e.g., ethylene, propylene and methanol. For the special case of commodities, a mass-based functional unit is reasonable. Furthermore, it is sufficient to limit the system boundaries of the design approach to the production process of the commodities (Seider et al., 2009). Use phase and end-of-life processes are typically not affected by an alternative commodity production and can thus be omitted (section 3.2.2.2.) If, however, new products with different performance and quality are designed, use phase and end-of-life processes are generally affected by different product properties. In these cases, product properties have to be considered in an integrated product-process design (Eden et al., 2004).

Another typical principle of LCA is the evaluation of co-products by alternative allocation methods. The influence of allocation methods has been thoroughly analyzed in LCA (Curran, 2007; Jung et al., 2013, 2014). In the context of process design, however, the impact of allocation methods has not been analyzed. Thus, the experience for co-product allocation should be transferred from LCA into process design. This chapter aims at providing an LCA-based process design approach in the context of CCU considering the described LCA features. In this thesis, an LCA-based process design approach is called *Life-Cycle Design* (Ramani et al., 2010).

7.1.1 Life-Cycle Design approaches for CCU

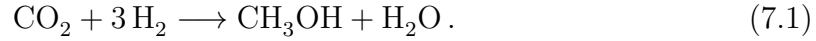
In this chapter, Life-Cycle Design (LCD) approaches are presented for two different CO₂ utilization options: CO₂ hydrogenation and CO₂-based polymers. CO₂ hydrogenation has the potential to provide bulk chemicals and fuels such as methanol. Thus, large volumes of CO₂-based products can be introduced in the existing value chain of the fossil-based counterpart. In contrast to CO₂ hydrogenation, the utilization volumes of CO₂ for polymers are limited. However, utilization of CO₂ for polymers can enable new process routes and provide materials with surpassing product properties (section 2.3.3). These different characteristics of CO₂ hydrogenation and utilization for polymers are also reflected in the following LCD approaches.

The first approach is an environmental *process design* for CO₂ hydrogenation reactions. For production of a compound of the form C_xH_yO_z, a cradle-to-gate system boundary for the production process is often sufficient. Since many CO₂ hydrogenation processes are still in very early design stages, it is not generally known which reactants and which amounts of reactants should be used in an environmentally favorable process. According to the first stage of process design in Sugiyama et al. (2008), only reaction information such as stoichiometry is available and should be used. Therefore, the presented process design approach identifies optimal reactants and reaction schemes in a systematical way for different conditions of reactant supply. Instead of generating and evaluating discrete process routes like in RNFA, a general reaction scheme is identified by relaxation of the stoichiometric coefficients. The approach is illustrated for production of methanol.

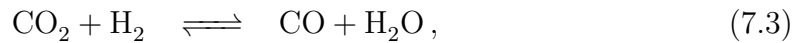
The second approach is an *integrated product and process design* based on LCA for the production of CO₂-based polymers. In addition to the direct utilization of CO₂ as feedstock, CO₂ can also be used indirectly to produce other feedstocks in the supply chain. Thus, direct and indirect utilization of CO₂ provide novel degrees of freedom to design the polymer supply chain. The supply chain is modeled by LCA unit processes similar to the RNFA approach. Incorporation of CO₂ and CO₂-based feedstocks into polymers also provides degrees of freedom regarding polymer properties. These degrees of freedom can be exploited to minimize environmental impacts in the design of a polyol polymer with desired properties and the associated processes in the supply chain. For this purpose, an integrated design of both product and processes coupled with LCA is developed and applied to CO₂-based polyol production. Since many co-products occur in the considered polyol supply chain, the effect of alternative co-product allocation methods on the optimal solution is analyzed.

7.2 LCA-based process design for CO₂-based methanol synthesis

As described in section 2.3.2.2, methanol can be produced from CO₂ in the reaction:



In sections 4.1.2 and 4.2.3, this particular reaction has been compared to conventional methanol synthesis via steam reforming of natural gas. In conventional methanol synthesis, natural gas and steam react to syngas according to the following two reactions:



where the syngas is then converted to methanol:

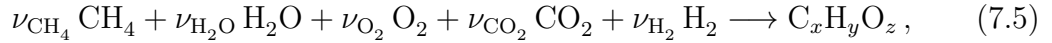


Lower GHG emissions of the CO₂-based route are not guaranteed and depend largely on the source of the reactants H₂ and CO₂. For CO₂ from air capture, the CO₂-based methanol synthesis has been found favorable in terms of global warming impacts if the required H₂ is produced by electrolysis and wind power (section 4.1.2). In contrast, if H₂ is produced by electrolysis and photovoltaics or by fossil-based steam reforming, the CO₂-based methanol synthesis causes larger GHG emissions than conventional methanol synthesis. In addition to air capture, CO₂ can be captured from alternative CO₂ sources, which provide CO₂ with largely different GHG emissions (chapter 6). Furthermore, the CO₂-based and conventional routes can be combined: already today, small amounts of CO₂ are added to syngas in methanol production (Peters et al., 2011b). Thus, the question arises which overall reaction scheme is environmentally favorable under different conditions for provision of the reactants H₂ and CO₂.

This section provides a graphical method to identify environmentally optimal reaction schemes for the production of methanol. The environmental impacts of H₂ and CO₂ provision are considered as free parameters. Thus, the graphical method allows to determine targets for H₂ production and CO₂ capture. The approach is not restricted to methanol synthesis but also directly applicable to other CO₂ hydrogenation options (see section 2.3.2.2) that lead to compounds of the form C_xH_yO_z.

7.2.1 Goal and scope definition

The goal of this work is to identify environmentally optimal reaction schemes for the production of methanol based on a process design framework by Patel et al. (2007). The considered reactants are limited to methane (CH₄), water (H₂O), oxygen (O₂), carbon dioxide (CO₂) and hydrogen (H₂). The generic reaction for a compound of the form C_xH_yO_z is used:



The stoichiometric coefficient ν_i of component i is negative as reactant and positive if the component is formed as by-product. Thus, a component can only be either reactant or by-product. The functional unit is defined as one mole of C_xH_yO_z and the stoichiometric coefficient of the product C_xH_yO_z is thus fixed to 1. The goal to identify environmentally optimal reaction schemes means to determine the stoichiometric coefficients ν_i for which the reaction causes minimal environmental impacts.

The scope of the approach focuses on the theoretical reaction (7.5) included in a black box process (Fig. 7.1). The black box consists of various, yet unknown unit operations such as multiple reactions steps, separation and recycling. In particular, heat generation is also part of the black box process. Nevertheless, the overall process must fulfill the mass, energy and entropy (in terms of Gibbs free energy) balances. The mass balances for the individual chemical elements are:

$$\text{C:} \quad 0 = \nu_{\text{CH}_4} + \nu_{\text{CO}_2} + x, \quad (7.6)$$

$$\text{H:} \quad 0 = 4\nu_{\text{CH}_4} + 2\nu_{\text{H}_2\text{O}} + 2\nu_{\text{H}_2} + y, \quad (7.7)$$

$$\text{O:} \quad 0 = \nu_{\text{H}_2\text{O}} + 2\nu_{\text{O}_2} + 2\nu_{\text{CO}_2} + z. \quad (7.8)$$

Standard conditions (298K, 1 bar) are assumed for the black box process. Furthermore, it is assumed that pure reactants enter and pure products leave the process. Under these assumptions, the energy and Gibbs free energy balances yield:

$$\Delta h = \Delta h_0^{\text{R}} = \Delta h_{\text{C}_x\text{H}_y\text{O}_z}^{f,0} + \sum_{i \in I} \nu_i \Delta h_i^{f,0} \leq 0, \quad (7.9)$$

$$\Delta g = \Delta g_0^{\text{R}} = \Delta g_{\text{C}_x\text{H}_y\text{O}_z}^{f,0} + \sum_{i \in I} \nu_i \Delta g_i^{f,0} \leq 0, \quad (7.10)$$

$$\text{where } i \in I = \{\nu_{\text{CH}_4}; \nu_{\text{H}_2\text{O}}; \nu_{\text{O}_2}; \nu_{\text{CO}_2}; \nu_{\text{H}_2}\}. \quad (7.11)$$

The energy balance represented by Eq. 7.9 includes potential heat supply by combustion of CH₄ or H₂ (Fig. 7.1).

Although the potential by-products are assumed to be separated and could thus be utilized as valuable products, CO₂ and CH₄ as by-products are assumed to be

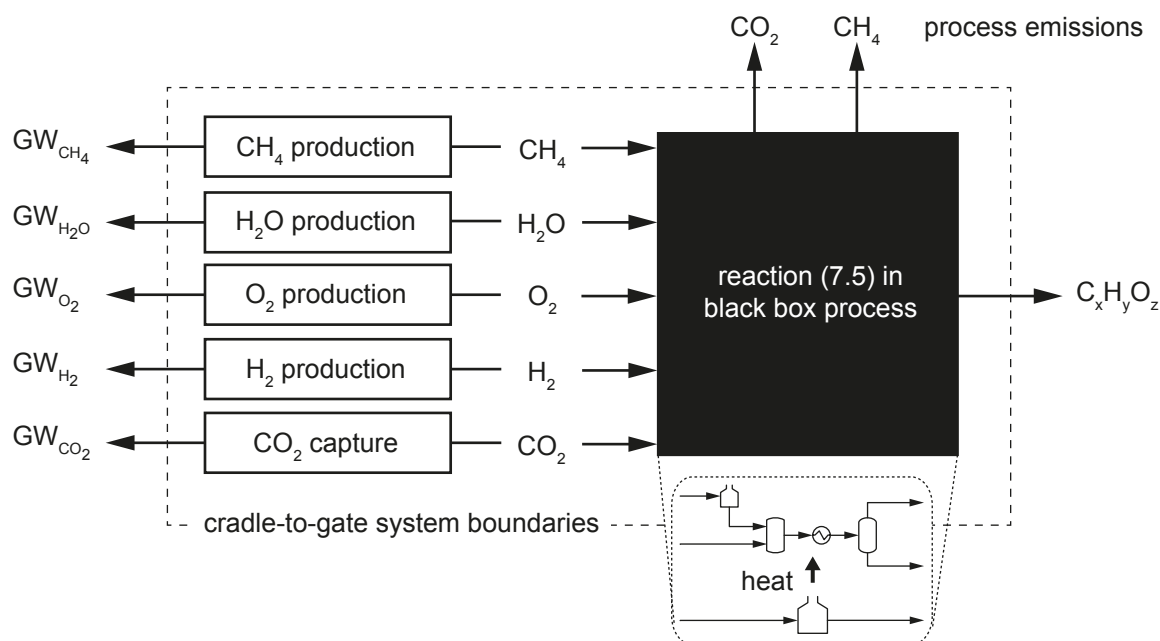


Figure 7.1: System boundary for environmentally optimal production of compound $C_xH_yO_z$ from alternative reactants including CO_2 .

emitted to the atmosphere. Thus, the by-products CO_2 and CH_4 of the reaction are not considered as products in an LCA context but as direct process emissions. Other potential by-products (O_2 , H_2 and H_2O) are not further considered, i.e., they are neither considered as process emissions nor are they given any environmental credit via allocation or avoided burden. These assumptions represent a worst case regarding the evaluation of the reaction's by-products.

In addition to the black box process, provision of reactants is included spanning a cradle-to-gate system boundary (Fig. 7.1). For provision of CH_4 , O_2 and H_2O , average impacts are taken from ecoinvent database (ecoinvent, 2010). The impacts for provision of H_2 and CO_2 are often particularly crucial for the overall environmental performance of CCU processes; however, they vary largely (Table 3.2 and chapter 6). In the presented approach, the environmental impacts of H_2 and CO_2 are treated as free parameters, which allows for identification of targets for their environmental impacts. For simplicity, the only considered environmental impact is global warming (GW). However, the methodology is also applicable for any other environmental impact.

7.2.2 Optimization formulation

The general optimization problem to minimize the cradle-to-gate global warming impact for the production of a compound $C_xH_yO_z$ is:

$$\begin{aligned} \min_{\nu} \quad & f(\nu), && \text{minimal environmental impact} \\ \text{s.t.} \quad & p(\nu) = 0, && \text{mass balances} \\ & q(\nu) \leq 0, && \text{energy and entropy balances} \end{aligned} \quad (7.12)$$

where ν is a vector of the stoichiometric coefficients as decision variables; $p(\nu)$ are the equality constraints from the mass balances and $q(\nu)$ are the inequality constraints from the energy and entropy balances¹¹.

To specify the general formulation, it is useful to introduce two auxiliary variables for the stoichiometric coefficients: $\nu_{R,i}$ is the stoichiometric coefficient for compound i if used as reactant; $\nu_{P,i}$ is the corresponding coefficient for occurrence as by-product:

$$\nu_{R,i} = \begin{cases} \nu_i & \text{if } \nu_i < 0 \\ 0 & \text{if } \nu_i \geq 0 \end{cases}, \quad \nu_{P,i} = \begin{cases} 0 & \text{if } \nu_i < 0 \\ \nu_i & \text{if } \nu_i \geq 0 \end{cases}. \quad (7.13)$$

To avoid the conditional expressions for reactants and products, the terms in Eq. (7.13) can be re-formulated using a *Big M* formulation (Türkay and Grossmann, 1996):

$$\left. \begin{aligned} \nu_i &= \nu_{R,i} + \nu_{P,i} \\ 1 &= \delta_{R,i} + \delta_{P,i} \\ \delta_{R,i} \nu_{R,i}^\infty &\leq \nu_{R,i} \leq 0 \\ 0 &\leq \nu_{P,i} \leq \delta_{P,i} \nu_{P,i}^\infty \end{aligned} \right\} \forall i \in I, \quad (7.14)$$

where $\nu_{R,i}^\infty$ and $\nu_{P,i}^\infty$ are the maximum amounts for compound i as reactant and product, respectively;

$\delta_{R,i}$ and $\delta_{P,i}$ are binary variables that denote the (non-)existence of compound i as reactant or product, respectively.

Global warming impacts are considered as representative environmental impact for production of $C_xH_yO_z$ to avoid further complexity with multi-objective optimization. The single objective function $f(\nu)$ is calculated from direct GHG process emissions (GWP_i) and the global warming impact (GW_i) of reactant supply:

$$f(\nu, \delta_P, \delta_R) = GW_{C_xH_yO_z} = \sum_{i \in I} \nu_i (\delta_{P,i} GWP_i - \delta_{R,i} GW_i). \quad (7.15)$$

¹¹Instead of frequently used h and g , p and q denote the equality and inequality constraints in this work to avoid confusion with enthalpy and Gibbs free energy.

For both GWP and GW , molar values are used. The objective function $f(\nu)$ is continuous with respect to ν_i but has a kink at $\nu_i = 0$ since the emission factor for ν_i in the objective function switches between GWP_i and GW_i . To avoid the bi-linear terms in Eq. (7.15), the objective function can be re-formulated:

$$f(\nu_P, \nu_R, \delta_P, \delta_R) = GW_{C_xH_yO_z} = \sum_i \nu_{P,i} GWP_i - \sum_i \nu_{R,i} GW_i. \quad (7.16)$$

Together with Eqs. (7.6)-(7.10), (7.14)-(7.16), the optimization problem (7.12) can be specified as mixed-integer linear program (MILP):

$$\begin{aligned} \min_{\nu_{CO_2}, \nu_{H_2}} \quad & \sum_i \nu_{P,i} GWP_i - \sum_i \nu_{R,i} GW_i \\ \text{s.t.} \quad & \nu_i = \nu_{R,i} + \nu_{P,i} \quad \forall i \in I \\ & 1 = \delta_{R,i} + \delta_{P,i} \quad \forall i \in I \\ & 0 = \nu_{CH_4} + \nu_{CO_2} + x \\ & 0 = 4\nu_{CH_4} + 2\nu_{H_2O} + 2\nu_{H_2} + y \\ & 0 = \nu_{H_2O} + 2\nu_{O_2} + 2\nu_{CO_2} + z \\ & \Delta h_{C_xH_yO_z}^{f,0} + \sum_i \nu_i \Delta h_i^{f,0} \leq 0 \\ & \Delta g_{C_xH_yO_z}^{f,0} + \sum_i \nu_i \Delta g_i^{f,0} \leq 0 \\ & \delta_{R,i} \nu_{R,i}^\infty \leq \nu_{R,i} \leq 0 \quad \forall i \in I \\ & 0 \leq \nu_{P,i} \leq \delta_{P,i} \nu_{P,i}^\infty \quad \forall i \in I \\ & \nu \in \mathbb{R}^5, \nu_R \in \mathbb{R}_-^5, \nu_P \in \mathbb{R}_+^5 \\ & \delta_R, \delta_P \in \{0; 1\}^5 \end{aligned} \quad (7.17)$$

The MILP (7.17) can be solved with standard optimization tools. However, a graphical solution for the not very complex problem is possible and can provide additional insights. Therefore, the following part presents a graphical solution for MILP (7.17).

7.2.3 Graphical targeting approach

An optimization problem refers to a set of equations that is under-determined. Thus, a solution space exists. Within this solution space, the degrees of freedom are exploited to find a single optimal solution. For the present problem with five possible reactants and three chemical elements, the resulting two degrees of freedom can be easily visualized in a 2D solution *area*. Since H₂ and CO₂ are the most important feedstocks

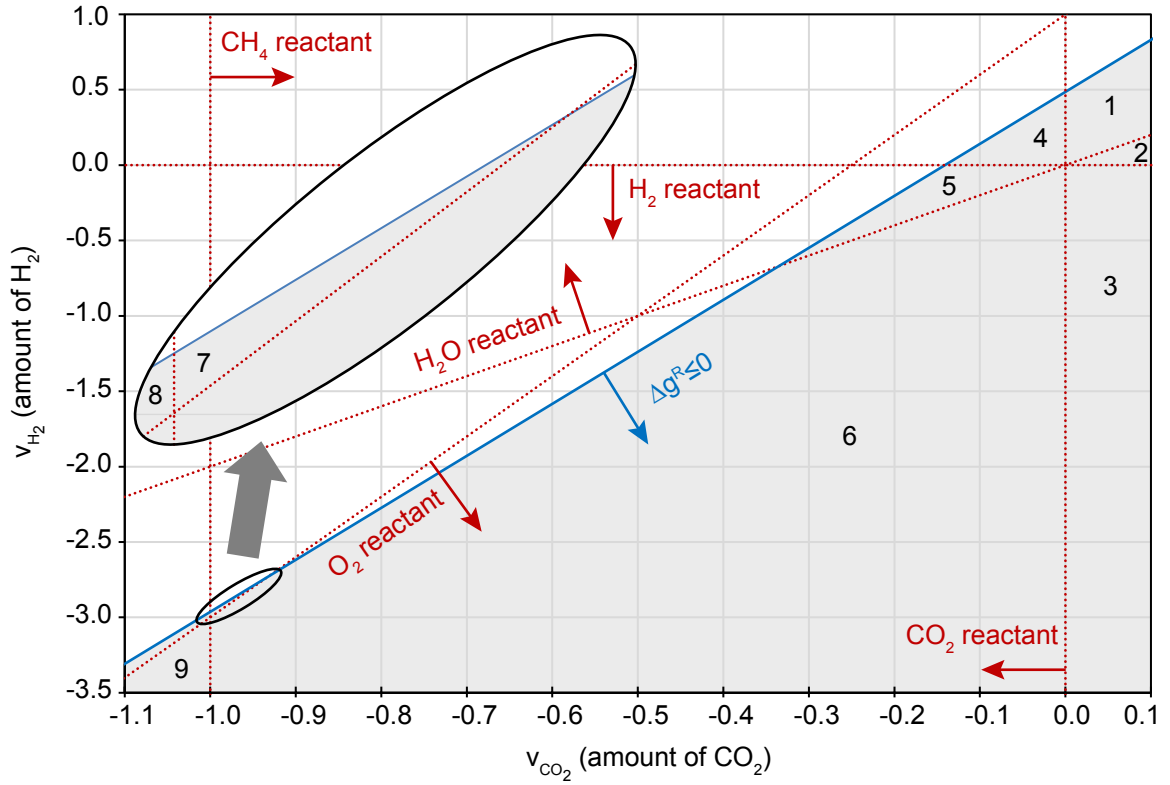


Figure 7.2: Solution area of MILP (7.17) for methanol synthesis with CO₂ as potential feedstock. The solution area is divided into nine regions with continuous objective functions.

for CO₂ hydrogenation, the solution area is illustrated for the stoichiometric coefficients of H₂ (ν_{H_2}) and CO₂ (ν_{CO_2}) as degrees of freedom (Fig. 7.2). The remaining stoichiometric coefficients are computed from the mass balances in Eqs. (7.6)-(7.8):

$$\nu_{\text{CH}_4} = -\nu_{\text{CO}_2} - x, \quad (7.18)$$

$$\nu_{\text{H}_2\text{O}} = 2\nu_{\text{CO}_2} - \nu_{\text{H}_2} + 2x - \frac{1}{2}y, \quad (7.19)$$

$$\nu_{\text{O}_2} = -2\nu_{\text{CO}_2} + \frac{1}{2}\nu_{\text{H}_2} - x + \frac{1}{4}y - \frac{1}{2}z. \quad (7.20)$$

The solution area is limited by the inequality constraints from the enthalpy and Gibbs free energy balances. In the case of methanol, the $\Delta h_0^{\text{R}} \leq 0$ constraint is dominated by the $\Delta g_0^{\text{R}} \leq 0$ constraint due to a negative reaction entropy and is neglected for better visualization in Fig. 7.2.

The objective function has a kink where a compound changes between reactant and by-product. At these kinks, the objective function is not differentiable. To be able to differentiate the objective function, the solution space can be decomposed

into k regions with differentiable objective functions f_k . The regions are conveniently determined by the graphical approach by Patel et al. (2007) using so-called zero lines. The zero lines represent a set of stoichiometric coefficients ν with zero amounts of a certain compound j ($\nu_j = 0$), with zero reaction enthalpy ($\Delta h_0^R = 0$) or with zero Gibbs free energy ($\Delta g_0^R = 0$). The zero-lines as functions of ν_{CO_2} and ν_{H_2} can be obtained from the mass balances in Eqs. (7.18)-(7.20) and from the energy and Gibbs free energy balances in Eqs. (7.9)-(7.10) and are given in Appendix D.1.1.

The objective function f_k is linear within each region k bounded by the zero lines. In Fig. 7.2, nine feasible regions ($k = 1, \dots, 9$) exist. For example in region $k = 6$, all compounds are reactants except for H₂O, which is formed as by-product. Although water vapor plays a vital role in absorption of solar irradiation, no *GWP* value is assigned to water by Stocker et al. (2013) and is therefore also neglected here. Thus, the objective function f_6 in region $k = 6$ is:

$$f_6 = -GW_{\text{CH}_4} \nu_{\text{CH}_4} - GW_{\text{O}_2} \nu_{\text{O}_2} - GW_{\text{CO}_2} \nu_{\text{CO}_2} - GW_{\text{H}_2} \nu_{\text{H}_2}. \quad (7.21)$$

For region $k = 8$, CH₄, O₂ and H₂O are formed as by-products whereas CH₄ is assumed to be emitted to the atmosphere. Hence, the global warming potential of CH₄ (GWP_{CH_4}) instead of the global warming impact (GW_{CH_4}) has to be considered in the objective function f_8 :

$$f_8 = +GWP_{\text{CH}_4} \nu_{\text{CH}_4} - GW_{\text{CO}_2} \nu_{\text{CO}_2} + GW_{\text{H}_2} \nu_{\text{H}_2}. \quad (7.22)$$

The objective functions f_k for all regions $k = 1, \dots, 9$ are given in Appendix D.1.2.

For the linear objective functions within each region, a formulation as linear program (LP) is possible. For a feasible LP, an optimal solution includes a corner. A vector $\vec{n}_{\text{S},k}$ pointing towards the local optimal (minimal) solution (S) can be defined as:

$$\vec{n}_{\text{S},k} = \begin{pmatrix} n_{\text{S},k,1} \\ n_{\text{S},k,2} \end{pmatrix} = \begin{pmatrix} -\partial f_k / \partial \nu_{\text{CO}_2} \\ -\partial f_k / \partial \nu_{\text{H}_2} \end{pmatrix}. \quad (7.23)$$

For region $k = 6$, the vector is given by:

$$\vec{n}_{\text{S},6} = \begin{pmatrix} GW_{\text{CH}_4} \frac{\partial \nu_{\text{CH}_4}}{\partial \nu_{\text{CO}_2}} + \frac{\partial \nu_{\text{O}_2}}{\partial \nu_{\text{CO}_2}} + GW_{\text{CO}_2} \\ GW_{\text{CH}_4} \frac{\partial \nu_{\text{CH}_4}}{\partial \nu_{\text{H}_2}} + GW_{\text{O}_2} \frac{\partial \nu_{\text{O}_2}}{\partial \nu_{\text{H}_2}} + GW_{\text{H}_2} \end{pmatrix}. \quad (7.24)$$

The partial derivatives for the stoichiometric coefficients can be calculated from Eqs. (7.18)-(7.20). The vector $\vec{n}_{\text{S},6}$ is finally given by:

$$\vec{n}_{\text{S},6} = \begin{pmatrix} -GW_{\text{CH}_4} - 2 GW_{\text{O}_2} + GW_{\text{CO}_2} \\ 1/2 GW_{\text{O}_2} + GW_{\text{H}_2} \end{pmatrix}. \quad (7.25)$$

Similarly for region $k = 8$, the vector $\vec{n}_{S,8}$ is:

$$\vec{n}_{S,8} = \begin{pmatrix} GWP_{CH_4} + GW_{CO_2} \\ GW_{H_2} \end{pmatrix}. \quad (7.26)$$

For given GW_i values for each compound i , the procedure to obtain the global optimal solution is as follows: the vectors $\vec{n}_{S,k}$ for $k = 1, \dots, 9$ point towards the local optimal corners. At these corners, the stoichiometric coefficients for H₂ and CO₂ can be read from Fig. 7.2. The remaining stoichiometric coefficients can be computed from Eqs. (7.18)-(7.20). Finally, the objective function values f_k are computed and compared to determine which of the identified corners constitutes the global optimal solution. This graphical solution procedure corresponds to the Simplex method (Dantzig and Thapa, 1997).

The above described procedure to obtain a global optimal solution is only feasible for fixed GW values. Here, however, GW_{CO_2} and GW_{H_2} are considered as free parameters. Eqs. (7.25)-(7.26) show that the vectors $\vec{n}_{S,k}$ for $k = 6$ and $k = 8$ depend on GW_{CO_2} and GW_{H_2} . As shown in Appendix D.1.3, all vectors $\vec{n}_{S,k}$ for $k = 3, \dots, 9$ depend on GW_{CO_2} and GW_{H_2} . Starting at chosen maximum values of $GW_{CO_2,max} = 0.4$ kg CO₂-eq/kg CO₂ and $GW_{H_2,max} = 12$ kg CO₂-eq/kg H₂, the vectors $\vec{n}_{S,k}$ turn counter-clockwise if GW_{CO_2} and/or GW_{H_2} decrease to chosen minimal values of $GW_{CO_2,min} = -1$ kg CO₂-eq/kg CO₂ and $GW_{H_2,min} = 0$ (Fig. 7.3). The counter-clockwise-turning vectors eventually point to different corners as local optimal reaction schemes where more CO₂ and H₂ are utilized as reactants. In other words, a provision of CO₂ and H₂ with fewer GHG emissions favors the utilization of CO₂ and H₂ as reactants, as one would expect.

However, the vectors do not point in all directions and thus, only certain corners are candidate optimal solutions. For example in Fig. 7.3, the vector $\vec{n}_{S,1}$ always points towards corner A and vector $\vec{n}_{S,2}$ always towards corner F. Corner F is also included in region $k = 1$. Since the objective function is continuous throughout the entire solution space, corner A dominates corner F. Thus, not all corners have to be considered as candidate global optimal solutions. Repeating the dominance considerations for all regions leads to corners A-E as candidate global optimal solutions. Interestingly, corners A-E are all on the $\Delta g_0^R = 0$ line.

The optimal solution moves from its current to a neighboring corner if the vector $\vec{n}_{S,k}$ is orthogonal to the zero-line connecting these corners (Fig. 7.3). In general, the orthogonality condition is fulfilled if:

$$m_{\text{zero-line}} = -\frac{n_{S,k,1}}{n_{S,k,2}}, \quad (7.27)$$

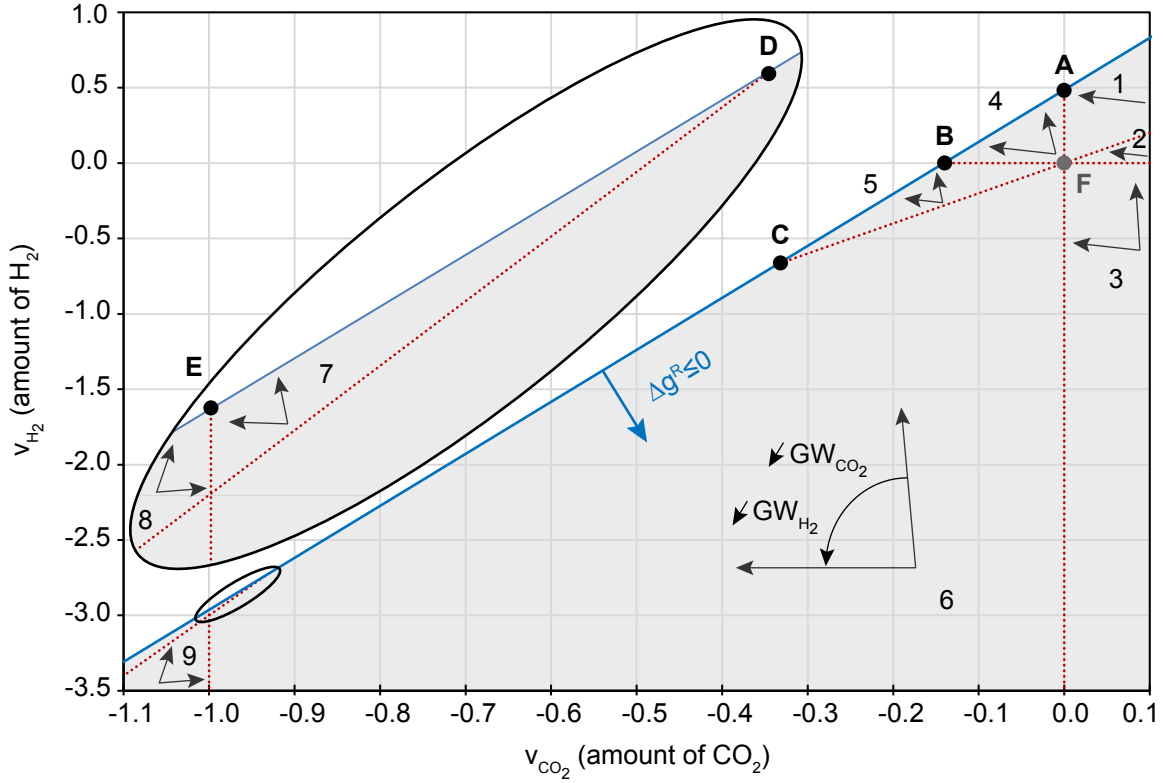


Figure 7.3: Range of vectors pointing towards the local optimal solution in each region $k = 1, \dots, 9$. The vectors for $k = 3, \dots, 9$ turn counter-clockwise if GW_{CO_2} or GW_{H_2} decreases. The corners A-E constitute candidates for the global optimal reaction schemes depending on the values of GW_{CO_2} and GW_{H_2} .

where $m_{\text{zero-line}}$ denotes the slope $\partial \nu_{H_2} / \partial \nu_{CO_2}$ of the zero line (see appendix D.1.1). The critical values $\overline{GW}_{CO_2}$ and $\overline{GW}_{H_2}$ that fulfill Eq. (7.27) are called threshold values since GW values just below or above the threshold values result in different optimal solutions. For the candidate optimal solutions A-E, threshold values are computed for the $\Delta g_0^R = 0$ line as connecting zero line in regions $k = 4 - 7$. Due to the two free parameters (GW_{CO_2} and GW_{H_2}), it is convenient to compute threshold *lines*. For example, the threshold line for region $k = 6$ is obtained as follows:

$$m_{\Delta g_0^R=0} = -\frac{n_{S,6,1}}{n_{S,6,2}}, \quad (7.28)$$

$$2 + \underbrace{\frac{\Delta g_{CO_2}^{f,0} - \Delta g_{CH_4}^{f,0}}{\Delta g_{H_2O}^{f,0}}}_{\Delta \tilde{g}} = \frac{GW_{CH_4} + 2 GW_{O_2} - \overline{GW}_{CO_2}}{1/2 GW_{O_2} + \overline{GW}_{H_2}}. \quad (7.29)$$

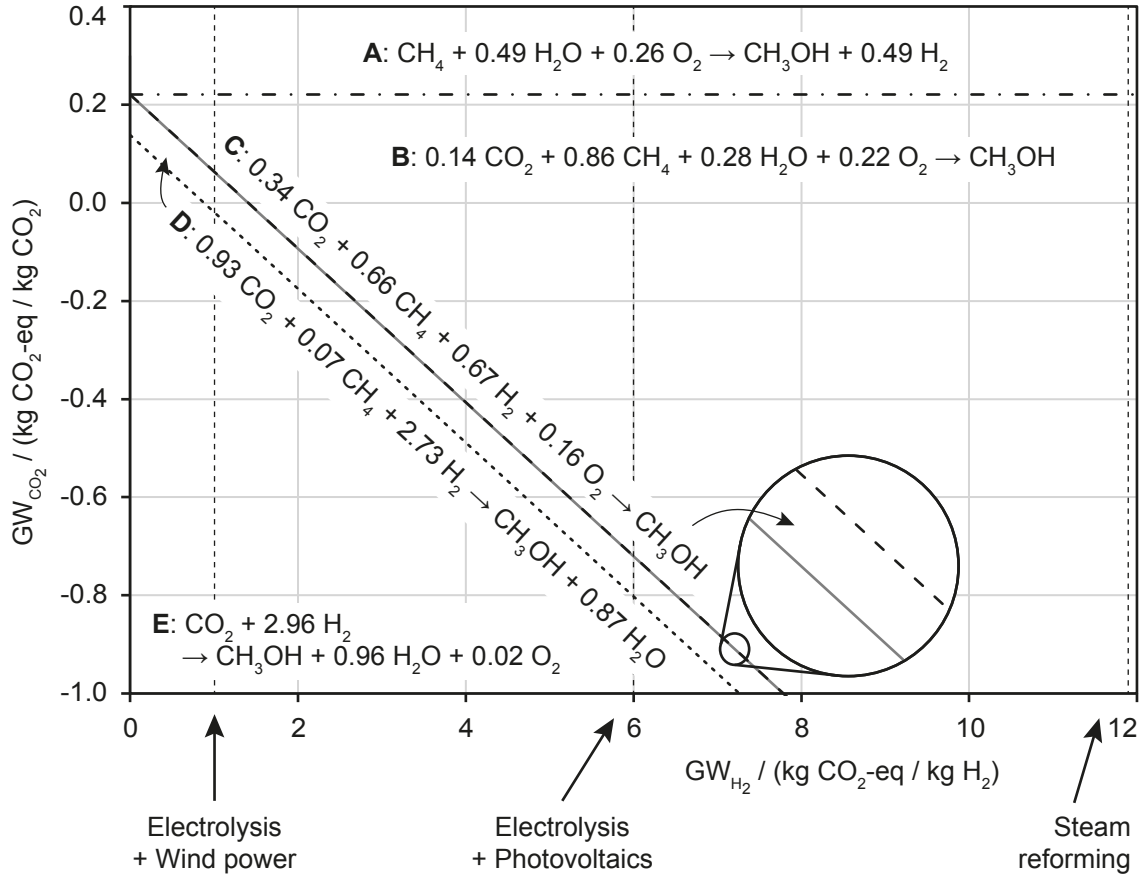


Figure 7.4: Environmentally optimal reaction schemes for methanol synthesis in dependence of the global warming impact of CO₂ (GW_{CO_2}) and H₂ provision (GW_{H_2}).

$$\Rightarrow \overline{GW}_{CO_2} = -(2 + \Delta\tilde{g}) \overline{GW}_{H_2} + GW_{CH_4} + (1 - \Delta\tilde{g}) GW_{O_2}. \quad (7.30)$$

The threshold lines for the other regions $k = 4, 5, 7$ are given in Appendix D.1.4.

7.2.4 Threshold values for optimal reaction schemes

The proposed method is used to determine the threshold values $\overline{GW}_{CO_2}$ and $\overline{GW}_{H_2}$ for global warming impacts of CO₂ and H₂ supply in the context of methanol synthesis. Five global environmentally optimal solutions have been found (corners A to E in Fig. 7.3). Hence, four threshold lines for regions $k=4-7$ can be computed (Fig. 7.4).

If GW_{CO_2} is above 0.22 kg CO₂-eq/kg CO₂, the use of CO₂ as a feedstock for methanol synthesis is environmentally not advisable and CH₄ should be employed as carbon source (scheme A). If GW_{CO_2} is below that value, it is always preferential to

(partially) use CO₂ as a carbon feedstock. How much CO₂ should be used, depends also on GW_{H_2} . For $GW_{H_2} > 7.7$ kg CO₂-eq/kg H₂, only minor amounts of 14 mol%_C CO₂ should be utilized (scheme B). Major amounts of CO₂ should be used, if $GW_{CO_2} \leq 0.22$ kg CO₂-eq/kg CO₂ and $GW_{H_2} \leq 7.7$ kg CO₂-eq/kg H₂ (scheme D and E).

Fig. 7.4 can be used to define GW targets for CO₂ capture and H₂ production technologies that allow for an entirely CO₂-based methanol synthesis. For example, if H₂ is produced via electrolysis and photovoltaics ($GW_{H_2} = 6$ kg CO₂-eq/kg H₂, Table 4.1), CO₂ should be captured from CO₂ sources where CO₂ capture leads to a reduction of at least 0.8 kg CO₂-eq/kg CO₂.

The threshold lines can also be coupled with the environmental-merit-order (EMO) curves for marginal global warming impacts of CO₂ supply (Fig. 7.5): For a given CO₂ source, the corresponding global warming impact for CO₂ supply can be read from the EMO curve (section 6.3.1). With this impact for CO₂ supply, the threshold value for H₂ supply can be read from Fig. 7.4. For example for the worst CO₂ source, the average marginal global warming impact of CO₂ supply is -0.42 kg CO₂-eq/kg CO₂. Even with the worst CO₂ source, methanol synthesis should employ at least small amounts of CO₂ as reactant (region B and E in Fig. 7.5), regardless of H₂ production. For the worst CO₂ source, an exclusively CO₂-based methanol synthesis requires clean H₂ production with maximum GHG emissions of $\overline{GW}_{H_2} = 3.58$ kg CO₂-eq/kg H₂.

The combination of EMO curves and threshold lines also allows to determine the total amount of environmentally favorable, exclusively CO₂-based methanol for a particular H₂ source. For example for H₂ supply with $GW_{H_2} = 6.50$ kg CO₂-eq/kg H₂, an exclusively CO₂-based methanol synthesis would require CO₂ supply with GW_{CO_2} below 0.86 kg CO₂-eq/kg CO₂. In this case, up to 0.21 Gt a⁻¹ CO₂ could be supplied limiting CO₂-based methanol synthesis to 0.15 Gt a⁻¹ methanol.

For H₂ from electrolysis with renewable electricity technologies, a similar EMO curve could be constructed for H₂ from electrolysis with renewable electricity technologies taking into account the potential supply amounts of H₂. For example, the EMO curve for H₂ might consider the total potential resources of renewable energy or the unused electricity in times of low demand and high supply by renewables, so-called surplus power (Sternberg and Bardow, 2015).

Please note that the marginal environmental impacts are obtained from a system-wide comparison of CO₂ sources with and without CO₂ sources. Thus, the combination of EMO curves with the threshold lines also represents a system-wide analysis including the full CO₂ reductions from CO₂ capture at the CO₂ source.

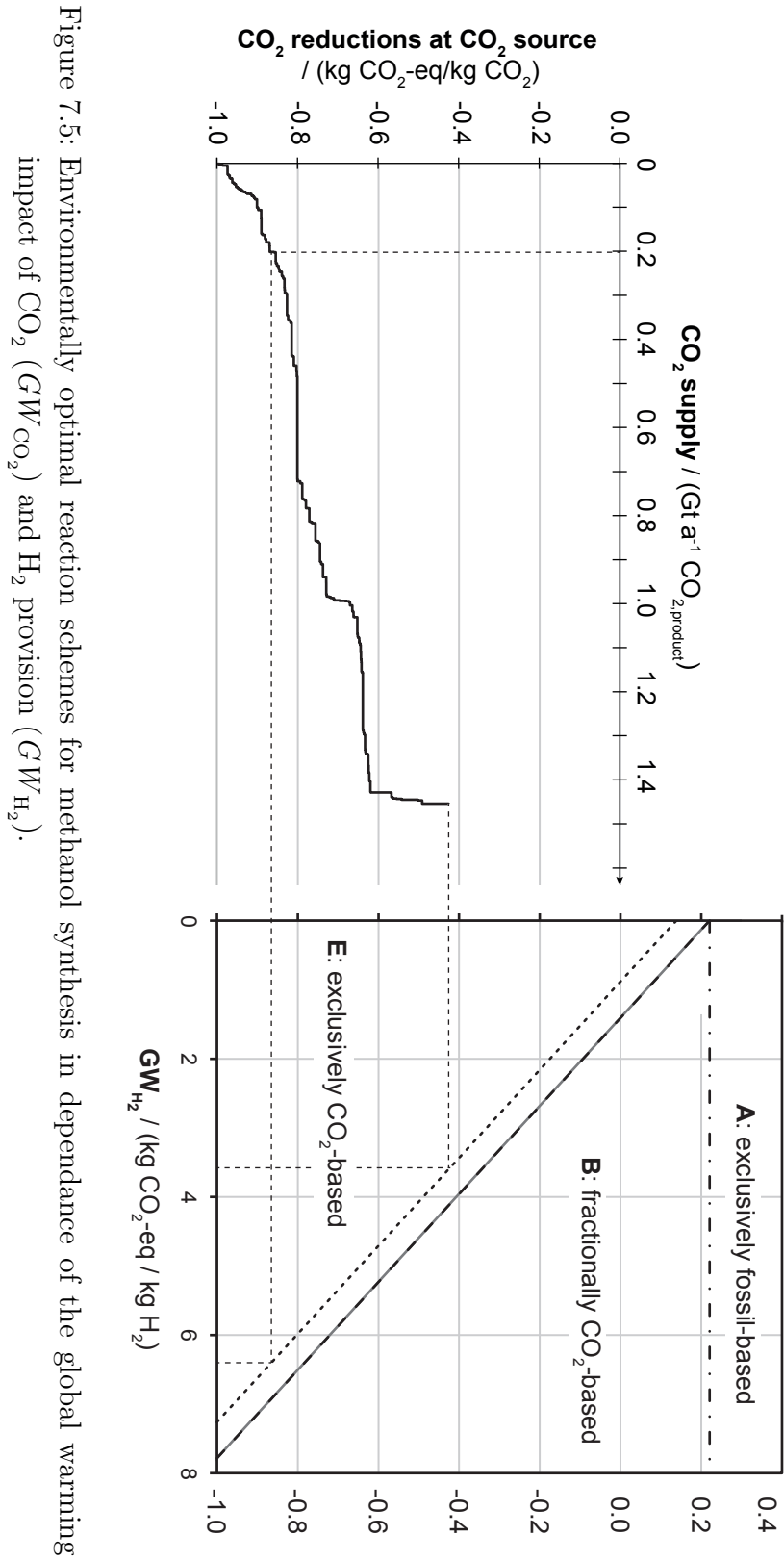


Figure 7.5: Environmentally optimal reaction schemes for methanol synthesis in dependance of the global warming impact of CO₂ (GW_{CO_2}) and H₂ provision (GW_{H_2}).

7.2.5 Summary and discussion for LCA-based process design for methanol from CO₂

Many bulk chemicals of the form C_xH_yO_z such as synthetic natural gas, methanol and other Fischer-Tropsch fuels can be synthesized via steam reforming of natural gas. Alternatively, these compounds can also be obtained by hydrogenation of CO₂. In very early stages of process design for C_xH_yO_z production, it is often unclear which overall reaction scheme is environmentally favorable: the conventional route via fossil resources, CO₂ hydrogenation or a mix of fossil- and CO₂-based processes.

Environmentally optimal reaction schemes for potentially CO₂-based production processes for compounds C_xH_yO_z can be obtained by introducing environmental impacts into the process design framework by Patel et al. (2007). The resulting graphically-based targeting method gives further valuable insights: if the global warming impacts of CO₂ and H₂ production are considered as free parameters, threshold values for these impacts can be derived that are tipping points between different environmentally optimal reaction schemes.

For synthesis of methanol, five environmentally optimal reaction schemes have been identified, which utilize no (scheme A), small (scheme B and C) or major amounts of CO₂ (scheme D) or exclusively CO₂ (scheme E) as carbon feedstock. Since the favorable reaction scheme depends on the global warming impacts of CO₂ provision (and of H₂), the presented design approach is particularly useful when coupled with the environmental-merit-order curves for CO₂ capture from CO₂ sources in chapter 6. Regardless of the CO₂ source employed, methanol synthesis should employ at least small amounts of CO₂ as reactant, regardless of H₂ production. An entirely CO₂-based methanol synthesis requires a clean H₂ production with maximum GHG emissions between 3.6 and 7.2 kg CO₂-eq/kg H₂, depending on the CO₂ source.

For process design in very early development stages, the presented approach can be applied even before any process flowsheet is known. So far, the approach considers only standard conditions for temperature and pressure as well as pure reactants and products. This means that pure reactants and products enter and leave the process with standard temperature and pressure; the reaction can actually take place at other temperatures and pressures. Nevertheless, an adaptation to other temperatures and pressures is possible. A limitation of the approach is the worst-case evaluation of the by-products. In particular in scheme A, about half a mole of pure H₂ is produced but not considered in terms of environmental impacts or benefits. Thus, a more detailed analysis of the by-products should be included into the process design at early stages. The possibility to give a credit of environmental impacts to certain by-products such as

H₂ could be easily incorporated into the objective function. Another, more systematic possibility for by-product evaluation in the context of an LCA-based design approach is presented in the following section.

7.3 LCA-based process and product design for CO₂-based polymers

As alternative and renewable carbon feedstock, CO₂ can be successfully utilized as building block for polyol polymers, as shown in chapter 5. In addition to the direct utilization of CO₂ as feedstock for polyols, CO₂ can also be used indirectly to produce further chemicals in the polyol supply chain. Both direct and indirect utilization of CO₂ provide novel degrees of freedom to design the polyol supply chain, and to modify the properties of the polyol itself. These degrees of freedom can be exploited to minimize environmental impacts in the design of a polyol polymer with desired properties and of the associated processes in the supply chain. For this purpose, an integrated design approach for both product and processes coupled with LCA is developed in this section.

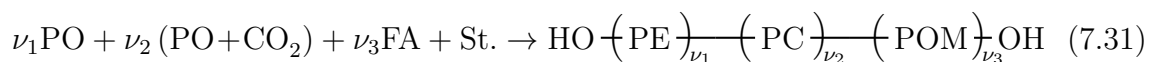
Integrated product and process design is a challenging problem by itself (Gani, 2004; Adjiman et al., 2014). Coupling the integrated design problem with LCA introduces further challenges; in particular, the evaluation of co-products has to be addressed since many products are co-produced in the chemical industry, e.g., in (bio-) refineries, steam crackers and also for CO₂ capture from CO₂ point sources (section 4.2). To allocate the environmental impacts to the individual co-products, a set of allocation methods exists in LCA (section 3.2.4). The choice of the allocation method is known to often lead to strongly varying product footprints (Curran, 2007). The existence of co-products is also often highlighted in process design (Kokossis and Yang, 2010; Sammons et al., 2007). However, to the best of the author's knowledge, the effect of alternative allocation methods has not been analyzed in the context of process design.

In this section, the effect of alternative allocation methods is analyzed for an LCA-based product and process design of polyols. The design approach consists of the integrated optimization of the polyol supply chain and the polyol composition with minimal environmental impacts. Product-specific property constraints ensure that polyols with comparable properties are designed. The polyol supply chain includes all processes for production of feedstocks and energy from cradle to gate. The influence of alternative allocation methods on both the optimal monomer composition and the supply chain of the polyol are illustrated. Finally, a recommendation is derived regarding allocation methods in LCA-based product and process design.

7.3.1 Goal and scope definition

The goal of this section is to identify a polyol composition and a corresponding supply-chain structure that allows for minimal environmental impacts while ensuring a specified product quality. As representative environmental impact, the global warming impact is chosen as single LCA metric to avoid further complexity due to multi-objective optimization. The functional unit is chosen as 1,000 kg polyol. A mass-based functional unit is appropriate since comparable product properties are guaranteed by property constraints in the design approach. In particular, the molar mass, the *OH* number and the glass transition temperature are considered (see section 7.3.3).

Poly-ether (PE) polyols are the most common type of polyols. They can be synthesized from the reaction of a multi-functional alcohol starter (glycerol in this work) with epoxides such as propylene oxide (PO). PO can partly be substituted by CO₂ making the overall process more energy efficient since the production of PO is energy intensive (section 5.3). Each molecule of CO₂ reacts with one molecule of PO forming a poly-carbonate (PC) unit in the polymer chains. In addition to PC units and the conventional poly-ether (PE) units from PO, poly-oxy-methylene (POM) units from complete polymerization of formaldehyde (FA) can also be incorporated into the polyol. FA is synthesized from oxidation of methanol. Since methanol can also be produced from CO₂ (section 7.2), incorporation of POM units offers the potential for indirect CO₂ utilization in polyols. The overall reaction for a hypothetical statistical polyol from the considered feedstocks and the starter (“St.”) is:



The considered cradle-to-gate system boundary in Fig. 7.6 includes the supply chain superstructure for production of polyols. The supply chain illustrates that CO₂ can be incorporated into the polyol both directly in PC units and indirectly in POM units through methanol and formaldehyde. The supply chain superstructure also shows that many co-products can potentially occur in the upstream processes of polyol production. In particular, the basic fossil-based processes such as steam cracking and catalytic reforming yield a large variety of co-products. In section 3.2.4, allocation methods for co-product evaluation in LCA are described. The goal of this section is twofold: First, an LCA-based product-process design is developed that can be employed for a large variety of polyol applications. Second, it is analyzed how alternative allocation methods affect the resulting polyol composition and supply chain structure.

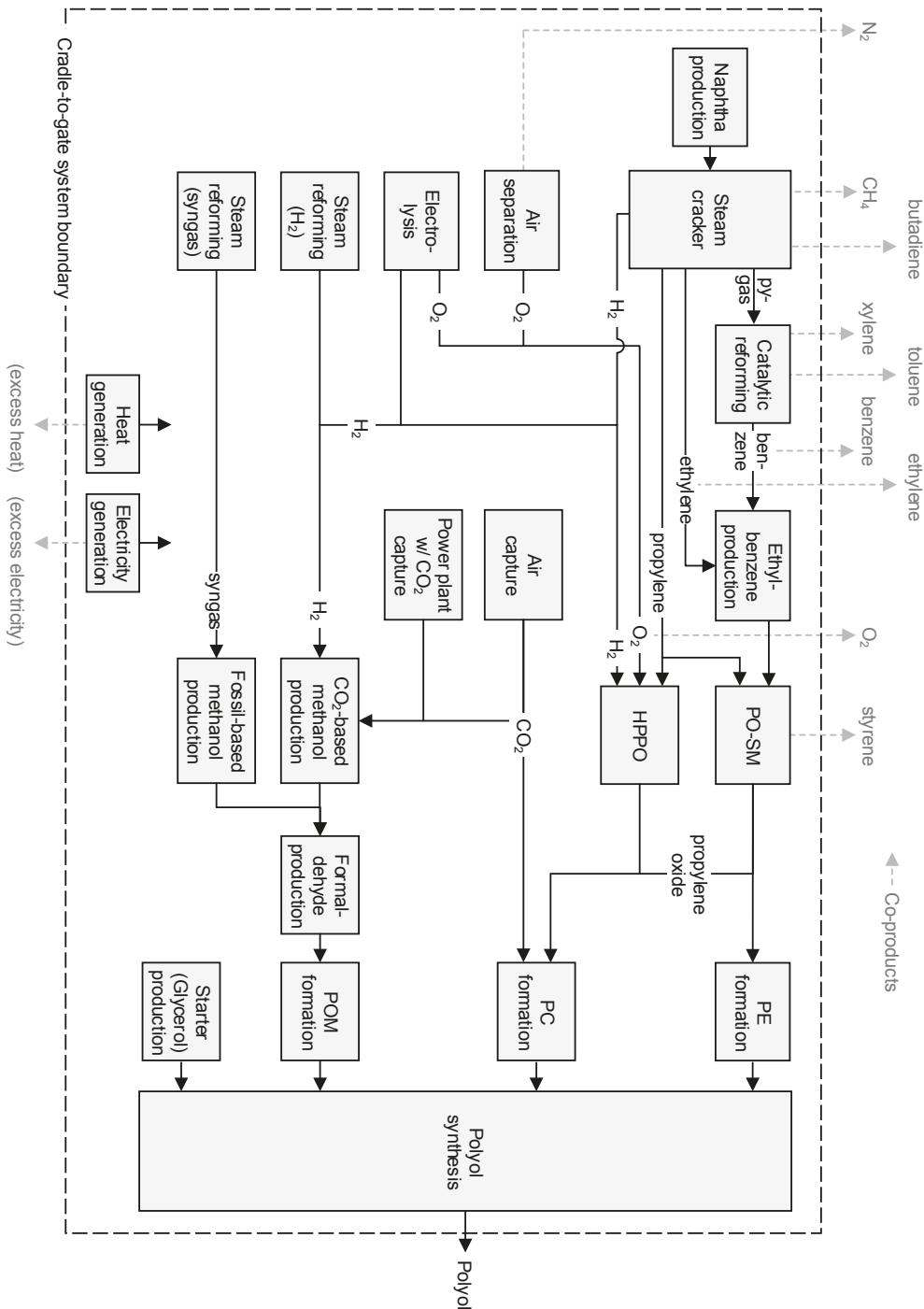


Figure 7.6: The supply chain superstructure for polyol production illustrating the major feedstocks propylene oxide, CO₂, and formaldehyde as well as glycerol as starter. Co-products in the upstream processes are shown as gray, dashed-arrows. Energy flows are considered but omitted in the Figure for better visualization.

7.3.2 Optimization formulation

The aim of LCA-based product and process design is to identify a product and its supply chain with minimal environmental impact. The design problem can be generally formulated as the following non-linear program (NLP):

$$\begin{aligned}
 \min_{s, \nu} \quad & f(s, \nu), && \text{minimal environmental impact} \\
 \text{s.t.} \quad & p(s, \nu) = 0, && \text{constraints from supply chain processes} \\
 & q(\nu) \leq 0, && \text{product design constraints} \\
 & s \in \mathbb{R}^m, && \text{process variables} \\
 & \nu \in \mathbb{R}^n, && \text{product structure variables}
 \end{aligned} \tag{7.32}$$

where $p(s, \nu) = 0$ describes the mass and energy balances for all processes in the supply chain as a function of process variables s and product structure variables ν ; and $q(\nu) \leq 0$ describes the product properties constraints as a function of the product structure variables ν . The following subsections specify the details of problem (7.32) for CO₂-based polyols.

7.3.3 Estimation methods and constraints for polyol properties

Reaction (7.31) is thermodynamically feasible for all combinations of ν_i since $\Delta g_0^R \leq 0$. However, the product composition ν_i alters the polyol properties. The following polyol properties are considered in this work:

- the molar mass M : the molar mass of a polymer indicates the length and degree of polymerization of a polymer.
- the OH number or hydroxyl value: the OH number for polyols is a defined metric for the number of functional OH groups per macro-molecule.
- the glass transition temperature T_g : at the glass transition temperature, a molecule changes from a glass-like to a rubbery state.

The properties are estimated from the polyol structure (ν) via group contribution methods (van Krevelen and te Nijenhuis, 2009):

$$M = \sum_i \nu_i M_i + M_{St}, \tag{7.33}$$

$$OH = \frac{1000 M_{KOH} F}{M}, \tag{7.34}$$

$$T_g = \frac{\sum_i \nu_i Y_{g,i} + Y_{g,St}}{M}. \tag{7.35}$$

The molar mass M of the polyol can be computed from the molar masses M_i of the monomer units PE, PC and POM, and the molar mass $M_{\text{St}} = 92$ g/mol of glycerol as starter. The OH number can be determined via M and the number F of hydroxyl groups in the starter molecule. The molar mass of potassium hydroxide (KOH) is $M_{\text{KOH}} = 56$ g/mol. The glass transition temperature T_g is obtained from the corresponding group contributions $Y_{g,i}$ and $Y_{g,\text{St}}$ of the monomers and starter, respectively.

The desired polyol properties are constrained by minimum and maximum values:

$$M_{\min} \leq M \leq M_{\max} , \quad (7.36)$$

$$OH_{\min} \leq OH \leq OH_{\max} , \quad (7.37)$$

$$T_{g,\min} \leq T_g \leq T_{g,\max} . \quad (7.38)$$

Since the number of hydroxyl groups $F = 3$ is fixed for glycerol in this work, bounds for OH are equivalent to further bounds on M :

$$\frac{1000 M_{\text{KOH}} F}{OH_{\max}} \leq M \leq \frac{1000 M_{\text{KOH}} F}{OH_{\min}} . \quad (7.39)$$

The desired properties depend largely on the application case. Thus, the application case determines whether the bounds for OH or M are tighter. Although Eq. (7.35) for calculation of T_g is non-linear with respect to ν_i , the product design constraints in Eq. (7.38) can be re-formulated as linear constraints:

$$\sum_i (T_{g,\min} M_i - Y_{g,i}) \nu_i \leq Y_{\text{St}} - T_{g,\min} M_{\text{St}} , \quad (7.40)$$

$$\sum_i (Y_{g,i} - T_{g,\max} M_i) \nu_i \leq T_{g,\max} M_{\text{St}} - Y_{\text{St}} . \quad (7.41)$$

7.3.4 Computational structure of allocation methods in LCA

To integrate the computational structure of co-product allocation of LCA in product-process design, it is helpful to review the general computational structure of LCA in matrix form. In LCA, process systems are typically modeled as set of linear equations. The product under study is specified in the functional unit as vector f . The dimension of vector f equals the number of economic flows of the process system. LCA process data are given as technology matrix A and intervention matrix B . Each entry $a_{i,j}$ of A quantifies the economic flow of product i to process j . To supply only the product flow in f , matrix A is scaled with a scaling vector s (Heijungs and Suh, 2002):

$$A(\nu) \cdot s = f . \quad (7.42)$$

For the process of polyol synthesis modeled by Eq. (7.31), the corresponding entries in A contain the product variables ν . Thus, the mass balances for PE, PC and POM in Eqs. (7.42) are non-linear with respect to the design variables s and ν . The environmental impacts h associated with production of the product flow in f are:

$$h = (Q \cdot B) \cdot s, \quad (7.43)$$

where matrix B contains the elementary flows (rows in B) exchanged between processes (columns in B) and the environment. Matrix Q contains characterization factors to aggregate elementary flows into environmental impact indicators (see Fig. 3.6).

The process superstructure in Fig. 7.6 shows that many upstream processes of polyol production generate co-products. Due to these co-products, the set of equations (7.42) is over-determined and, in general, no scaling vector s exists to supply only the polyol without any co-products. To still obtain specific environmental impacts for polyol production, three methods exist in LCA to introduce additional degrees of freedom: system expansion, avoided burden and allocation¹² (section 3.2.4). The computational structure of these methods is briefly explained in the following section to illustrate that the optimization problem remains structurally identical. Furthermore, the additional degrees of freedom are highlighted. Details regarding the computational structure and the construction of involved matrices can be found in Heijungs and Suh (2002) and Jung et al. (2014).

System expansion. System expansion includes all co-products in an expanded functional unit $f_{\text{exp}} = f + \tilde{f}$, where f contains only the original product, here the polyol, and $\tilde{f}$ contains the unknown quantities of the co-products. Thereby, the environmental impacts are determined for a basket of products. For system expansion, the first two equations of NLP (7.32) can be specified as follows (see Appendix D.2.1):

$$\begin{aligned} \min_{s, \nu, \tilde{f}} \quad & h = Q \cdot B \cdot s, \\ \text{s.t.} \quad & \begin{pmatrix} A(\nu) & -I \end{pmatrix} \cdot \begin{pmatrix} s \\ \tilde{f} \end{pmatrix} = f. \end{aligned} \quad (7.44)$$

Avoided burden. The co-products of the polyol supply chain can be considered to avoid the production of these products by alternative processes. The alternative processes cause environmental burdens. These burdens can thus be avoided by co-production. The co-products are therefore credited with an ‘avoided burden’. Process data of the alternative ‘avoided burden’ processes are contained in matrices A_{avo} and

¹²In this section, allocation methods refer to system expansion, avoided burden and allocation. Allocation alone refers to the proportional allocation based on mass, energy or price.

B_{avo} . For the avoided burden approach, the first two equations of NLP (7.32) can be re-formulated as follows:

$$\begin{aligned} \min_{s, s_{\text{avo}}, \nu} \quad & h = Q \cdot (B - B_{\text{avo}}) \cdot \begin{pmatrix} s \\ s_{\text{avo}} \end{pmatrix}, \\ \text{s.t.} \quad & (A(\nu) - A_{\text{avo}}) \cdot \begin{pmatrix} s \\ s_{\text{avo}} \end{pmatrix} = f. \end{aligned} \quad (7.45)$$

Allocation. Allocation splits a process with n co-products into n processes with only one product each. The inputs in A and emissions in B are allocated to the single-product processes according to the co-products' share in mass, energy content or economic value. The allocation criteria can be cast into a matrix C (Jung et al., 2014). With matrices T_1 , T_0 and U that handle the process splitting, the first two equations of NLP (7.32) can be re-formulated for allocation as follows (Jung et al., 2014):

$$\begin{aligned} \min_{\tilde{s}, \nu} \quad & h = Q \cdot (B \cdot T_0) \cdot \tilde{s}, \\ \text{s.t.} \quad & [U \circ (A(\nu) \cdot T_1)] \cdot C \cdot \tilde{s} = f. \end{aligned} \quad (7.46)$$

Since the process splitting increases the number of processes, the dimension of $\tilde{s}$ in Eqs. (7.46) is also increased compared to s in Eqs. (7.42)-(7.43).

7.3.5 Application of allocation methods in life-cycle design

The presented allocation methods in Eqs. (7.44)-(7.46) show structural similarities. For example, the structure of system expansion is identical to avoided burden with $A_{\text{avo}} = I$ and $B_{\text{avo}} = 0$. This means that system expansion is equivalent to avoided burden where no credits are assigned to the co-products (see Appendix D.2.1).

Furthermore, all methods introduce additional degrees of freedom ($\tilde{f}$, s_{avo} , $\tilde{s}$) that are required to obtain a feasible solution. However, not all degrees of freedom are necessarily required for a feasible solution. Moreover, allowing for all degrees of freedom might not even be reasonable as discussed for each allocation method in the following. Therefore, the application of allocation methods in life-cycle design is not trivial.

System expansion. In general, *all* economic flows could be added to $\tilde{f}$. This would allow for production of unlimited amounts of co-products and also intermediate products. In most cases, the design approach minimizes production of co-products and intermediate products since their production is associated with GHG emissions. Hence, allowing the production of unlimited amounts of all products is typically not problematic. However, direct air capture (DAC) provides CO₂ with net negative GHG

emissions (section 6.3.1). Thus, the design approach minimizes the overall GHG emissions h by maximizing the amount of CO₂ provided by DAC. Consequently, the optimal expanded functional unit f_{exp} includes the polyol and an infinite amount of CO₂ from DAC ($\tilde{f}_{\text{DAC}}, s_{\text{DAC}} \rightarrow \infty$). However, this solution is degenerate since DAC is employed far beyond the amount of CO₂ actually needed for polyol production. To avoid these solutions, any product i that can be produced with net negative GHG emissions should be produced only in the amount actually required for polyol production. This can be achieved by setting $\tilde{f}_i = 0$. This means these products are not allowed to ‘leave’ the system boundaries. However, the a-priori identification of processes with net negative GHG emissions might not be obvious for highly integrated supply chains. Nevertheless, system expansion can be used to identify inevitable co-products: if setting $\tilde{f}_i = 0$ still yields a feasible solution, the economic flow i is an evitable co-product; if not, co-product i is inevitable.

Avoided burden. Avoided burden processes could be added to the superstructure for *all* products from multi-product processes. However, if the CO₂ credit v from the avoided burden is larger than the CO₂ emissions u of the multi-product process, a net GHG sink is created ($u - v < 0$; Fig. 3.5), leading to a similar problem as discussed for DAC in system expansion: Both the multi-product process i and the avoided burden process j are employed infinitely ($s_i, s_{\text{avo},j} \rightarrow \infty$). To prevent the infinite employment of both processes in this case, the avoided burden process should be limited ($s_{\text{avo},j} \leq \hat{s}_{\text{avo},j}$): if the co-product is evitable, it is possible to set $s_{\text{avo},j} = 0$; if the co-product is inevitable, a reasonable upper bound ($\hat{s}_{\text{avo},j}$) should be selected that reflects the technically possible substitution potential of the avoided burden process.

Allocation. Applying allocation to *all* multi-product processes in the supply chain can also lead to degenerated optimization due to artificial decoupling of the co-production. For example for the power plant with CO₂ capture, a mass-based allocation yields CO₂-free electricity since all CO₂ emissions are allocated to captured CO₂ as feedstock. CO₂-free electricity leads to employment of air-capture to provide CO₂ for PC and POM units while captured CO₂ from the power plant is simply discarded. To maintain the coupled production of multi-product processes where possible, allocation should not be applied to evitable co-products.

7.3.6 Environmentally optimal polyols and supply chain

For minimal global warming impacts, polyol composition and supply chain details are presented in Table 7.1 for alternative allocation methods. The top part presents the product property constraints and obtained properties as well as the polyol compositions. The bottom part gives production amounts of selected supply chain processes.

First, common features of the optimal solution are discussed for the alternative allocation methods. Then, the distinct features are presented separately for each allocation method.

For all considered allocation methods, the molar mass M equals the upper bound $M_{\max}$. This is due to the large global warming impact of the considered glycerol production process via epichlorohydrin (PE International, 2012). Since the impact of considered glycerol production is larger than the impacts of the polyol building blocks, the LCD approach minimizes the mass content of glycerol in polyols to 3 % by extending the polyols to the maximum chain length and thus maximum molar mass $M_{\max}$. Alternatively, glycerol can be obtained as abundant co-product from bio-diesel production with expectedly lower global warming impact (Ciriminna et al., 2014). For extremely low impacts of glycerol, the minimal chain length for polyols might be then optimal. Another common feature among allocation methods is that no poly-ether (PE) units are incorporated into the polyol. This is due to the fact that the impact of PE is larger than the impacts of the other building blocks regardless of the considered allocation method. Regarding the supply chain, methanol required for POM is produced exclusively by the CO₂/H₂ process. In almost all cases, CO₂ is captured from the power plant. H₂ is always produced in the fossil-fueled processes steam cracker and steam reforming.

System expansion. The optimal polyol composition is based mainly on POM units (79 %) and on PC units (18 %) and the starter (3 %). POM units are used since the POM supply chain provides only a few co-products. In total, 408 kg of co-products are produced along the entire supply chain including 145 kg styrene, 101 kg N₂, 63 kg CH₄, 51 kg butadiene, 26 kg toluene, 19 kg ethylene, and 3 kg xylene. Not all potential co-products, i.e., benzene, O₂, heat and electricity, are included in $\tilde{f}$.

Avoided burden. The optimal polyol consists of mostly PC units (84 %) and of POM units (14 %) and the starter (3 %). Further incorporation of PC units is limited by $T_{g,\max}$ since PC units have the largest group contribution $Y_{g,PC}$ to T_g of the considered polyol building blocks. The limitation by T_g underlines the importance to consider product properties in the design approach. PC units are always produced together with various co-products. In particular, many co-products occur in the significantly employed steam cracker. For production of 1,000 kg polyol, this approach leads to assigning credits for 1854 kg of co-products including 661 kg styrene, 460 kg N₂, 285 kg CH₄, 232 kg butadiene, 118 kg toluene, 85 kg ethylene and 13 kg xylene. Hence, the avoided burden approach favors co-production compared to system expansion where no credits are assigned to co-products.

Allocation. For the considered allocation criteria mass, energy and price, the optimal polyols consist of glycerol, POM and PC units. PC content is highest for mass allocation and no PC units are incorporated for economic allocation. PO for PC units is exclusively produced in the PO-SM process where a large share of emissions are allocated to the co-product styrene monomer (SM). For mass- and energy-based allocation, CO₂ is exclusively obtained from the power plant. For economic allocation, the

Table 7.1: Polyol composition and production amounts in kg of selected intermediates in the polyol supply chain for minimal carbon footprints of 1,000 kg polyol for alternative allocation methods. Property values are marked with an asterisk (*) if a corresponding constraint is active.

			System expansion	Avoided burden	Allocation by:		
					Mass	Energy	Price
Properties	min	max					
M [g/mol]	2000	3500	3500*	3500*	3500*	3500*	3500*
OH [-]	40	100	48	48	48	48	48
T_g [K]	173	233	191	233*	206	202	177
Product composition in wt%	Starter PC POM	 (no PE units incorporated for all allocation methods)					
Intermediate	Process						
PO [kg]	HPPO		39	152	0	0	0
	PO-SM		66	260	214	183	0
Methanol [kg]	CO ₂ /H ₂		948	298	717	782	1169
	Syngas		0	0	0	0	0
CO ₂ [kg]	Air capture		0	0	0	0	1276
	Power plant		1382	723	1148	1214	331
H ₂ [kg]	Steam cracker		9	34	134	147	219
	Electrolysis		0	0	0	0	0
	Steam ref.		171	29	0	0	0
Sum of all co-products leaving the system boundary [kg]			408	1854	-	-	-

non-allocated power plant process alone cannot provide enough CO₂ required for PC and POM units and thus, CO₂ is also obtained from air capture. The opposite effect can be observed for H₂: Although large amounts of H₂ are required (134-219 kg), H₂ is exclusively obtained from the allocated steam cracker process. The allocated steam cracker process can be employed independently from the originally coupled co-products in the steam cracker. In the physical reality, however, co-products in the steam cracker are produced and utilized or disposed. Thus, application of allocation in LCA can lead to physically non-meaningful supply chains.

7.3.7 Recommendation for allocation methods in LCD

The application of alternative allocation methods leads to large variations in the optimal polyol composition and supply chain characteristics. Thus, the question remains which allocation method should be chosen and, derived from this choice, how polyols should be synthesized optimally. In the following, allocation methods are interpreted in the specific context of life-cycle *design*. This interpretation for LCD is contrasted with the conclusions for allocation methods in product-specific life-cycle *assessment* (section 4.2). Finally, a recommendation for allocation methods is derived for LCD.

The purpose of LCD is to identify an environmentally optimal product composition and supply chain that together lead to minimal environmental impacts. This environmentally optimal solution is *better* than any other feasible solution. Hence, the LCD approach has a *comparative* character and is more similar to comparative and consequential LCA than to attributional LCA. This requires the numerous feasible solutions to be comparable to each other. Furthermore, in LCD, one is not primarily interested in the absolute value of the environmental impacts. Rather, LCD aims at identifying the optimal process and product parameters that lead to minimal environmental impacts. In the following, the alternative multi-functionality approaches are verified with respect to comparability and physical meaningfulness of feasible solutions.

System expansion is frequently recommended as first-choice method to treat multi-functionality problems in LCA, for both comparative and attributional LCA studies (cf. LCA framework for CCU in Fig. 4.9). The application of system expansion in LCD is expected to lead to supply chains with few co-products since no credits are assigned (see Appendix D.2.1). However, different amounts of co-products will most likely occur in the expanded functional units $\tilde{f}$ for the numerous feasible solutions, which prohibits a sound comparison of feasible solutions for each iteration of the optimization. Alternatively, one could define a common expanded functional unit that all feasible solutions have to fulfill. However, it cannot be guaranteed that such a common expanded functional unit exists. While the motivation of LCD is to find the

optimum among a large number of feasible solutions, this large number of alternative solutions now prohibits the comparison of alternatives. In contrast to LCD, only a single or handful alternatives are typically assessed in LCA, where system expansion is advisable. For LCD however, the author does not recommend system expansion due to the missing comparability of numerous alternatives.

Comparative LCA studies typically favor the application of avoided burden (Pelletier et al., 2015). Avoided burden implies a comparison and is therefore well suited for multi-functionality treatment in LCD. For product-specific footprints in LCA, the avoided burden approach has been found to be problematic mainly due to offsetting the absolute footprint values (section 4.2). The offsetting problem is not relevant in LCD since the primary goal of LCD is not to determine minimal absolute footprints but to identify environmentally optimal product and process parameters leading the a maximum footprint reduction. For LCD, the author recommends to apply avoided burden if infinite employment of avoided burden processes can be prevented and if avoided burden data are available.

If avoided burden data are not available, it might be necessary to apply allocation to introduce the required degrees of freedom. While allocation is preferred for obtaining absolute product-specific LCA-footprints for labeling and reporting (section 4.2 and Pelletier et al. (2015)), allocation can lead to physically non-meaningful solutions in LCD. This is problematic since the goal of LCD is to find an optimal but also technically feasible and meaningful product and process system. In contrast, in section 4.2, allocation is recommended for ‘bare’ accounting purposes of existing or already designed and thus technically meaningful systems. For LCD however, the author does not recommend allocation as first-choice method to treat multi-functionality due to possible non-meaningful solutions.

In the author’s opinion, the avoided burden approach is best suited in the considered LCD for polyols due to comparability and physical meaningfulness of feasible solutions. Allocation should only be applied if avoided burden processes and data are not available. This recommendation for avoided burden and allocation in LCD is in line with the framework for comparative LCA presented by Jung et al. (2013). Following the recommendation in the case study, polyols should be synthesized mainly from PC units and to a minor extent from POM units. However, the optimal polyol composition is only valid for the considered application (i.e., property constraints) and the chosen avoided burden processes. In other case studies, other allocation methods might be favorable. In any case, the effect of alternative allocation methods should always be systematically assessed in LCA-based process design.

7.3.8 Summary for life-cycle design of polymers

In this section, an approach is presented for coupling an integrated product and process design with LCA. This life-cycle design (LCD) approach allows to simultaneously exploit the degrees of freedom in product and supply chain design while minimizing environmental impacts. The LCD approach has been applied to polyols that can be directly and indirectly synthesized from CO₂. In the example, CO₂ should always be incorporated into polyols, directly via PC and/or indirectly via methanol and POM units. The direct incorporation of CO₂ is, however, limited by the desired product properties underlining the importance to include product properties in LCD.

Furthermore, allocation methods from LCA are systematically integrated to account for co-products in the supply chain. The influence of allocations methods on LCA results has received much attention in the literature. However, alternative allocation methods have not yet been analyzed systematically in an environmental design approach. Thus, the experience from LCA regarding allocation methods should be transferred to LCD. However, this section shows that already the application of allocation methods itself is not trivial in LCD: the optimization algorithm of LCD also exploits choices in allocation methods leading to degenerate solutions. To prevent degenerate solutions, unnecessary allocation choices should be limited manually.

For CO₂-based polyols, the alternative allocation methods lead to very different optimal polyol compositions and supply chain structures. To determine the environmentally optimal polyol and supply chain, one must select an appropriate allocation method. While system expansion and economic allocation have been recommended for accounting purposes in product-specific life-cycle *assessment*, the author recommends avoided burden as first-choice method and proportional allocation as last resort for the purpose of life-cycle *design*. In the author's opinion, avoided burden reflects best the comparative character of LCD and guarantees comparability and technical meaningfulness of the numerous feasible solutions. However, the developed recommendation for LCD serves only as starting point. The LCD approach including the recommendation for allocation methods should be applied to other case studies to verify their applicability and validity.

Summary and conclusions

Carbon dioxide (CO₂) Capture and Utilization (CCU) is primarily motivated by providing an alternative carbon source and reducing CO₂ emissions. However, CCU is inherently challenging due to the substantial energy demands for capture and conversion of CO₂. The intuitively expected benefits are not given by default. Thus, a reliable environmental assessment is required.

A reliable environmental assessment typically needs comprehensive data such as mass and energy balances. However, many CCU processes are at early design stages where data availability is limited. Therefore, easily accessible ad-hoc metrics are frequently used as indicators for environmental impacts of CCU. However, it is shown that these metrics are not suited for assessing the actual environmental impacts of CCU (section 2.4.2). For this purpose, Life-Cycle Assessment (LCA) is advocated as suitable methodology. Despite the suitability of LCA, its application to CCU is not yet common practice due to the limited data availability and the apparent complexity of LCA.

To facilitate the application of LCA for CCU, this thesis provides a jargon-free introduction to LCA specifically for CCU and directed at LCA novices (chapter 3). Although the general concept of LCA is easily understandable, three particularly important pitfalls have been identified (chapter 4). The first pitfall is to intuitively consider the utilized CO₂ as negative greenhouse gas (GHG) emission. Instead, CO₂ should be considered as feedstock with its own production emissions. Therefore, the CO₂ source and the capture process should be included in the assessment. Since CO₂ point sources provide a main product and co-produce CO₂ as feedstock, the overall CCU system also delivers two products: the original main product at the CO₂ point source and the CO₂-based product or service from the utilization process. If product-specific LCA results are desired, the second pitfall is how to allocate the environmental impacts to the individual products. Whenever the scope of the study allows, system expansion should be used and environmental impacts should be expressed for a

basket of products. In system expansion, ambiguous choices are avoided. If, however, product-specific LCA results are required, economic allocation should be used as only generally applicable allocation criterion. Assigning credits for avoided burdens might lead to misleading negative global warming impacts and does not generate environmental incentives for all involved parties. The third pitfall is using the CO₂ storage duration as equally important metric as the global warming impact. Integration of the CO₂ storage duration into a time-corrected global warming metric shows that the beneficial effect of the CO₂ storage duration on the climate is generally overestimated. To avoid the pitfalls, a framework is presented.

The presented framework for LCA of CCU is applied to an industrial case study for production of CO₂-based polyols for polyurethane production (chapter 5). This LCA constitutes one of the first LCA studies for CO₂-based polymers. In this study, CO₂ is obtained from a pilot plant for CO₂ capture from power plant flue gases. In a nearby pilot plant for polyol production, up to 30 wt% can be incorporated into polyols with suitable properties for polyurethane production. A cradle-to-gate LCA for CO₂-based polyol production shows that the overall CCU process is not a GHG sink. However, utilization of CO₂ allows for significant reductions of GHG emissions, fossil fuel use, and other environmental impacts. The origin of the environmental impacts includes the obvious effect of capturing instead of emitting CO₂ at the power plant. The much larger effect is the substitution fossil-based feedstocks that are energy- and emission-intensive. In total, GHG emissions are reduced by up to 3 kg CO₂-eq per kg CO₂ utilized.

In contrast to the industrial case study, many CCU processes are at early design stages. Here, degrees of freedom can still be exploited to optimize product and process performance and to minimize associated environmental impacts. One such degree of freedom for CCU processes is the selection of the CO₂ source. So far, CO₂ capture is often limited to fossil-fueled power plants. The scope for CO₂ capture is extended to analyze all considered CO₂ sources for CO₂ utilization in an environmental assessment (chapter 6). To select CO₂ sources with minimal environmental impacts, the environmental-merit-order (EMO) curve is introduced. The EMO curves ranks CO₂ sources according to the environmental impact due to CO₂ capture from these sources over their amounts of available CO₂ supply. The EMO curves for Europe underline the CO₂ concentration as decisive factor for the energy demand and thus the environmental impacts of CO₂ capture. Therefore, CO₂ should generally be captured from almost pure sources such as in production of hydrogen, ammonia and ethylene oxide, in natural gas processing, and in IGCC power plants, followed by pulp and paper plants, power plants and iron and steel plants. Due to the low CO₂ concentration in

ambient air, air capture has the largest energy demand and thus causes highest fossil resource depletion at lowest CO₂ emission reductions. For expected CO₂ demands, the environmentally favorable CO₂ point sources can provide enough CO₂. Finally, environmentally favorable locations for CO₂ supply, so-called CO₂ oases, are identified to be sited in the center of Europe. Nevertheless, large amounts of CO₂ can be obtained anywhere in Europe with low environmental impacts from CO₂ capture.

Having identified favorable CO₂ sources, environmentally promising processes for CO₂ utilization should be designed. For this purpose, process design is coupled with LCA to rigorously minimize the environmental impacts of CO₂ utilization processes (chapter 7). For CO₂ hydrogenation reactions, an LCA-based process design approach is presented to identify optimal reaction schemes (section 7.2). A graphical solution provides useful insights on threshold relations for the provision of the reactants CO₂ and H₂. The approach is applied to methanol synthesis from the potential reactants CO₂, hydrogen (H₂), methane, water and oxygen. The threshold relations for methanol synthesis are combined with the EMO curve for CO₂ capture. The combination allows determining the maximum viable global warming impact for H₂ production that is required to still render an exclusively CO₂-based methanol synthesis environmentally favorable. An exclusively CO₂-based methanol synthesis requires H₂ production from renewable energy sources such as electrolysis powered by wind turbines. For H₂ from fossil-based steam reforming, only small amounts of CO₂ should be used, as already done today.

While the considered products from CO₂ hydrogenation typically yield commodity chemicals with indistinguishable properties, utilization of CO₂ for polymers provides novel degrees of freedom to modify the polymer properties. Furthermore, direct and indirect utilization of CO₂ allow for new process routes in the entire supply chain of polymers. These degrees of freedom are exploited to minimize environmental impacts in the design of polyols with desired properties and associated processes in the supply chain. For this purpose, an LCA-based integrated product-process design approach is presented for CO₂-based polyols (section 7.3). This design approach allows simultaneously exploiting the degrees of freedom in product and supply chain design while minimizing environmental impacts. In the example, incorporation of CO₂ is limited by the desired product properties, which underlines the importance to include product properties in the design approach. To account for co-products in the polyol supply chain, alternative allocation methods from LCA are systematically integrated. Alternative allocation methods have been found to lead to very different polyol compositions and employed processes in the polyol supply chain. Thus, a recommendation for allocation methods in LCA-based process design approaches is given.

In summary, the presented tutorial and framework facilitate the application of LCA for CCU. The LCA-based design approaches support the selection of CO₂ sources, the identification of optimal reaction schemes of CO₂ hydrogenation processes at early stages, and the identification of an optimal polymer composition and corresponding supply chain.

The illustrative examples and polyol case study and show that CCU processes for production of chemicals do typically not act as GHG sink. Furthermore, CO₂ will usually be released at the end of the product life cycle and thus, the cradle-to-grave GHG emissions for CCU are strictly positive. Nevertheless, CCU processes have the potential to significantly reduce GHG emissions and fossil resource depletion compared to the fossil-based alternative. A pre-requisite for many CCU processes to reduce environmental impacts is the provision of clean energy. However, energy provision has so far been the major cause of both fossil resource depletion and GHG emissions.

No general assertions can be made regarding the environmental benefits of CCU. Instead, LCA studies for specific CCU processes are required. Since the environmental benefits are not always guaranteed, LCA should be included in scientific research, political discussions and regulatory legislation.

CO₂ capture

A.1 CO₂ capture concepts for combustion processes

For combustion processes, CO₂ capture concepts are classified according to where and how the combustion takes place in post-combustion, pre-combustion, oxy-fuel combustion, and chemical looping combustion (Fig. A.1).

Post-combustion capture. Post-combustion capture can be considered as retro-fit option for existing stacks where CO₂ is separated from the combustion flue gases. Due to combustion with air, these flue gases contain large fractions of N₂. Depending on the fuel type and the air-fuel ratio, the CO₂ concentration in combustion flue gases is typically between 3 and 15 % (Thambimuthu et al., 2005).

Pre-combustion capture. In pre-combustion capture, CO₂ is captured before combustion (Markewitz et al., 2012; Thambimuthu et al., 2005). For this purpose, the fuel is partially oxidized with oxygen to syngas. In a subsequent water-gas shift reaction, CO is converted to CO₂ and the resulting gas contains only H₂ and 15-60 % CO₂ (Thambimuthu et al., 2005). The higher CO₂ concentration and also higher pressure compared to post-combustion capture allow for easier CO₂ separation. However, air separation, gasification and shift processes have also be taken into account in the assessment of pre-combustion capture. Finally, H₂ is combusted without any CO₂ emissions.

Oxy-fuel combustion. Oxy-fuel combustion (OFC) refers to a combustion of fuels with pure oxygen and recycled flue gas. The flue gas contains only CO₂ and water vapor, which is easily separated by condensation. However, gas separation is still required for provision of pure oxygen. Here, cryogenic air-separation (Mac Dowell et al., 2010) and polymeric or ceramic membranes (Engels et al., 2010) are typi-

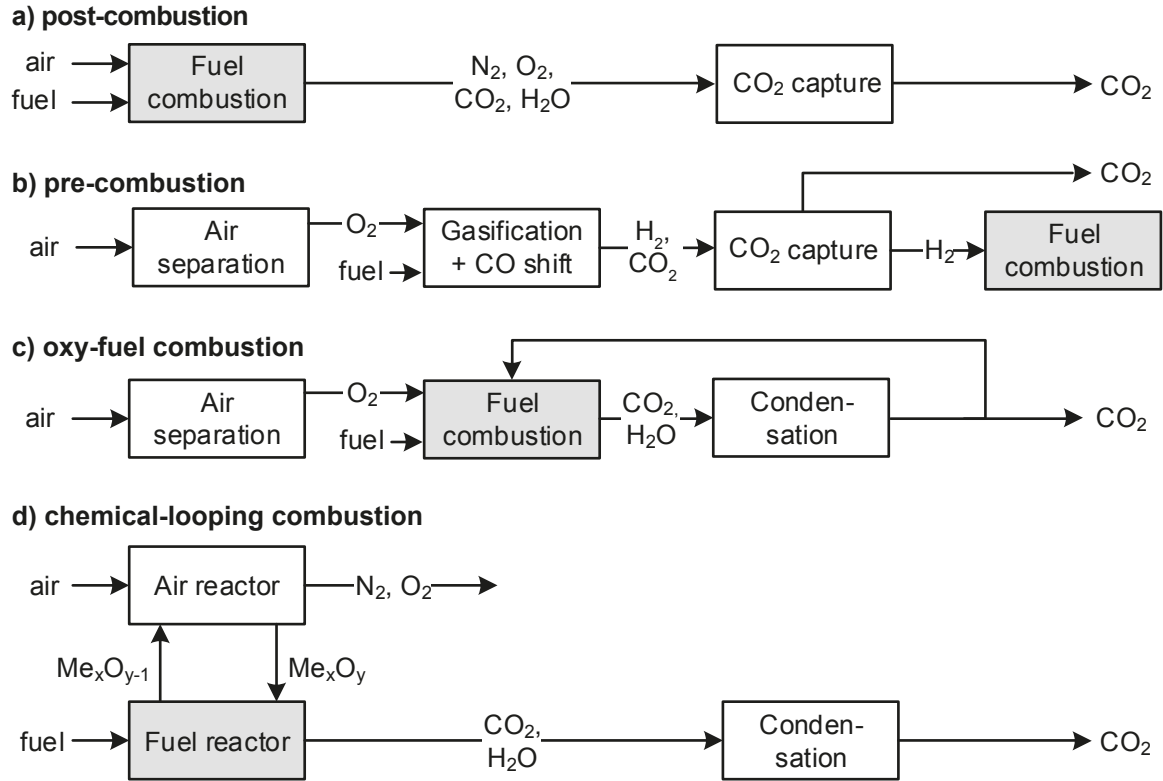


Figure A.1: CO_2 capture concepts for combustion processes.

cally used. For coal-fired power plants, oxy-fuel combustion leads to an overall lower energy penalty compared to post-combustion capture, improved process flexibility, improved combustion efficiency and reduced NO_x and SO_x formation (Boot-Handford et al., 2014). Furthermore, a circulating fluidized bed combustion allows (co-)firing of biomass fuels (Boot-Handford et al., 2014) giving oxy-fuel combustion the potential to act as net CO_2 sink.

Chemical-looping combustion. In chemical-looping combustion (CLC), flue gases contain only CO_2 and H_2O . For chemical-looping combustion, the fuel is not in direct contact with oxygen in contrast to oxy-fuel combustion. Instead, oxygen is provided indirectly by an oxygen-carrier material (Lyngfelt et al., 2001). Typical oxygen-carrier materials are metal oxides such as copper and iron oxide (Cao et al., 2006; Lyngfelt et al., 2001). In a fuel reactor, the metal oxide is reduced releasing oxygen and the fuel is combusted to CO_2 and H_2O . Pure CO_2 is easily recovered by condensation of H_2O . The reduced metal oxide is recycled to an air reactor, loaded with oxygen from air and thereby oxidized back to its original state. The reaction in the fuel reactor

is endothermic but the reaction in the air reactor is highly exothermic. An overall energy balance shows that the net heat production is similar to conventional fuel combustion. Since no gas separation is required, CLC has the potential of a low energy penalty for CO₂ capture in power plants, particularly in power plants firing solid fuels (Boot-Handford et al., 2014).

CLC can also be implemented for hydrogen reforming with integrated CO₂ capture. Due to a reduced reactor temperature, chemical-looping based steam reforming has an even increased reforming efficiency compared to conventional steam reforming (Boot-Handford et al., 2014).

A.2 CO₂ capture technologies

For separation of CO₂ from other gases, four main unit operations are frequently used: membranes, cryogenic distillation, adsorption, and physical and chemical absorption (Ebner and Ritter, 2009).

Membrane gas separation. Since CO₂ is smaller than most other gases except for helium (He) and H₂, CO₂ can be separated from many gas streams by being selectively permeated through a porous membrane. The advantages of membrane separation are that no phase change, no solvent and thus no regeneration are involved (Ebner and Ritter, 2009). Furthermore, the equipment is rather simple as only fans and membranes are required. A disadvantage of membrane separation is a trade-off between selectivity and permeability (Aaron and Tsouris, 2005). Thus, capturing a large fraction of high-purity CO₂ from a gas stream requires an increased pressure to drive the separation making the separation energy intensive.

Cryogenic distillation. Cooling a gas mix liquifies its components in order of their boiling points. Cryogenic distillation for CO₂ separation provides very pure and already liquid CO₂, thus facilitating transport. However, cryogenic distillation is extremely energy intensive and requires pre-treatment to remove NO_x, SO_x, water and oxygen (Aaron and Tsouris, 2005).

Adsorption. CO₂ adsorption is the physical adherence of gaseous CO₂ molecules to a solid surface. Low-temperature adsorbent materials include silicate sieves, zeolites, activated carbon and metal organic frameworks (MOFs) (Aaron and Tsouris, 2005; Boot-Handford et al., 2014). CO₂ can be liberated from the adsorbent by decreasing the pressure or increasing the temperature. Typically, the pressure is passed back and forth between two adsorption chambers. This so-called pressure swing adsorption (PSA) generally has a lower energy demand and higher regeneration rate than

temperature swing adsorption (TSA). Whereas adsorption does not require complex equipment, it is only applicable for low concentrations between 0.04 and 1.5 %; moreover, it is often not selective enough resulting in N₂ impurities (Aaron and Tsouris, 2005).

So-called *Calcium Looping* (CaL) is a high-temperature adsorption process where calcium oxide (CaO) and CO₂ react to CaCO₃. Since both the carbonation (=sorption) and calcination (=desorption) processes occur at 700-900 °C, an efficient heat integration is often possible (Boot-Handford et al., 2014). Thereby, CaL results in a relatively low energy penalty of about 6-8 % in power plants (Lin et al., 2011; Martínez et al., 2012). A drawback of CaL is the fast decay of CaO in repeated sorption cycles requiring a large make-up of fresh limestone as CaO source. Therefore, CaL is best integrated in the cement industry, where CaO is the main precursor to cement and already available.

Absorption. CO₂ absorption describes the physical or chemical “incorporation” of CO₂ into the solvent (Aaron and Tsouris, 2005). In physical absorption, the solvent favors the absorption of CO₂ over other components without a chemical reaction taking place. Current physical solvents have a low CO₂ solubility and selectivity. Since CO₂ solubility increases with increasing pressure, physical absorption is preferred under high pressure (Zhenhong et al., 2014). The solvent can be regenerated by reducing the pressure. While the energy demand for regeneration is relatively low, much energy is required for compression of the mixed gas to the required pressure for effective absorption. Typical solvents are methanol in the Rectisol process (Linde, 2014) or glycol ethers in the Selexol process (DOW, 2014) which are industrially implemented for cleaning of natural gas, syngas or hydrogen.

In addition to physical absorption, hydrogen and natural gas cleaning are also using chemical absorption of CO₂ with alkanol-amines (Boot-Handford et al., 2014). Chemical absorption is also the most frequently considered CO₂ capture technology for power plants. Typical solvents are mono-ethanol amine (MEA) (Wagener and Rochelle, 2011) and piperazine (PZ) (Freeman et al., 2009; Rochelle et al., 2011). The desorption is achieved by lowering the pressure and/or more often by increasing the temperature. Heating the regeneration column to desorption temperatures of 120-150 °C requires substantial amounts of energy (Boot-Handford et al., 2014). A low thermal stability of most solvents results in solvent make-up in significant amounts. Furthermore, direct solvent loss due to high volatility and indirectly formed nitrosamines are considered as potential environmental and health hazards (Nielsen et al., 2012; Boot-Handford et al., 2014).

As “green” alternative with no solvent loss, ionic liquids are frequently proposed

(Ramdin et al., 2012). Ionic liquids offer a potentially lower energy demand, are non-flammable, more thermally stable and easier to recycle (Boot-Handford et al., 2014). A main barrier for implementation of ionic liquids for CO₂ capture are their high costs (Mac Dowell et al., 2010).

Alternative absorption processes use inorganic chemisorbents in aqueous solution, e.g., calcium hydroxide (Ca(OH)₂), potassium hydroxide (KOH) and sodium hydroxide (NaOH). Since NaOH can capture CO₂ from very dilute streams, it is often considered in CO₂ capture from ambient air (Goeppert et al., 2012). To avoid the energy-intensive evaporation of large amounts of aqueous sodium carbonate (Na₂CO₃) solution, the solution is recovered by reaction with Ca(OH)₂ to CaCO₃. The formed CaCO₃ precipitates and can be recovered by calcination with oxy-fuel combustion similar to regeneration in Calcium Looping (Keith et al., 2006). The main drawback remains the large energy requirement for regeneration (Goeppert et al., 2012).

Industrial case study: LCA for CO₂-based polymers

B.1 Potential differences in downstream processes

Polyurethane production. The viscosity of polyols increases exponentially with the CO₂ content (Langanke et al., 2014b). An increased viscosity might require extra or stronger pumps in polyurethane processing. However, Langanke et al. (2014b) report that CO₂-based polyols were “*readily processed with standard equipment used in industry for the preparation of polyurethane foams.*” For production of polyurethanes from polyol blends, an extra storage tank for CO₂-based polyols will become necessary.

Polyurethane use. Polyurethane flexible foams from CO₂-based polyols provide similar properties as flexible foams from conventional polyols according to the same recipe (Langanke et al., 2014b). Some properties of CO₂-based foams are even expected to be superior to conventional foams (BMS, 2014). The enhanced properties might allow for a reduced material demand or longer product lifetime. However, these expectations still have to be verified.

Polyurethane end-of-life treatment. End-of-life treatment of polyurethanes depends on the polyurethane application. As first application, polyurethane foams for mattresses are projected. Due to sanitary restrictions, mattresses are incinerated and thermal energy is recovered. With increasing CO₂ content, the heat of combustion of polyurethanes decreases. Therefore, CO₂-based mattresses reduce the recovered energy in thermal utilization. For polyols with 20 wt% CO₂, the heat of combustion is lowered by about 12 % (BMS, 2014). The reduced heat of combustion is also considered as appreciated safety feature for polyurethanes (cf. polyurethane use).

B.2 List of data sources

The following Tables B.1-B.2 contains used datasets from GaBi LCA database (PE International, 2012).

Table B.1: List of LCA process data for conventional and CO₂-based polyols. Part 1.

Process	Name of dataset	Year	Country
CO ₂ source / electricity generation			
Lignite	Lignite mix	2010	DE
CO ₂ capture solvent	Monoethanolamine ^a	2010	RER
Water for CO ₂ cleaning	Tap water; water purification treatment; production mix, at plant; from surface water	2012	EU-27
CO ₂ transport by truck	Truck; diesel driven, Euro 4, cargo; technology mix; 28-32t gross weight/ 22t payload capacity	2012	GLO
Fuel for truck	Diesel mix at refinery; 10 ppm sulphur, 5.75 wt.% bio components	2010	DE
Electricity compensation			
Grid mix	Electricity grid mix; AC, technology mix; consumption mix, at consumer; <1kV	2010	DE

^a LCA data for monoethanolamine as proxy for amine-based solvent were taken from ecoinvent v2.01 database (ecoinvent, 2010) as integrated in GaBi software (PE International, 2012).

Table B.2: List of LCA process data for conventional and CO₂-based polyols. Part 2.

Process	Name of dataset	Year	Country
CO ₂ utilization / polyol production			
Propylene oxide (CHPO)	Propylene oxide (Chlorohydrin process with Cell Liquor)	2012	DE
Propylene oxide (CHPO)	Propylene oxide (Chlorohydrin process with Ca(OH) ₂)	2012	DE
Propylene oxide (PO/TBA; PO/MTBE)	Propylene oxide (Oxirane process); by-product t-butanol	2012	DE
Ethylene oxide	Ethylene oxide (EO) via O ₂ /methane	2012	DE
Glycerol	Glycerine (from Epichlorohydrine)	2012	DE
Steam	Process steam from natural gas 90 %; 90 % efficiency	2010	DE
Compressed air	Compressed air; 7 bar, low efficiency	2010	EU-27
Process water	Process water; ion exchange; production mix, at plant; from groundwater	2012	EU-27
Nitrogen	Nitrogen, via cryogenic air separation	2012	EU-27
Electricity	Electricity grid mix; AC, technology mix; consumption mix, at consumer; <1kV	2010	DE

B.3 Allocation alternatives for cyclic propylene carbonate (cPC)

In chapter 5, the standard allocation procedure for cPC is based on different criteria: feedstocks (PO, CO₂ and glycerin) are allocated according to the feedstock masses incorporated in polyols and cPC, respectively. For example, glycerin is only incorporated into polyols and therefore fully assigned to the polyols. The catalyst is also fully assigned to the polyols. Other inputs (utilities such as steam and electricity) are allocated according to polyol and cPC masses. The effect of alternative allocation options for cPC is assessed (Fig. B.1):

- Mass allocation
- Economic allocation (assumed prices are 1.90 €/kg polyols and 1.20 €/kg cPC)
- 100 % allocation to polyols (worst-case allocation for polyols)

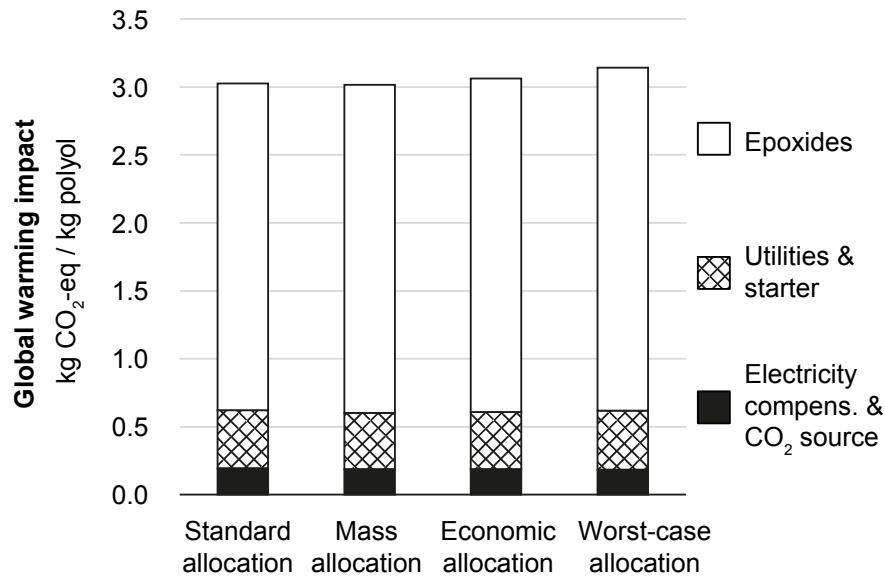


Figure B.1: Global warming impact for polyethercarbonate polyols with 20 wt% CO₂ for alternative allocation options for the by-product cPC: left to right: standard allocation, mass allocation, economic allocation and worst-case allocation. The global warming impacts for alternative allocation options change by only -0.3% (mass allocation) to $+3.8\%$ (worst case allocation) compared to standard allocation.

B.4 Midpoint impact categories

In addition to impact on global warming and fossil resource depletion, other impact categories have also been analyzed. The following Figures B.2-B.8 show midpoint LCA results for (freshwater and marine) eutrophication, ionizing radiation, ozone depletion, particulate matter formation, photochemical oxidant formation, and terrestrial acidification using ReCiPe 1.08 (Hierarchist) methodology (Goedkoop et al., 2013).

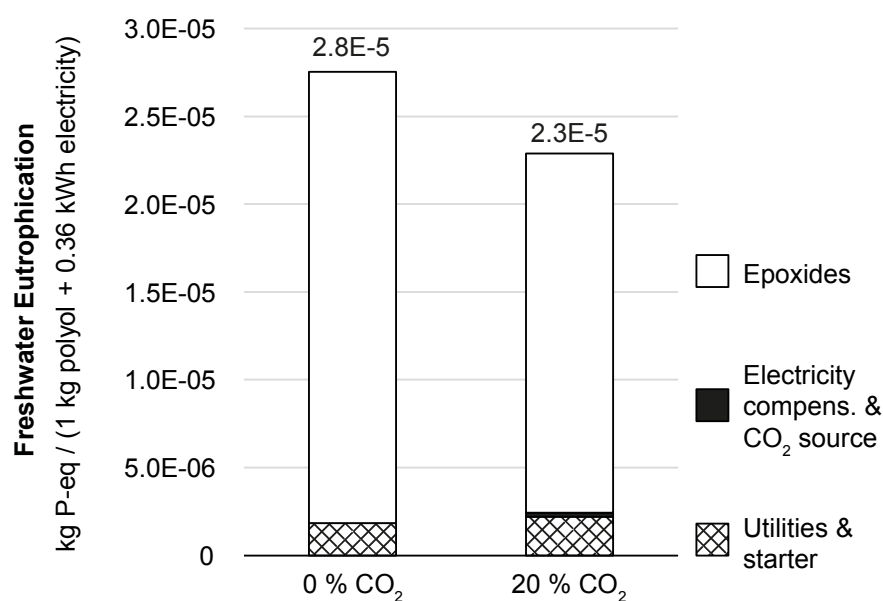


Figure B.2: Freshwater eutrophication in kg P-equivalents for product system of conventional polyether polyols (0 % CO₂, left) and CO₂-based polyether-carbonate polyols (20 % CO₂, right).

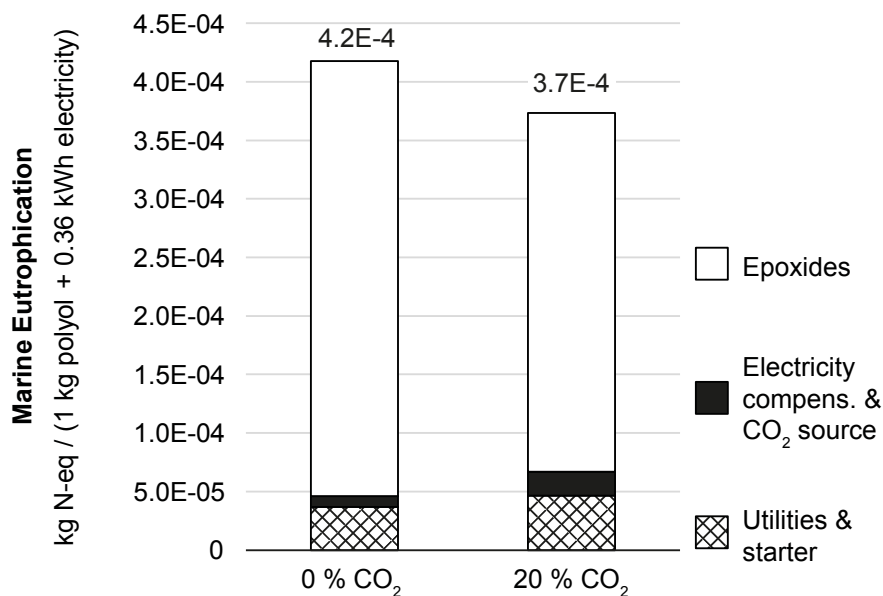


Figure B.3: Marine eutrophication in kg N-equivalents for product system of conventional polyether polyols (0 % CO₂, left) and CO₂-based polyethercarbonate polyols (20 % CO₂, right).

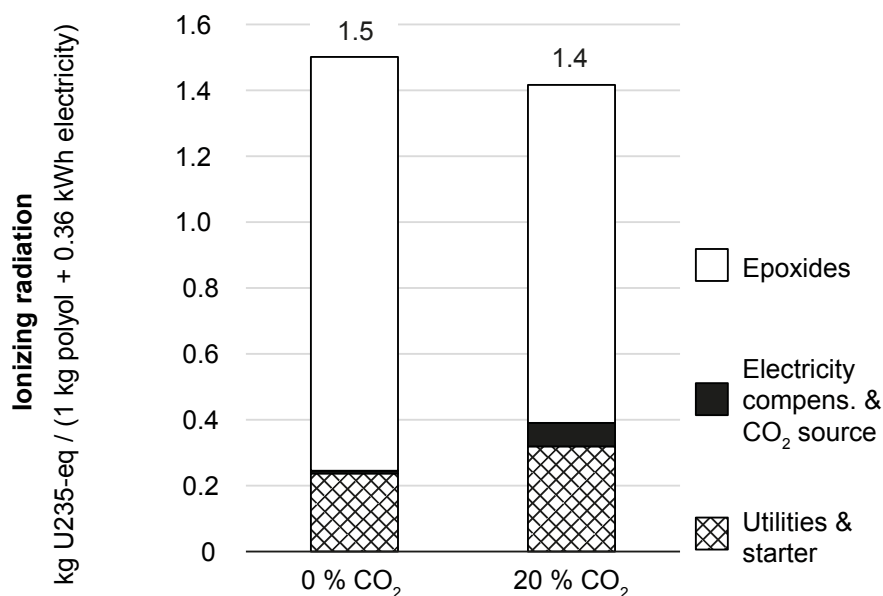


Figure B.4: Ionizing radiation in kg U235-equivalents for product system of conventional polyether polyols (0 % CO₂, left) and CO₂-based polyethercarbonate polyols (20 % CO₂, right).

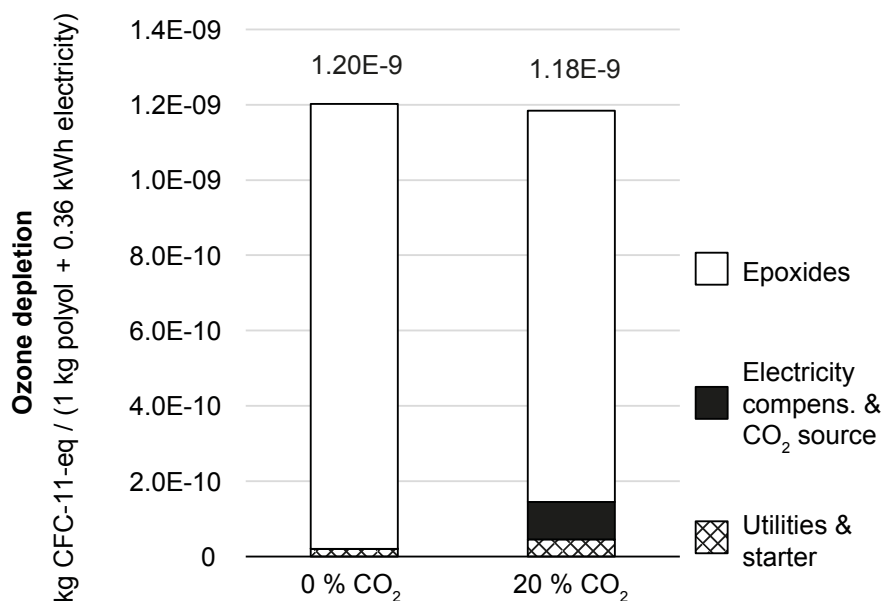


Figure B.5: Ozone depletion in kg CFC-11-equivalents for product system of conventional polyether polyols (0 % CO₂, left) and CO₂-based polyethercarbonate polyols (20 % CO₂, right).

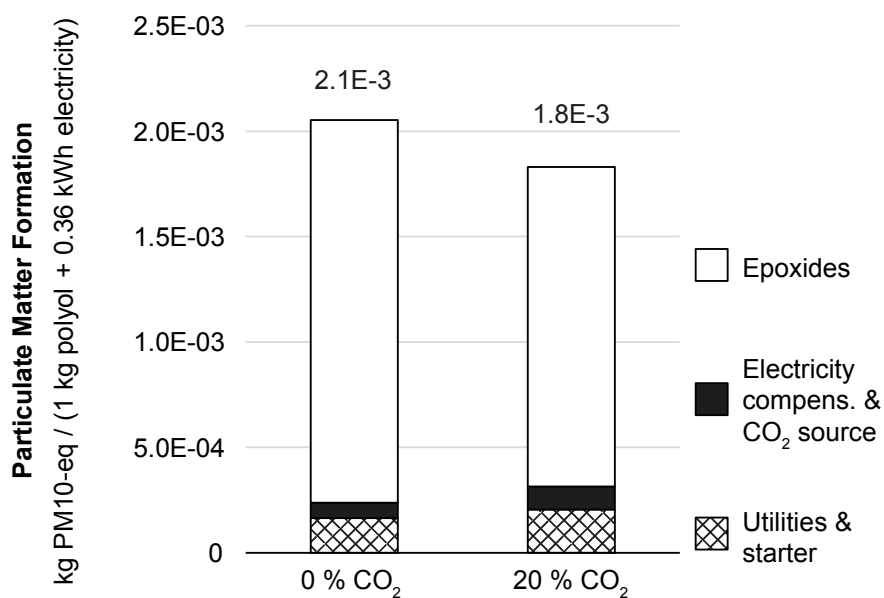


Figure B.6: Particulate matter formation in kg PM1011-equivalents for product system of conventional polyether polyols (0 % CO₂, left) and CO₂-based polyethercarbonate polyols (20 % CO₂, right).

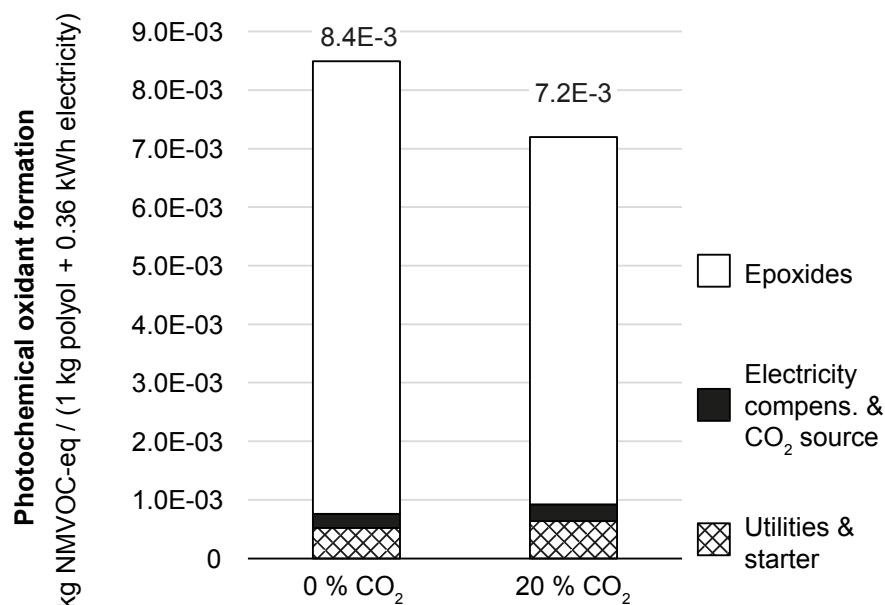


Figure B.7: Photochemical oxidant formation (“summer smog”) in kg NMVOC-equivalents for product system of conventional polyether polyols (0 % CO₂, left) and CO₂-based polyethercarbonate polyols (20 % CO₂, right).

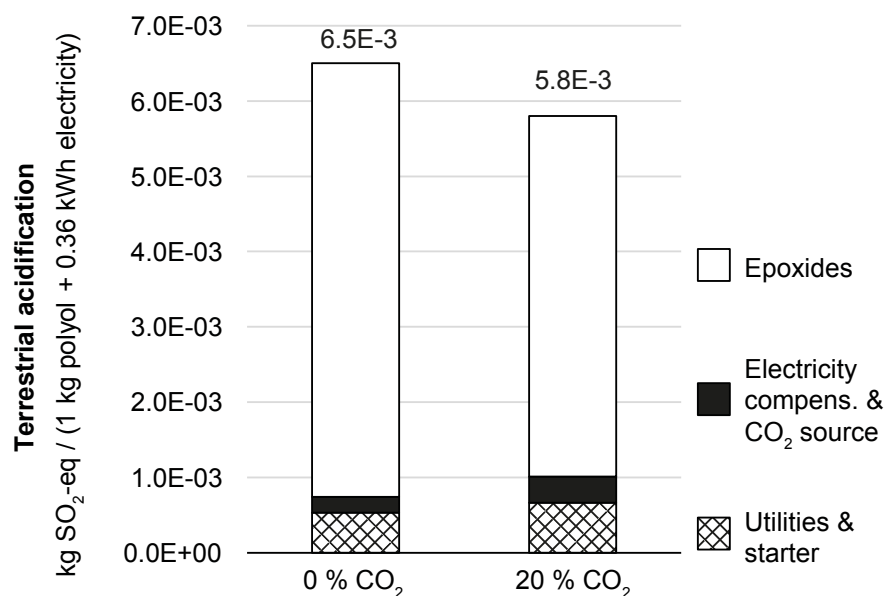


Figure B.8: Terrestrial acidification in kg SO₂-equivalents for product system of conventional polyether polyols (0 % CO₂, left) and CO₂-based polyethercarbonate polyols (20 % CO₂, right).

B.5 Normalized midpoint impact categories

Figs. 5.3 and 5.6 in the chapter 5 and Figs B.2-B.8 show how the benchmark system (polyols with 0 wt% CO₂) and the CCU system (polyols with 20 wt% CO₂) perform in different environmental impact categories. To compare these different categories, one approach is normalization. Normalization can be achieved by dividing the environmental impacts (e.g. in kg CO₂-eq, kg oil-eq etc. per functional unit) by average per-capita emissions (e.g. in kg CO₂-eq/(person-eq · year)) to obtain impact results in a common unit ((person-eq · year) per functional unit). Fig. B.9 shows normalized midpoint impact category results for the benchmark and the CCU system using average per-capita emissions in Europe.

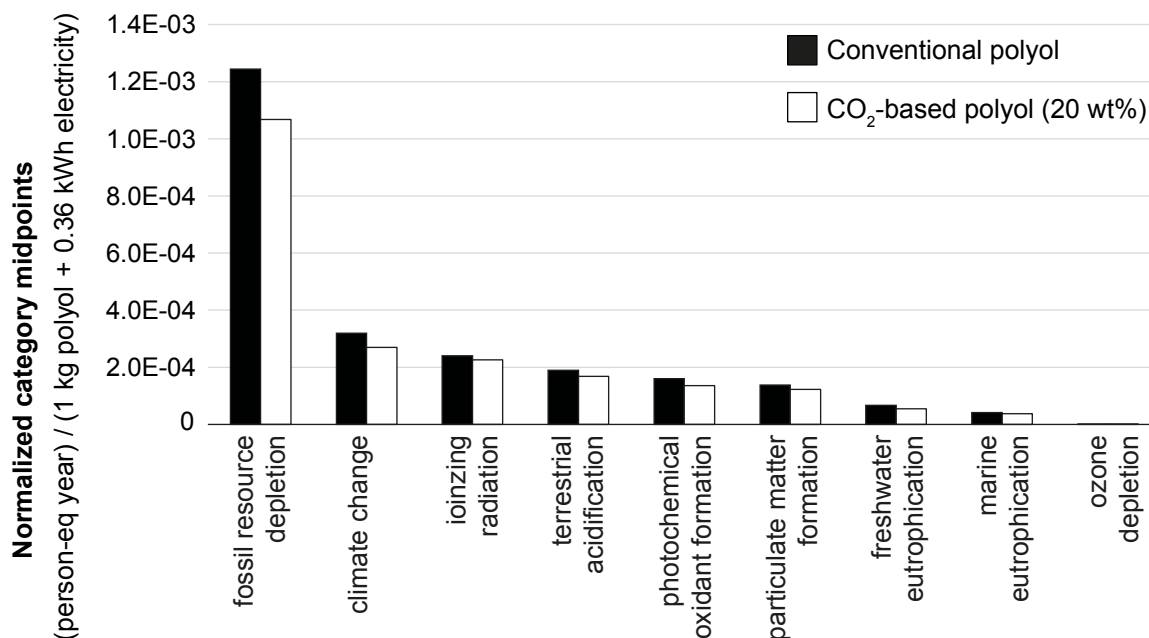


Figure B.9: Normalized midpoint impact categories for product system of conventional polyether polyols (0 % CO₂, left) and CO₂-based polyethercarbonate polyols (20 % CO₂, right) using ReCiPe 1.08 normalization data for Europe. In normalization, initial midpoint results are divided by average European emissions per capita. According to this normalization procedure, fossil resource depletion can be considered as most important environmental impact category for polyol production.

APPENDIX C

Selecting CO₂ sources for CO₂ utilization

C.1 Marginal CO₂ emissions for CO₂ point sources

Marginal CO₂ emissions for CO₂ point sources are obtained by comparing CO₂ emissions of the point source with CO₂ capture (1) to the point source without CO₂ capture (2), divided by the amount of product CO₂ (*cf.* Fig. 1a in section 6.2):

$$m_{\text{CO}_2\text{-eq,marginal}} = \frac{m_{\text{CO}_2\text{-eq,(1)}} - m_{\text{CO}_2\text{-eq,(2)}}}{m_{\text{CO}_2,\text{product}}} . \quad (\text{C.1})$$

Inserting the CO₂ flows for CO₂ point sources as illustrated in Fig. 1a in section 6.2 yields:

$$m_{\text{CO}_2\text{-eq,marginal}} = (m_{\text{CO}_2,\text{el}} + m_{\text{CO}_2,\text{th}} + m_{\text{CO}_2,\text{fuel-supply}} + m_{\text{CO}_2,\text{offgas}} + m_{\text{CO}_2,\text{transport}} - m_{\text{CO}_2,\text{fluegas}}) / m_{\text{CO}_2,\text{product}} . \quad (\text{C.2})$$

The CO₂ emissions $m_{\text{CO}_2,\text{el}}$ from electricity generation are proportional to the specific electricity demand W_{el} per product CO₂, to the amount $m_{\text{CO}_2,\text{product}}$ of product CO₂, and to the CO₂ emissions factor GW_{el} for electricity generation:

$$m_{\text{CO}_2,\text{el}} = m_{\text{CO}_2,\text{product}} W_{\text{el}} GW_{\text{el}} . \quad (\text{C.3})$$

Likewise, the CO₂ emissions $m_{\text{CO}_2,\text{th}}$ from heat generation are proportional to the specific heat demand Q_{th} per product CO₂, to the amount $m_{\text{CO}_2,\text{product}}$ of product CO₂, and to the CO₂ emissions factor GW_{th} for heat generation:

$$m_{\text{CO}_2, \text{th}} = m_{\text{CO}_2, \text{product}} Q_{\text{th}} GW_{\text{th}} . \quad (\text{C.4})$$

Again, the CO₂ emissions $m_{\text{CO}_2, \text{fuel-supply}}$ from fuel supply are proportional to the specific fuel demand Q_{fuel} per product CO₂, to the amount $m_{\text{CO}_2, \text{product}}$ of product CO₂, and to the CO₂ emissions factor $GW_{\text{fuel-supply}}$ for fuel supply:

$$m_{\text{CO}_2, \text{fuel-supply}} = m_{\text{CO}_2, \text{product}} Q_{\text{fuel}} GW_{\text{fuel-supply}} . \quad (\text{C.5})$$

Please note, that $GW_{\text{fuel-supply}}$ only includes the CO₂ emissions from fuel *supply*. CO₂ emissions from fuel *combustion* ($m_{\text{CO}_2, \text{fuel}}$) are proportional to the fuel demand per product CO₂ (Q_{fuel}), to the amount of product CO₂ ($m_{\text{CO}_2, \text{product}}$), and to the specific CO₂ emissions factor for fuel combustion ($e_{\text{CO}_2, \text{fuel}}$):

$$m_{\text{CO}_2, \text{fuel}} = m_{\text{CO}_2, \text{product}} Q_{\text{fuel}} e_{\text{CO}_2, \text{fuel}} . \quad (\text{C.6})$$

CO₂ emissions from fuel combustion ($m_{\text{CO}_2, \text{fuel}}$) can be added to the CO₂-rich flue gas stream from the CO₂ point source. The total amount of CO₂ mixed flue gas stream is denoted as $m_{\text{CO}_2, \text{mixed-fluegases}}$:

$$m_{\text{CO}_2, \text{mixed-fluegases}} = m_{\text{CO}_2, \text{fluegas}} + m_{\text{CO}_2, \text{fuel}} . \quad (\text{C.7})$$

The CO₂ in the flue gas stream from the CO₂ point source is proportional to the amount of product CO₂ ($m_{\text{main-product}}$), and to the CO₂ emissions factor for the main product of the CO₂ point source ($GW_{\text{main-product}}$):

$$m_{\text{CO}_2, \text{fluegas}} = m_{\text{main-product}} GW_{\text{main-product}} . \quad (\text{C.8})$$

A fraction CR of CO₂ in the mixed flue gas stream is then captured. The capture ratio CR is the ratio of obtained product CO₂ and total CO₂ in the waste stream:

$$CR = \frac{m_{\text{CO}_2, \text{product}}}{m_{\text{CO}_2, \text{fluegas}} + m_{\text{CO}_2, \text{fuel}}} \quad (\text{C.9})$$

$$m_{\text{CO}_2, \text{product}} = CR \left(m_{\text{CO}_2, \text{fluegas}} + m_{\text{CO}_2, \text{fuel}} \right) . \quad (\text{C.10})$$

Re-arranged for $m_{\text{CO}_2, \text{fluegas}}$ and combined with Equation (C.6):

$$m_{\text{CO}_2, \text{fluegas}} = \frac{1}{CR} m_{\text{CO}_2, \text{product}} - m_{\text{CO}_2, \text{fuel}} \quad (\text{C.11})$$

$$= m_{\text{CO}_2, \text{product}} \left(\frac{1}{CR} - Q_{\text{fuel}} e_{\text{CO}_2, \text{fuel}} \right). \quad (\text{C.12})$$

The remaining fraction of not captured CO₂ ($m_{\text{CO}_2, \text{offgas}}$) is released to the atmosphere:

$$m_{\text{CO}_2, \text{offgas}} = (1 - CR) (m_{\text{CO}_2, \text{fluegas}} + m_{\text{CO}_2, \text{fuel}}) \quad (\text{C.13})$$

$$= \frac{1 - CR}{CR} m_{\text{CO}_2, \text{product}}. \quad (\text{C.14})$$

The CO₂ emissions from CO₂ transport can be written as:

$$m_{\text{CO}_2, \text{transport}} = m_{\text{CO}_2, \text{product}} GW_{\text{transport}}. \quad (\text{C.15})$$

Combining the expression for the CO₂ flows in Equations (C.3)-(C.15) with Equation (C.2) yields:

$$m_{\text{CO}_2\text{-eq}, \text{marginal}} = W_{\text{el}} GW_{\text{el}} + Q_{\text{th}} GW_{\text{th}} + Q_{\text{fuel}} GW_{\text{fuel-supply}} + \frac{1 - CR}{CR} + GW_{\text{transport}} - \left(\frac{1}{CR} - Q_{\text{fuel}} e_{\text{CO}_2, \text{fuel}} \right). \quad (\text{C.16})$$

With $\frac{1 - CR}{CR} - \frac{1}{CR} = -1$, Equation (C.16) can be re-written as:

$$m_{\text{CO}_2\text{-eq}, \text{marginal}} = -1 + W_{\text{el}} GW_{\text{el}} + Q_{\text{th}} GW_{\text{th}} + Q_{\text{fuel}} (GW_{\text{fuel-supply}} + e_{\text{CO}_2, \text{fuel}}) + GW_{\text{transport}} \quad (\text{C.17})$$

The term $(GW_{\text{fuel-supply}} + e_{\text{CO}_2, \text{fuel}})$ now includes both CO₂ emissions from fuel supply and fuel combustion. Introducing the CO₂ emissions factor $GW_{\text{fuel}} = GW_{\text{fuel-supply}} + e_{\text{CO}_2, \text{fuel}}$ for fuel supply including combustion, one obtains Equation (2) in section 6.2.2:

$$m_{\text{CO}_2\text{-eq}, \text{marginal}} = -1 + W_{\text{el}} GW_{\text{el}} + Q_{\text{th}} GW_{\text{th}} + Q_{\text{fuel}} GW_{\text{fuel}} + GW_{\text{transport}} \quad (\text{C.18})$$

C.2 Marginal CO₂ emissions for air capture

Marginal CO₂ emissions for CO₂ capture from the atmosphere are the CO₂ emissions of the air-capture system, divided by the amount of product CO₂ (*cf.* Fig. 1b in the main article):

$$m_{\text{CO}_2\text{-eq,marginal}} = \frac{m_{\text{CO}_2\text{-eq,air-capture}}}{m_{\text{CO}_2,\text{product}}} \quad (\text{C.19})$$

It is assumed that air capture units are installed close to the CO₂ utilization site. Thus, impacts from transport are neglected. Inserting the CO₂ flows for CO₂ point sources as illustrated in Fig. 1b in the main article yields:

$$m_{\text{CO}_2\text{-eq,marginal}} = \frac{-m_{\text{CO}_2,\text{air}} + m_{\text{CO}_2,\text{el}} + m_{\text{CO}_2,\text{th}} + m_{\text{CO}_2,\text{fuel-supply}} + m_{\text{CO}_2,\text{offgas}}}{m_{\text{CO}_2,\text{product}}} . \quad (\text{C.20})$$

In the case of air-capture, the amount of product CO₂ corresponds to:

$$m_{\text{CO}_2,\text{product}} = CR \left(m_{\text{CO}_2,\text{air}} + m_{\text{CO}_2,\text{fuel}} \right) . \quad (\text{C.21})$$

Re-arranged for $m_{\text{CO}_2,\text{air}}$ and combined with Equation (C.6):

$$m_{\text{CO}_2,\text{air}} = m_{\text{CO}_2,\text{product}} \left(\frac{1}{CR} - Q_{\text{fuel}} e_{\text{CO}_2,\text{fuel}} \right) . \quad (\text{C.22})$$

Combining the expression for the CO₂ flows in Equations (C.3)-(C.5), (C.14), (C.15), (C.22) with Equation (C.20) yields Equation (C.16). Thus, marginal CO₂ emissions for CO₂ capture from the atmosphere can also be obtained Equation (C.18) (Equation (2) of the main article) with $GW_{\text{transport}} = 0$.

C.3 Marginal fossil resource depletion

To obtain impacts on fossil resource depletion, only flows of fossil resources have to be considered. For both cases (CO₂ point sources and air-capture), the following processes use fossil resources:

- electricity generation
- heat generation

- fuel supply
- CO₂ transport

Impacts factors regarding fossil resource depletion are denoted as FD_i . Using a notation analogous to marginal CO₂ emissions, one can calculate the marginal impacts on fossil resource depletion for CO₂ capture with the following Equation:

$$m_{\text{resources,marginal}} = W_{\text{el}} FD_{\text{el}} + Q_{\text{th}} FD_{\text{th}} + Q_{\text{fuel}} FD_{\text{fuel}} + FD_{\text{transport}} \quad (\text{C.23})$$

C.4 Emission factors

Table C.1: Environmental impacts for electricity and heat generation and for fuel combustion (including fuel supply).

Environmental impact		Value	
Global warming		kg CO ₂ -eq / GJ	kg CO ₂ -eq / MWh
electricity generation	GW_{el}	133	477
heat generation	GW_{th}	75	271
natural gas combustion	GW_{NG}	68	244
coal combustion	GW_{coal}	105	378
biomass combustion	GW_{biomass}	5	18
Fossil resource depletion		kg oil-eq / GJ	kg oil-eq / MWh
electricity generation	FD_{el}	39	139
heat generation	FD_{th}	32	116
natural gas combustion	FD_{NG}	29	104
coal combustion	FD_{coal}	26	93
biomass combustion	FD_{biomass}	1	4

C.5 Energy demand

Table C.2: Actual energy demands for CO₂ capture from alternative CO₂ sources.

CO ₂ source / description	Actual energy demands / GJ (t CO _{2,product}) ⁻¹					References
	Electricity	Heat	Natural gas	Coal	Biomass	
Air-capture						
Wet air capture, NaOH + MEA	0.43		7.67			123
Wet air capture, NaOH + MEA	0.37		7.67			123; 250
Wet air capture, NaOH + CaO + oxyfuel calcination	0.98		5.78			16; 250
Wet air capture, NaOH + CaO + oxyfuel calcination	1.96			3.65		250
Wet air capture, NaOH + CaO + oxyfuel calcination	1.26		4.19			7; 152
Wet air capture, NaOH + CaO + oxyfuel, M-250Y, C _{cap}	1.84		4.19			152
Wet air capture, NaOH + CaO + oxyfuel, M-250Y, C _{avo}	1.04		4.19			152
Wet air capture, NaOH + CaO + oxyfuel, M-500Y, C _{cap}	1.58		4.19			152
Wet air capture, NaOH + CaO + oxyfuel, M-500Y, C _{avo}	1.02		4.19			152
Wet air capture, NaOH + CaO + oxyfuel, M-CC, C _{cap}	1.28		4.19			152
Wet air capture, NaOH + CaO + oxyfuel, M-CC, C _{avo}	1.00		4.19			152
NGCC power plant						
Post combustion, MEA	2.38					224
Post combustion, MEA	1.59					224
Post combustion, MEA	1.66					224
Post combustion, KS-1	1.22					224
Post combustion, MEA	1.90					224
Post combustion, MEA	1.61					224
Natural gas fired boiler, KS-1	0.79					223

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CO ₂ source / description	Actual energy demands / GJ (t CO _{2,product}) ⁻¹					References
	Electricity	Heat	Natural gas	Coal	Biomass	
Refineries and steam cracker						
Steamcracker, chemical absorption	0.48	4.21				70
Combined stack, post-combustion, MEA, steam import	0.55	3.85				131
Combined stack, post-combustion, MEA, onsite NG-CHP	-0.10		5.70			131
Combined stack, oxyfuel (cryogenic), power import	2.00					131
Combined stack, oxyfuel (cryogenic), onsite power	-0.20		2.50			131
Combined stack, pre-combustion (WGSMR)	-0.10		4.50			131
Catalytic cracker, post-combustion, MEA, steam import	0.60		4.60			131
Catalytic cracker, oxyfuel (cryogenic)	2.50	-3.30				131
Coal power plant						
Subcritical bituminous coal power plant, MEA retrofit, FGD upgrade	1.70					224
Subcritical sub-bituminous coal power plant, MEA retrofit, new FGD	1.65					224
Subcritical sub-bituminous coal power plant, MEA retrofit, FGD upgrade	1.60					224
Subcritical sub-bituminous coal power plant, MEA retrofit, FGD upgrade	1.84					224
Pulverized coal power plant, MEA retrofit	1.36					203
Simulations for MEA solvent, rich equilibrium pCO ₂ =5kPa	0.86					74

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Appendix C Selecting CO₂ sources for CO₂ utilization

CO ₂ source / description	Actual energy demands / GJ (t CO ₂ ,product) ⁻¹					References
	Electricity	Heat	Natural gas	Coal	Biomass	
Simulations for PZ solvent, rich equilibrium pCO ₂ =5kPa	0.80					74
Simulations for PZ solvent, rich equilibrium pCO ₂ =7.5kPa	0.78					74
Simulations for MEA solvent, simple stripper	0.80					241
Simulations for MEA solvent, interheated column	0.76					241
Integrated pulp and paper mill (Kraft)						
Integrated pulp and paper mill, w/o CO shift	0.65					158
Integrated pulp and paper mill, with CO shift	0.04		1.57			158
Integrated pulp and paper mill, biofuel boiler	-0.27				4.02	101
Integrated pulp and paper mill, heat pump	1.09		0.97			101
Market pulp mill (Kraft)						
Market pulp mill, w/o CO shift	1.23					158
Market pulp mill, with CO shift	1.29					158
Market pulp mill with heat integration, Alternative 1	0.24		1.00			100
Market pulp mill with heat integration, Alternative 2	0.56					100
Iron and steel plant						
Capture from blast furnace, MDEA	0.35	3.42				70
Capture from air-blown blast furnace, MEA	0.54	4.40				131
Capture from air-blown blast furnace, KS-1	0.51	3.00				131
Capture from air-blown blast furnace, adv. Solvent	0.50	2.50				131
Capture from air-blown blast furnace, Selexol	0.77					131

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CO ₂ source / description	Actual energy demands / GJ (t CO _{2,product}) ⁻¹					References
	Electricity	Heat	Natural gas	Coal	Biomass	
Capture from air-blown blast furnace, Shift + physical absorption (Selexol)	0.91	0.62				131
Capture from air-blown blast furnace, sel. carbon membrane (long term)	0.76					131
Capture from oxygen-blown blast furnace with top gas recycling, MEA	0.62	3.30				131
Capture from oxygen-blown blast furnace with top gas recycling, PSA	0.94					131
Capture from oxygen-blown blast furnace with top gas recycling, Selexol	0.93	0.21				131
Capture from oxygen-blown blast furnace with top gas recycling, sel. carbon membrane (long term)	0.88					131
Capture from oxygen-blown blast furnace with top gas recycling, hydrate crystallization (long term)	1.50					131
Capture from COREX smelter, MEA, setup 1	0.62	3.30				131
Capture from COREX smelter, MEA, setup 2	0.94					131
Capture from COREX smelter, MEA, setup 3	0.45	4.40				131
Capture from COREX smelter, Selexol	0.97					131
Capture from COREX smelter, Shift + physical absorption (Selexol)	0.60	0.63				131
Cement plant						
Post combustion capture, MEA, steam import	0.73	3.70				131
Post combustion capture, MEA, NG-CHP	0.13		3.60			131

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Appendix C Selecting CO₂ sources for CO₂ utilization

CO ₂ source / description	Actual energy demands / GJ (t CO ₂ ,product) ⁻¹					References
	Electricity	Heat	Natural gas	Coal	Biomass	
Post combustion capture, MEA, coal-CHP	-0.35			5.50		131
Post combustion capture, KS-1, coal-CHP	-0.38			4.00		131
Post combustion capture, adv. solvents, steam import	0.54	2.70				131
Oxyfuel kiln, pre-calciner only, coal	0.73			0.06		131
Oxyfuel kiln, entire kiln, coal	0.99			0.86		131
Calcium looping, pre-calciner only, coal	0.54			1.60		192; 131
Post combustion capture, MEA, coal-CHP	-0.39			6.12		18
Oxyfuel kiln, pre-calciner only, coal	0.80			0.07		18
Calcium looping, entire kiln, with heat recovery, coal	-0.49			4.82		193
Calcium looping, entire kiln, w/o heat recovery, coal				4.82		193
Oxyfuel kiln, pre-calciner only, with heat recovery, coal	-0.44			4.49		193
Oxyfuel kiln, pre-calciner only, w/o heat recovery, coal				4.49		193
Ammonia plant						
100 % CO ₂ stream, compression only	0.40	0.01				70
Ethylene oxide plants						
100 % CO ₂ stream, compression only	0.40	0.01				70
Gas processing						
100 % CO ₂ stream, compression only	0.40	0.01				70
Hydrogen plant (steam cracker)						

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CO ₂ source / description	Actual energy demands / GJ (t CO _{2,product}) ⁻¹					References
	Electricity	Heat	Natural gas	Coal	Biomass	
100 % CO ₂ stream, compression only	0.40	0.01				70
Steam methane reforming, amine scrubbing	0.52					224
H ₂ from coal	0.29					224
H ₂ and electricity from coal, Selexol	0.25					224
H ₂ and electricity from coal, Selexol	0.27					224

Table C.3: References

Reference Number	Reference Name
7	APS physics (2011)
16	Baciocchi et al. (2006)
18	Barker et al. (2009)
70	Farla et al. (1995)
74	Freeman et al. (2009)
100	Hektor and Berntsson (2007)
101	Hektor and Berntsson (2009)
123	Keith et al. (2006)
131	Kuramochi et al. (2012)
152	Mazzotti et al. (2013)
158	Möllersten et al. (2004)
192	Rodríguez et al. (2008)
193	Rodríguez et al. (2012)
203	Schreiber et al. (2009)
224	Thambimuthu et al. (2005)
223	Tatsumi et al. (2011)
241	Wagener and Rochelle (2011)
250	Zeman (2007)

C.6 CO₂ transport distances

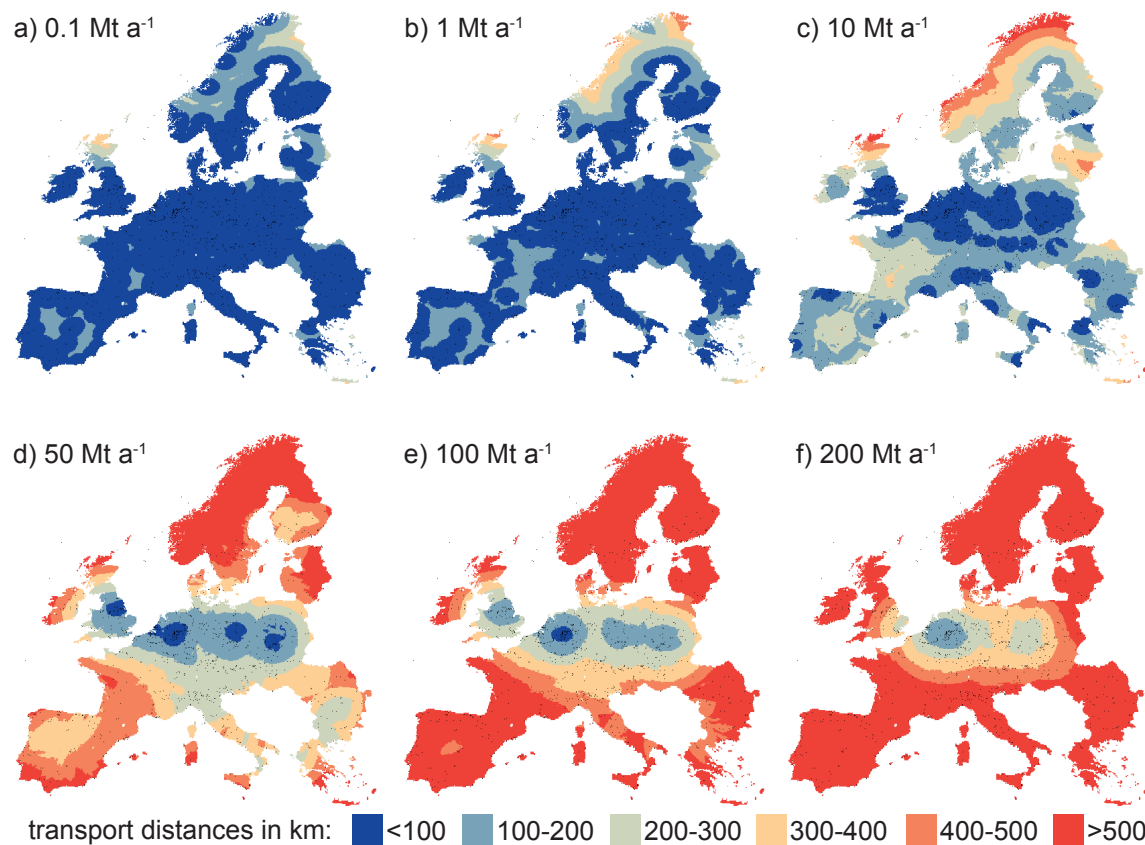


Figure C.1: CO₂ desert maps for Europe illustrating the maximum CO₂ transport distances required to satisfy a CO₂ demand of a) 1, b) 10, and c) 50 Mt a⁻¹.

APPENDIX D

Towards life-cycle design of CO₂-based chemicals

D.1 LCA-based process design for CO₂-based methanol synthesis

D.1.1 Zero lines as functions of ν_{CO_2} and ν_{H_2}

The zero lines as functions of ν_{CO_2} and ν_{H_2} for zero amounts of compound j ($\nu_j = 0$), for zero reaction enthalpy ($\Delta h_0^{\text{R}} = 0$) and for zero Gibbs free energy ($\Delta g_0^{\text{R}} = 0$) are:

$$\nu_{\text{CH}_4} = 0 : \quad \nu_{\text{CO}_2} = -x, \quad (\text{D.1})$$

$$\nu_{\text{H}_2\text{O}} = 0 : \quad \nu_{\text{H}_2} = 2\nu_{\text{CO}_2} + 2x - 1/2 y, \quad (\text{D.2})$$

$$\nu_{\text{O}_2} = 0 : \quad \nu_{\text{H}_2} = 4\nu_{\text{CO}_2} + 2x - 1/2 y + z. \quad (\text{D.3})$$

$$\nu_{\text{CO}_2} = 0 : \quad \nu_{\text{CO}_2} = 0, \quad (\text{D.4})$$

$$\nu_{\text{H}_2} = 0 : \quad \nu_{\text{H}_2} = 0, \quad (\text{D.5})$$

$$\begin{aligned} \Delta h_0^{\text{R}} = 0 : \quad \nu_{\text{H}_2} = & \left(2 + \frac{\Delta h_{\text{CO}_2}^{f,0} - \Delta h_{\text{CH}_4}^{f,0}}{\Delta h_{\text{H}_2\text{O}}^{f,0}} \right) \nu_{\text{CO}_2} \\ & - 2x - 1/2 y + \frac{\Delta h_{\text{C}_x\text{H}_y\text{O}_z}^{f,0} - x \Delta h_{\text{CH}_4}^{f,0}}{\Delta h_{\text{H}_2\text{O}}^{f,0}}, \end{aligned} \quad (\text{D.6})$$

$$\Delta g_0^{\text{R}} = 0 : \quad \nu_{\text{H}_2} = \left(2 + \frac{\Delta g_{\text{CO}_2}^{f,0} - \Delta g_{\text{CH}_4}^{f,0}}{\Delta g_{\text{H}_2\text{O}}^{f,0}} \right) \nu_{\text{CO}_2}$$

$$-2x - 1/2 y + \frac{\Delta g_{\text{C}_x\text{H}_y\text{O}_z}^{f,0} - x \Delta g_{\text{CH}_4}^{f,0}}{\Delta g_{\text{H}_2\text{O}}^{f,0}}. \quad (\text{D.7})$$

D.1.2 Objective functions for divided regions

The specific objective function f_k from Eq. (7.16) for all regions $k = 1, \dots, 9$ are as follows:

$$f = \begin{pmatrix} f_1 \\ f_2 \\ f_3 \\ f_4 \\ f_5 \\ f_6 \\ f_7 \\ f_8 \\ f_9 \end{pmatrix} = \underbrace{\begin{pmatrix} -GW_{\text{CH}_4} & -GW_{\text{H}_2\text{O}} & -GW_{\text{O}_2} & GWP_{\text{CO}_2} & 0 \\ -GW_{\text{CH}_4} & 0 & -GW_{\text{O}_2} & GWP_{\text{CO}_2} & 0 \\ -GW_{\text{CH}_4} & 0 & -GW_{\text{O}_2} & GWP_{\text{CO}_2} & -GW_{\text{H}_2} \\ -GW_{\text{CH}_4} & -GW_{\text{H}_2\text{O}} & -GW_{\text{O}_2} & -GW_{\text{CO}_2} & 0 \\ -GW_{\text{CH}_4} & -GW_{\text{H}_2\text{O}} & -GW_{\text{O}_2} & -GW_{\text{CO}_2} & -GW_{\text{H}_2} \\ -GW_{\text{CH}_4} & 0 & -GW_{\text{O}_2} & -GW_{\text{CO}_2} & -GW_{\text{H}_2} \\ -GW_{\text{CH}_4} & 0 & 0 & -GW_{\text{CO}_2} & -GW_{\text{H}_2} \\ GWP_{\text{CH}_4} & 0 & 0 & -GW_{\text{CO}_2} & -GW_{\text{H}_2} \\ GWP_{\text{CH}_4} & 0 & -GW_{\text{O}_2} & -GW_{\text{CO}_2} & -GW_{\text{H}_2} \end{pmatrix}}_{\mathbf{C}} \cdot \underbrace{\begin{pmatrix} \nu_{\text{CH}_4} \\ \nu_{\text{H}_2\text{O}} \\ \nu_{\text{O}_2} \\ \nu_{\text{CO}_2} \\ \nu_{\text{H}_2} \end{pmatrix}}_{\boldsymbol{\nu}}. \quad (\text{D.8})$$

D.1.3 Vectors pointing towards the local optimal solution

The vectors pointing $\vec{n}_{\text{S},k}$ towards the local optimal solution can be summarized in the vector $\vec{n}_{\text{S}}$:

$$\vec{n}_{\text{S}} = \begin{pmatrix} n_{\text{S},k,1} & n_{\text{S},k,2} \end{pmatrix} = \begin{pmatrix} -\frac{\partial f}{\partial \nu_{\text{CO}_2}} & -\frac{\partial f}{\partial \nu_{\text{H}_2}} \end{pmatrix} = -\mathbf{C} \cdot \begin{pmatrix} \frac{\partial \nu}{\partial \nu_{\text{CO}_2}} & \frac{\partial \nu}{\partial \nu_{\text{H}_2}} \end{pmatrix} \quad (\text{D.9})$$

$$\vec{n}_{\text{S}} = - \begin{pmatrix} -GW_{\text{CH}_4} & -GW_{\text{H}_2\text{O}} & -GW_{\text{O}_2} & GWP_{\text{CO}_2} & 0 \\ -GW_{\text{CH}_4} & 0 & -GW_{\text{O}_2} & GWP_{\text{CO}_2} & 0 \\ -GW_{\text{CH}_4} & 0 & -GW_{\text{O}_2} & GWP_{\text{CO}_2} & -GW_{\text{H}_2} \\ -GW_{\text{CH}_4} & -GW_{\text{H}_2\text{O}} & -GW_{\text{O}_2} & -GW_{\text{CO}_2} & 0 \\ -GW_{\text{CH}_4} & -GW_{\text{H}_2\text{O}} & -GW_{\text{O}_2} & -GW_{\text{CO}_2} & -GW_{\text{H}_2} \\ -GW_{\text{CH}_4} & 0 & -GW_{\text{O}_2} & -GW_{\text{CO}_2} & -GW_{\text{H}_2} \\ -GW_{\text{CH}_4} & 0 & 0 & -GW_{\text{CO}_2} & -GW_{\text{H}_2} \\ GWP_{\text{CH}_4} & 0 & 0 & -GW_{\text{CO}_2} & -GW_{\text{H}_2} \\ GWP_{\text{CH}_4} & 0 & -GW_{\text{O}_2} & -GW_{\text{CO}_2} & -GW_{\text{H}_2} \end{pmatrix} \cdot \begin{pmatrix} -1 & 0 \\ 2 & -1 \\ -2 & 1/2 \\ 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (\text{D.10})$$

The explicit single vectors $\vec{n}_{S,k}$ for $k = 1, \dots, 9$ are:

$$\vec{n}_{S,1} = \begin{pmatrix} -GW_{CH_4} + 2 GW_{H_2O} - 2 GW_{O_2} - GWP_{CO_2} \\ -GW_{H_2O} + 1/2 GW_{O_2} \end{pmatrix} \quad (D.11)$$

$$\vec{n}_{S,2} = \begin{pmatrix} -GW_{CH_4} - 2 GW_{O_2} - GWP_{CO_2} \\ 1/2 GW_{O_2} \end{pmatrix} \quad (D.12)$$

$$\vec{n}_{S,3} = \begin{pmatrix} -GW_{CH_4} - 2 GW_{O_2} - GWP_{CO_2} \\ 1/2 GW_{O_2} + GW_{H_2} \end{pmatrix} \quad (D.13)$$

$$\vec{n}_{S,4} = \begin{pmatrix} -GW_{CH_4} + 2 GW_{H_2O} - 2 GW_{O_2} + GW_{CO_2} \\ -GW_{H_2O} + 1/2 GW_{O_2} \end{pmatrix} \quad (D.14)$$

$$\vec{n}_{S,5} = \begin{pmatrix} -GW_{CH_4} + 2 GW_{H_2O} - 2 GW_{O_2} + GW_{CO_2} \\ -GW_{H_2O} + 1/2 GW_{O_2} + GW_{H_2} \end{pmatrix} \quad (D.15)$$

$$\vec{n}_{S,6} = \begin{pmatrix} -GW_{CH_4} - 2 GW_{O_2} + GW_{CO_2} \\ 1/2 GW_{O_2} + GW_{H_2} \end{pmatrix} \quad (D.16)$$

$$\vec{n}_{S,7} = \begin{pmatrix} -GW_{CH_4} + GW_{CO_2} \\ GW_{H_2} \end{pmatrix} \quad (D.17)$$

$$\vec{n}_{S,8} = \begin{pmatrix} GWP_{CH_4} + GW_{CO_2} \\ GW_{H_2} \end{pmatrix} \quad (D.18)$$

$$\vec{n}_{S,9} = \begin{pmatrix} GWP_{CH_4} - 2 GW_{O_2} + GW_{CO_2} \\ 1/2 GW_{O_2} + GW_{H_2} \end{pmatrix} \quad (D.19)$$

D.1.4 Threshold lines

The threshold lines $GW_{CO_2} = f(GW_{H_2})$ for the four regions $k = 4, 5, 6, 7$ (in this order) are:

$$GW_{CO_2} = GW_{CH_4} + \Delta\tilde{g} GW_{H_2O} + (1 - \Delta\tilde{g}) GW_{O_2} \quad (D.20)$$

$$GW_{CO_2} = -(2 + \Delta\tilde{g}) GW_{H_2} + GW_{CH_4} + \Delta\tilde{g} GW_{H_2O} + (1 - \Delta\tilde{g}) GW_{O_2} \quad (D.21)$$

$$GW_{CO_2} = -(2 + \Delta\tilde{g}) GW_{H_2} + GW_{CH_4} + (1 - \Delta\tilde{g}) GW_{O_2} \quad (D.22)$$

$$GW_{CO_2} = -(2 + \Delta\tilde{g}) GW_{H_2} + GW_{CH_4} \quad (D.23)$$

where:

$$\Delta\tilde{g} = \frac{\Delta g_{\text{CO}_2}^{f,0} - \Delta g_{\text{CH}_4}^{f,0}}{\Delta g_{\text{H}_2\text{O}}^{f,0}}. \quad (\text{D.24})$$

D.2 LCA-based process and product design for CO₂-based polymers

D.2.1 Computational structure of system expansion

System expansion includes all co-products in an expanded functional unit $f_{\text{exp}} = f + \tilde{f}$, where f contains only the original product and $\tilde{f}$ contains the unknown quantities of the co-products. Equation (7.42) can be re-written as follows:

$$A(\nu) \cdot s = f_{\text{exp}} = f + \tilde{f} = f + I \cdot \tilde{f}, \quad (\text{D.25})$$

where I is the identity matrix. Re-arranging terms yields:

$$\begin{aligned} A(\nu) \cdot s - I \cdot \tilde{f} &= f \\ \left(A(\nu) \quad -I \right) \cdot \begin{pmatrix} s \\ \tilde{f} \end{pmatrix} &= f. \end{aligned} \quad (\text{D.26})$$

Comparing the formulation of NLP (7.32) for system expansion

$$\begin{aligned} \min_{s, \nu, \tilde{f}} \quad & h = Q \cdot B \cdot s, \\ \text{s.t.} \quad & \left(A(\nu) \quad -I \right) \cdot \begin{pmatrix} s \\ \tilde{f} \end{pmatrix} = f. \end{aligned} \quad (\text{D.27})$$

and avoided burden

$$\begin{aligned} \min_{s, s_{\text{avo}}, \nu} \quad & h = Q \cdot \left(B \quad -B_{\text{avo}} \right) \cdot \begin{pmatrix} s \\ s_{\text{avo}} \end{pmatrix}, \\ \text{s.t.} \quad & \left(A(\nu) \quad -A_{\text{avo}} \right) \cdot \begin{pmatrix} s \\ s_{\text{avo}} \end{pmatrix} = f. \end{aligned} \quad (\text{D.28})$$

shows that the two approaches will yield identical results for s and h if (i) A_{avo} is invertible and (ii) $B_{\text{avo}} = 0$. The first condition is usually fulfilled since A_{avo} typically comprises aggregated, mono-functional processes. In this case, the system expansion

approach is equivalent to an avoided burden approach where co-products are assigned no credits ($B_{\text{avo}} = 0$). In other words, co-products in system expansion are not considered in the environmental assessment, although the co-products are technically included in the expanded functional unit $\tilde{f}$. In a mathematical sense, the co-products only exist to be able to solve the set of equations.

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