THESIS FOR THE DEGREE OF DOCTOR OF TECHNOLOGY

Environmental Assessment of Emerging Routes to Biomass Based Chemicals

The Case of Ethylene

CHRISTIN LIPTOW

Environmental Systems Analysis
Department of Energy and Environment

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2014

Environmental Assessment of Emerging Routes to Biomass Based Chemicals
The Case of Ethylene
CHRISTIN LIPTOW
ISBN 978-91-7385-998-1

Doktorsavhandlingar vid Chalmers tekniska högskola
Ny serie nr 3679
ISSN 0346-718X

Environmental Systems Analysis
Department of Energy and Environment
Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone + 46 (0)31-772 1000

Reproservice Chalmers
Gothenburg, Sweden 2014

Environmental Assessment of Emerging Routes to Biomass Based Chemicals
The Case of Ethylene
CHRISTIN LIPTOW
Department of Energy and Environment
Chalmers University of Technology

ABSTRACT
The production of bulk chemicals from biomass instead of fossil resources is perceived as one promising option to decrease society's environmental impact. However, though considerable research and development efforts aim at such production, it might take several more years before biomass based bulk chemicals are fully commercialized. This leaves room for investigating the environmental impact of such production, as well as, identifying improvement options along the related life cycles using environmental assessment tools such as life cycle assessment (LCA).

This thesis aims at providing guidance for the development and production of biomass based ethylene, using life cycle assessment as a method of choice. It achieves this by: (1) identifying environmental hot spots along its life cycle and (2) by comparing the environmental impact of a sugarcane, a wood fermentation, and a wood gasification route to ethylene to each other, as well as to a fossil alternative.

In addition, the thesis contributes to the methodological development of LCA to better fit the assessment of emerging routes to biomass based products (1) by determining methodological challenges linked to the assessment of products (e.g. biomass based chemicals) produced via emerging technologies; and (2) by identifying application and methodological challenges related to the climate impact assessment of land use and of time lags between CO_2 release and uptake from wood.

A number of potential hot spots were revealed for the production of biomass based ethylene. These include e.g. enzyme production and the energy consumption of the ethylene production process and further development such as decreased enzyme and energy consumption is needed.

From a global warming perspective, all three biomass routes can outperform the fossil alternative. However, this finding is significantly influenced by the assessment of time lags for biomass CO_2 (wood routes), and of emissions from indirect land use change (sugarcane route). Both factors can significantly increase the global warming potential of the biomass routes, making them comparable to the fossil alternative. Therefore, the production of biomass must induce as few changes as possible regarding land use and related decreases in carbon stocks. In addition, consideration needs to given on how to use wood based ethylene to best mitigate potential effects of time lags between CO_2 uptake and release from biomass.

As regards the other investigated impacts (acidification, eutrophication, and photochemical ozone creation) the biomass routes were found to be in clear need for further development before competing with the fossil route.

To ensure the relevance of assessments, two factors were found to be critical: (1) the consideration of the needs and demands of different stakeholders, and (2) the use of process simulation as a means to provide data for emerging technologies.

Finally, the climate impact assessment of land use and time lags in CO_2 release and uptake was found to encounter a number of methodological and practical issues, including inconsistent modeling for forestry and agricultural and poor data availability. These challenges need to be addressed, in order to consistently assess the climate impact of land use and time lags.

Keywords: life cycle assessment, LCA, biomass based chemicals, fermentation, gasification, wood sugarcane, land use, time lags

Acknowledgment

During the time of my PhD there have been many people helping and supporting me and I would like to thank them here.

Thanks go to my supervisor Prof. Anne-Marie Tillman (Chalmers University) for her thoughtful guidance through the challenges of LCA and her commitment to my work. I would also like to thank my co-supervisor Prof. Glenn A. Taylor (University of New Mexico) for never getting tired of pushing me, staying calm when I couldn't and for keeping up with my 'German Style' sentences. Another person I would like to thank is my co-supervisor Assistant Prof. Matty Janssen (Chalmers University) who always had five minutes for me, which then suddenly turned into twenty.

This work has been financially supported by Formas (the Swedish Research Council for Environment, Agricultural Science and Spatial Planning), as well as by Tetra Pak (Lund, Sweden) and Trioplast AB (Smålandsstenar, Sweden).

The three case studies being part of this thesis were supported by a number of people inside and outside of Chalmers University, whom I would like to thank here. Many thanks goes to my industrial reference group for the many critical discussions and for bringing new perspectives to my work: Dr. Thorbjörn Andersson from Tetra Pak, Christer Forsgren from Stena Metall, Dr. Bernt-Åke Sultan from Borealis and Susanne Thygesson from Trioplast AB.
My gratitude also goes to Dr. Ola Wallberg (Lund University) who supported me in my work for Paper 2 and to Johan Isaksson (Chalmers University), whose gasification model I have used in Paper 3 and who answered all my questions about gasification.
Another group of people that supported me on my way were my colleagues here at ESA, whom I thank for all the funny and interesting moments in the kitchen, the corridor, the copy room and where ever else we came together. Ein besonderes Danke schön geht an Birgit, die immer ein offenes Ohr für mich hatte und mir oft mit Rat und Tat zur Seite gestanden hat. Danke auch an Jutta für unsere Gespräche über LCA.

A big 'thank you' goes to my friends. You are of unbelievable value to me and I promise I'll be around more often after my defense.

Ich danke meiner Familie - danke, dass Ihr nie müde geworden seid, mich daran zu erinnern, dass das Leben nicht nur aus Arbeit besteht, sondern auch aus Spaziergängen, Kuchen backen, ins Kino gehen und was man sonst noch alles zum Leben braucht. Danke auch für die 'Westpackete' und all Eure Briefe, auch wenn die Schwedische Post sie meist im Schneckentempo überbracht hat.

Last but not least, I would like to thank Georgios - you are my working hero und sowieso und überhaupt bist Du Der Beste, und zusammen sind wir Die Besten.

Table of Contents

Table of Figures

Table of Tables

Appended Papers

Paper 1: Liptow C, Tillman AM (2012) A comparative life cycle assessment study of polyethylene based on sugarcane and crude oil. Journal of Industrial Ecology 16 (3):420-435

Paper 2 (as accepted)**:** Liptow C, Tillman A-M, Janssen M, Wallberg O, Taylor GA (2013) Ethylene based on woody biomass—what are environmental key issues of a possible future Swedish production on industrial scale. The International Journal of Life Cycle Assessment 18 (5):1071-1081

Paper 3 (submitted)**:** Liptow C, Tillman A-M, Janssen M (2014) Life cycle assessment of biomass based ethylene production in Sweden - is gasification or fermentation the environmentally preferable route?

Paper 4 (manuscript): Liptow C, Tillman A-M, Janssen M (2014) Accounting for effects of carbon flows in LCA of biomass-based products - exploration and evaluation of existing methods

May 9, 2013 - on that specific day, just roughly 12 months ago, the atmospheric concentration of CO_2 surpassed, for the first time since measurements have started in 1958, the 400 parts per million (ppm) mark [1]. Though this number in itself does not say much, it gets a meaning when put in context with other numbers. In particular, when put with the numbers 350 and 500, which represent the critical range in atmospheric CO_2 concentration (ppm) that many scientists argue for we need to stabilize at in order to avert the worst impacts of climate change [2-4]. Under this perspective, 400 is an enormous ringing alarm bell which calls for actions.

1 Intro

1.1 Biomass based chemicals and materials

The call for actions to stabilize the atmospheric CO_2 concentration is responded to in different ways, including the replacement of fossil resources with biomass based alternatives. This is especially true for the fuel and energy industry which has, during the last decade, continuously increased its production of biofuels such as bioethanol and biodiesel. As a matter of fact, the production of these two fuels more than doubled from 46.6 billion liters in 2005 to 97.4 billion liters in 2012 [5] for bioethanol and from 5.3 billion liters to 27.4 billion liters for biodiesel [5].

However, despite its dominating role as regards to the replacement potential of fossil with biomass alternatives, the fuel and energy industry is not the only industry with an interest in such a replacement. Other industries currently operating on fossil resources, such as the chemical industry, are interested as well, and are investigating the development and production of biomass based products. In fact, there are already a number of biomass based chemicals and materials commercially available. This includes, among others, biodegradable plastics such as polylactic acid (PLA) and starch blends, whose production capacity increased from 226 000 tonnes in 2009 to 486 000 tonnes in 2011. Moreover, traditionally fossil based chemicals such as succinic acid, acrylic acid and ethylene, are now produced from biomass [6-8].

The feedstocks currently used for the above chemicals and materials are mainly of agricultural origin and include plant oils and fats such as palm oil, as well as sugar and starch sourced from e. g. sugarcane, wheat and corn [9]. However, the steadily growing debate on using agricultural products for fuels or other non-food applications (food vs. fuel or here food vs. chemicals) [10-12] has opened up the search for new feedstock options. This was further fostered by a number of scientific studies, such as Fargione et al. [13], Searchinger et al. [14], Faus et al. [15], Hill [16] and Havlik et al. [17], which show that using agricultural feedstocks can lead to severe releases of CO_2 emissions due to land clearings (land use change (LUC)). Furthermore, water shortages due to irrigation needs, water pollution due to run-off and soil erosion can be observed for these processes.

Among others, lignocellulosic biomass such as wood is seen as a potential feedstock source [16-18], especially for countries with abundant forest areas such as Sweden. However, with new feedstocks also come new demands on the conversion process, which is why the search for feedstocks also led to a search for feasible and applicable conversion processes. One process or rather technology heavily investigated for the conversion of lignocellulosic biomass is fermentation (biochemical conversion). It converts, with the help of microorganisms, chemicals and biochemicals (enzymes) lignocellulose to acids or alcohols [19], which can then be used as chemicals or as intermediates for other chemicals or materials. Another alternative is the conversion via thermochemical technology such as gasification with subsequent synthesis, which uses heat and metal catalysts to produce desired chemicals or intermediates [20, 21].

Though bio- and thermochemical technologies for conversion of lignocellulosic material are very different from each other, one thing they have in common is their status as emerging technologies. Currently, there are only few commercial scale plants, whose products are, however, mainly supplying the fuel and energy industry [22]. This means that plants supplying the production of bulk chemicals, such as ethylene, have yet to be planned or constructed. Though this might add to the time needed before lignocellulose based bulk chemicals are commercially produced, it also leaves more time for thorough investigation of the potential environmental impact of such productions and the overall life cycles they are embedded into, as well as, improving these life cycles.

1.2 Life Cycle Assessment of biomass based chemicals and materials

A tool that can help in this process is Life Cycle Assessment (LCA). As the name indicates, LCA models the life cycle of a product or service from its cradle to its grave, i.e. from raw material acquisition to final waste treatment. This also includes the collection of data with regard to inputs and outputs to the life cycle (e.g. crude oil and CO_2) and their translation into potential environmental impacts such as global warming potential [23].

At its beginning, in the late 1960s and 70s, LCA was primarily used for the assessment of packaging materials and related waste handling issues. For example, one of the first LCA studies was conducted by the Coca-Cola Company in order to investigate the environmental impact of various packing materials [24]. Moreover, in the 1970s several governmental agencies such as the U.S. EPA (Environmental Protection Agency) and the German Federal Ministry of Education and Science conducted and commissioned LCAs on packaging materials and their contribution to experienced waste issues [24, 25]. However, over time the range of products and services under assessment broadened and LCA became a common tool for product development and marketing, as well as a tool to support procurement decisions and to learn about the potential environmental impact of a product or service under a life cycle perspective [26-28].

A product group that is being subjected to LCA studies from a very early stage are biomass based products. While at the beginning it was mainly packaging related products such as molded pulp trays [24], today all kinds of products ranging from food, feed, materials, fuels and chemicals are assessed in LCAs. In fact, chemicals and related materials have been increasingly assessed over the last decades, providing plenty material for several reviews (e.g. [29-32]) with the major following findings:

Findings with regard to the overall environmental impact:

- Biomass based products have the potential to save greenhouse gases (GHG) and non-renewable energy (NREU) in comparison to their fossil alternatives. However, such conclusions are drawn from studies that do not consider potential GHG effects of land use change (LUC) and land use (LU).
- For other impacts such as acidification and eutrophication, the preferability of bio-based products is less clear. It needs to be pointed out that these other impacts were less commonly assessed in the reviewed studies compared to NREU and global warming potential (GWP).
- LCA results can vary considerably depending on data used and methodological choices.

Findings with regard to environmental hot spots:

- When LUC is included in the assessment, it can have a considerable impact on the overall global warming potential.
- Cultivation and related activities such as fertilizer production are of importance, particularly in the case of annual crops.
- Especially for fine chemicals and pharmaceuticals the energy consumption of the conversion process makes up a considerable share of the overall energy use. The same applies to the use of solvents.

A feature regarding the review studies as such is their focus on studies that assess biochemical product routes, though assessment for thermochemical routes exists (see e.g. [33-36]). However, in comparison to fermentation assessments, they are fewer and potentially not numerous enough to conduct a review study.

The assessment of biomass based chemicals and material spurred various methodological debates and developments. In particular, these focus on the following issues, which can be grouped into more general LCA issues, and issues that are of special relevance for biomass based products [32, 37-39]:

General LCA related issues:

- Which system boundaries should be applied - is a cradle-to-gate perspective sufficient or does one need a cradle-to-grave perspective? Where does the natural system end and where does the technical system start (e.g. is land part of the technical system)?
- Which allocation method/s should be applied?
- Which LCA approach (attributional vs. consequential) should be used?

Issues especially relevant for biomass based products:

- Which potential impacts should be investigated (e.g. impact biodiversity, water consumption and pollution)?
- Which method should be used to assess the impact from e.g. carbon stock changes due to land use, time lags between release and uptake of CO_2 from biomass, as well as, water use?

Especially for the biomass product relevant issues, it needs to be stated that there has been a lot of method development during recent years (e.g. [40-42]). However based on their recent state, most of the methods are still in need for more extended testing and reflection of what implications it might have to use one method instead of another.

A further challenge related to the assessment of biomass based products is the circumstance that a multitude of them are intended to be produced via currently emerging technologies. This introduces additional methodological issues such as [43-46]:

- Under which development state should the emerging technology be assessed (e.g. a potential future development state right after commercialization or a potential state reached after several years of operation in a large number of facilities)?
- With which (future or otherwise) fore- and background data should the technology assessment be conducted?

Apart from that, data availability and quality are other issues related to the assessment of emerging technologies, including the ones used for the production of biomass based products [44, 47].

2 Aim and Scope

2.1 Thesis aims

The aim of the thesis is two-fold. The first aim is to provide guidance for the development and production of biomass based ethylene by:

- Identifying environmental hot spots along the life cycle,
- Investigating potential improvement options, and by
- Comparing different production routes .

The second aim is to contribute to the methodological development of life cycle assessment by:

- Determining methodological challenges related to the assessment of products produced via emerging technologies, and
- Identifying methodological and application challenges related to the climate impact assessment of land use and of time lags between CO_2[1] release and uptake from biomass.

2.2 Thesis scope

The research aims stated above set the scope of the thesis and are investigated in the four papers comprising this thesis. The papers relate to each other and the thesis' aims as shown in Figure 1 and described in the following section.

Paper 1 is an assessment for the sugarcane ethanol based production of polyethylene (PE). The choice to investigate this particular case was based on the following two reasons:

(1) At the time of starting the thesis, the large-scale industrial production of PE from sugarcane ethanol was close to realization [48], which generated a great interest in its environmental impact, as well as, in its potential environmental hot spots.
(2) The production of PE is one the of major applications of ethylene [49].
The assessment focuses on the production of PE via fermentation of sugarcane in Brazil but also includes a comparison with the fossil alternative. Moreover, the paper investigates how the inclusion of land use change emissions might affect the overall impact and the hot spots

[1] For slow growing biomass such as trees, there is a considerable time lag between CO_2 being released from a product produced from the tree and an equal amount of CO_2 being taken up by the tree. It is currently debated on how to assess these time lags and the thesis explores methodological issue related to currently suggested methods.

of the sugarcane PE. For this purpose, two extremes of a potential range of LUC emissions were included into the assessment.

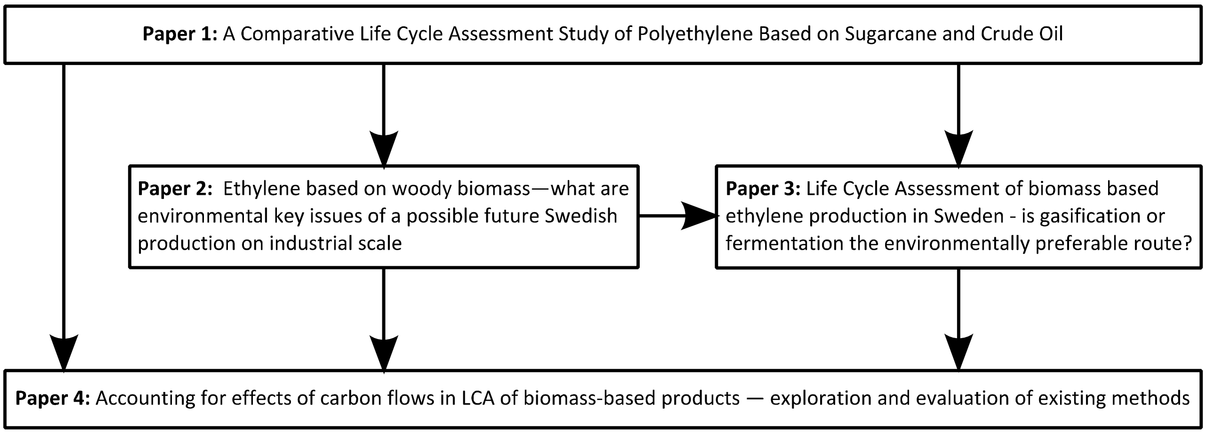

Figure 1 Connection between the four papers

The choice to investigate the environmental impact and related hot spots for a potential future production of ethylene from wood based ethanol in Sweden in Paper 2, was directly influenced by the environmental hot spots determined in Paper 1. The study was conducted in cooperation with researchers at Lund University, who developed the process simulation model for the fermentation and ethanol upgrading process used in the assessment. Moreover, numerous conversations with employees of an enzyme producer, a Swedish wood ethanol pilot plant, and various forestry related agencies formed the basis for the investigated feedstock and enzyme product consumption scenarios.

A biochemical (fermentation) route is only one possible option to produce biomass based ethylene in the near future. Another option could be the use of a thermochemical (gasification) route via methanol. Paper 3 investigates one such potential future gasification route for two different woody biomass feedstock scenarios (tops and branches, wood mix), in a Swedish context. In particular, the paper focuses on the potential environmental hot spots related to a gasification route and how they might be influenced by the choice of feedstock. In addition, the paper also presents a comparison between the gasification and the fermentation routes. This also includes a comparison between their inventories of biogenic CO_2.

During the course of time that this thesis evolved, much discussion and development occurred on how to account for the impact from land use and time lags between CO_2 release and uptake from biomass. Both issues are of high relevance and Paper 4 tests and explores some of these methods and related application and methodological challenges on the case of sugarcane and wood PE (as one possible application of biomass ethylene). Specifically the paper focuses on the impact from carbon emissions related to land use and to time lags occurring between carbon release and uptake from biomass. The emissions of the latter were already found to be of significant quantity in Paper 3.

Though there are additional types of environmental impacts related to the production of biomass based products, such as e.g. impact on biodiversity, water availability and quality [50], these were out of the scope of this thesis.

2.3 Thesis outline

The thesis is structured as follows:
The next chapter provides a more detailed description of the emerging wood fermentation and gasification process being part of the assessment in Paper 2 and Paper 3. This is followed in chapter 4 by a general overview of the methods used during the work on this thesis. Chapter 5 is dedicated to the thesis' results and their discussion and is divided into two parts. The first part presents the case study findings, including the overall environmental impact of the investigated biomass routes, their respective hot spots and potential options on how to approach them. The second part describes the methodological findings that contribute to an increased applicability of LCA for the environmental assessment of biomass based chemicals produced via emerging technologies. Conclusions with regard to the case studies and the methodological findings are presented in chapter 6. The thesis concludes with suggestions for future work, in chapter 7. The papers comprising this thesis are appended.

3 Technology Background

In order to facilitate the understanding of the assessments, Chapter 3 gives a brief overview of the emerging fermentation and gasification processes assessed in Paper 2 and Paper 3 for the production of wood based ethylene.

3.1 Fermentation process

The wood fermentation process studied in Paper 2, is based on a process developed by Barta et al. and Sassner et al. [51-53] and can be summarized as follows.
The fermentation process begins with a SO_2 -catalyzed steam pretreatment during which the hemicellulose in the wood is converted to fermentable sugars. This is followed by a simultaneous saccharification and fermentation (SSF) i.e. the enzymatic hydrolysis needed to convert the cellulose part of the wood into fermentable glucose, and the fermentation with baker's yeast to ethanol are occurring in the same vessel.

The SSF delivers low concentrated ethanol (the fermentation broth), which is further purified in a two step procedure. Step one is distillation, which delivers highly concentrated ethanol (top product of distillation) and stillage (bottom product of distillation). Step two is the further purification of the ethanol with molecular sieves to a concentration of 99.8%(wt). The stillage from step one is anaerobically digested, resulting in biogas and some remnant, which is then aerobically digested forming sludge and water. The latter is fed back into the process after a treatment with ozone. While the sludge and parts of the biogas are burned to cover the energy demand of the various processes.

3.2 Gasification process

In this thesis (Paper 3), the gasification route to ethylene was assessed assuming a gasification process with subsequent synthesis to methanol. Specifically the process was based on a study by Isaksson et al. [54], which can be summarized as presented below.
The first step in the gasification process is the pretreatment of the biomass, including its chipping (if needed) and drying to a moisture content of 15%. This is followed by the gasification of the biomass using an oxygen- and steam- blown circulating fluidized bed gasifier. The latter operates at a temperature of 850°C and a pressure of 25 bar. Moreover, to facilitate the downstream conversion to methanol, Isaksson et al. [54] propose the use of oxygen as oxidizing medium. It prevents the dilution of the product gas with nitrogen.

The gasification is subsided by a cleaning and condition procedure. During this procedure, tars and other hydrocarbons contained in the product gas are cracked into hydrogen and carbon monoxide. This is followed by the removal of particles and other impurities using a sequence of cyclone, bag filter, and finally wet scrubber.

After the cleaning and condition, the product gas is reformed in an oxygen-blown autothermal reformer (ATR). This is done in order to convert hydrocarbons (e.g. methane) still present in the gas into hydrogen and carbon monoxide. Following the reforming, the gas' hydrogen to carbon monoxide ratio is adjusted with the water-gas-shift reaction. The reaction results in a hydrogen to carbon monoxide ration of 2:1, which is needed for the downstream synthesis to methanol.

The next step is the conversion of the cleaned and conditioned gas to methanol at a temperature of 240°C, a pressure of 90 bar and under a Cu/Zn/Al catalyst. Apart from methanol, the conversion also results in a gaseous by-product, which is used to fuel the process. While the methanol is purified using a series of flashes and separation columns.

4 Methods

For pursuing the aims of this thesis a set of methods was used, which will be described in the following sections. In the beginning of the chapter, the methods used for the assessment of the environmental impact related to the production of biomass based ethylene are being presented. This includes the method of Life Cycle Assessment (LCA) and scenario development within LCA, as well as a short section on the use of process simulation for LCA purposes. After this more case focused section, the text will proceed with a short description on the research process applied to derive methodological insight. Finally, there will be a general overview of methods related to the assessment of land use and of time lags for biomass CO_2, and how they have been tested in this thesis.

4.1 Life Cycle Assessment

Life cycle assessment as part of Environmental Systems Analysis

One of the aims of the thesis is to provide, from an environmental perspective, guidance for the development and production of biomass based ethylene. For this purpose, the environmental impact of ethylene was assessed using the method of Life Cycle Assessment (LCA). Life Cycle Assessment belongs to the family of Environmental Systems Analysis methods, which also includes methods such as Environmental Accounting, Material Flow Analysis and Life Cycle Costing [55, 56], and which has the following features:

A common feature of all systems analysis methods is their systems approach. This approach differs from a reductionist approach in that it focuses on the different components in a system and how they interconnect and relate to each other, rather than looking at them in isolation [57, 58].

A further feature is the use of system models, which are simplified models of the real world problem under investigation [59]. Since these models are based on the individual choices of the analyst, the same problem can be modeled in various ways, depending on the analyst. As a consequence, there might be many solutions to a problem, all of which can be difficult to reproduce [60].

Finally, systems analysis methods have an interdisciplinary approach, combining method and knowledge from different fields such as natural science and engineering [59, 61], with LCA being a very good example of this.

Life cycle Assessment (LCA)

LCA is a method that assesses quantitatively the potential environmental impact of a product, process, or service along its life cycle by accounting for related energy and material inputs, as well as emissions and wastes released, followed by an assessment of their respective impacts. Apart from providing an overall insight of a product's, process' or service's environmental impact, LCA can also support the identification of the life cycle activities contributing the most to the overall impact, the so called hot spots, and indicate improvement potentials. The procedure of how to conduct an LCA is standardized in the ISO 14040 and 14044 standards [23, 62] and consists of four phases (see Figure 2). These are described in the following paragraphs, first on a more general level and then more specifically with regard to the LCA case studies included in this thesis.

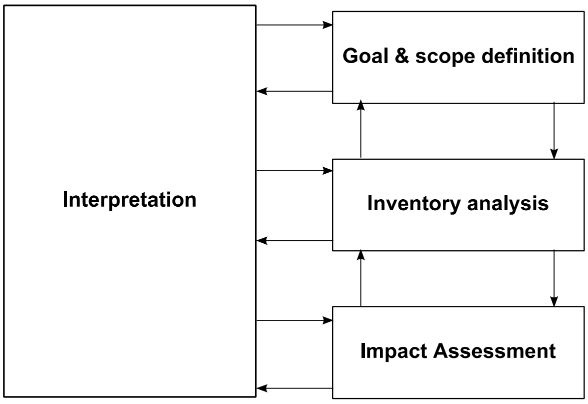

Figure 2 The four phases of an LCA according to ISO 14044 [62]

The first phase of an LCA is the Goal and Scope Definition. It consists of the definition of the assessment's purpose, including the intended application, the reasons for carrying out the study and the intended audience. The purpose determines what type of assessment is done, meaning whether the assessment is of the accounting (attributional) or change-oriented (consequential) type. Though the ISO standard does not explicitly distinguish between these two approaches, the LCA community commonly differentiates between them. For example, Curran et al. [63] define an attributional LCA as an LCA that sets out to describe the system at a certain point in time, including the attribution of the system's environmental impact to the various products produced within the system. In comparison, a consequential LCA intends to estimate how changes within a system influence the system's resource and pollution flows [64]. Both approaches were used in Paper 1, while the studies in Paper 2 and Paper 3 were conducted under an attributional approach, based on their purposes - see Table 1. The choice of approach also influences which data to use for the assessment. Attributional

LCA commonly uses average or supplier-specific data, while consequential LCA uses marginal data (e. g.[65]). Where available, data according to these principles were applied throughout Paper 1-3. However, for the emerging technology part of the studies (wood fermentation and gasification process) it needs to be pointed out, that though, data were intended to represent average site-specific production, this could not be verified. This also applies to the ethylene production processes, for which data availability was an issue too.

Data related issues were also experienced for the assessment of land use, as well as, for the assessment of time lags for biomass CO_2 in Paper 1 (land use change) and Paper 4 (land use and time lags). This was approached by estimating emission release and uptake based data and models found in literature.

A further part of the Goal and Scope Definition is the definition of the assessment's scope. This includes the following important modeling choices: definition of system boundaries, allocation procedure, level of detail, limitations and assumptions, and impact categories. Moreover, the functional unit, to which all flows are related to, is chosen.
All system boundaries have to be chosen in accordance with the purpose of the assessment. A "full" LCA study includes all life cycle activities from resource acquisition to waste management (cradle-to-grave). However, in some cases a so-called cradle-to-gate study is conducted, in which resource acquisition and subsequent production of the product under assessment are included. Both types of system boundaries were used in the case studies reported in this thesis, see Table 1.

Allocation is used when a process provides several products or functions, in order to allocate the environmental burden of the process between the different products or functions.
This can be done in various ways, with the ISO standard [62] ranking the different options as follows:

(1) Allocation should be avoided whenever possible by either an increased level of detail or by system enlargement.
When allocation is unavoidable the following ranking is applicable:
(2) Physical partitioning - the environmental burden of the system is partitioned between the different functions or products of the system based on underlying physical relationships.
(3) Partitioning based on other relationships - when physical relationships cannot be found or applied, the environmental burden of the system is partitioned between the different functions or products of the system based on other relationships such as price.

However, this ranking is debatable since it does not adequately reflect the purposes and related causal relationships investigated in LCAs [66]. For example, an attributional LCA describes the relationships between a system and its causes and an allocation based on the causes for the existence of a particular technical system seems therefore more appropriate. Such an allocation would be e.g. the partitioning on an economic basis, since economic profit can be one of the causes for a system to exist [66]. In contrast, a consequential assessment focuses on the relationships between a system and effects of changes to it. Therefore, allocation based on system enlargement seems more suitable.

Following Tillman [66], allocation through partitioning was applied throughout the attributional assessments in Paper 1-3, while system expansion was used for the consequential assessment in Paper 1.

Table 1 Overview of goals and scope of the life cycle assessment conducted in Papers 1-3

	Goal	Functional unit	System boundaries	Environmental impact
Sugarcane based PE via fermentation (Paper 1)	- identify first set of hot spots and raise awareness for them, as well as for knowledge gaps - compare sugarcane route with fossil alternative to get insight into whether sugarcane has lower impact in comparison - compare potential near term state with further future expansion	1 kg PE	cradle-to-grave: from biomass acquisition to final disposal	global warming, acidification, eutrophication, photochemical ozone creation
Wood based ethylene via fermentation (Paper 2)	- identify first set of hot spots for a potential future state in order to provide guidance for development	50 000 t ethylene	cradle-to-gate: from biomass acquisition to ethylene plant's gate	global warming, acidification, eutrophication, photochemical ozone creation

Continuation of **Table 1**

Wood based ethylene via gasification (Paper 3)	- identify first set of hot spots for a potential future state in order to provide guidance for development - give insight into whether gasification or fermentation process route could be preferable, also in comparison to a fossil route	50 000 t ethylene	cradle-to-gate: from biomass acquisition to ethylene plant's gate exception for global warming - emissions from final oxidation included since they influence the relative difference between fossil and biomass ehtylene	global warming, acidification, eutrophication, photochemical ozone creation

The next phase in the procedure of an LCA is the inventory analysis. This phase starts with the construction of the life cycle flow chart, which is followed by a data collection for all relevant inputs (energy and material) and outputs (emissions and wastes) along the life cycle. Finally, the collected data are put in relation to the functional unit defined in the Goal and Scope Definition.

The third phase of an LCA consists of the impact assessment, which is divided into classification followed by characterization. During the classification, the inventory results are related to their respective impacts. Subsequently in the characterization, all inventory results are multiplied with the equivalence factors of the different impacts and finally summed up into the various impacts. In this thesis, equivalence factors as provided in the CML guidelines [67] were used. In some cases, weighting might be applied to further aggregate the results into a single impact score. However, such an aggregation is not mandatory for an LCA and is not part of this thesis.

The fourth and final phase is the interpretation during which the results of inventory analysis and the impact assessment are interpreted and conclusion and recommendations with respect to the aim of the assessment are given. The interpretation might also include a discussion of potential sensitivities and uncertainties, as well as limitations.

4.1.1 Uncertainties of LCA

According to Huijbregts et al. [68] and Lloyd et al.[69], uncertainties related to LCA can be grouped into the following three categories:

- Parameter uncertainty, which is the uncertainty in the data used (due to imprecise estimates, assumptions or measurements).
- Model uncertainty, which stands for the uncertainty in the models used to represent the real world, including uncertainties due to the absence of suitable characterization factors or an insufficient spatial differentiation.
- Scenario uncertainty, which is related to value choices such as allocation, system boundaries and choice of impacts.

In the context of this thesis, parameter uncertainty was found to be of particular relevance for the emerging technology parts of the different life cycles. In fact, an estimation of whether the data used could serve in the assessments was challenging. However, it seems the challenge is more fundamental than that and rather turns into the question of whether to use certain data in order to conduct any assessment at all or whether to continue searching for other data that might not even exists yet. Of course, this should not be understood as a pledge for deliberately using the first set of data one might find. Instead, the intention here is to increase awareness for the fact that data is an issue for emerging technologies and that results need to be interpreted with this in mind.

Model uncertainty for biomass based products is particularly important with regard to time lags between CO_2 release and uptake from biomass. Currently, there is no agreed upon method on how to assess their impact in LCA, leading to considerable uncertainty in assessment results. An additional uncertainty for biomass products, is the impact assessment of land use. Though, a guideline for such assessment has recently been released [50], it is still far from every day application. In this thesis, model uncertainty for time lags and land use were approached by testing and investigating different methods for their assessments.

A value choice of importance is the one on allocation. While in this thesis allocation based on economic partitioning was prevailing, this might be debated. For example, Tuvfesson et al. [32] argue that allocation based on system expansion should be applied for biomass based bulk chemicals. However, they [32] also point that this might introduce more uncertainty to the analysis. In addition, also Pawelzik et al. [38] reason that system expansion would be a feasible option for biomass based materials. However, at the same time they [38] also state that economic partitioning is more justifiable than energy based partitioning, since biomaterials are produced for material and not for energy purposes.

The case studies present in Papers 1-4 were conducted using scenarios with set locations, scales and processes. However, especially the value choices of scale and process are prone to uncertainty, since emerging technologies can/will evolve in scale, as well as, in their process set up. For this reason, the findings of this thesis, should be seen as one step on the way of identifying potential environmental hot spots for biomass based bulk chemicals, and additional and /or other hot spots might be found with assessments at later points in time.

The previous paragraphs have discussed the uncertainties related to LCA and consequently the results it provides. However, every event is uncertain until the moment it actually happens. For this reason, uncertainty in results should not be taken as a justification for total halt. Instead, results should be seen as a means to create awareness and to spark discussions and actions, on how to approach the identified problems in a creative and versatile manner [70, 71].

4.1.2 Limitations of LCA

Though LCA is a useful tool to get an impression of a product's or process' potential environmental impact, it also has its limitations like every tool (see e. g. [72-75]).
One limitation of particular relevance for emerging technologies is that LCA assesses things as if in steady-state, without considering what might happen over time to the technology under assessment. Moreover, LCA has commonly a low temporal resolution, however (especially for biomass based products) the consideration of emission timing could be decisive for LCA results as shown in e. g. Cherubini et al. [76] and Repo et al.[77].
Finally, traditionally LCA does not consider economic and social aspects. These, however, are also important for real world problems, which is why LCA should be combined with other tools to get a more diverse impression of the problem under investigation.

4.2 Scenario Development within LCA

The SETAC guidelines on 'Scenarios in Life Cycle Assessment' [64] define a scenario in the context of LCA as "a description of a possible future situation relevant for specific LCA applications, based on specific assumptions about the future and, when relevant, a description of a path from the present to the future" [64]. Moreover, the guidelines [64] provide a differentiation of three types of scenarios, including valuation scenarios, environmental scenarios, and technology scenarios. Particularly the last type (technology scenario) was relevant for the cases investigated as part of the thesis.

A further important part of the guidelines is the description of principles for the construction of scenarios, which are grouped into what-if and cornerstone (see Table 2 for major features). Though more differentiating groupings have been suggested (see e. g. [78-80]), their overall features seem to generally match with one of the two SETAC categories. For example, the Predictive Scenario approach described in Börjesson et al. [78], which aims for near-term future scenarios and builds on a fairly good knowledge of the object under study and its surroundings, could be grouped under the guideline's what-if approach. Similar, their Explorative Scenario [78] with its long time horizon, the wide span of investigated options and the potentially unknown surroundings, resembles several features of the cornerstone approach.

Using the guideline's approaches and considering the time horizon under assessment (near-term future), the technology scenarios in Paper 1-3 were constructed using a composite of what-if and cornerstone approach. On the one hand, the scenarios are dealing with a study object that is at an emerging state (biomass based production of ethylene via emerging fermentation and gasification processes) with the aim to support the development of this object; a clear feature of the cornerstone approach. On the other hand, the scenarios were developed with very specific assumptions, that are not necessarily covering the outer limits of possible developments regarding e. g. process choices and conditions, feedstock options and origins, as well as scale.

Table 2 Major features of cornerstone and what-if approach based on [64]

Cornerstone approach	What-if approach
new field of research	well known research field
complex research object	simple research object
purpose: to increase the understanding	purpose: to investigate consequences of specific, discrete uncertainties and assumptions
used for development and design purposes	used for comparison of existing systems

Apart from the approaches, the method/s used for the development of a scenario are of importance as well. Different authors (e. g. [64, 78, 81]) suggest a variety of methods including workshops, extrapolation, and optimizing modeling. For this thesis, scenarios were mainly developed using participatory methods [64]. This included the discussion with experts such as process developers for fermentation and gasification processes, as well as enzyme producers (Papers 2 and 3). Moreover, discussions with other industrial stakeholders (e.g. polyethylene producers and users), forest agencies, and the scanning of published studies investigating e. g. feedstock options for future gasification based fuels in Sweden and land use change emissions in Brazil, played an important role in the development of the scenarios in Papers 1-3.

4.3 Process simulation and LCA

Over the years, the use of data generated by process simulations has been shown to be a useful approach to inventory life cycle processes. For example, LCAs on the production of chemicals and solvents such as phosphoric acid, ammonia or acrylic acid (e.g. [82-84]), as well as, on the production of steel (e.g. [85, 86]) have made use of data originating from process simulations. Process simulation has also been used for the assessment of coal fired power plants and water treatment processes [87, 88]. Moreover, it is also frequently used as a basis for the assessments of biofuels (see e.g. [89-93]).

In this thesis, data based on process simulations were used for the following processes:

(1) The **wood fermentation process** including the upgrading of the ethanol was based on process simulation data provided by researchers at Lund University, Lund, Sweden (Ola Wallberg and colleagues). The simulation, which is set up in AspenPlus, was based on lab scale experiments (see [51-53]) conducted at Lund University.

(2) The **wood gasification process** including conversion to methanol was investigated using data from Isaksson et al. [54]. Their data are based on process simulations conducted with the software AspenPlus in combination with calculations based on literature values.

(3) The **conversion of ethanol to ethylene** was based on historical literature data in Paper 1 and Paper 2. However, for Paper 3 the inventory data for the process were updated, using more recent data generated by Arvidsson and Lundin [94]. They modeled the process in the process simulation AspenPlus using literature and communications with experts.

4.4 Research Process for method contributions

Under a method perspective, the aim of this thesis is to contribute to the methodological development of life cycle assessment. For this purpose, the procedure depicted in Figure 3 was applied. In principle this procedure is a case study methodology as applied in social science or management research [95, 96]. However, while in these areas case studies are used to get an insight into, develop, test and extend /refine qualitative theories [95, 96], in this thesis they were used to:

- Test quantitative methods, in order to discover potential methodological and practical challenges, which can be used as a further guide to method development and harmonization.

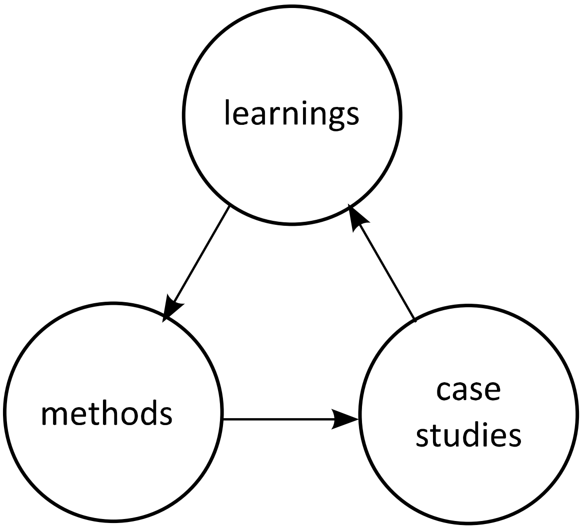

Figure 3 Research process for method contributions

4.5 Methods tested for the assessment of Land Use and Time Lags

The following chapter provides an overview about the methods tested for the global warming impact assessment of land use and time lags for CO_2 uptake and release from biomass. It starts with a brief overview on the current state of method development, followed by the description of the testing procedure and the methods tested.

4.5.1 Introduction to Land Use

The assessment of land use is still a challenging task for LCA and various assessment methods have been proposed within recent years. However, before describing these different methods, the following paragraph will give a short overview on what is considered as land use.

In general land use can be divided into two components (1) land occupation and (2) land transformation [97]. Land occupation is the maintenance of man-made land properties (e. g. keeping land under agricultural use) [98].

In contrast, land transformation, also called land use change[2], is the man-made change in the use of land [99] (e.g. the change from forestry to agriculture). Land use change can be further divided into direct and indirect land use change (ILUC), with direct land use change (DLUC) being the change on the land directly used to produce a crop or feedstock [100]. In comparison, indirect LUC is the change in land "caused by cultivating biomass... on land which previously was used for other cultivation," if the demand for the product "formerly produced in the land would remain... [and] would have to occur elsewhere." [101].

The assessment of the different types of environmental impact related to land use has long been recognized as important, but "difficult" in LCA. Land use causes environmental impact in many aspects, including biotic production, climate regulation, water purification, freshwater regulation and erosion regulation [50] and might be estimated in many different ways, including global mean surface temperature change [102] , biotic production potential or biodiversity damage potential [103], to name just a few. However, in this thesis only the global warming impact related to carbon flows is further discussed, notwithstanding the importance of the others.

As is often the case in the scientific community, methodologies for the assessment of a certain aspect develop along different lines. This also applies for the methods on land use, and the following section will give a brief overview of these developments. Moreover, in Chapter 4.5.1.3 the topic of time lags is introduced together with land occupation, since these two topics can be seen as related.

4.5.1.1 Indirect land use change - ILUC

Fueled by the studies of Searchinger et al. [14], Fargione et al. [13], and Fritsche [104], the topic of land use change (LUC) and related emissions has, over recent years, evolved into a central issue for biomass based products. However, despite the steadily increasing awareness for the potential environmental impact of emissions from land use change, there is currently no commonly agreed method on how to account for these emissions in environmental assessments such as LCA. Especially the issues of whether and how to approach indirect land use change (ILUC) emissions are still heavily debated. For example, the British Publicly Available Specification (PAS) 2050 for the greenhouse gas assessment of goods and services

[2] Please note that hereafter the term land use change will be used for land transformation.

[105], explicitly excludes ILUC emissions from their framework, while including emissions from direct land use change (DLUC). Also the European Parliament (within the European Renewable Fuel Directive (RED) [106] only recently provided ILUC emission factors, though already in previous versions of the Directive the need to assess ILUC emissions was clearly stated [107].

In contrast, two agencies estimating ILUC emissions at a very early state were the California Environmental Protection Agency (EPA) and the United States (US) EPA. They published data for ILUC emissions already in 2009 and 2010, respectively. However, despite assessing the same biofuels, the two agencies provide very different ILUC data. For example, while the California EPA [108] estimates the ILUC emissions for sugarcane ethanol to 46 g CO_2 eq /MJ ethanol, the US EPA [109] gives approximately 3.7 g CO_2 eq /MJ ethanol. This is a considerable range, which is mainly caused by differences in the underlying models (partial equilibrium model versus global general equilibrium model), the LUC emission factors applied (data "factors by region within a country" versus "factor by land type within a region"), and the time horizon under consideration (from 2010 to 2022 versus from 2001 to 2015) [110]. The significant difference between the ILUC emissions factors from the California EPA [108] and the US EPA [109] stresses the severe uncertainties related to the assessment of ILUC effects and related emissions. These are mainly caused by [111-116]:

- The theoretical models used for the estimation of land use change effects (emissions) and their underlying assumptions as regards to e. g. market developments, time horizons, crop yields and management, as well as area under change,
- The way greenhouse gas emissions are allocated between different crops,
- Amortization period over which the emissions are distributed and,
- The spatial resolution of the data used.

Based on these uncertainties ILUC is commonly not part of life cycle assessments. However, some methods have recently been proposed, in order to include this important issue into LCA. For example, Schmidt et al. [117] provide a preliminary method which considers the ILUC effects of intensification and displacement and which uses a fate function for CO_2 instead of amortization. In addition, also Kløverpris et al. [118] suggested a method for the assessment of ILUC emissions. Their method uses a dynamic baseline to estimate yearly ILUC emissions instead of using annualized data and considers ILUC from the perspective of accelerated expansion and delayed reversion.

4.5.1.2 Direct land use change - DLUC

The issue of whether to account for emissions from direct land use change (DLUC) seems less controversial, in comparison to ILUC, although also for DLUC methods are still varying. For example, the European Renewable Energy Directive RED [107] prescribes that emissions from DLUC are accounted for as the difference between the carbon stock under land use and under a reference state, which is the state in January 2008 (or later, depending on the assessment). The difference is annualized over 20 years.

Annualization over a 20-year period is also used in the PAS2050 [105], which however uses January 1990 as its reference state (or later, depending on the assessment). Moreover, also Cherubini and Jungmeier [119], García et al. [120] and Meul et al. [121] annualize the difference in carbon stock over 20 years.

Another method or rather guideline using 20 years of annualization is the UNEP-SETAC guideline on global land use impact assessment [50], which builds on several methods and frameworks including among others Müller-Wenk and Brandão [42], Milà i Canals [98] and Brandão et al. [122]. However, in comparison to the aforementioned methods (e.g. Cherubini and Jungmeier [119]) the guideline distributes the DLUC 'burden' (DLUC does not lead to emission release in every case) not evenly over the 20 years of annualization. Instead the 'burden' gradually decreases from year to year, resulting in a high burden for the first years and a low burden for the final years.

Though 20 years of annualization seems to be common, there are also studies that investigate the effect of using other annualization periods. For example, Reijnders and Huijbregts [123] use 10 and 25 years to annualize DLUC emissions and Cederberg et al. [124] go even further by applying a range of one to fifty years. In addition, Cederberg et al. [124] also consider changes in productivity and changes in the area used to produce beef during the amortization time, as well as, potential emissions from decaying processes (e. g. decay of biomass residuals from LUC). Moreover, they suggest to distribute emissions from DLUC not only over the product produced directly at the changed land, but to also put some of the burden to the product that drove the LUC. Using their example [124], this would mean that emissions from DLUC are not only distributed to the beef produced directly from the changed land, but also to beef for export, which could then be seen as ILUC for this exported beef.

Yet another method, the time correction factor (TCF), to account for DLUC was suggested by Kendall et al. [125]. They noticed a discrepancy between the GWP calculated by considering

DLUC emissions as an emission pulse at year zero and an amortization of DLUC emission over a specific time and proposed to bridge this discrepancy with a time correction factor.
As can be seen from the above examples, there are still several methodological and practical challenges to overcome, to consistently assess effects DLUC. Among others, the choice of annualization time, as well as, the choice of reference state and data ([126], [124]), are in further need for research and harmonization .

4.5.1.3 Land occupation and time lags for biomass CO_2

As pointed out in the UNEP-SETAC guideline [50], another important aspect of land use, apart from land use change (transformation), is land occupation. The guideline suggests calculating the impact from land occupation by multiplying the difference in land quality (e.g. carbon stock) between a reference state and the occupation state, together with the amount of time the occupation is lasting and the area under occupation. Similar approaches are also used by the methods underlying the guideline e.g. the *CRP* [42] (see Table 3 for more details on the method).

An important assumption used in the UNEP-SETAC guideline [50] is that land quality stays constant during the time of occupation, however, from a carbon perspective this assumption might be questioned. Particularly for long rotation crops such as wood, a constant carbon stock might be debated, since their long growing times lead to varying carbon stocks and related time lags between CO_2 release and uptake from biomass. In fact various methods have been proposed, in order to assess the climate impact of these time lags. For example, Väisänen et al. [40] propose to take long growing times into account with the help of a weighting factor (see Table 3 for more details). Another method proposed for such assessments is the GWP_{bio} characterization factor developed Cherubini et al. [41] and the GWP_{netbio} characterization factor proposed by Pingoud et al. [127] (see Table 3 for more details) .
In addition to the above methods, there are a number of other methods taking differences in carbon stocks over time into account see e.g. [128, 129].

4.5.2 Assessment and Method Testing for land use and time lags

Land use
In this thesis, the impact of land use has been assessed under two approaches.

Approach 1

Approach one was 'learning by doing' for the case of sugarcane based ethylene (Paper 1). In more detail, Paper 1 assessed the global warming effect of indirect land use change emissions for Brazilian sugarcane in the below described manner.

At the time of conducting the assessment of Paper 1 (and still at the time of writing), a fully developed method for the assessment of LUC was missing, therefore a preliminary method as summarized below was applied.

The study for sugarcane PE includes an attributional and a consequential assessment, which were intended to represent a near-term future state (attributional) and the consequences of a further expansion of sugarcane due to increased sugarcane demand (consequential). Based on these scenarios, for the attributional assessment emissions for direct LUC were assumed to be zero (based on that recent expansions had taken place into areas already used for agriculture [130]). For the consequential assessment the main share of future expansion was assumed to be occurring into areas already used for agricultural activities, with a minor share expanding into virgin areas [131]. Moreover, emissions from indirect LUC were included into both the consequential and the attributional assessment. For the attributional assessment, this was based on discussions at a European expert work shop [132] which recommended to include effects of ILUC into attributional assessments in cases of a recent, rapid land use changes. This recommendation was made, in spite of ILUC being an inherently consequential concept.

Land use change was not considered for the studies where the feedstock came from forest that have been managed for a long time, i.e. Swedish forests, where the change from natural to managed forest occurred a long time ago.

Approach 2

The second approach with regard to climate impact assessment of land use (Paper 4) was the testing of two currently proposed methods on the thesis' cases (see below for more detail on the cases), in order to:

- Determine the potential global warming effect of land use for this thesis' cases.
- Explore their methodological and application challenges and with this support and guide further development and harmonization.

The two tested methods, which hereafter are referred to as land use methods, are:

- *CRF* - climate regulation potential [42], and

- GWP due to changes in soil organic carbon content [122], hereafter referred to as *GWP soil*

The major features of the two methods are listed in Table 3.

The two methods were chosen, since they the focus on the global warming impact of land use and since they were specifically developed for the application in LCA. In addition, they clearly differentiate between impact from direct land use change (called transformation in the studies) and from land occupation, making results transparent. Finally, they are among the methods, which form the background for the recently released UNEP-SETAC guideline [50].

Time lag

Another, still critically discussed issue related to the assessment of biomass is the assessment of time lags between CO_2 release and uptake from biomass. In this thesis (Paper 4), three methods for the global warming impact assessment of time lags were tested on the thesis' cases. The purpose of this test was to:

- Determine the potential global warming effect of time lags for this thesis' cases.
- Explore methodological challenges and challenges related to the practical application of these methods, in order to support and guide further method development and harmonization.

The tested methods are:

- GWP_{bio} [41]
- GWP_{netbio} [127]
- *WF* (weighting factor) [40]

Their major features are presented in Table 3 and the methods are hereafter referred to as carbon cycle methods.

The GWP_{bio} was chosen, since it is currently one of the most discussed methods for the assessment of time lags in LCA. The GWP_{netbio} can be seen as an extension of the GWP_{bio}, which considers avoided emissions from the avoided production of an alternative product and the potential impact due to lost uptake. Finally, the underlying principles of *WF* are similar to the GWP_{bio}, however, its modeling is much simpler.

Major modeling assumptions

As has already been stated, the land use and carbon cycle (time lag) methods were tested by applying them to the three biomass routes investigated in this thesis. More specifically, the test case was polyethylene (PE) packaging, which is incinerated at the end of life. PE was used here, as it is one of the major applications of ethylene.

For the GWP_{bio} and the GWP_{netbio}, the growth of biomass was modeled using a forest growth function [41] for the wood routes, and a probability density function [76] for the sugarcane route. The growth modeling for the *WF* was based on a simple linear function for the wood and the sugarcane routes.

For the *CRP* applied to the wood routes, no direct LUC was assumed, since in Sweden the change from natural to managed forest occurred a long time ago. Moreover, the impact from land occupation was calculated based on the average land occupation flow over the whole of Sweden. The *CRP* for the sugarcane route considered both land occupation and direct LUC. The latter was based on data from the FAO statistics [133], while the impact from land occupation was the difference in carbon stock between sugarcane and grassland (Cerrado). The *GWP soil* for the sugarcane route was based on soil carbon sequestration data as stated in Anderson-Teixera et al. [134]. For the wood routes, the GWP soil was assumed to be zero, since there is no difference in soil carbon between a natural and a managed forest.

Analysis of the land use and carbon cycle methods

The analysis of the methods built upon a framework developed by Helin et al. [135], particularly on the following four questions:

(1) Does the method use a reference situation?

(2) Does the method account for potential timing differences between emissions release and uptake?

(3) Does the method consider all carbon pools (above and below ground) related to the biomass system?

(4) Does the method account for temporary carbon storage in biomass-based products?

Table 3 Major features of the land use and carbon cycle methods

Feature	Land use methods		Carbon Cycle methods		
	CRP	GWP_{soil}	GWP_{bio}	GWP_{netbio}	*WF*
Carbon pools considered	above and below ground carbon	soil organic carbon	depends on available data - always above ground carbon in growing biomass	depends on available data - always above ground carbon in growing biomass	above ground carbon in grow-ing biomass only
Modeling	direct land use change: change in carbon stock due to transformation multiplied with duration factor for transformation occupation: difference between occupation state and reference state multiplied with duration factor for occupation and with area	direct land use change: transformation impact is allocated to the 100 years following the transforma-tion occupation: carbon sequestration or release rate multiplied with area and time of oc-cupation	growth function (or other data) in combination with Bern carbon cycle model to derive characterization factor	growth function (or other data) in combination with Bern carbon cycle model to derive characterization factor	simple, linearly distributed up-take to derive inventory factor

Continuation of **Table 3**

Additional remarks	no guidance on whether or how to annualize the land use change impact		considers actual timing of emission release and uptake on a continuous basis	considers actual timing of emission release and uptake on a continuous basis considers lost uptake also interpreted as land occupation impact [103] considers avoided fossil emissions	assumes all emissions to occur at time of harvest, emissions uptake considered on yearly instead of continuous basis

5 Results & Discussion

The two aims of the thesis are (1) to provide guidance for the development and production of biomass based ethylene and (2) to contribute to the methodological development of life cycle assessment. The results in this respect are presented and discussed in the subsequent chapter, which is structured as follows:

- Section 5.1 presents and discusses the hot spots identified for the three investigated biomass routes to ethylene. Moreover, measures on how to lower the impact of these hot spots are proposed.

- Section 5.2 presents and discusses the results for the comparison between the biomass routes and a fossil route.

- Section 5.3 presents and discusses the methodological contributions of the thesis. The section is divided into (1) contributions for the assessment of emerging products (i.e. products that are produced via currently emerging technologies), and (2) contributions with regard to the climate impact assessment of land use and time lags for biomass CO_2.

5.1 Potential Hot Spots for biomass based ethylene and Improvement Suggestions

In this section the hot spots identified for the production of biomass based ethylene are presented and discussed. In addition, improvement options to tackle these hot spots are proposed. The section starts with the sugarcane route, followed by the wood fermentation route, and closes with the wood gasification route. As a reminder, Paper 1 used a consequential and attributional approach for the assessment of sugarcane based ethylene, while Papers 2 and 3 used only an attributional approach.

5.1.1 Sugarcane based ethylene via fermentation - Paper 1

The choice to investigate the production of ethylene from sugarcane ethanol was influenced by developments at the start of this thesis. In fact, the large-scale industrial production of PE from sugarcane ethanol was just close to realization [48] at that point, creating a great interest in the environmental impact of sugarcane based ethylene and polyethylene, as well as, in its potential environmental hot spots. The findings for the latter are presented in the following paragraphs and are detailed in Paper 1.

The production of sugarcane based ethylene has hot spots along its entire life cycle.
A number of common hot spots were revealed for the attributional and consequential assessment of sugarcane based ethylene in Paper 1. These included for the global warming potential the activities related to the sugarcane cultivation (called 'biomass acquisition' in Figure 4) and the ethylene production (this is a new finding in comparison to Paper 1, which is based on updated process data [94]), and the long sea transport and the ethanol production for the acidification and eutrophication potential (see Figure 4). In addition, ethylene emissions stemming from the conversion of ethanol to ethylene were most important for the photochemical ozone creation potential (this is a new finding in comparison to Paper 1, which is based on updated process data [94]).

There are various ways to reduce the potential environmental impact.
Based on the hot spots identified, there are various options to reduce the impact of a sugarcane based production of ethylene, including for example the use of cleaner fuels. In addition, the production of more valuable co-products and an increase in efficiency (e.g. increased ethanol yield) could lower the impact stemming from the ethanol production.

Emissions from indirect land use change need to be considered.
The assessment of land use change, particularly indirect land use change, is still a delicate issue in LCA. However, the preliminary assessment conducted in the thesis highlighted that emissions from indirect land use change can affect the hot spots for global warming considerably. In fact, as can be seen in Figure 4, they can turn the focus completely towards land use change (ILUC is included under biomass acquisition in Figure 4). For this reason, potential land use changes need to be considered when selecting feedstocks.

5.1.2 Wood based ethylene via fermentation - Paper 2

Influenced by the hot spots identified for the sugarcane case, Paper 2 investigated a potential future Swedish production of ethylene from wood. In particular, the assessment focused on a fermentation based process route, supplied with sawmill chips (a by-product from sawmills) as the feedstock. The study revealed a list of potential hot spots, which will be discussed in the following paragraphs.

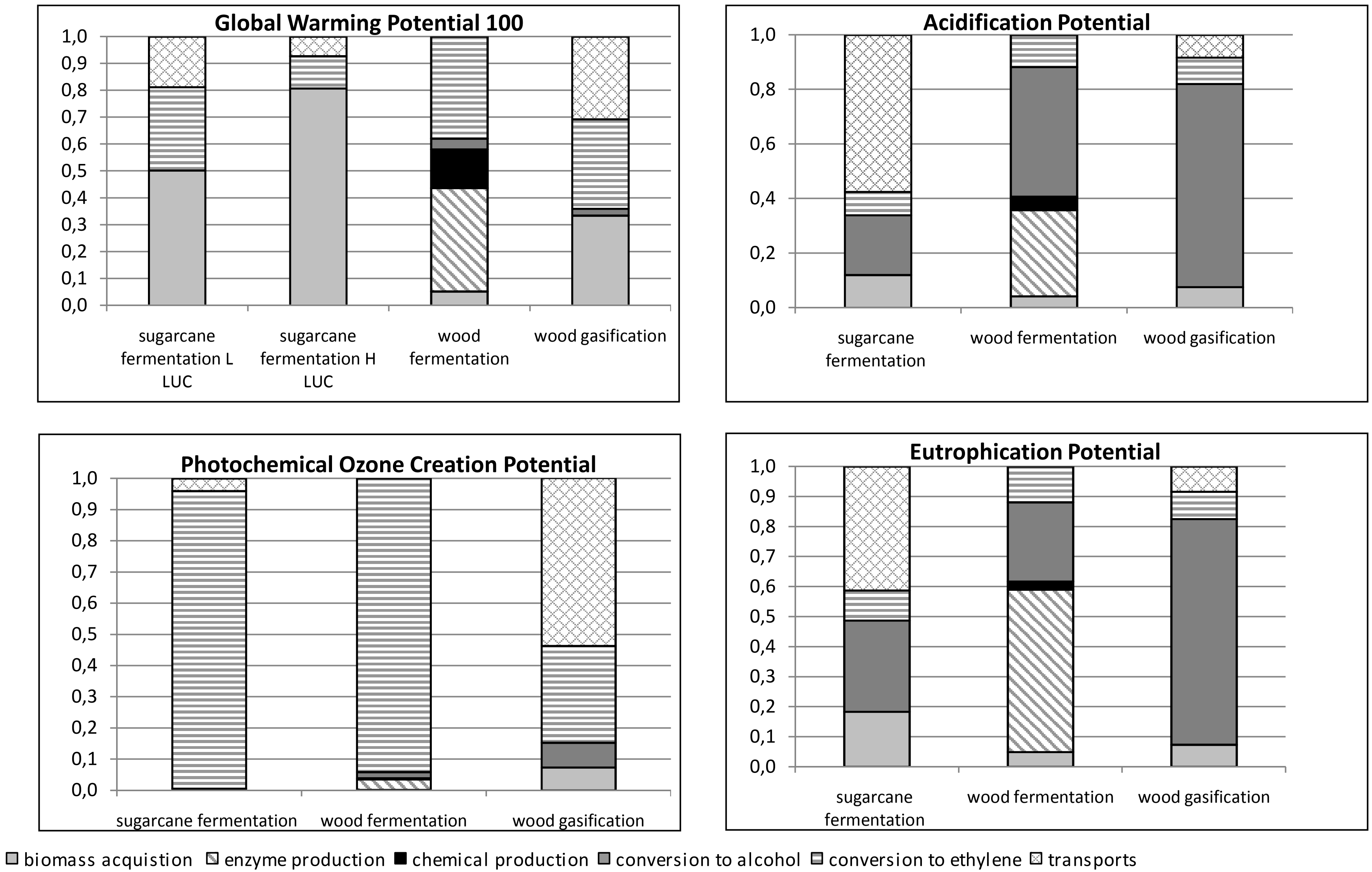

Figure 4 Hot spots for the three biomass routes to ethylene, please note that since hot spots were similar, the figure only shows the results for the attributional assessment of the sugarcane route; the same applies to the gasification route, hot spots are only shown for the GROT route. Moreover, the results for the wood fermentation route are only presented for the scenario under low enzyme product consumption. sugarcane H LUC = scenario with high estimate for ILUC emissions; sugarcane L LUC = scenario with low estimate for ILUC emissions

Off-site enzyme production cannot be neglected.

The off-site production of enzymes[3] was identified as an environmental hot spot for the global warming, acidification and eutrophication potential of the wood fermentation route (see Figure 4). This is a significant finding, since e.g. Wiloso et al. [136] point out that enzyme production is many times not even included in LCAs for bio-ethanol. However, also Slade et al. [137] found off-site enzyme production to be important for the global warming potential of wood ethanol. In addition, even when produced on-site, enzymes are still a hot spot for the global warming potential, as revealed by Gonzalez-García et al.[138] in their study on Swedish wood based ethanol.

There are different possibilities to lower the environmental impact related to the fermentation's hydrolysis step.

An option to lower the impact of the enzyme on the environmental impact of the fermentation is to lower the process' enzyme consumption by e.g. increasing the activity of the enzyme. Moreover, lowering the impact of the enzyme production process itself would be of significance and further investigations are recommended.

Apart from enzymatic hydrolysis, there is a variety of other processes to hydrolyze wood, including e.g. diluted and concentrated acid hydrolyzing processes. However, using either of these two processes could add considerably to the overall equipment cost, due to the need for corrosive resistant equipment [139]. An additional drawback, at least for the dilute acid process, is the formation of compounds toxic to the yeast, which leads to low ethanol yields [140-142]. In comparison, low yields are not an issue for the concentrated acid process, however, it has problems with the energy intensive recovery of the acid used in the process [143]. Comparing the environmental impact of a diluted acid with the enzymatic process, Slade et al. [137] found the diluted acid process to have a lower impact. The opposite seems to be the case for the concentrated acid process, as found by Kadam et al. [144]. However, it needs to be noted that they [144] use a process with on-site production of enzymes for their comparison. The latter allows for a process integration of the enzyme production with the rest of the ethanol production, lowering the impact of the former.

The conversion of biomass to ethanol (fermentation including distillation) needs to be further developed.

Another hot spot for the wood fermentation route is the fermentation process itself, including post-processing (distillation) to anhydrous ethanol (in Figure 4 labeled as 'conversion to al-

[3] Enzymes are used to hydrolyze the wood before the actual fermentation.

cohol'). These process steps were found to considerably contribute to the environmental impact of ethylene based on wood, in terms of acidification and eutrophication potential. Similar findings are also presented by Gonzalez-García et al. [138] and further development of the fermentation process would be of importance. This could, for example, include measures to increase the ethanol yield or measures to produce other high value co-products. Moreover, it needs to be noted that the ethylene production process does not necessarily need anhydrous ethanol. The use of hydrous ethanol instead would decrease the energy consumption of the fermentation process, and related emissions, by approximately 5%.

The conversion of ethanol to ethylene needs further attention.
The production of ethylene from ethanol was found to be of relevance from two aspects. One is its fuel consumption, which contributes considerably to the global warming potential of the route (this is a new finding in comparison to Paper 2, and is based on updated process data [94]). The other is its ethylene emissions, which cause a considerable share of the photochemical ozone creation potential. Both aspects need to be addressed including measures such as the reduction of ethylene emissions, the reduction of the process' fuel consumption, and an increase in ethylene yield.

5.1.3 Wood based ethylene via gasification - Paper 3

Another potential option to produce ethylene from biomass is via gasification. In fact, several gasification plants are planned to be built in the near term or are currently under construction [22, 145]. However, even though these plants are dedicated to fuel production (e.g. ethanol, methanol), future plants might as well supply the chemical industry. For this reason, a potential future production of ethylene via gasification of wood to methanol in Sweden was investigated in Paper 3. In particular, the production from a feedstock of tops and branches only (tops and branches are called GROT in Swedish) and from a mix of different woody feedstocks was assessed, revealing the following potential hot spots.

Biomass acquisition is a hot spot also for feedstocks based on by-products.
The acquisition of the biomass was found to be a potential hot spot, both for the mixed feedstock, as well as, for the GROT feedstock scenario. For the latter, also the transport of the biomass to the gasification plant was of special importance and further improvement, such as increased efficiency or use of cleaner fuels, would be of relevance. Moreover, it would be worthwhile reflecting on the issue whether a less distributed feedstock would be more suitable.

The conversion of biomass to methanol (gasification including synthesis to methanol) is of importance.
The gasification process, including synthesis to methanol (in Figure 4 labeled as 'conversion to alcohol'), influenced the acidification and eutrophication potential of the gasification route considerably, as shown in Figure 4. Similar findings are also presented in Bright and Strømman [91], who found the gasification process to be key for the acidification potential of wood ethanol. For this reason, measures such as NO_x removal would be recommended to lower the impact of the process.

The inventory of biogenic CO_2 confirms the role of the gasification process as a hot spot.
In Paper 3, biogenic CO_2 was accounted for as a separate item in the inventory. The results showed that the gasification process is a major source of biogenic CO_2. This confirms findings by Daystar et al. [146] and Kikuchi et al. [34] and further improvements with regard to conversion efficiency would need to be investigated.

The conversion of methanol to ethylene needs to be addressed.
The production of the ethylene from methanol was a considerable contributor to the global warming and photochemical ozone creation potential of the gasification route. For this reason, further development regarding the process' energy consumption need to be strived for.

To summarize, the production of biomass based ethylene is linked to a variety of potential hot spots, which need to be addressed throughout subsequent development phases.

5.2 Comparison of the different routes

Section 5.2 presents and discusses the findings for the comparison between the fossil and the biomass routes, in the following order:

- Comparison with regard to Global Warming Potential including the effect of land use and time lags
- Comparison with regard to Acidification, Eutrophication and Photochemical Ozone Creation Potential

Global Warming

One of the main drivers for the investigation into biomass based bulk chemicals is the expectation of a reduced global warming impact, in comparison to a fossil alternative. This thesis'

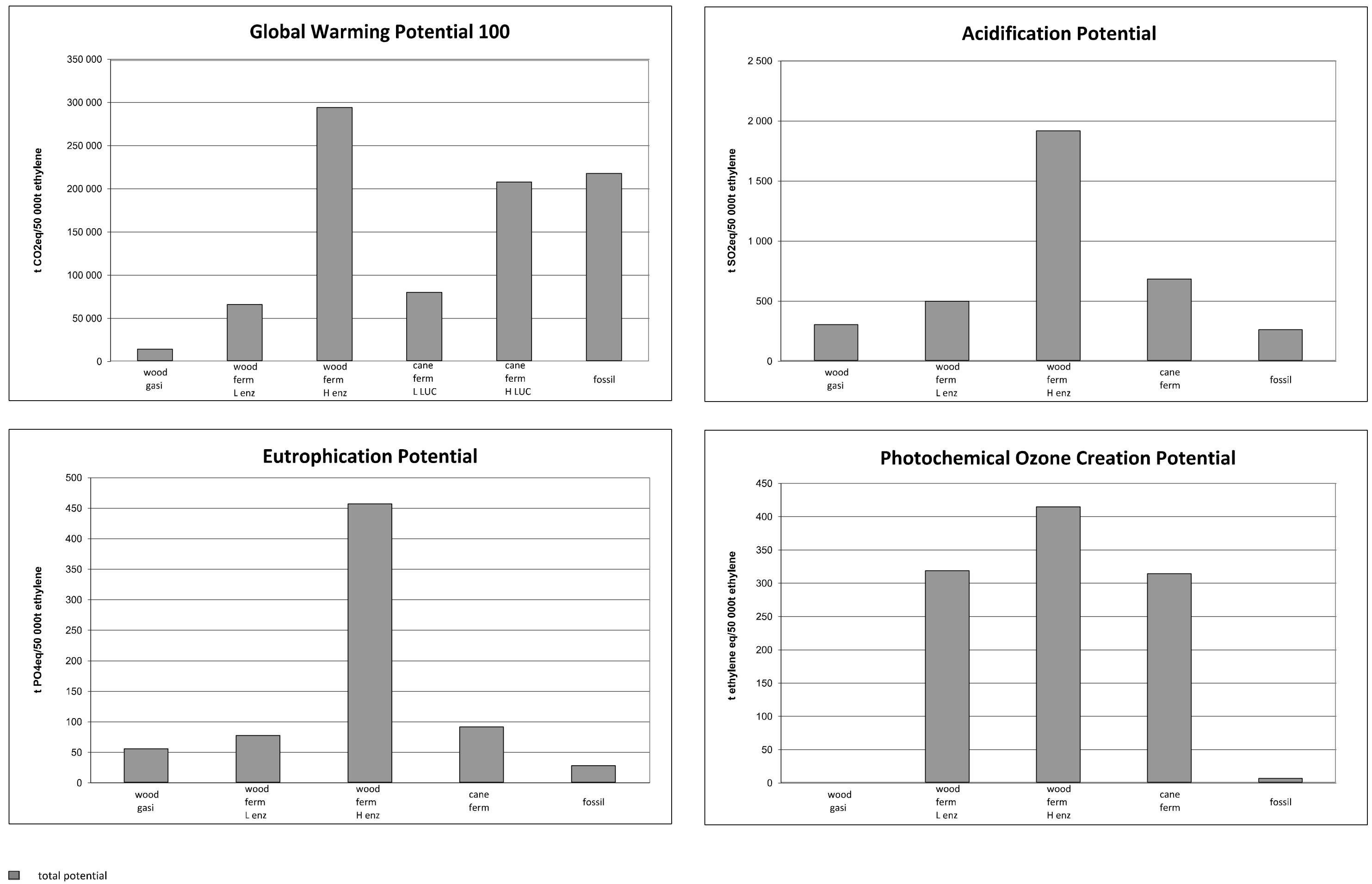

Figure 5 Environmental impact potentials of the different biomass routes and the fossil route; Please note: (1) the Global Warming Potential for the fossil route also contains the potential CO_2 emissions from the ethylene, (2) only GROT results are presented for the gasification route since results were similar between the two feedstock scenarios. wood gasi = GROT gasification route, wood ferm L enz = wood fermentation route low enzyme consumption, wood ferm H enz = wood fermentation route high enzyme consumption, cane ferm L LUC = sugarcane fermentation route low ILUC emissions, cane ferm H LUC = sugarcane fermentation route high ILUC emissions, cane ferm = sugarcane fermentation route, fossil = fossil route

results show (see Figure 5) that with respect to global warming, and if enzyme consumption is estimated low, as well as, if possible global warming effects of biogenic CO_2 and indirect land use change are disregarded, all three biomass routes were better than the fossil route. For the sugarcane route similar results are also presented by Hermann et al.[147], Chen et al. [148] and Kikuchi et al. [149], who assess the production of polyethylene from sugarcane. Also Alvarenga et al. [150] finds sugarcane based PVC to have a lower global warming potential in comparison to the fossil alternative.

However, there is a ranking regarding the preferability of the different biomass routes. Under the current state of development, the gasification route could outperform the fermentation routes. For the wood alternative this was also found in Bright and Strømman [91], who investigated the production of wood ethanol via fermentation and gasification. Also Mu et al. [151] state that, depending on the variety of co-products, a gasification route to ethanol could be environmentally preferable to a fermentation route.

The ranking between the sugarcane and the wood fermentation route depends mainly on whether the enzyme consumption of the wood route can be reduced. If enzyme consumption is assumed to be high, the wood route turns out less preferable than the sugarcane alternative and even gives emissions in line with those of the fossil route. When a low consumption of enzyme is assumed, the wood fermentation and the sugarcane routes had a comparable impact.

Land use and its effect on global warming

Though the above comparison could be seen as straight forward, there are a number of potential issues that need to be taken into consideration and that could influence the preferability of the biomass routes. One such issue is land use: as has been stated in Section 4.5, land use can be divided into land occupation and land use change, the latter of which can be further grouped into direct and indirect land use change.

In this thesis, the issue of indirect land use change was investigated for the sugarcane based ethylene (Paper 1). It was found that, emissions from indirect land use change could more than double the sugarcane's global warming potential, making it comparable to the fossil route (see Figure 5). Moreover, though this finding was highly depended on the choice of emission data, it shows that ILUC emission could backfire, making biomass not an inherently better choice.

Regarding the issue of direct land use change and land occupation, Paper 4 tested the following methods (denoted as land use methods):

- *CRP* [42], and
- the *GWP soil* [122] to assess the impact of these two factors on the biomass routes.

Specifically, the test case was biomass based polyethylene packaging incinerated at the end of life - results are shown in Table 4.

The test provided different results for the two methods, with the *GWP soil* having no effect for the wood routes and a positive effect (carbon uptake) for the sugarcane route. In comparison, the *CRP* method resulted in some increase in global warming for the sugarcane route and a considerable increase for the wood routes, highlighting the importance of an efficient use of biomass, in order to minimize the impact from land use. However, despite these increases, the biomass routes were still preferable to the fossil alternative.

The differences in results between the two methods are caused by differences in the considered carbon pools - the *CRP* takes below and above ground carbon into account, while the *GWP soil* only considers soil carbon. Moreover, the difference between the sugarcane and the wood routes is mainly caused by the following factors:

- For the *GWP soil*: The soil carbon of the wood routes is the same under management and natural vegetation [152, 153]. For the sugarcane route, soil carbon was found to increase during occupation [134].
- For the *CRP*: The fast growth of the sugarcane leads to a very short occupation time when compared to the wood routes.

Time lags and their effect on global warming

An additional issue of importance is the assessment of potential time lags between CO_2 release and uptake from biomass. This is especially debated for long rotation crops such as wood [41], since their long growing times could lead to considerable time lags between CO_2 uptake and release. For this reason, three methods for the assessment of time lags were tested in Paper 4. These methods were:

- GWP_{netbio} [127]
- GWP_{bio} [41]
- *WF* [40]

Also here, the test case was polyethylene packaging.

As can be seen in Table 4, for the wood routes, the effects of applying two of these methods (GWP_{bio} and *WF*) were significant. In fact, the GWP_{bio} and *WF*, make the wood routes comparable to the fossil alternative. A less severe effect was found for the GWP_{netbio}, since it not only considers the carbon release and uptake of the wood, but also the avoided emissions from the replaced fossil product.

The reason for the critical increase in global warming is the methodological choice of using the full grown forest stand as starting point. Using this point, the trees are harvested and turned into packaging, which is disposed of after a short life time, releasing CO_2 emissions to the atmosphere. An equal amount of CO_2 is eventually taken up by the re-growing trees (the trees do not differentiate between CO_2 of different origin), however, meanwhile the atmospheric CO_2 concentration stays elevated, inducing global warming (see 5.3.2 for more discussion on this starting point).

Table 4 Global Warming Potential for the biomass routes for the land use and the carbon cycle methods, also including the fossil route

	Carbon cycle methods			Land use methods		GWP for fossil CO_2 & other GHG	GWP fossil PE
	GWPbio TH 100 [t CO_{2eq}/t PE]	GWPnetbio TH 100 [t CO_{2eq}/t PE]	WF [t CO_{2eq}/t PE]	CRP [t CO_{2eq}/t PE]	GWP soil C [t CO_{2eq}/t PE]	TH 100 [t CO_{2eq}/t PE]	TH 100 [CO_{2eq}/tPE]
Sugarcane, fermentation	0.0	-3.3	0.0	0.29	-0.26	1.7	4.4
Wood, fermentation	3.1	1.4	3.5	0.87	0	1.5	
Wood, gasification	4.1	1.7	4.6	1.1	0	0.4	

For the sugarcane route, the consideration of time lags has no effect, when applying the *WF* and the GWP_{bio} method. This is caused by the fast re-growth of the sugarcane, which leads to an almost instantaneous uptake of CO_2. Moreover, the GWP_{netbio} results even in a net decrease of global warming, due to the consideration of avoided fossil emissions.

In summary, the consideration of time lags could lead to a significant increase in global warming potential and a change in ranking between the biomass routes.

Acidification, Eutrophication and Photochemical Ozone Creation

In addition to the potential impact on global warming, this thesis also investigated the potential impact on photochemical ozone creation, acidification, and eutrophication. As can be seen in Figure 5, for the last two impacts, all three biomass routes performed worse than the fossil alternative, with the gasification route being more preferable than the fermentation routes. As regards the wood routes, also Bright and Strømman [91] found gasification to be more preferable than fermentation for the production of wood based ethanol. Moreover, also

Hermann et al. [147] found a higher acidification and eutrophication potential for sugarcane polyethylene when compared to a fossil alternative.

The major causes for the higher acidification and eutrophication of the biomass routes are the NO_x and SO_2 emissions released during the conversion of the biomass to ethanol or methanol. Moreover, for the sugarcane route the long distance transport, and for the wood fermentation route the production of enzymes, are decisive. For this reason, further optimization and improvements of these processes are necessary.

Regarding the photochemical ozone creation, the sugarcane and the wood fermentation route showed a significantly higher impact than the fossil and the gasification route. For both routes, this was due to the ethylene emissions released during the conversion of ethanol to ethylene. In comparisons, for the gasification route, ethylene emissions were not documented. Therefore its results for the photochemical ozone creation potential need to be considered preliminary.

In summary, the biomass routes were found to perform better or worse depending on:

- *The impact under investigation,*
- *The route under assessment, and*
- *The assessment of land use and time lags.*

However, overall, it needs to be considered that the biomass routes are still at an emerging state, leaving room for further improvements.

5.3 Methodological Contributions

Section 5.3 presents the methodological contributions of this thesis. It starts with the contributions to the assessment of products produced via currently emerging technologies, which is followed by the contributions to the global warming impact assessment of land use and time lags.

5.3.1 LCA for emerging technologies

The life cycle assessment of products produced via emerging technologies is related to a number of methodological challenges. This thesis focuses on two of these challenges, the development of scenarios and the conducting of the inventory analysis. They are discussed in the following paragraphs.

Scenario development

The development of an assessment scenario is one of the first and most important steps in an LCA, since it determines whether the assessment is of relevance towards its purpose. However, especially for assessments on emerging products, (i.e. products produced via currently emerging technologies) the development of scenarios is a challenge, since it involves numerous choices about how a future state could or should look like [43].

In order to develop scenarios representing a potential biomass ethylene production in Papers 1-3, discussions with different stakeholders were conducted. The stakeholders comprised of both stakeholders that will be and stakeholders that will affect this development, including:

- Forestry agencies,
- Process developers for fermentation and gasification processes, but also
- Other industrial stakeholders such as enzyme producers and polyethylene producers, as well as, industrial users of PE (industries that use PE in their products).

This combination was found to be very efficient, since it provided essential insights into the various needs and demands that will come together during the further development of biomass chemicals. All these considerations need to be taken into account when developing scenarios for a future production of biomass based ethylene.

In summary, the discussion with different stakeholders is critical for the development of relevant future scenarios.

Process simulation

After the Goal and Scope Definition, the next step in an LCA is the Inventory Analysis. However, especially for emerging technologies, this is a critical issue, since industrial scale production data are not available. In the thesis, this challenge was approached by using data based on process simulation. Though the use of process simulation for LCA purposes is not novel (see 4.3) it is especially useful for the assessment emerging technologies for the following reasons.

(1) Process simulation can provide data as close as possible to an industrial scale process, without building an actual plant. Its use therefore allows a first insight into the environmental impact of the emerging technology under a potential industrial scale application.

(2) Due to the simulations' flexibility, they can cover a wide range of potential process set-ups and conditions. This is especially relevant for emerging technologies, as a variety of set-ups and conditions is conceivable and plausible.

However, though the advantages of process simulations are apparent, there are some issues that need to be considered. One issue is that a simulation is only as good as the parameters with which it is set up, which is why process simulations should be developed in cooperation with or by experts. Moreover, a process simulation only covers the conditions it was created for and this needs to be considered when using data and interpreting LCA results. Finally, process simulations need lab or other data as background; however, these might not always be available, particularly for emerging technologies.

Though process simulation should be used with care, it is a powerful tool that can help in the assessing of the environmental impact of an emerging technology and guide its further development. This development might directly aim at the technology itself but might also apply to the overall life cycle the technology is embedded into.

5.3.2 LCA for biomass based products - the issue of land use and time lags for biomass CO_2

One of the last steps in an LCA is the impact assessment. However, for some of the topics occurring during the life cycle of biomass based products, LCA is still encountering difficulties on how to assess their impact. This thesis contributes to the overcoming of these difficulties by identifying methodological and application issues related to the assessment of time lags for biomass CO_2 and of land use. The results of this are presented and discussed in the following sections.

The discussion consists of two parts: the first part focuses on the methodological issues revealed for the global warming impact assessment of time lags and of land use and the second part deals with application issues encountered during testing.
As a reminder, the following methods were tested:

Land use methods:

- *GWP soil*
- *CRF*

Time lag methods referred to as Carbon Cycle methods:

- GWP_{bio}

- GWP_{netbio}
- WF

5.3.2.1 Methodological Issues

The following paragraphs present and discuss the methodological challenges identified for the land use and carbon cycle methods.

Reference states and Reference points

A methodological challenge identified for the land use and the carbon cycle methods, is the need to define a reference state.

Though the tested land use methods (as well as the UNEP-SETAC guideline [50] clearly recommend the use of potential natural vegetation (PNV), PNV is not easily defined. Especially for forestry, this poses a challenge, since the carbon stocks of a mature managed and a natural forest are very similar.

For the carbon cycle methods, the definition of a reference state was particularly an issue for GWP_{netbio}. This was because it uses not only one, but two reference states. One is the state under 'not harvesting but letting the plant continue to grow' (lost uptake), the other is the avoided alternative product system. The latter might be anything from e.g. a coal to a natural gas based product system, and it is up to the practitioner to decide upon this alternative. Since this decision is very case specific, one of the criticisms for the GWP_{netbio} is its case specificity. Moreover, the integration of avoided emissions into an impact factor is unsuitable, as already stated by Helin et al. [135].

The lost uptake used in the GWP_{netbio} has similarities with the assessment of land occupation in the land use methods, and Helin et al. [103] even interpret it as such. However, independent of how lost uptake might be interpreted, its modeling is still a challenge. This is especially true for short rotation crops, such as sugarcane, since the method provides no guidance for this specific application.

It can be argued that, in addition to a reference state, the carbon cycle methods also use a less explicit point of reference. This point is the fully grown forest, which is used as a starting point in all three methods. However, as for example stated by Levasseur et al. [154], this point is not self-evident, but rather depends on the aim of the assessment.

In their study, they [154] propose to use a 'just beginning to grow' forest as reference point, when assessing afforestation projects. This could be understood as a consequential assessment, one that assesses the decision to plant trees (afforest a plot of land). However, a consequential assessment does not necessarily have to apply a 'just beginning to grow' forest as a point of reference. Instead the 'fully grown forest' might be used, e.g. when assessing the impact of cutting down a forest. For attributional assessments, the point of reference seems rather a question of consensus, which is still under way.

To conclude, independent of the assessment approach, the choice of reference point is highly value laden and should be stated explicit in order to allow for discussion.

Carbon Pools under consideration

The question of which carbon pools to consider is clearly defined for the land use methods. The *CRP* method considers above and below ground carbon pools. In comparison, the *GWP soil* method only takes soil carbon pools into consideration, however without claiming that this would capture the full carbon effects of land use.

For the carbon cycle methods, the question of carbon pools is less clearly defined. In fact, it seems to be rather a question of data availability. Cherubini et al. [155], for example, consider not only changes in the carbon pools of growing but also of decaying biomass. However, such data might not always be available.

Spatial Boundaries - Stand vs. Landscape

A methodological challenge for the carbon cycle methods, particular in context with forest, is the issue of stand versus landscape approach.

The investigated methods apply a stand approach i.e. they consider the re-growth on the same stand as harvested. In combination with the 'fully grown forest' point of reference, this can lead to a high impact factor for wood based CO_2 emissions. Additionally, the life time of the wood product (GWP_{bio}) (see Cherubini et al. [156]) and the avoided emissions (avoided alternative) (GWP_{netbio}) determine whether emissions from wood based products have a high impact factor.

Though, the tested methods use a stand approach, this is not self-evident and other authors use a landscape approach instead (e.g. Sedjo [157]). This approach regards managed forest as being in a steady state, with some plots being ready for harvest, some plots being newly harvested and other plots having varying ages between these two points. As pointed out by Helin et al.[135], the most critical factor for this approach is the choice of an appropriate reference state, one that considers the independent evolution of the forest.

Approaches towards time in land use and carbon cycle methods
An additional methodological difference between the land use and the carbon cycle methods is the way they consider time.
The land use methods appear to have a rather static approach, using time only to determine and distribute emissions over time. In detail, this means that (1) emissions from land transformation are amortized over several years of occupation (20 years are typically used), and that (2) for the impact from land occupation delayed relaxation time is used as a basis for calculations.

In contrast, the carbon cycle methods have a quite dynamic approach towards time. Especially for the GWP_{netbio} and the GWP_{bio}, the accounting for the actual timing of emission release and uptake is the essence of the method. In comparison, the WF is less dynamic and considers emission uptake on a yearly instead of a continuous basis.

A possible explanation for the different approaches towards time in the carbon cycle and the land use methods is their approach on land quality (carbon stocks) during occupation. For example, the UNEP-SETAC guideline [50] and the *CRP* method [42] apply the simplification that carbon stocks stay constant during occupation. This might be founded by their mainly agricultural background, as agricultural crops usually have a short rotation period, making the consideration of timing seem less pressing. However, for long rotation crops, the assumption of constant carbon stocks can be questioned. Indeed, the carbon cycle methods argue against this assumption and advocate for the consideration of long rotation cycles and of the timing of emission uptake.

Temporary carbon storage
Temporary carbon storage is an issue particular for the carbon cycle methods. It is handled differently, depending on the method. For example, the *WF* does not consider temporary storage, but instead assesses the oxidation of the product as if occurring at the time of harvest. In comparison, the GWP_{netbio} and the GWP_{bio} consider the actual timing of the oxidation and cut off emissions released past the assessment time horizon. The latter corresponds to the Lashof method, which in LCA is used to assess temporary carbon storage [158].

5.3.2.2 Application challenges

A practical challenge experienced for all tested methods was the availability of data. Particularly for the GWP_{netbio}, data that could represent a continuous re-evolution to natural vegetation might be difficult to find. Therefore, though out the scope of this thesis, more extended searches for potential data sources are recommended.

A further challenge related to data is their consistency and quality. For example, considering carbon pools in growing, as well as decaying, biomass could have a notable impact on the carbon cycle results. For this reason, data quality needs to be consistent in order to allow for comparability between results.

Moreover, their considerable computational effort and related time needs make the GWP_{netbio} and GWP_{bio} factor non-functional for every day application. In addition, though pre-calculated factors exist, they might not be suitable in every context [135].

A final challenge experienced for the methods is the one of acceptance. When presenting the test's case results to different stakeholders (researchers developing biomass conversion technology and industry), they were seen rather skeptical. This can be seen as a point for concern, since results might not be acted upon and assessments might be seen as meaningless. However, this should not lead to a halt in method development and application, but rather as a starting point to make methods and assessments more understandable and open to discussion.

In summary, in their current state, the land use and the carbon cycle methods still encounter a number of methodological and practical challenges, which need to be further investigated and harmonized. However, in spite of this, it is important to consider land use and time lags in LCA, at least in sensitivity analysis, to not miss out their potential environmental impact.

6 Conclusions

6.1 Guidance for the development of biomass based ethylene

This thesis has shown that for the further development of biomass based ethylene a number of potential environmental hot spots need to be addressed. These hot spots can be grouped as follows:

- Hot spots related to the biomass acquisition phase such as land use change and feedstock transport.

- Hot spots related to the biomass-to-alcohol conversion phase such as the production of enzymes, the fermentation process including post-processing and the gasification process including synthesis to methanol.

- Hot spots related to the alcohol-to-ethylene conversion phase, namely the conversion of ethanol or methanol to ethylene.

- Other hot spots such as the long distance sea transport in the sugarcane route.

Considering the diversity of these hot spots, it becomes also clear that this development needs to be pursued from various sides. These include the developers of fermentation and gasification processes, who need to tune the processes with regard to their enzyme and feedstock consumption, their NO_x and SO_2 release, as well as their output of high value co-products and their efficiency. Improvements in efficiency are also needed for the ethylene production processes, in addition to a reduction in energy consumption. Moreover, the contributions of enzyme producers, such as an increased enzyme activity and an improved environmental performance of the production processes, are crucial. Finally, consideration also needs to be given to the origin and the distribution of the feedstock.

The major driver for exchanging fossil with biomass based chemicals is the expectation of a lowered environmental impact. However, this thesis has revealed that this is not self-evident, especially for the impact on global warming. As long as biomass CO_2 emissions are considered climate neutral and ILUC emissions, along with enzyme consumption, are assumed low, the biomass routes have a lower impact than the fossil alternative, with the following ranking: the wood gasification route is most preferable, while the sugarcane and the wood

fermentation routes are comparable. However, this ranking changes when assuming ILUC emissions to be high. In such case, the sugarcane route becomes comparable to the fossil route. For this reason, though methods and data for ILUC are still highly uncertain, the production of biomass needs to induce as little carbon stock decreasing land use changes as possible.
Moreover, time lags for biomass CO_2 can increase the impact of the wood routes significantly. Therefore, further investigations on how to use wood based ethylene to best mitigate potential effects of time lags between CO_2 release and uptake from biomass need to be included into coming development phases.

With regard to the other investigated impacts (acidification, eutrophication and photochemical ozone creation); the biomass routes are clearly in need for further development, in order to compete with the fossil alternative.

6.2 Methodological Contributions

To ensure a low environmental impact, the development of currently emerging routes to biomass based chemicals needs to be accompanied by environmental assessments to identify environmental hot spots and improvement potentials. The thesis has shown that LCA is a useful method for such purposes. However, as demonstrated in this thesis, to ensure the relevance of results, the needs and demands of different stakeholders need to be considered when developing assessment scenarios. Moreover, relevance is not only a question of scenario but also of the data used for the assessment. In this thesis, process simulation was found to be a powerful means with this respect and the combination of LCA with process simulation is essential to guide the development of emerging technologies and related life cycles. The impact of land use and time lags between CO_2 release and uptake were revealed as a potential threat specifically for biomass based products. However, in their current state, assessment methods are restrained, due to practical, as well as, and methodological issues. These include:

- The inconsistent modeling for forestry and agriculture.
- The varying approaches towards time (static vs. dynamic).
- The insufficient guidance on how to define a reference state.
- The implicit use of the full grown forest as a reference point for the climate impact assessment of time lags for biomass CO_2.

- Poor data availability, inconsistent data, data with insufficient spatial resolution

Despite this, already 'preliminary' assessments can provide important, first insights. Specifically, for the time lag assessment of short lived products, the WF method appears currently more applicable (out of the three methods tested here) for two reasons:
(1) It provides results similar to the more complex GWP_{bio} method.
(2) It is transparent since it works on the inventory level and therefore does not mix inventory and impact assessment, as is the case for the GWP_{netbio}.
For long lived products, the *WF* might be less suitable though, since it does not consider the effect of temporary carbon storage.

With regard to the impact assessment of land use, out of the two tested methods, the *CRP* seems more relevant, since it considers above and below ground carbon, providing a richer overall picture of land use impact.

7 Future Work

The biomass routes to ethylene studied in this thesis provide a first insight into the potential environmental impact related to the biomass based production of today's fossil based bulk chemicals. In the future it can be expected that routes additional to the ones investigated here will emerge and will be in need for environmental guidance. For this reason, further assessments investigating into alternative feedstocks (e.g. algae), processes (e. g. combination of fermentation and gasification processes) and process outputs (e.g. high value chemicals) are a natural continuation of this work.

Apart from these mainly technology related issues; it is also of importance to make LCA more suitable for the assessment of biomass based chemicals and products in general. This thesis revealed some of the issues related to this challenge, but further research is needed to make LCA even more suitable for the assessment of impact specific to biomass products such as impacts from land and water use. In addition, efforts need to be also spent on applicability matters. For instance, data availability is a key issue affecting the applicability of qualitative methods such as LCA. Therefore further data aggregation into formalized databases, as well as, generation of new data, will increase the applicability of impact assessment methods for biomass specific issues such as land use. Additional factors related to applicability are comprehensiveness and time needs. The land use and time lag (carbon cycle) methods tested in this thesis could be developed further to optimize towards these characteristics.

8 References

1. U.S. National Oceanic and Atmospheric Administration (NOAA). *Carbon Dioxide at NOAA's Mauna Loa Observatory reaches new milestone: Tops 400 ppm http://www.esrl.noaa.gov/news/2013/CO2400.html*. [cited 2013 November 25,].
2. Hansen, J., et al., *Target atmospheric CO2: Where should humanity aim?* arXiv preprint arXiv:0804.1126, 2008.
3. Rockström, J., et al., *Planetary boundaries: exploring the safe operating space for humanity.* Ecology and society, 2009. **14**(2).
4. Stocker, T., D. Qin, and G. Platner, *Climate Change 2013: The Physical Science Basis.* Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Summary for Policymakers (IPCC, 2013), 2013.
5. OECD (Organisation for Economic Co-operation and Development) and FAO (Food and Agriculture Organization of the United Nations), *OECD-FAO Agricultural Outlook 2013 Chapter 3 - Biofuels*. 2013.
6. Lane, J. *Myriant starts-up biosuccinic production in Lousiana. http://www.biofuelsdigest.com/bdigest/2013/06/17/myriant-starts-up-biosuccinic-production-in-lousiana/*. [cited 2014 January 31,].
7. Reverdia. *Biosuccinium™ Sustainable Succinic Acid. http://www.reverdia.com/biosuccinium/*. [cited 2014 January 31,].
8. Braskem. *Green Products. http://www.braskem.com/site.aspx/green-products-USA*. [cited 2014 January 31,].
9. Carus, M. and A. Raschka, *Agricultural Resources for Bioplastics.* bioplastics Magazine, 2011. **6**(6).
10. Pimentel, D., et al., *Food versus biofuels: environmental and economic costs.* Human ecology, 2009. **37**(1): p. 1-12.
11. Abbott, P.C., C. Hurt, and W.E. Tyner, *What's driving food prices? March 2009 Update*, 2009, Farm Foundation.
12. Timilsina, G.R. and A. Shrestha, *Biofuels: markets, targets and impacts*, 2010, The World Bank.
13. Fargione, J., et al., *Land clearing and the biofuel carbon debt.* Science, 2008. **319**(5867): p. 1235-1238.
14. Searchinger, T.D., et al., *Fixing a critical climate accounting error.* Science, 2009. **326**(5952): p. 527.
15. Dominguez-Faus, R., et al., *The water footprint of biofuels: A drink or drive issue?* Environmental Science & Technology, 2009. **43**(9): p. 3005-3010.
16. Hill, J., *Environmental costs and benefits of transportation biofuel production from food-and lignocellulose-based energy crops. A review.* Agronomy for Sustainable Development, 2007. **27**(1): p. 1-12.
17. Havlik, P., et al., *Global land-use implications of first and second generation biofuel targets.* Energy Policy, 2011. **39**(10): p. 5690-5702.
18. Yuan, J.S., et al., *Plants to power: bioenergy to fuel the future.* Trends in plant science, 2008. **13**(8): p. 421-429.
19. Paustian, T. *Metabolism - Fermentation. http://dwb4.unl.edu/Chem/CHEM869P/CHEM869PLinks/www.bact.wisc.edu/microtextbook/metabolism/Fermentation.html*. 2000 [cited 2013 December 1,].
20. Ciferno, J.P. and J.J. Marano. *Benchmarking Biomass Gasification Technologies for Fuels, Chemicals and Hydrogen Production. http://www.netl.doe.gov/technologies/coalpower/gasification/pubs/pdf/BMassGasFinal.pdf*. 2002 [cited 2013 November 12,].

21. Bos, H.L. and J.P.M. Sanders, *Raw material demand and sourcing options for the development of a bio-based chemical industry in Europe. Part 1: Estimation of maximum demand.* Biofuels, Bioproducts and Biorefining, 2013. **7**: p. 246–259.
22. Advanced Ethanol Council (AEC). *Cellulosic Biofuels Industry Progress Report 2012-2013. http://ethanolrfa.3cdn.net/d9d44cd750f32071c6_h2m6vaik3.pdf*. [cited 2013 December 18,].
23. ISO, *International Organization for Standardization: ISO 14040:2006 Environmental management—Life cycle assessment—Principles and framework*, 2006: Geneva, Switzerland.
24. Hunt, R.G., W.E. Franklin, and R. Hunt, *LCA—How it came about.* The international journal of life cycle assessment, 1996. **1**(1): p. 4-7.
25. Baumann, H. and A. Tillman, *The Hitch Hiker's Guide to LCA. 2004.* Lund: Studentlitteratur. **543**.
26. Weidema, B., *Application typologies for life cycle assessment.* The International Journal of Life Cycle Assessment, 1998. **3**(4): p. 237-240.
27. Lindfors, L.-G., *Nordic Guidelines on Life-cycle Assessment: Nord 1995: 20*. 1995: Nordic Council of Ministers.
28. Wenzel, H., L. Alting, and M. Hauschild, *Environmental assessment of products. Vol. 1, Methodology, tools and case studies in product development*. 1997, London: Chapman & Hall.
29. Weiss, M., et al., *A review of the environmental impacts of biobased materials.* Journal of Industrial Ecology, 2012. **16**(s1): p. S169-S181.
30. Carus, M., A. Raschka, and S. Piotrowski, *Entwicklung von Förderinstrumenten für die stoffliche Nutzung von nachwachsenden Rohstoffen in Deutschland (Kurzfassung) Volumen, Struktur, Substitutionspotenziale, Konkurrenzsituation und Besonderheiten der stofflichen Nutzung sowie Entwicklung von Förderinstrumenten, Mai 2010, nova Institut*, 2010.
31. Yates, M.R. and C.Y. Barlow, *Life cycle assessments of biodegradable, commercial biopolymers—A critical review.* Resources, Conservation and Recycling, 2013. **78**: p. 54-66.
32. Tufvesson, L.M., et al., *Life cycle assessment in green chemistry: overview of key parameters and methodological concerns.* The International Journal of Life Cycle Assessment, 2013. **18**(2): p. 431-444.
33. MAYUMI, K., Y. KIKUCHI, and M. HIRAO, *Life Cycle Assessment of Biomass-Derived Resin for Sustainable Chemical Industry.* CHEMICAL ENGINEERING, 2010. **19**.
34. Kikuchi, Y., K. Mayumi, and M. Hirao, *Integration of CAPE and LCA tools in environmentally-conscious process design: a case study on biomass-derived resin.* Computer Aided Chemical Engineering, 2010. **28**: p. 1051-1056.
35. Nouri, S. and A.-M. Tillman, *Evaluating synthesis gas based biomass to plastics (BTP) technologies*, 2005, Chalmers University of Technology.
36. Gilbert, P., et al. *Ammonia from Biomass Gasification. https://www.escholar.manchester.ac.uk/uk-ac-man-scw:64628*. [cited 2013 December 15].
37. Cherubini, F., *GHG balances of bioenergy systems–Overview of key steps in the production chain and methodological concerns.* Renewable Energy, 2010. **35**(7): p. 1565-1573.
38. Pawelzik, P., et al., *Critical aspects in the life cycle assessment (LCA) of bio-based materials–Reviewing methodologies and deriving recommendations.* Resources, Conservation and Recycling, 2013. **73**: p. 211-228.
39. Bier, J.M., et al., *Life cycle assessments of bioplastics: Applications and issues.* International Journal of Environmental, Cultural, Economic and Social Sustainability, 2011. **7**(4): p. 145-157.
40. Väisänen, S., T. Valtonen, and R. Soukka, *Biogenic carbon emissions of integrated ethanol production.* International Journal of Energy Sector Management, 2012. **6**(3): p. 381-396.

41. Cherubini, F., A.H. Strømman, and E. Hertwich, *Effects of boreal forest management practices on the climate impact of CO2 emissions from bioenergy.* Ecological Modelling, 2011. **223**(1): p. 59-66.
42. Müller-Wenk, R. and M. Brandão, *Climatic impact of land use in LCA—carbon transfers between vegetation/soil and air.* The International Journal of Life Cycle Assessment, 2010. **15**(2): p. 172-182.
43. Hospido, A., et al., *A review of methodological issues affecting LCA of novel food products.* The international journal of life cycle assessment, 2010. **15**(1): p. 44-52.
44. Hetherington, A.C., et al., *Use of LCA as a development tool within early research: challenges and issues across different sectors.* The International Journal of Life Cycle Assessment, 2013: p. 1-14.
45. Hillman, K., *Environmental Assessment and Strategic Technology Choice: The Case of Renewable Transport Fuels*, in *Energy and Environment*2008, Chalmers University of Technology: Göteborg.
46. Karlström, M., *Environmental Assessment of Polymer Electrolyte Membrane Fuel Cell Systems. Consequences of an Evolutionary Perspective on Technology Development*, in *Energy and Environment*2004, Chalmers University of Technology: Göteborg.
47. Bakshi, B.R. and N.U. Ukidwe. *The role of thermodynamics in life cycle assessment of existing and emerging technologies*. in *Electronics and the Environment, 2006. Proceedings of the 2006 IEEE International Symposium on*. 2006. IEEE.
48. Schut, J.H. *What's Ahead for 'Green' Plastics: Look for More Supply, More Varieties, Better Properties. http://www.ptonline.com/articles/what%27s-ahead-for-%27green%27-plastics-look-for-more-supply-more-varieties-better-properties*. [cited 2008 October 25,].
49. Zimmermann, H. and R. Walzl, *Ethylene*, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2009, Wiley-VCH Verlag GmbH & Co. KGaA.
50. Koellner, T., et al., *UNEP-SETAC guideline on global land use impact assessment on biodiversity and ecosystem services in LCA.* The International Journal of Life Cycle Assessment, 2013. **18**(6): p. 1188-1202.
51. Barta, Z., et al., *Process design and economics of on-site cellulase production on various carbon sources in a softwood-based ethanol plant.* Enzyme Res, 2010. **2010**.
52. Barta, Z., K. Reczey, and G. Zacchi, *Techno-economic evaluation of stillage treatment with anaerobic digestion in a softwood-to-ethanol process.* Biotechnol Biofuels, 2010. **3**: p. 21.
53. Sassner, P., M. Galbe, and G. Zacchi, *Techno-economic evaluation of bioethanol production from three different lignocellulosic materials.* Biomass bioenergy 2008. **32**(5): p. 422-430.
54. Isaksson, J., et al., *Integration of biomass gasification with a Scandinavian mechanical pulp and paper mill–Consequences for mass and energy balances and global CO2 emissions.* Energy, 2012. **44**.
55. Baumann, H. and S.J. Cowell, *An Evaluative Framework for Conceptual and Analytical Approaches Used in Environmental.* Greener Management International, 1999(26).
56. Finnveden, G. and Å. Moberg, *Environmental systems analysis tools–an overview.* Journal of Cleaner Production, 2005. **13**(12): p. 1165-1173.
57. Checkland, P., *Systems thinking, systems practice: includes a 30-year retrospective.* 1999.
58. Aon, M.A. and C. S., *Biochemistry, Chaotic Dynamics,Noise, and Fractal Space in; Encyclopedia of Complexity and Systems Science*, R.A. Meyers, Editor 2009, Springer.
59. Björklund, A., *Environmental systems analysis waste management.* Stockholm, Sweden: Department of Chemical Engineering and Technology, Royal Institute of Technology, 1998.
60. Baumann, H., *Decision making and Life Cycle Assessment*, in *Department of Technical Environmental Planning, Chalmers University of Technology, Göteborg, Sweden,*1995, Chalmers University of Technology: Göteborg.

61. Miser, H.J. and E.S. Quade, *Handbook of systems analysis*. 1985, Chichester, England: John Wiley & Sons.
62. ISO, *International Organization for Standardization: ISO 14044:2006 Environmental management—Life cycle assessment—Requirements and Guidelines*, 2006: Geneva, Switzerland.
63. Curran, M.A., M. Mann, and G. Norris, *The international workshop on electricity data for life cycle inventories.* Journal of Cleaner Production, 2005. **13**(8): p. 853-862.
64. Rebitzer, G. and T. Ekvall, *Scenarios in Life Cycle Assessment*, 2004, Society of Environmental Toxicology and Chemistry (SETAC).
65. Ekvall, T., A.-M. Tillman, and S. Molander, *Normative ethics and methodology for life cycle assessment.* Journal of Cleaner Production, 2005. **13**(13): p. 1225-1234.
66. Tillman, A.-M., *Significance of decision-making for LCA methodology.* Environmental Impact Assessment Review, 2000. **20**(1): p. 113-123.
67. Leiden University Institute of Environmental Sciences *Characterization factors* 2010, Leiden University, The Netherlands.
68. Huijbregts, M.A., et al., *Evaluating uncertainty in environmental life-cycle assessment. A case study comparing two insulation options for a Dutch one-family dwelling.* Environmental science & technology, 2003. **37**(11): p. 2600-2608.
69. Lloyd, S.M. and R. Ries, *Characterizing, Propagating, and Analyzing Uncertainty in Life-Cycle Assessment: A Survey of Quantitative Approaches.* Journal of Industrial Ecology, 2007. **11**(1): p. 161-179.
70. Jacobsson, S. and A. Bergek, *Transforming the energy sector: the evolution of technological systems in renewable energy technology.* Industrial and corporate change, 2004. **13**(5): p. 815-849.
71. Lönnroth, M., T.B. Johansson, and P. Steen, *Solar versus nuclear: choosing energy futures*. 1980: Pergamon Press.
72. Haes, H.A.U., et al., *Three strategies to overcome the limitations of life-cycle assessment.* Journal of industrial ecology, 2004. **8**(3): p. 19-32.
73. Wrisberg, N., et al., *Analytical tools for environmental design and management in a systems perspective: the combined use of analytical tools*. 2002: Kluwer Dordrecht,, The Netherlands.
74. Guinée, J., *Handbook on life cycle assessment—operational guide to the ISO standards*. Vol. 6. 2001, Leiden, the Netherlands: Kluwer Academic Publishers. 255-255.
75. Reap, J., et al., *A survey of unresolved problems in life cycle assessment.* The International Journal of Life Cycle Assessment, 2008. **13**(5): p. 374-388.
76. Cherubini, F., et al., *CO2 emissions from biomass combustion for bioenergy: atmospheric decay and contribution to global warming.* GCB Bioenergy, 2011. **3**(5): p. 413-426.
77. Repo, A., M. Tuomi, and J. Liski, *Indirect carbon dioxide emissions from producing bioenergy from forest harvest residues.* GCB Bioenergy, 2011. **3**(2): p. 107-115.
78. Börjeson, L., et al., *Scenario types and techniques: towards a user's guide.* Futures, 2006. **38**(7): p. 723-739.
79. Finnveden, G., et al., *Recent developments in life cycle assessment.* Journal of environmental management, 2009. **91**(1): p. 1-21.
80. Höjer, M., et al., *Scenarios in selected tools for environmental systems analysis.* Journal of Cleaner Production, 2008. **16**(18): p. 1958-1970.
81. Bishop, P., A. Hines, and T. Collins, *The current state of scenario development: an overview of techniques.* Foresight-The journal of future studies, strategic thinking and policy, 2007. **9**(1): p. 5-25.
82. Bojarski, A.D., et al., *Life cycle assessment coupled with process simulation under uncertainty for reduced environmental impact: Application to phosphoric acid production.* Industrial & Engineering Chemistry Research, 2008. **47**(21): p. 8286-8300.

83. Mendivil, R., et al., *A New LCA Methodology of Technology Evolution (TE-LCA) and its Application to the Production of Ammonia (1950-2000)(8 pp).* The International Journal of Life Cycle Assessment, 2006. **11**(2): p. 98-105.
84. Hossain, K.A., F.I. Khan, and K. Hawboldt, *E-Green-A robust risk-based environmental assessment tool for process industries.* Industrial & Engineering Chemistry Research, 2007. **46**(25): p. 8787-8795.
85. Norgate, T., S. Jahanshahi, and W. Rankin, *Assessing the environmental impact of metal production processes.* Journal of Cleaner Production, 2007. **15**(8): p. 838-848.
86. Iosif, A.-M., et al., *Reduction of CO 2 emissions in the steel industry based on LCA methodology.* TMS-CO2 Reduction Metallurgy, San-Francisco, 2009.
87. Strube, R., G. Pellegrini, and G. Manfrida, *The environmental impact of post-combustion CO< sub> 2</sub> capture with MEA, with aqueous ammonia, and with an aqueous ammonia-ethanol mixture for a coal-fired power plant.* Energy, 2011. **36**(6): p. 3763-3770.
88. Mery, Y., et al., *An integrated "process modelling-life cycle assessment" tool for the assessment and design of water treatment processes.* The International Journal of Life Cycle Assessment, 2013. **18**(5): p. 1062-1070.
89. Budsberg, E., et al., *Life-cycle assessment for the production of bioethanol from willow biomass crops via biochemical conversion.* Forest Products Journal, 2012. **62**(4): p. 305.
90. González-García, S., et al., *Comparative life cycle assessment of ethanol production from fast-growing wood crops (black locust, eucalyptus and poplar).* biomass and bioenergy, 2012. **39**: p. 378-388.
91. Bright, R.M. and A.H. Strømman, *Life cycle assessment of second generation bioethanols produced from Scandinavian Boreal forest resources.* Journal of Industrial Ecology, 2009. **13**(4): p. 514-531.
92. Xiao, J., et al., *Integrated analysis of energy, economic, and environmental performance of biomethanol from rice straw in China.* Industrial & Engineering Chemistry Research, 2009. **48**(22): p. 9999-10007.
93. Morais, S., et al., *Simulation and life cycle assessment of process design alternatives for biodiesel production from waste vegetable oils.* Journal of Cleaner Production, 2010. **18**(13): p. 1251-1259.
94. Arvidsson, M. and B. Lundin, *Process integration study of a biorefinery producing ethylene from lignocellulosic feedstock for a chemical cluster*, in *Energy and Environment*2011, Department of Energy and Environment, Chalmers University of Technology Göteborg (Sweden).
95. Voss, C., N. Tsikriktsis, and M. Frohlich, *Case research in operations management.* International journal of operations & production management, 2002. **22**(2): p. 195-219.
96. Flyvbjerg, B., *Five misunderstandings about case-study research.* Qualitative inquiry, 2006. **12**(2): p. 219-245.
97. Lindeijer, E., *Review of land use impact methodologies.* Journal of Cleaner Production, 2000. **8**(4): p. 273-281.
98. Milà i Canals, L., et al., *Key elements in a framework for land use impact assessment within LCA.* International Journal of Life Cycle Assessment, 2007. **12**(1): p. 2-4.
99. IPCC. *Intergovernmental Panel on Climate Change: Climate Change 2007: Working Group I: The Physical Science Basis Glossary E-O* 2007 [cited 2011 24 January]; Available from: http://www.ipcc.ch/publications_and_data/ar4/wg1/en/annex1sglossary-e-o.html.
100. IEA Bioenergy. *Bioenergy – The Impact of Indirect Land Use Change Summary and Conclusions from the IEA Bioenergy ExCo63 Workshop, Rotterdam, the Netherlands*. 12 May 2009.
101. Fritsche, U.R., K. Hennenberg, and H. Fehrenbach, *GBEP Workshop on Indirect Land Use Change (ILUC):Status of and Perspectives on Science-Based Policies; Briefing paper; supported*

by the German Federal Ministry for Environment, Nature Protection and Nuclear Safety, Oeko-Institut and IFEU, Editors. 2009: Darmstadt/Heidelberg.
102. Ericsson, N., et al., *Time-dependent climate impact of a bioenergy system–methodology development and application to Swedish conditions.* GCB Bioenergy, 2013. **5**(5): p. 580-590.
103. Helin, T., A. Holma, and S. Soimakallio, *Is land use impact assessment in LCA applicable for forest biomass value chains? Findings from comparison of use of Scandinavian wood, agro-biomass and peat for energy.* The International Journal of Life Cycle Assessment, 2014: p. 1-16.
104. Fritsche, U.R., *Bioenergy life cycle analysis: beyond biofuels; ETC/ACC Technical paper 2008/18*, 2008, European Topic Centre on Air and Climate Change Bilthoven.
105. BSi, *British Standards Institution :PUBLICLY AVAILABLE SPECIFICATION PAS 2050:2008 Specification for the assessment of the life cycle greenhouse gas emissions of goods and services*, 2008.
106. European Parliament. *European Parliament legislative resolution of 11 September 2013 on the proposal for a directive of the European Parliament and of the Council amending Directive 98/70/EC relating to the quality of petrol and diesel fuels and amending Directive 2009/28/EC on the promotion of the use of energy from renewable sources (COM(2012)0595 – C7-0337/2012 – 2012/0288(COD)) http://www.europarl.europa.eu/sides/getDoc.do?type=TA&reference=P7-TA-2013-0357&language=EN&ring=A7-2013-0279*. 2013 [cited 2014 March 5].
107. European Commission Energy, *DIRECTIVE 2009/28/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC*, 2009.
108. California EPA, *Proposed Regulation to Implement the Low Carbon Fuel Standard, Volume I, Staff Report: Initial Statement of Reasons*, 2009, California EPA Air Resource Board: Sacramento.
109. US EPA, *Renewable Fuel Standard Program (RFS2) Regulatory Impact Analysis EPA-420-R-10-006 February 2010*, 2010.
110. Rosenfeld, J. and J. Pont, *Indirect Land Use Change Comparative Analysis Final Report Prepared for State of Oregon Department of Environmental Quality*, T. LLC, Editor 2010.
111. Börjesson, P., *Good or bad bioethanol from a greenhouse gas perspective–what determines this?* Applied Energy, 2009. **86**(5): p. 589-594.
112. Broch, A., S.K. Hoekman, and S. Unnasch, *A review of variability in indirect land use change assessment and modeling in biofuel policy.* Environmental Science & Policy, 2013. **29**: p. 147-157.
113. Finkbeiner, M., *Indirect land use change (iLUC) within life cycle assessment (LCA) – scientific robustness and consistency with international standards.Association of the German Biofuel Industry, Verband der ölsaatenverarbeitenden Industriein Deutschland, Berlin, Germany*, V.d.ö.I.D. Association of the German Biofuel Industry, Berlin, Germany, Editor 2013.
114. Kim, H., S. Kim, and B.E. Dale, *Biofuels, land use change, and greenhouse gas emissions: some unexplored variables.* Environmental Science & Technology, 2009. **43**(3): p. 961-967.
115. Liska, A.J. and R.K. Perrin, *Indirect land use emissions in the life cycle of biofuels: regulations vs science.* Biofuels, Bioproducts and Biorefining, 2009. **3**(3): p. 318-328.
116. Sanchez, S.T., et al., *Accounting for indirect land-use change in the life cycle assessment of biofuel supply chains.* Journal of The Royal Society Interface, 2012. **9**(71): p. 1105-1119.
117. Schmidt, J.H., J. Reinhard, and B.P. Weidema. *A model of indirect land use change*. in *Proceeding of the 8th International Conference on Life Cycle Assessment in the Agri-Food Sector (LCA Food 2012)*. 2012.

118. Kløverpris, J.H. and S. Mueller, *Baseline time accounting: considering global land use dynamics when estimating the climate impact of indirect land use change caused by biofuels.* The International Journal of Life Cycle Assessment, 2013. **18**(2): p. 319-330.
119. Cherubini, F. and G. Jungmeier, *LCA of a biorefinery concept producing bioethanol, bioenergy, and chemicals from switchgrass.* The International Journal of Life Cycle Assessment, 2010. **15**(1): p. 53-66.
120. García, C.A., et al., *Life-cycle greenhouse gas emissions and energy balances of sugarcane ethanol production in Mexico.* Applied Energy, 2011. **88**(6): p. 2088-2097.
121. Meul, M., et al., *Carbon footprint of five pig diets using three land use change accounting methods.* Livestock Science, 2012. **149**(3): p. 215-223.
122. Brandão, M., L. Milà i Canals, and R. Clift, *Soil organic carbon changes in the cultivation of energy crops: Implications for GHG balances and soil quality for use in LCA.* Biomass and Bioenergy, 2011. **35**(6): p. 2323-2336.
123. Reijnders, L. and M. Huijbregts, *Biogenic greenhouse gas emissions linked to the life cycles of biodiesel derived from European rapeseed and Brazilian soybeans.* Journal of cleaner production, 2008. **16**(18): p. 1943-1948.
124. Cederberg, C., et al., *Including carbon emissions from deforestation in the carbon footprint of Brazilian beef.* Environmental Science & Technology, 2011. **45**(5): p. 1773-1779.
125. Kendall, A., B. Chang, and B. Sharpe, *Accounting for time-dependent effects in biofuel life cycle greenhouse gas emissions calculations.* Environmental science & technology, 2009. **43**(18): p. 7142-7147.
126. Persson, U.M., S. Henders, and C. Cederberg, *A method for calculating a land-use change carbon footprint (LUC-CFP) foragricultural commodities – applications to Brazilian beef and soy, Indonesian palm oil.* under publication.
127. Pingoud, K., T. Ekholm, and I. Savolainen, *Global warming potential factors and warming payback time as climate indicators of forest biomass use.* Mitigation and Adaptation Strategies for Global Change, 2012. **17**(4): p. 369-386.
128. Holtsmark, B., *Harvesting in boreal forests and the biofuel carbon debt.* Climatic Change, 2012. **112**(2): p. 415-428.
129. McKechnie, J., et al., *Forest bioenergy or forest carbon? Assessing trade-offs in greenhouse gas mitigation with wood-based fuels.* Environmental science & technology, 2010. **45**(2): p. 789-795.
130. Lal, R., et al., *Carbon Sequestration in Soils of Latin America*. 2006, Binghamton, NY: The Haworth Press, Inc.
131. Zuurbier, P. and J. van de Vooren, *Sugarcane ethanol - Contributions to climate change mitigation and the environment*, 2008, Wageningen Academic Publishers: Wageningen, the Netherlands.
132. Tillman, A.M., *Personal communication with A.-M. Tillman, professor, Chalmers University. During the Workshop on Methodological Issues in Quantifying Emissions of Greenhouse Gases (GHGs) Associated with Food Production and Supply, Den Haag, 4–5 June 2009.* 2009.
133. Food and Agricultural Organization of the United Nations. *FAOSTAT Domains, http://faostat3.fao.org/faostat-gateway/go/to/download/R/RL/E*. [cited March 2014 13].
134. Anderson-Teixeira, K.J., et al., *Changes in soil organic carbon under biofuel crops.* GCB Bioenergy, 2009. **1**(1): p. 75-96.
135. Helin, T., et al., *Approaches for inclusion of forest carbon cycle in life cycle assessment–a review.* GCB Bioenergy, 2012.
136. Wiloso, E.I., R. Heijungs, and G.R. de Snoo, *LCA of second generation bioethanol: A review and some issues to be resolved for good LCA practice.* Renewable and Sustainable Energy Reviews, 2012. **16**(7): p. 5295-5308.

137. Slade, R., A. Bauen, and N. Shah, *The greenhouse gas emissions performance of cellulosic ethanol supply chains in Europe.* Biotechnol Biofuels, 2009. **2**(15): p. 1–19.
138. González-García, S., B. Mola-Yudego, and R.J. Murphy, *Life cycle assessment of potential energy uses for short rotation willow biomass in Sweden.* The International Journal of Life Cycle Assessment, 2013. **18**(4): p. 783-795.
139. Galbe, M., et al., *Process Engineering Economics of Bioethanol Production*, Springer-Verlag, Editor 2007: Heidelberg.
140. Galbe, M. and G. Zacchi, *Pretreatment of lignocellulosic materials for efficient bioethanol production.* Biofuels, 2007: p. 41-65.
141. Verardi, A., et al., *Hydrolysis of lignocellulosic biomass: current status of processes and technologies and future perspectives*, 2011, Bioethanol.
142. Wesolowski, D., *The Sustainability of Ethanol Fuel in the United States*, 2005.
143. Jeihanipour, A., *Waste Textiles Bioprocessing to Ethanol and Biogas*. 2011: Chalmers University of Technology.
144. Kadam, K.L., et al., *Environmental life cycle implications of fuel oxygenate production from California biomass*. 1999: National Renewable Energy Laboratory.
145. VärmlandsMetanol AB. *VärmlandsMetanol AB http://www.varmlandsmetanol.se/dokument/Folder%20VM%202011.pdf* [cited 2013 February 14,].
146. Daystar, J., et al., *Life-Cycle Assessment of Bioethanol from Pine Residues via Indirect Biomass Gasification to Mixed Alcohols.* Forest Products Journal, 2012. **62**(4).
147. Hermann, B.G., K. Blok, and M.K. Patel, *Twisting biomaterials around your little finger: environmental impacts of bio-based wrappings.* The International Journal of Life Cycle Assessment, 2010. **15**(4): p. 346-358.
148. Chen, G.-Q. and M.K. Patel, *Plastics derived from biological sources: present and future: a technical and environmental review.* Chemical Reviews, 2011. **112**(4): p. 2082-2099.
149. Kikuchi, Y., et al., *Environmental Performance of Biomass-Derived Chemical Production: A Case Study on Sugarcane-Derived Polyethylene.* Journal of Chemical Engineering of Japan, 2013. **46**(4): p. 319-325.
150. Alvarenga, R.A., et al., *Life cycle assessment of bioethanol-based PVC.* Biofuels, Bioproducts and Biorefining, 2013. **7**(4): p. 386-395.
151. Mu, D., et al., *Comparative life cycle assessment of lignocellulosic ethanol production: biochemical versus thermochemical conversion.* Environmental management, 2010. **46**(4): p. 565-578.
152. Simon, G., et al., *Carbon stocks and net ecosystem production changes with time in two Italian forest chronosequences.* European Journal of Forest Research, 2012. **131**(5): p. 1297-1311.
153. Chen, J., et al., *Carbon budget of Ontario's managed forests and harvested wood products, 2001–2100.* Forest Ecology and Management, 2010. **259**(8): p. 1385-1398.
154. Levasseur, A., et al., *Biogenic carbon and temporary storage addressed with dynamic life cycle assessment.* Journal of Industrial Ecology, 2013. **17**(1): p. 117-128.
155. Cherubini, F., R.M. Bright, and A.H. Strømman, *Site-specific global warming potentials of biogenic CO2 for bioenergy: contributions from carbon fluxes and albedo dynamics.* Environmental Research Letters, 2012. **7**(4): p. 045902.
156. Cherubini, F., G. Guest, and A.H. Strømman, *Application of probability distributions to the modeling of biogenic CO2 fluxes in life cycle assessment.* GCB Bioenergy, 2012. **4**(6): p. 784-798.
157. Sedjo, R., *Carbon Neutrality and Bioenergy: A Zero-Sum Game?* Resources for the Future Discussion Paper, 2011(11-15).

158. Levasseur, A., et al., *Valuing temporary carbon storage.* Nature Climate Change, 2011. **2**(1): p. 6-8.