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The Environmental Performance of biobased 1,3-propanediol production from glycerol compared to conventional production pathways

A Life Cycle Assessment

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ABSTRACT

Due to environmental concerns and the reliance on depleting fossil resources the conventional chemical industry is facing increasing pressure to alter their production methods towards a sustainable direction. Despite having also its disadvantages like the land-use issue, biomass is considered to have a major potential as a more sustainable feedstock for the future chemical production. Research in this area is increasing, but profitable business models for biobased products are still lacking. A good example for a biobased chemical product which already found its way to the markets is 1,3-propanediol (PDO), a platform-chemical with a wide range of possible uses and a rapidly growing market. It has been commercially implemented and environmentally assessed by DuPont, an American chemical company. While DuPont produces PDO from glucose based on corn, there is also the possibility to use glycerol as a biological feedstock. Glycerol is a by-product of the large biodiesel production and is thus currently facing an over-supply on the market which cannot be accommodated by the conventional uses of glycerol. As research has indicated, it could be an attractive solution to use it as a cheap feedstock for the production of PDO.

However, so far no analysis of the environmental impacts of this production pathway has been conducted. This thesis therefore assesses what the environmental impacts of the glycerol-based PDO production are and indicates how they relate to impacts of other biobased and petrochemical alternatives of PDO-production. Hence, a cradle-to-gate Life Cycle Assessment was conducted, assessing the greenhouse gas emissions and the non-renewable energy use of the glycerol-based PDO production. This assessment includes a contributional analysis and an extensive sensitivity analysis which develops three scenarios. The results of those scenarios are compared to results of other studies assessing environmental aspects of alternative fossil- and biobased production pathways for PDO.

This benchmarking between the different production pathways indicates that the glycerol-based production route is environmentally preferable compared to fossil alternatives and might be competitive with biobased PDO from glucose, if the production process is further optimized. The contributional analysis revealed that the process of PDO recovery and purification shows the biggest environmental impact, which is mainly due to its intensive steam use from fossil sources. Moreover, the study gave insight to the future development of the biodiesel market, which might negatively influence the prospects of a glycerol-based PDO production on long term.

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LIST OF ACRONYMS

ADEME	French Environment and Energy Management Agency
DBFZ	Deutsches Biomasseforschungszentrum
EEA	European Environmental Agency
EC	European Commission
EP	European Parliament
EU	European Union
FU	Functional Unit
GHG	Greenhouse Gases
GREET	Greenhouse gases, Regulated Emissions and Energy use in Transportation
ILUC	Indirect Land Use Change
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LCC	Life Cycle Costing
NREU	Non-renewable Energy Use
PDO	1,3-Propanediol

1 INTRODUCTION

1.1 CONTEXT AND PROBLEM DEFINITION

1.1.1 BIOMASS AS A FEEDSTOCK FOR THE PRODUCTION OF CHEMICALS

The conventional chemical industry as we know it is currently subject of change. In general, one might even say that we are facing the start of a *"historic transition"* from a mainly petroleum-based economy towards a more diversified economy with renewable biomass as an important feedstock. (Dale & Kim 2006)

The current chemical industry relies to a large extent on the depleting fossil resources and is furthermore facing critics about their environmental impacts. Its environmentally damaging production processes and toxic by-products are thereby as well subject of criticism as their not readily recyclable or degradable products. Hence, the industry is experiencing increasing pressure to alter their production methods towards a more sustainable direction. (Hatti-Kaul et al. 2007)

Expecting a shortage of petrochemicals the hopes are that biomass has the potential to be a major feedstock for the production of chemicals in the future (Langeveld et al. 2010). But so far only a small part of the chemical output is derived from biobased raw materials. Nevertheless, the rising oil prices and the concerns mentioned before created a *"momentum"* that might accelerate a shift in the production of chemicals (Hatti-Kaul et al. 2007).

However, also the limitations of biomass-supply have to be considered. The cultivation of biomass requires land which is a limited resource. Hence, biomass for chemical production could face competition with other land uses, e.g. for food or energy production (Hoogwijk et al. 2003; Kretschmer et al. 2009).

Fact is that biomass as an input for the production of polymers, lubricants, solvents, surfactants and bulk chemicals[1] *"is receiving more and more attention"*. But the challenge still lies in creating profitable business models for biobased products. (Langeveld et al. 2010)

Biobased products can be defined as commercial or industrial products (other than food or feed) that are *"composed, in whole or in significant part, of biological products [...] or an intermediate ingredient or feedstock"* (110th Congress of the United States of America 2008).

[1] Bulk chemicals refer to basic or technical chemicals (e.g. methanol and ethylene) which are *"either directly used or further processed for the production of large-volume and value-added products in the chemical industry."* (Zeng & Biebl 2002)

Numerous reasons speak in favor of substituting fossil oil with biomass in the chemical production. Scenarios predict significant savings in non-renewable energy use (NREU) and reductions in Greenhouse-gas-emissions (GHG) compared to production from fossil oil (Dornburg et al. 2008). Furthermore a potential for cost reductions in production is seen, which can be reached by reduced processing costs and using the cheaper biomass raw materials compared to oil (Dale 2003). One study predicts production cost savings of up to 65 billion Euro for the EU 25 alone oil (Dornburg et al. 2008).

Other advantages include the higher biodegradability of products, less waste generation (Hatti-Kaul et al. 2007) and the reduced dependence on imported petroleum if the feedstock is cultivated inside the country. A socio-economic benefit could be the strengthening of rural areas due to the increased or maintained production and processing of the plant raw materials. Moreover previously unexploited residues from agriculture and forestry as well as organic municipal waste might become valuable which would enhance the efficiency and productivity of agriculture. Under the condition that it is developed properly, many scientists imagine a biobased economy that is *"more economically and environmentally sustainable"* than the current, petroleum based economy. (Dale 2003)

However there also critics doubting that biobased chemicals have a significantly lower environmental impact than petrochemicals. And reservations are reasonable as it is not completely clear how far biobased products are per-se better than oil-based products from a life-cycle perspective. Studies have shown that the environmental superiority of using biomass as feedstock is not necessarily valid in all situations and concerning all aspects (Hatti-Kaul et al. 2007). While the use of renewable feedstocks might decrease the environmental impact in some categories like energy consumption they might at the same time increase the problems in other categories like land-use (Urban & Bakshi 2009).

A sound environmental assessment is therefore as well necessary as a continuing search for better production processes or use of different resources as input. A widely used method to assess environmental impacts of products is the Life Cycle Assessment (LCA), which in the meanwhile also became a valuable tool in the chemical industry (Hatti-Kaul et al. 2007). While there already exist a decent amount of LCA studies on conventional chemical processes and products, there is a comparably limited amount of studies analyzing biobased chemicals (Hatti-Kaul et al. 2007).

1.1.2 1,3-PROPANEDIOL AS AN EXAMPLE FOR BIOBASED CHEMICALS

For some biobased chemicals the commercialization is already taking place. For example DuPont developed a method to produce 1,3-propanediol (PDO) from corn (Muska & Alles 2005). PDO is a platform –chemical that can be used for a wide range of purposes (Saxena et al. 2009). Next to its use as solvent, lubricant, functional fluid (e.g. antifreeze) and as precursor for the pharmaceutical and chemical industry, PDO can furthermore be applied as additive in foods, paintings, printing inks, cosmetics and liquid detergents (Posada et al. 2013). But it is mainly used for the manufacture of polytrimethylene terephthalate (PTT) where it shows various advantages concerning its chemical and mechanical properties[2] compared to other polyesters based on 1,4-butanediol, ethylene glycol and terephthalic acid (Kraus 2008; Posada 2011). Another advantage of PDO is that it makes plastics easier biodegradable (Posada et al. 2013).

As it already has a large and still growing market (Kraus 2008; Dasari et al. 2005) it seems to be a good example for biobased chemicals that is worth a closer analysis. A study of 2012 estimated that the global PDO market will grow from $ 157 million in 2012 to $ 560 million by 2019 with an annual growth rate of 15,7 % (MarketsandMarkets 2012). The same study also predicts a rise of demand in biobased products and sees for bio-derived PDO good market opportunities.

DuPont already conducted a LCA to compare the NREU and GHG-emissions of their biobased PDO production process from corn-derived glucose with their conventional, chemical one based on acrolein (Muska & Alles 2005; Zeng & Biebl 2002). Also further studies compared the PDO-production from glucose with fossil production pathways (Urban & Bakshi 2009; Anex & Ogletree 2006).

While DuPont is using corn as an input for its biobased PDO-production there are also several methods for producing it with glycerol as raw material. Glycerol can be gained as a by-product from the biodiesel production. Linking the chemical production to the bio-energy industries seems like a promising approach as it is increasing significantly (Hatti-Kaul et al. 2007). This development lead to an oversupply of glycerol (Pagliaro & Ciriminna 2007; Johnson & Taconi 2007) which makes glycerol a cheap feedstock for chemical synthesis (Posada et al. 2013; Johnson & Taconi 2007). In the light of this development options for a value-added conversion of glycerol were assessed, with the anaerobic fermentative production of PDO being regarded as the *"most promising"* one by some authors (Johnson & Taconi 2007). Apparently a commercial implementation of this pathway is on its way. The France-based company METabolic Explorer and its Malaysian partner Bio-XCell intend to go ahead

[2] Those advantages include: better stretching and stretch-recovery characteristics, lower dyeing temperature, more resistant to stains, better washfastness, better resistance against UV-degradation, application of a wider range of colors possible (Kraus 2008)

with their plans to build a biobased PDO facility that uses crude glycerol as feedstock and has a capacity of 50.000 tons per year (Guzman 2013).

Posada et al. (2013) proposed and assessed a technology scheme for PDO-production from glycerol. Considering the previously described developments of the glycerol market this production pathway might be a viable alternative to existing production of PDO from oil or corn like adapted by DuPont. Making use of glycerol as a by-product from the biodiesel production seems furthermore promising from an environmental perspective as it does not require additional land for crop cultivation like corn. Instead it adds value to a by-product whose oversupply can currently not be fully accommodated by conventional uses of glycerol (Johnson & Taconi 2007) and which is therefore mainly disposed by incineration (Pollitt 2008). Also the European Union discovered the potential of glycerol and currently fosters research about the production of value-added products from glycerol coming from the biodiesel production.[3]

1.2 RESEARCH QUESTION

While there exist environmental assessments of other PDO production schemes (Urban & Bakshi 2009; Anex & Ogletree 2006; Muska & Alles 2005), so far no assessment of the environmental impact of the glycerol-based PDO production was conducted. Addressing this knowledge gap, this paper aims at answering the following question:

> *What are the environmental impacts of the production of biobased 1,3-propanediol from glycerol and how do the results relate to existing studies of the petrochemical production of propanediol as well as the biobased production from corn?*

The tool for assessing the environmental impacts will be the widely used Life Cycle Assessment (LCA) which is standardized by the ISO 14040 series. This LCA will enable us to answer the following subquestions:

1. *What are the energy and material inputs and outputs throughout the production of 1,3 propanediol from glycerol?*
2. *What are the most contributing sub-processes in the production of 1,3-propanediol from glycerol?*

A short literature review will furthermore look at the production of glycerol in Europe (as a by-product of the biodiesel-production) from different feedstocks. This review should prepare the

[3] From November 2013 on the European Union finances the *"GRAIL"*-project: *„Glycerol Biorefinery Approach for the Production of High Quality Products of Industrial Value"* (European Commission 2013; DBFZ 2014)

decision on which glycerol production pathway will be chosen for this analysis as input to the PDO production. Often the choice of the raw material proves to be an important aspect of the life cycle performance of a product (Hatti-Kaul et al. 2007). Therefore the following sub-questions were formulated:

3. *What are predominant glycerol / biodiesel production pathways in Europe and how is their relative environmental performance?*
4. *How do the environmental impacts of the 1,3-propanediol production from glycerol relate to the initial glycerol production?*
5. *What are future trends in the European glycerol / biodiesel production and how could they influence the glycerol-based 1,3-propanediol production?*

As this paper just serves the purpose of a first screening comparison between different production pathways of PDO, the analysis will be just focused on the impact-categories Greenhouse gas emissions (GHG) and non-renewable energy use (NREU). Those are relatively easy and sound assessable compared to more complex but equally important categories like indirect land-use which face many inaccuracies and calculation difficulties (Cherubini et al. 2009). This limitation in scope also facilitates the comparison of the results to other studies which will be the next step. Moreover, a sound analysis and interpretation of a more encompassing environmental assessment including further impact categories would have been difficult within the frame this thesis allows. A limitation in scope was therefore necessary.

The results of this study will be compared to environmental assessments of petrochemical as well as other biobased production pathways of PDO. Three fitting studies have been identified for this purpose: DuPont Tate & Lyle n.d.; Anex & Ogletree 2006; Urban & Bakshi 2009.

This comparison leads to the 5th sub-question:

6. *How do the aggregated results (GHG emissions & Non-renewable energy use) of the 1,3-propanediol production from glycerol relate to the propanediol production from corn and fossil oil?*

Since conducting a LCA and especially a comparison based on different LCA-studies involves many inaccuracies and uncertainties an extensive analysis of the limitations of the study's results is indispensable. Hence a 6th sub-question was formulated:

7. *What are the limitations of such an analysis and comparison?*

1.3 STRUCTURE

An initial chapter about the research methodology describes the way those research questions are intended to be answered and introduces the LCA-methodology (chapter 2). In the following chapter 3 a brief introduction is given to the different possibilities that exist to produce PDO. Chapter 4 will then be dedicated to the feedstock for the PDO production analysed in this chapter: Glycerol. After giving an overview of the biodiesel / glycerol production in Europe different studies will be analysed to inform a decision about which production route will be chosen for the analysis. This chapter also provides insights into the future developments of the biodiesel / glycerol market. In chapter 5 the results of a literature review of LCA studies on PDO production are presented. This and the previous chapter 4 lay the ground for the following chapter 6, in which the Life Cycle Assessment of the glycerol-based PDO production is conducted. This LCA chapter mainly follows the structure proposed by the ISO 14040 standard and includes the Goal & Scope definition, the Life Cycle Inventory, the contributional as well as the sensitivity analysis of the results of the Life Cycle Impact Assessment (LCIA) and finally the limitations of the study.

The following chapter 7 benchmarks the results of the LCA to the results of the other studies analysed in chapter 5. The results will be discussed and some conclusion will be drawn, considering the limitations of the comparison. Finally, chapter 8 presents a summary of the findings and conclusions concerning the research questions posed in chapter 1.2 and provides a short outlook on possible further research and developments.

2 RESEARCH METHODOLOGY

To answer the research questions first two initial literature reviews will be conducted to prepare the further steps. A literature review about studies on biodiesel / glycerol production (step 1) will deliver information about the developments and environmental performance of different biodiesel production routes within Europe to lay the ground for the decision on which pathway to choose for the LCA of the glycerol-based PDO production. The second literature review will identify LCA-studies on different PDO-production routes (step 2) to provide input to the design of this paper's LCA study and to prepare a following comparison of the results. The third step is the conduction of the LCA study on the PDO production from glycerol, using information of step 1 and 2. The fourth step is the benchmarking of the obtained results with the results of the studies analysed in step 2. Finally the results of the LCA study and its comparison will be discussed and interpreted in step 5.

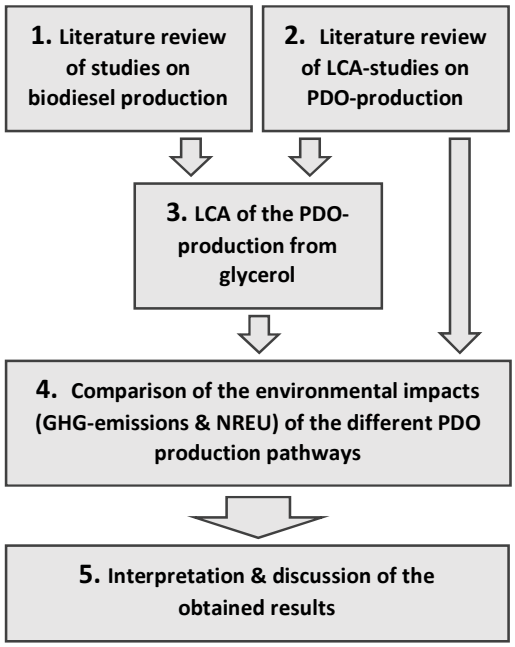

FIGURE 1: RESEARCH FRAMEWORK

The research framework is displayed in Figure 1 and will be further explained in chapters 2.1 – 2.5.

2.1 LITERATURE REVIEW OF STUDIES ANALYSING THE BIODIESEL / GLYCEROL PRODUCTION IN EUROPE

As stated in chapter 1.2 the choice of raw material can have a significant influence on the life cycle performance of a product. Since biological glycerol can be produced from various oil based crops (Hou et al. 2011), a choice of feedstock has to be made for this assessment. The aim is to identify a suitable, relevant European production pathway that preferably has a low environmental impact and for which assessable data is available for the LCA.

This task will be addressed by a literature review on studies dealing with the biodiesel production in Europe. In a first step relevant glycerol feedstocks in a European context will be identified. Additionally, future trends in the biodiesel / glycerol production will be identified to discuss their possible impact on the PDO production from glycerol. Afterwards studies analysing the environmental performance of production pathways based on those feedstocks will be examined.

Finally, a choice will be made that is based on three factors: relevance, environmental performance and practicality for this study (e.g. data availability).

2.2 LITERATURE REVIEW OF LCA-STUDIES ON 1,3-PROPANEDIOL PRODUCTION

The aim of this literature review is to identify studies that can be considered for benchmarking and that provide input for the design of this paper's LCA.

To achieve a high comparability of the results of the different studies it is important that the LCA-methodologies applied are as similar as possible. An adaption to the methodology and scope of the already existing studies chosen for comparison seems therefore advisable.

The identified studies will first be individually analysed concerning their methodology and scope applied. The observed similarities and differences will then be summarized and compared to provide a basis for benchmarking and insights for the design of the LCA on the glycerol-based PDO production.

2.3 LIFE CYCLE ASSESMENT OF THE 1,3-PROPANEDIOL PRODUCTION FROM GLYCEROL

A conventional process-based LCA using the SimaPro software will be conducted, guided by the principles of the ISO 14040 series. A LCA identifies and quantifies the environmental impacts occurring within the life cycle of a product, ideally in a cradle-to-grave analysis ranging from raw material acquisition through production, use and end-of-life treatment (ISO 14044 2006).

A LCA can help to select relevant indicators to measure environmental performance and thus inform decision makers in industry as well as in governmental and non-governmental organizations for the purpose of strategic planning or product and process design. It can help to identify opportunities to improve the environmental performance of a process or product by pointing out the most influential life cycle stages and processes. Furthermore it is a tool that can be used for marketing purposes (e.g. ecolabelling). (ISO 14040 2006)

A LCA consists of four different stages which are displayed in Figure 2: Goal and Scope definition, inventory analysis, impact assessment, interpretation. Those four phases will be explained in chapters 2.3.1 - 2.3.4, following the ISO 14040 (2006) and ISO 14044 (2006) standards. Chapter 2.3.5 will shortly explain how the LCA concept will be applied for this study. LCAs also frequently face criticism due to their limitations. Those limitations will be addressed in chapter 6.6.

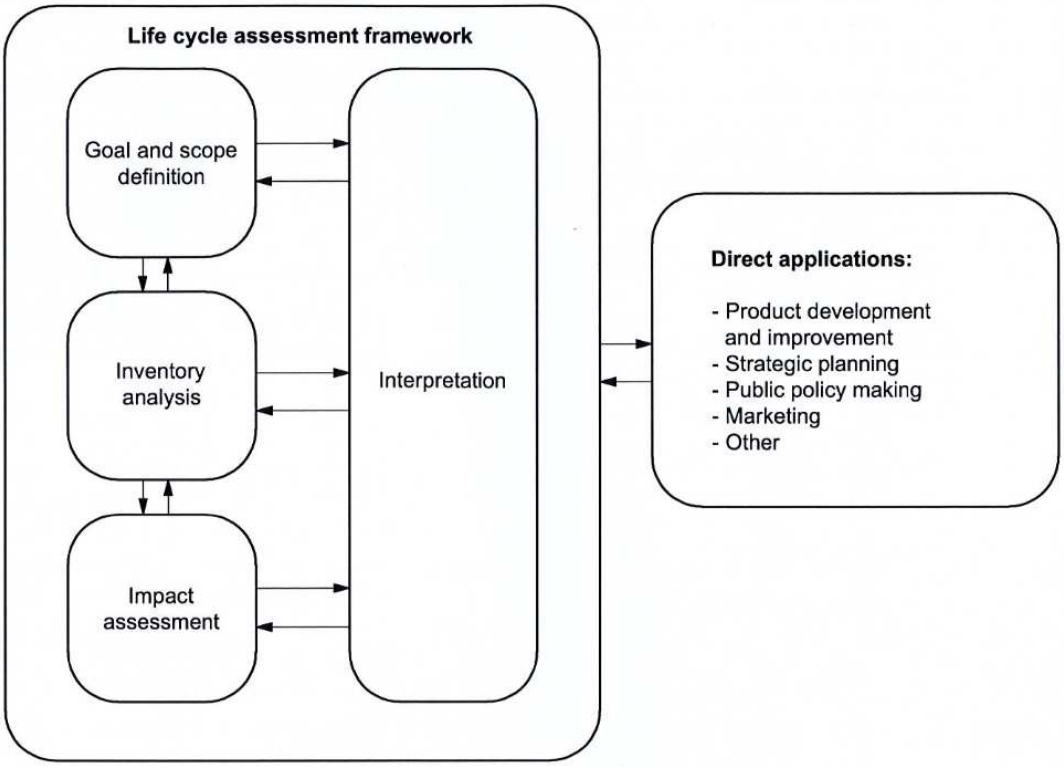

FIGURE 2: THE STAGES OF AN LCA AND ITS APPLICATIONS (ISO 14040 2006)

2.3.1 GOAL AND SCOPE DEFINITION

The goal and scope definition provides the framework of the LCA. The goal definition states the aims and the intended application of the study. It furthermore presents the reasons for conducting the study and names the audience the LCA is dedicated to.

The following scope definition has to be consistent with the goal definition. It is one of the most crucial parts of a LCA since it defines the product system to study, elaborates on the function and functional unit of the system and establishes the system limits, i.e. the system boundary. Moreover it defines allocation procedures, data requirements, impacts to be evaluated and interpreted and the methodology applied for assessing those impacts.

The purpose of the functional unit is to provide a reference to which input and output data will be related to. It enables a comparison to other product systems that perform the same function. The system boundary defines which processes of the life cycle will be included in the analysis and argues why others are excluded.

2.3.2 INVENTORY ANALYSIS

The goal & scope definition will be followed by a life cycle inventory analysis (LCI), which according to ISO 14044 should inform on all input/output data within the system boundaries and throughout the different life cycle stages that will be assessed. The different steps for conducting a LCI are illustrated in Figure 3.

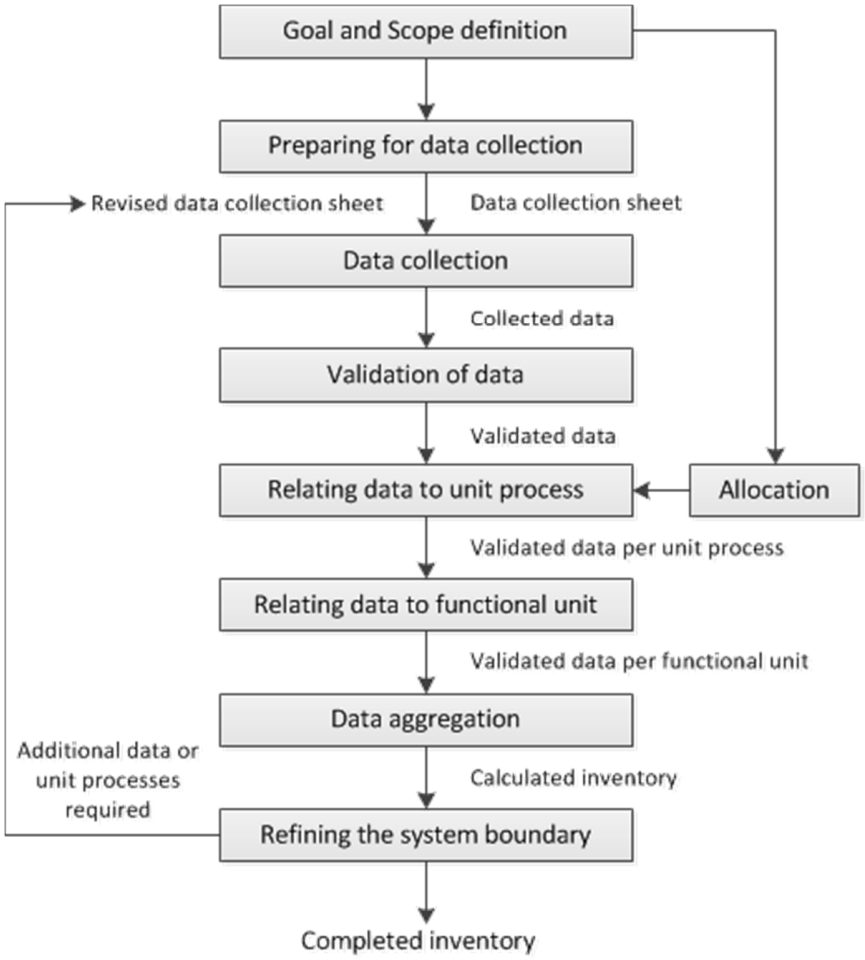

FIGURE 3: PROCEDURES FOR THE INVENTORY ANALYSIS (ADAPTED FROM ISO 14044)

This phase includes the collection of data and its validation. The data will be related to each process unit and classified in categories (e.g. material or energy input, emission, product etc.). The calculation procedures have to be explicitly documented and all assumptions explained.

Finally, the input / output data will be related to the functional unit chosen in the scope definition and furthermore aggregated. Sometimes the LCI-phase also results in the refinement of the system's boundaries.

2.3.3 IMPACT ASSESSMENT

The next step is the Life Cycle Impact Assessment (LCIA) which uses the results of the life cycle inventory to evaluate the potential environmental impacts. A LCIA consists mandatorily of 3 steps and further optional elements (see Figure 4).

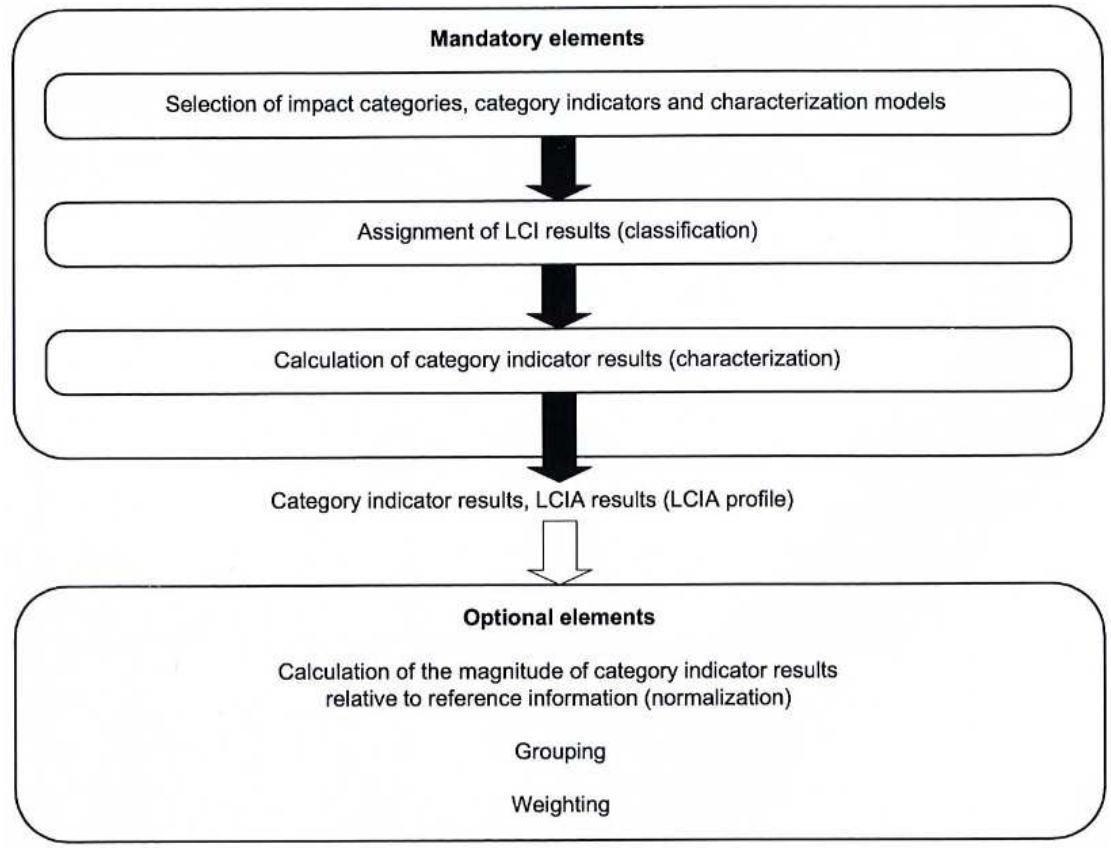

FIGURE 4: ELEMENTS OF THE LCIA-PHASE (ISO 14040 2006)

First, the impact categories and its indicators as well as the characterization models are chosen. In the following classification phase the inventory will be associated with the specific impact categories and their indicators. Finally, the category indicator results will be calculated. This process is labelled as characterization and will provide the LCIA-results. There are different methodologies for this which are usually defined in the goal and scope definition.

Optionally also a normalization can be done to compare the magnitude of the impact categories to each other. Further optional elements include grouping and weighting. Those optional elements will however not be considered in this study (see explanation in chapter 6.1.6)

2.3.4 INTERPRETATION

Once the results are obtained an LCA concludes with the interpretation of results. This phase consists of three elements:

- The identification of significant issues based on the results of the LCI and the LCIA
- The evaluation of the results, considering checks for their completeness, consistency and sensitivity
- Conclusions and recommendations, considering the limitations of the study

Together with the Goal and Scope definition the interpretation phase frames the study.

2.3.5 APPLICATION OF THE LCA CONCEPT FOR THIS STUDY

This paper will assess the production process from glycerol to 1,3-propanediol in a so called cradle-to-gate analysis (see chapter 6). The process analysed is taken from (Posada 2011).
Using the input from the literature reviews on glycerol and PDO production (see chapter 2.1 and 2.2) a LCA-methodology (Goal & scope definition) will be designed that fits to the data available while at the same time serving the purpose of the study, which also requires an easy comparability to the other studies as far as possible.

After having calculated the LCI an LCIA will be conducted, using the IMPACT 2002+ methodology to calculate the results for the midpoint-indicators GHG-emissions and NREU. To interpret the results a contributional analysis will be done that identifies the key processes, inputs and outputs responsible for the total NREU and GHG-emissions of the PDO production. Furthermore a sensitivity analysis will be implemented to examine how the results change if various factors are altered (e.g. methodological and data assumptions). From this sensitivity analysis different scenarios will be derived that are then used for the benchmarking in step 4 (see chapter 2.4).

The interpretation finishes with conclusions and an assessment of the limitations of the LCA. The general limitations of a LCA will be addressed via literature review and the specific limitations of this study will be critically evaluated on basis of the data used and the choices made (e.g. system boundaries).

2.4 COMPARISON OF THE DIFFERENT PATHWAYS OF 1,3-PROPANEDIOL PRODUCTION

To answer the second part of the main research question the results of the conducted LCA for the GHG-emissions and NREU will be benchmarked to the results of the studies chosen for comparison in step 2.

The basis for understanding and discussing the comparison is provided by the literature review on the LCA studies of alternative PDO production routes (step 2, see chapter 2.2).

2.5 INTERPRETATION AND DISCUSSION OF THE RESULTS

This study uses the tool LCA to assess the environmental impacts of the PDO production from glycerol and furthermore includes a comparison to other LCA-studies to answer the research question. As a LCA faces many limitations and comes along with various inaccuracies it is elemental to discuss the value of the obtained results. The comparison between different LCA studies implies even further difficulties which also have to be thoroughly addressed. This will help to appraise the quality of the statements about the environmental performance of the production processes that are derived from the comparison.

Considering the limitations of the study, the results will be interpreted to provide some valid statements for the conclusions.

3 1,3-PROPANEDIOL PRODUCTION PATHWAYS

PDO can be produced from four different feedstocks: Ethylene oxide, acrolein, glycerol and glucose. (Kraus 2008). This chapter gives a brief overview of those production pathways, starting with the petrochemical routes and closing with the glycerol-pathway, which will be assessed in this paper.

3.1 PETROCHEMICAL PDO PRODUCTION FROM ETHYLENE OXIDE

One petrochemical way to produce PDO is the hydroformylation of ethylene oxide. In this two-stage process ethylene oxide first reacts with carbon monoxide and an organometallic catalyst (Kraus 2008) to 3-hydroxypropanal, which is then hydrogenated to PDO (Zeng & Biebl 2002).

Shell combined these two steps into a single reaction with an approximately 90% yield (see Figure 5) using a bimetallic catalyst (cobalt and ruthenium compounds) and a 1,2-diphospholanoethane ligand. In the presence of synthesis gas in methyl tert-butyl ether and under elevated temperatures and pressures the catalyst then reacts with ethylene oxide to PDO. (Kraus 2008)

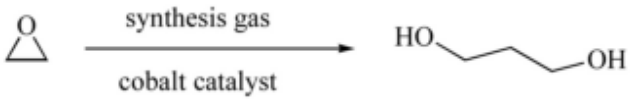

FIGURE 5: HYDROFORMYLATION OF ETHYLENE OXIDE (KRAUS 2008)

Besides the environmental concerns that the reaction uses petrochemical materials, a further disadvantage of this production route is that the generated PDO contains ten times more impurities than PDO produced via fermentation processes (Kraus 2008).

3.2 PETROCHEMICAL PDO PRODUCTION FROM ACROLEIN

A further petrochemical pathway is the PDO production from acrolein which involves a two-stage process (see Figure 6). Adding water to acrolein (mediated by acid catalysts) 3-hydroxy propionaldehyde is obtained which is then hydrogenated to generate PDO. (Kraus 2008; Zeng & Biebl 2002)

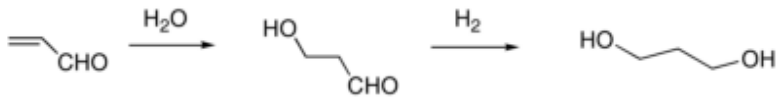

FIGURE 6: CONVERSION OF ACROLEIN TO PDO (KRAUS 2008)

DuPont uses a rubidium catalyst and high pressure (90 bar) for the hydrogenation step (Zeng & Biebl 2002). Studies have shown that with ruthenium catalyst the reduction of 3-hydroxy propionaldehyde to PDO can achieve yields of up to 98 %. (Kraus 2008)

The feedstock acrolein is usually obtained via the oxidation of propylene (Zeng & Biebl 2002), but also glycerol can be used to produce acrolein using *"catalytic quantities of sulphuric acid in hot compressed water"* (Kraus 2008).

3.3 BIOBASED PDO PRODUCTION FROM GLUCOSE

Besides its petroleum-based PDO production DuPont (in cooperation with Tate & Lyle) also designed and commercialized a biobased route for PDO production from D-glucose based on corn, using genetically engineered E.coli in a fermentation process which harvests PDO at a ratio of 0,51 kg / kg glucose, a titer of 135 g/L and a rate of 3,5 g/L/h (Nakamura & Whited 2003; Kraus 2008). Figure 7 shows the biobased PDO production process from glucose as depicted by Urban & Bakshi (2009) and Anex & Ogletree (2006), who tried to match the production process of DuPont. After the fermentation and separation PDO is recovered in a four-step distillation process.

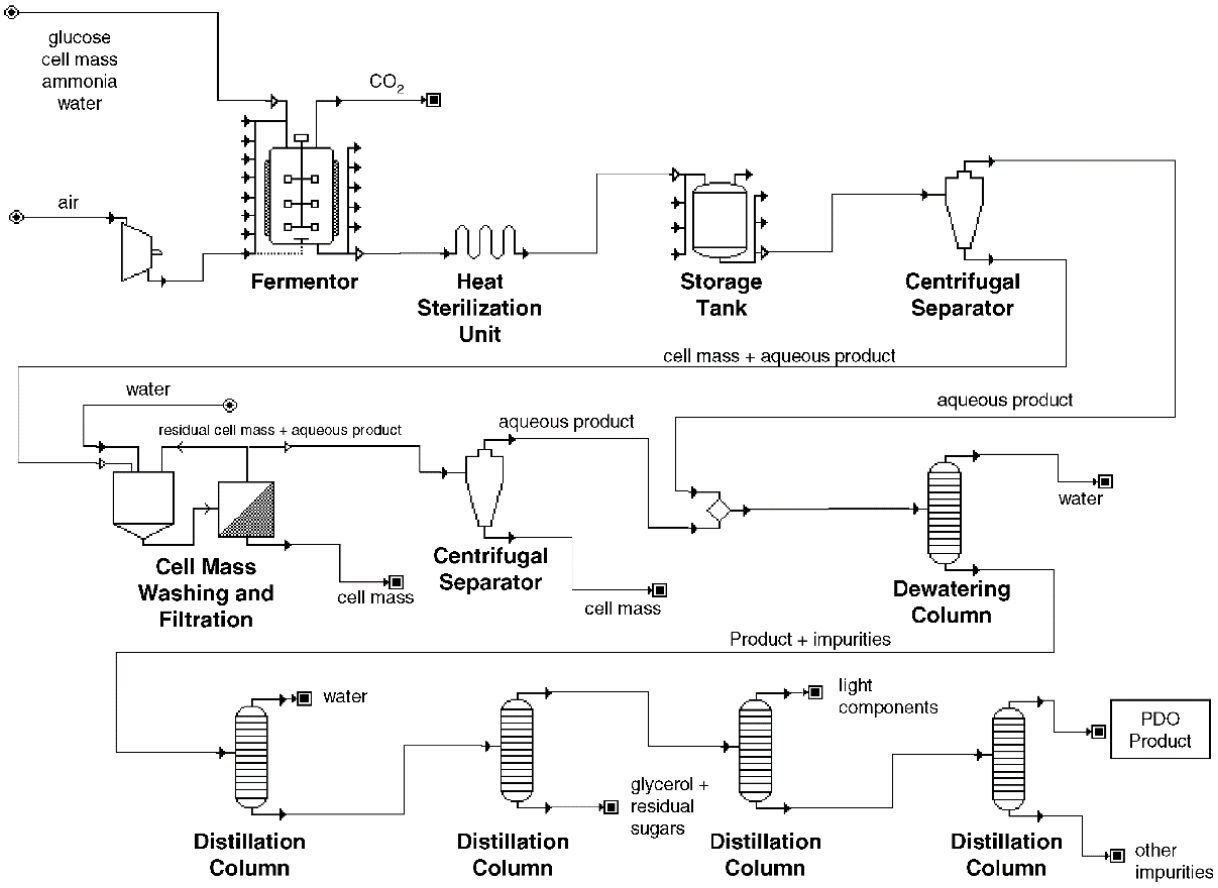

FIGURE 7: PROCESS FLOWSHEET FOR BIOBASED PDO PRODUCTION FROM CORN (URBAN & BAKSHI 2009)

But there are also further possibilities developed to obtain PDO from glucose. First research results indicate that PDO can also be generated from D-glucose in a one pot reaction using a Saccharomyces cerevisiae strain (Rao et al. 2008; Kraus 2008).

3.4 BIOBASED PDO PRODUCTION FROM GLYCEROL

Since almost 120 years a bacterial fermentation process has been known that generates PDO from glycerol. However it took till the 1990s that this naturally existing process was also considered for modern biotechnology. (Zeng & Biebl 2002)

Several bacteria strains can be used for the fermentation of glycerol to PDO, e.g. Klebsiella pneumoniae, Citrobacter freundii, Enterobacter agglomerans, Clostridium butyricum and Clostridium acetobutylicum. Of those Klebsiella pneumonia and Clostridium butyricum are considered as the commercially best performing strains due to their *"high yield, productivity, and resistance to both substrate and product inhibition"* (Posada 2011). Also Johnson & Taconi (2007) suggest that Klebsiella pneumonia shows the greatest productivity as it is able to tolerate much higher concentrations of glycerol.

The production process assessed in this paper is the one analyzed by Posada (2011), who assessed the PDO production by glycerol fermentation using *K. pneumoniae* DSM-2026 in one and two continuous fermentation stages. As a complex biological mechanism glycerol bioconversion to PDO faces many constraints. The challenge therefore lies in a thorough process analysis to come up with efficient configurations that provide a high yield, concentration and productivity. Posada (2011) assessed four different culture configurations and optimized all processes. The best performing process (scenario 3 in Posada 2011) is sketched in Figure 8.

The first step is the purification of the raw glycerol input, followed by the glycerol fermentation. While in the corn-based PDO production glucose is fermented in one fermentation tank (see chapter 3.3) the fermentation from glycerol is a two stage fermentation process, with the first tank achieving a concentration of 0,377 mol_{PDO}/L at a rate of 0,106 mol/L per hour and the second tank reaching 0,412 mol_{PDO}/L with a productivity of 0,109 mol/L per hour (Posada et al. 2013). The downstream processes consist of the PDO recovery and purification. For more explanations and information on the process please refer to Posada et al. (2013) and to Posada (2011).

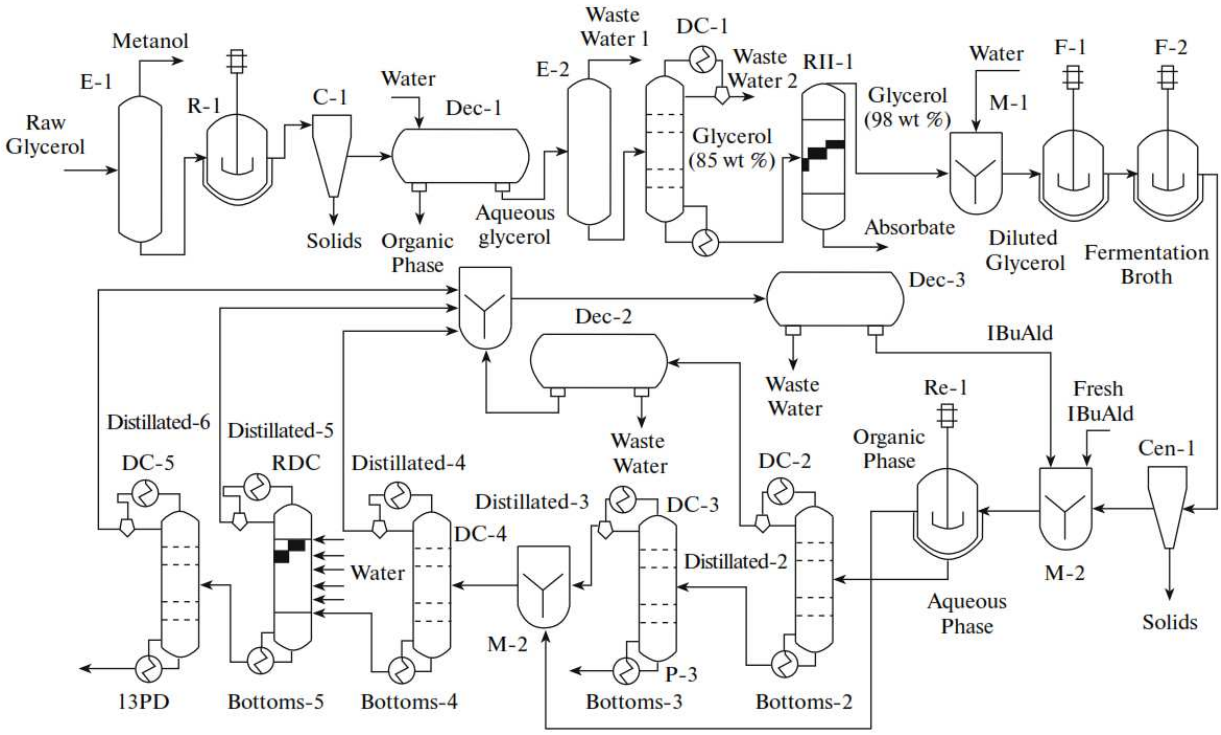

FIGURE 8: SIMPLIFIED FLOWSHEET FOR PDO PRODUCTION FROM RAW GLYCEROL: E—Evaporator, R—Reactor, C—Centrifuge, DEC—Decanter, DC—Distillation Column, M—Mixer, F—Fermentator, RE—Reactor Extractor, RDC—Reactive Distillation Column. (Posada Et Al. 2013)

4 GLYCEROL PRODUCTION

4.1 CURRENT BIODIESEL / GLYCEROL PRODUCTION

Glycerol, also known as glycerine, is an organic chemical with the formula $C_3H_8O_3$. Just less than 10% of glycerol is obtained by synthetic production while the vast majority of 90% comes from natural sources. (Jungbluth et al. 2007)

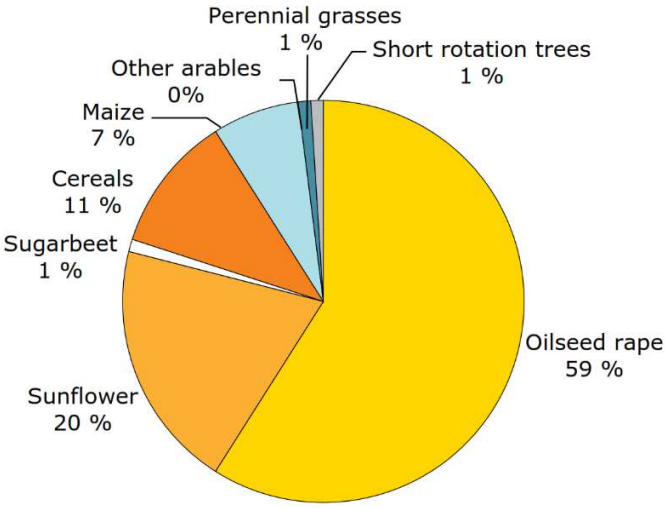

FIGURE 9: RECENT MIX OF ENERGY CROPS IN EUROPE (2006-2008 DATA)
(European Environmental Agency 2013)

Today glycerol is to a large extent obtained as a by-product of the biodiesel production. Biodiesel is produced from oil based crops like rapeseed, sunflower and waste edible oils. It can also be produced from palm trees, jatropha bushes and microalgae (Hou et al. 2011). But the most used feedstock in Europe is rapeseed (Jungbluth et al. 2007), followed by sunflower (see Figure 9). The production of rapeseed almost doubled (growth of 93%) in the European Union between 2000 and 2009 (European Environmental Agency 2013). Especially in Germany rapeseed plays a dominating role, as in 2013 84,7 % of the biodiesel production was based on it (Verband der Deutschen Biokraftstoffindustrie 2013). However, even if still increasing, recent data has shown that the growth of the biofuel production in the EU has slowed down in the past years (European Environmental Agency 2013).

4.2 FUTURE TRENDS IN BIODIESEL / GLYCEROL PRODUCTION

By 2020 the European Union (EU) aims at a 20%-share of renewable sources in the final energy consumption. Part of this goal should be fulfilled by the transport sector in which 10 percent of transport fuel should come from renewable sources by 2020. (European Union 2009)

Together with other motivations like energy security this lead to an increased interest in biofuel production. As they are mostly still not competitive to conventional fuels many supportive measures have been implemented by the EU member states like direct production subsidies, quotas or tax exemptions which resulted in an increased production of biofuels. (Kretschmer et al. 2009)

This governmental support of biofuels was however increasingly criticized, cumulating in the *"food vs. fuel"*- debate, raised by the rapidly rising food prices in 2007/2008. The reasoning behind this debate was that the growing production of biofuels fosters land use competition which eventually raises the agricultural and consequentially the food prices. (Kretschmer et al. 2009)

Also the European Environmental Agency (EEA) included those growing concerns in their research and highlights the importance of indirect land-use change (ILUC)[4] and recommends to include this issue into all political decisions on bioenergy (European Environmental Agency 2013).

In a report published in 2013 the EEA considers new developments like the ILUC issue to re-evaluate the potential of bioenergy in the EU and its environmental impacts. One of the key messages is that *"current energy cropping trends are not "environmentally compatible""* if the criteria developed by an EEA report from 2006 (European Environmental Agency 2006) are applied. A shift away from first generation biofuels to advanced second or third generation biofuels is proposed. (European Environmental Agency 2013)

The EEA assessed various storylines to come up with different scenarios for 2020. Figure 10 contrasts the recent energy mix that is characterized by a dominating role of first generation biofuels (especially of rape seed) with a projection of an environmentally compatible crop mix by 2020. This comparison highlights the significant change that the EEA postulates. Rape seed would experience a drastic drop from 59% to only 5%. (European Environmental Agency 2013)

[4] ILUC defines a situation in which e.g. crops for biofuel production occupy land which was previously dedicated to other agricultural products, e.g. food. As at the same time the demand for the other agricultural products remains the same this replacement will lead to a land conversion at some other place to meet the still existing demand for the replaced products. This might lead to land use change of e.g. forest to agricultural land which would result in CO_2 emissions and biodiversity loss. (European Commission 2012a; Cherubini et al. 2009)

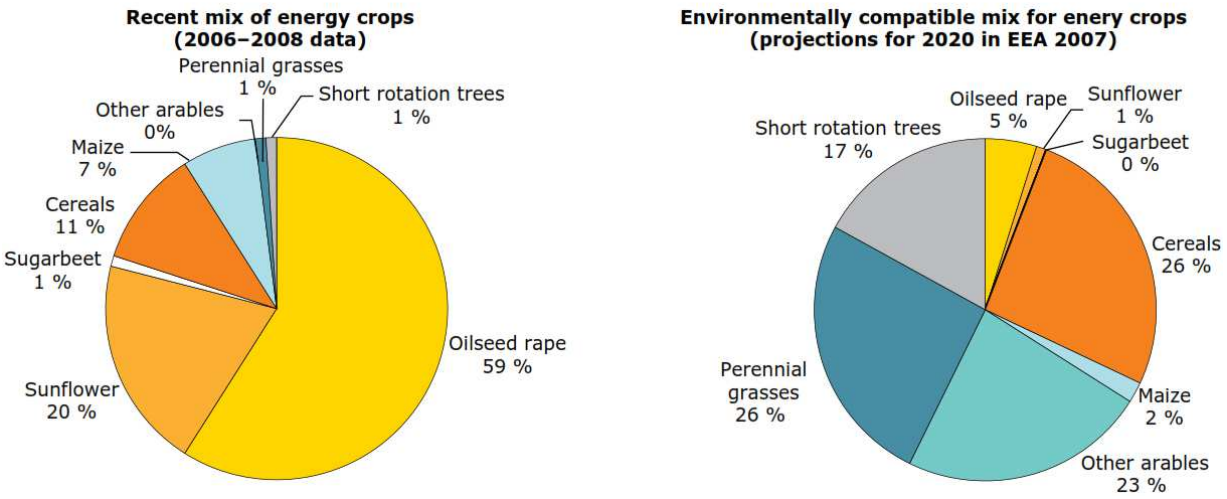

FIGURE 10: COMPARISON OF RECENT MIX OF ENERGY CROPS WITH EEA-PROJECTIONS FOR AN ENVIRONMENTALLY COMPATIBLE MIX FOR ENERGY CROPS BY 2020
(European Environmental Agency 2013)

Following the criticism of biofuel production and the new scientific insights also the politics took up that issue and worked on alterations of the biofuel policies. In 2012 the European Commission (EC) proposed a directive that is supposed to prevent providing the wrong incentives in biofuel production. It includes inter alia a 5% cap on the amount of biofuels from cultivated biomass in the EU's transport mix by 2020 and the announcement that public subsidies for biofuels after 2020 will end, if they cannot demonstrate *"substantial greenhouse gas savings"*. Furthermore the proposal included a threshold for new biofuel installations of at least 60% GHG-savings compared to fossil fuel from july 2014 on, an aim which was originally set for 2018 in the Renewable Energy Directive of 2009. Besides that the EC also sets incentives for second-generation biofuels and proposes a review of policy and scientific evidence on ILUC. This proposal for a directive was already a compromise and excluded previous plans to introduce mandatory accounting for indirect GHG-emissions (European Union 2009; Neslen 2012)

In a Memo accompanying the proposal the EC states its view that *"biofuels made from food crops and which do not lead to substantial greenhouse gas savings"* should not be subsidized after 2020. Until then, the EC aims at stabilizing the consumption of first generation fuels. (European Commission 2012a)

The follow-up of this proposal was characterized by intense disputes. The ministers of the EU member states failed to agree on an adapted version of the EC-proposal (European Commission 2012b) in 2013 (EurActiv & Reuters 2013; Council of the European Union 2013). Finally, in 2014 the energy ministers agreed on an again adapted proposal which now includes a 7% cap for biofuels from cultivated biomass instead of the 5% initially proposed by the EC and the 6% proposed by the

European Parliament (EP) (Hall 2014a). Another alteration compared to the version rejected in 2013 is the declaration of a now non-binding goal for advanced biofuels (e.g. from agricultural waste and residues) of 0,5 % (Hall 2014b). The accepted proposal will now go through the newly elected EP for a second reading, presumably in autumn 2014 (Hall 2014a).

Even if the European directive is not passed yet and the proposal does not include more drastic measures as expected by some actors (Hall 2014a) it seems clear that the trend goes towards advanced biofuels and that subsidies for first generation biofuels like from rape seed will be phased out. This will ultimately also affect the production of biobased chemicals like PDO from glycerol, as the glycerol feedstock is mostly produced as a side-product of those food-based biofuels from rape seed, sunflower or soybean. If the production of first generation biofuels will be reduced as a consequence of changed policies, less and more expensive glycerol will be on the market.

This scenario has therefore to be taken serious when thinking about fostering the production of biobased chemicals from glycerol (see GRAIL-project by EU, mentioned in chapter 1.1).

4.3 CHOICE OF GLYCEROL PRODUCTION PATHWAY FOR THIS STUDY

As the focus of this study lies on Europe, just the crops displayed in Figure 9 were considered as feedstock for the glycerol production. Of those sunflower and rapeseed are the only oil-based crops with a substantial contribution to the total production of energy crops in Europe. From a pure scale perspective rapeseed clearly recommends itself to be used in this paper's LCA as an example for a glycerol production pathway. However, also the environmental performance of the different glycerol production possibilities should play a role in the choice of the pathway used in the analysis.

A LCA comparison of biodiesel production from rapeseed, sunflower and soybean conducted by Sanz Requena et al. (2011) has shown that of those the seed production of sunflower has the highest environmental impact. This is mainly due to its higher land use which results in a greater use of fertilizer and herbicides. Consequentially the study recommends the use of rapeseed and soybean for biofuel production.

A very extensive study of the environmental impacts of first generation biofuels used in France has been issued by inter alia two French ministries and was conducted by the *"French Environment and Energy Management Agency"* (ADEME) in 2010 (ADEME 2010). Their results on their *"from fields to wheels"* analysis show a better performance of sunflower in GHG-emissions and furthermore also a slightly lower NREU than rape seed. But sunflower performs worse in eutrophication and also slightly

in human toxicity. However, the study did not include direct or indirect land use changes (ADEME 2010). Hence, the performance of sunflower in relation to rapeseed might be actually different. Especially when considering the results of Sanz Requena et al. (2011) which named the higher land use of sunflower cultivation as a decisive factor for the, according to their results, worse performance of sunflower compared to rapeseed.

Alone the comparison between those two studies on glycerol production already shows that it is difficult to get a clear picture about the environmental performance of different production pathways. The study results depend too heavily on differences in methodology and scope applied. They used different functional units (1 kg of biofuel and moving a vehicle over 1 km), different system boundaries (e.g. inclusion / exclusion of transport) and different LCIA-methodologies and indicators. Therefore the environmental performance could not be a decisive factor in choosing the sample pathways for this study.

Concerning data availability rape-seed is the most practical choice, as there is a readily available model for European glycerol production based on rape seed in the ecoinvent database. The only alternatives in the database are Glycerol from vegetable oil (France), from palm oil (Malaysia) and soybean (Brasil, USA) which all do not play a relevant role in Europe. (Jungbluth et al. 2007).

As no clear preference in environmental performance could be found, the scale of production and the data availability were the only decisive factors that lead to the choice of rape seed as the feedstock for glycerol production used in this analysis.

5 LITERATURE REVIEW OF LCA STUDIES ON PDO PRODUCTION

This chapter will review available LCA studies on the PDO production and conclude with a summarized comparison. The aim of this review is to prepare a critical comparison between those results and the result of the LCA about the glycerol-based PDO production which will be conducted in chapter 6. The focus will therefore be on methodological issues which should furthermore provide input for the design of the LCA study conducted in this paper. This chapter can be considered as a mere collection of information about the studies. The comparison of the results and the discussion about the actual influence of the different process designs on the benchmarking will follow in chapter 7.

5.1 DUPONT STUDY (MUSKA & ALLES 2005)

In 2000 the cooperation between Tate & Lyle and DuPont started the process piloting of the biobased PDO production from glucose using a genetically modified E.coli strain (Nakamura & Whited 2003) which lead to the start-up of a commercial plant in 2006. As part of their analysis they conducted a cradle-to-gate LCA of the process, which is used for benchmarking against the fossil alternative, process development and marketing. This LCA should be complemented by a gate-to-grave analysis in future. (Muska & Alles 2005)

Unfortunately there is almost no information available about the details of the study. No functional unit was given. Also the LCIA-methodology calculating the NREU and the GHG-emissions was not specified.

5.1.1 BIOBASED PDO PRODUCTION

Concerning the system boundaries it seems like the impacts have been assessed from raw-material acquisition to factory gate, including transport (DuPont Tate & Lyle 2009).

Figure 11 shows the Bio-PDO LCA system assessed by DuPont. In the fermentation the PDO is harvested at a ratio of 0,51 g PDO / g glucose, a titer of 135 g/L and at a rate of 3,5 g/L/h (Nakamura & Whited 2003).

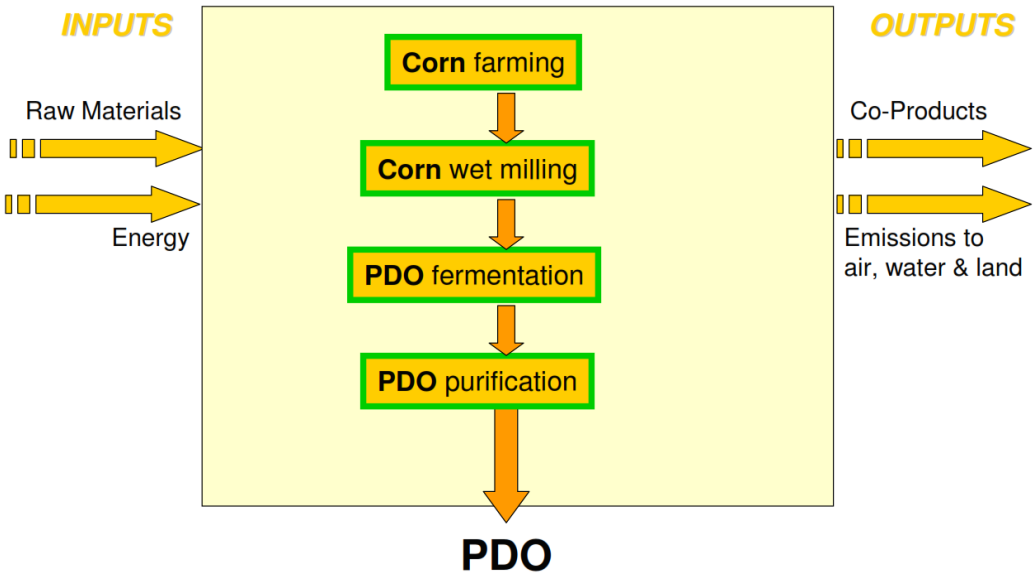

FIGURE 11: BIO-PDO LCA SYSTEM OF THE LCA CONDUCTED BY DUPONT (Muska & Alles 2005)

5.1.2 FOSSIL PDO PRODUCTION

Even less information is available about the fossil PDO production pathway DuPont chose as a benchmark (see Figure 12). Most likely they assessed the pathway that consists of the hydration of acrolein followed by a hydrogenation route (shortly explained in chapter 3.2). According to Kraus (2008) the acrolein approach *"has been rigorously evaluated by researchers at [...] DuPont"* (Kraus 2008) and was furthermore implemented for their commercial PDO production (IHS Chemical 1999; Zeng & Biebl 2002). Acrolein is obtained by catalytic oxidation of propylene (Anex & Ogletree 2006; Kraus 2008), which is mentioned as input in Figure 12. This information indicates that DuPont chose the acrolein production path as a reference.

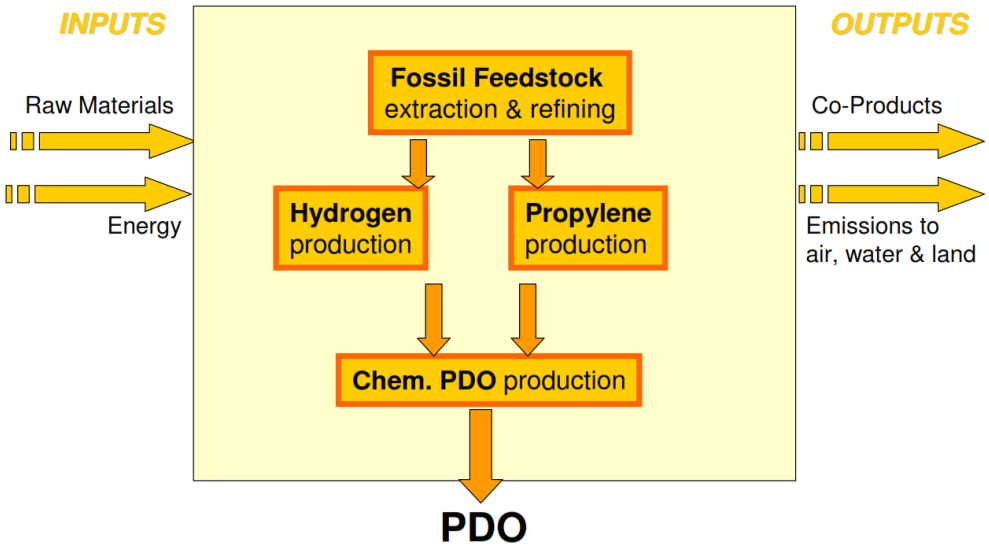

FIGURE 12: FOSSIL PDO PRODUCTION SYSTEM OF THE LCA CONDUCTED BY DUPONT (Muska & Alles 2005)

No statement could be found on how the study dealt with one of the biggest advantages of a biobased production compared to a fossil one: The CO_2-sequestration during the cultivation of the feedstock which usually balances the CO_2-emissions occurring when the PDO is disposed (e.g. incinerated) at the end of its lifetime. This natural balance does not exist for fossil PDO which therefore emits additional CO_2 to the atmosphere when disposed compared to biobased PDO (see explanation in chapter 7.1). As the study is from cradle-to-gate it has to be assumed that this factor was not considered.

5.2 ANEX & OGLETREE 2006

Anex & Ogletree (2006) analyze a PDO production system from glucose, trying to match the one developed by DuPont. For the fossil production pathway they chose however a production based on ethylene oxide, while DuPont most probably analyzed the acrolein pathway (see chapter 5.1.2). According to the authors the study should serve as a preliminary benchmark estimate of how a biobased process could perform, what trade-offs are made and furthermore as an indication which processes should be improved.

The functional unit of the study is 1 kg of PDO. Emission Categories applied are NREU, agricultural land use, GHG and NOx emissions. The results of those categories are expressed in equivalence factors, e.g. all GHG are converted to the common basis of kg CO_2 equivalent. An allocation based on mass was chosen to distribute the impact among the different system outputs.

5.2.1 BIOBASED PDO PRODUCTION

The system boundaries of the biobased PDO production are displayed in Figure 13, in which "Ag chemical" stands for agricultural chemicals like pesticides. Anex & Ogletree also conducted a cradle-to-gate analysis.

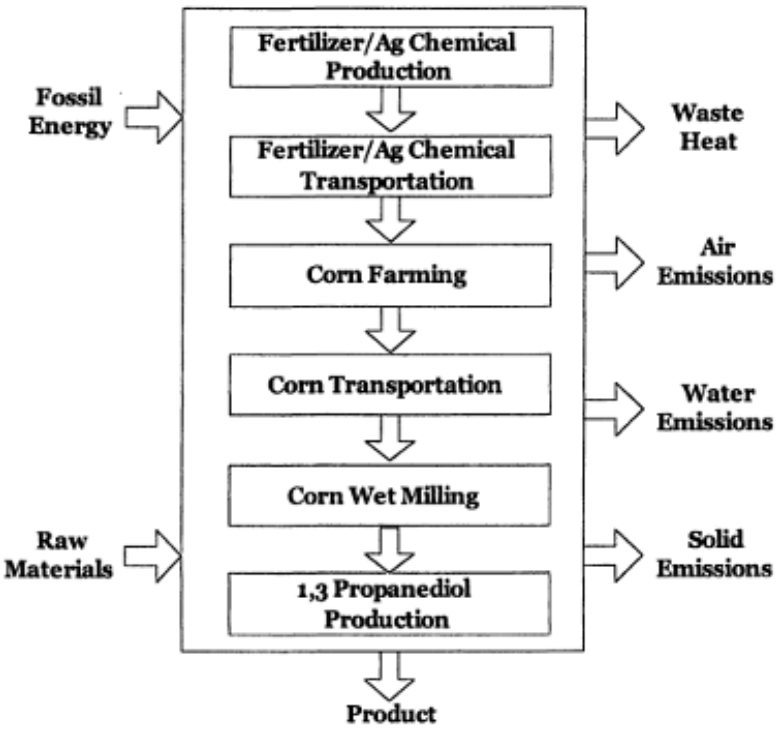

FIGURE 13: SYSTEM BOUNDARIES FOR THE BIOBASED PDO PRODUCTION ASSESSED BY ANEX & OGLETREE (2006)

Important aspects and assumptions concerning the applied scope are listed below:

- Manufacture of farm equipment was not included
- Transport included for: moving feedstock for fertilizer & chemical production, moving fertilizers & chemicals to the farm and moving corn from the farm to the mill
- But: no transportation of glucose to PDO facility (assumed to be at same place)
- All distillation processes were assumed to operate under vacuum to reduce operating temperatures.
- Location: Midwest United States (Illinois, Iowa, Minnesota and Nebraska)
- No climate change credit is taken for carbon sequestration in the soil, as it is assumed that all CO_2 fixed in the corn plant will be re-emitted during processing of the biomass.

The data used for the LCA is from various sources. For the cultivation (first four steps in Figure 13) the data is taken from the "GREET"-model, which stands for: "Greenhouse gases, Regulated Emissions and Energy use in Transportation". For the corn wet milling industry data was used and complemented with data reported in literature.
The PDO production process was designed to match the one of DuPont. For the fermentation the same yield (0,51 kg PDO / kg Glucose) and other publicly available variables were adopted. For the downstream processes (PDO recovery and purification) the process was predicted based on *"best practice engineering design"* (not specified) and *"some guidance"* of DuPont (personal communication, not revealed).

5.2.2 FOSSIL PDO PRODUCTION

Also Anex & Ogletree benchmarked their results of the biobased PDO production with results of a fossil based production pathway. The comparison is limited to the system boundary (cradle-to-gate) and does not include the benefits of CO_2-sequestration which is a big advantage of the biobased production compared to a fossil one (see chapter 7.1). In contrast to DuPont they did not choose the acrolein pathway but opted for the PDO production from ethylene oxide (see chapter 3.1).
To model the fossil production pathway from ethylene oxide Anex & Ogletree use the information of a private consulting firm which is not publicly available. The Life Cycle Inventory data for that process was than derived from a combination of hydrogen production data from a not specified SimaPro database and syngas production data from another literature source.

5.3 URBAN & BAKSHI 2009

This study compares the environmental impacts of PDO production from a fossil feedstock to those of biological feedstock. The specific fossil based production route they analyze is the reaction of syngas with ethylene oxide using a catalyst to form PDO. The biobased process consists of the fermentation of glucose to PDO using a genetically modifies strain of E. coli.

The authors want to verify the results of the study by Anex & Ogletree by reproducing it and adding additional data. The study produces results of three different LCA methods: A process-based LCA[5], a hybrid Economic Input-Output (EIO) LCA[6] and an Ecologically-Based LCA (Eco-LCA)[7]. As in this thesis a process based LCA is conducted, just their process-LCA will be analyzed and benchmarked in this paper.

As functional unit the study chose 1kg of PDO. Using the SimaPro Software the emissions were aggregated with the CML Baseline method. Instead of endpoint indicators the study chose midpoint indicators, e.g. CO_2 equivalent to display the GHG-emissions.

They chose both – mass and economic allocation for the outputs of the wet milling process (dry germ, gluten feed, gluten meal and starch). Since the outcome was almost the same[8], just the mass-based allocation was displayed in the results.

5.3.1 BIOBASED PDO PRODUCTION

As Urban & Bakshi aim at verifying the results of Anex & Ogletree they also adapt their process design to their study. Hence, they use the same fermentation performance (yield of 0,51 kg PDO / kg Glucose) and also adopt the downstream process design (PDO recovery and purification) of Anex & Ogletree. Therefore also the total energy need of the fermentation and PDO recovery and purification was set to be the same (26 MJ).

[5] Process LCA: A production system is divided into a series of unit processes with their specific inputs, outputs and the respective environmental impacts of those inputs and outputs. In the end the environmental impact of all unit processes are accumulated to obtain total impact of the production. (Davidson 2012)

[6] EIO-LCA: Using information about industry transactions (material exchanges between industries) in combination with information about the environmental impact of those industry sectors the EIO-LCA method estimates the total emissions of a production process. (Carnegie Mellon University n.d.)

[7] An Eco-LCA widens the scope of conventional LCAs by including the ecosystem goods and services into the assessment which also contribute to the analysed production process. (Zhang 2008)

[8] According to mass-based allocation 66,7 % is allocated to starch, according to economic allocation 65,2 % (Urban & Bakshi 2009)

The system boundaries of the biobased production pathway are displayed in Figure 14. The boxes dashed in red indicate that those processes were modeled via SimaPro. They mainly used US-models but also made use of European models if no US equivalents were available.

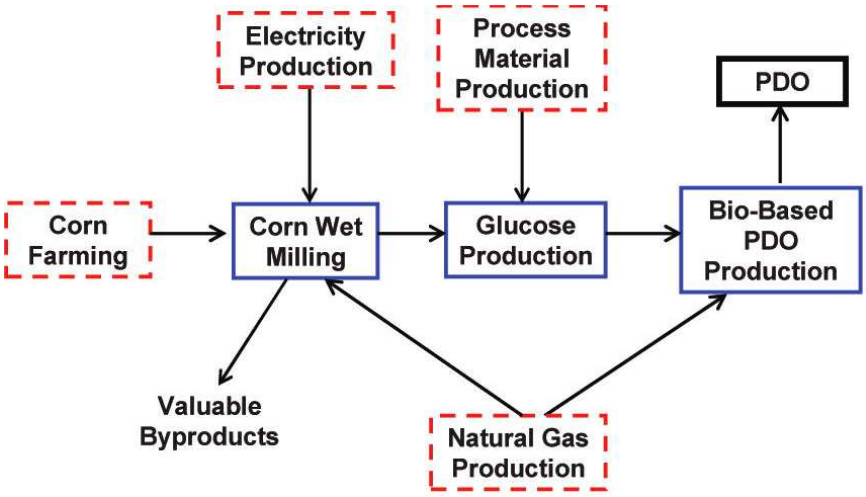

FIGURE 14: SYSTEM BOUNDARIES OF THE BIOBASED PDO PRODUCTION ASSESSED BY URBAN & BAKSHI (2009)

It is assumed that corn farming, wet milling and PDO production take all place close to each other. Therefore the transportation from the farm to the mill and from the mill to the PDO facility are not within the scope of the analysis. For the corn farming the study makes use of the SimaPro-process corn-farming. Therefore transportation of fertilizers and pesticides might be included within the scope of the LCA. However, there is no information which exact SimaPro-process was used.

Like in the study of Anex & Ogletree no building materials for the production facilities and no material for equipment and machinery are assessed. Natural gas is assumed for the heating processes while electricity use is just assessed for centrifugal separation after the fermentation but neglected for other processes.

For the glucose production emissions and energy consumption was ignored, because of apparently *"very little processing energy is required for starch hydrolysis".*

5.3.2 FOSSIL PDO PRODUCTION

Like Anex & Ogletree also Urban & Bakshi chose the fossil PDO production based on ethylene oxide as a benchmark. However, unlike for the biobased production they did not choose the same process design as Anex & Ogletree. Instead they took their design from a CHEMCAD process simulation (based on patent information and reaction stoichiometry) from an undergraduate design project. The

process consists of a reactor, a compressor and a membrane separator. Their key assumption is that for 1 kg of PDO 0.646 kg Ethylene oxide and 0.763 kg syngas are needed.

Process level information for the ethylene production was obtained via a literature review. As this was not easily possible for syngas production literature information for the hydrogen production by steam reforming of natural gas was chosen as an estimate.

In Figure 15 the system boundaries for the fossil PDO production is depicted. Again, the boxes dashed in red indicate that Sima Pro was used for those processes. Some processes were omitted from the LCA as there was no model for them provided by Sima Pro. For those cases the authors assumed that their impact was negligible.

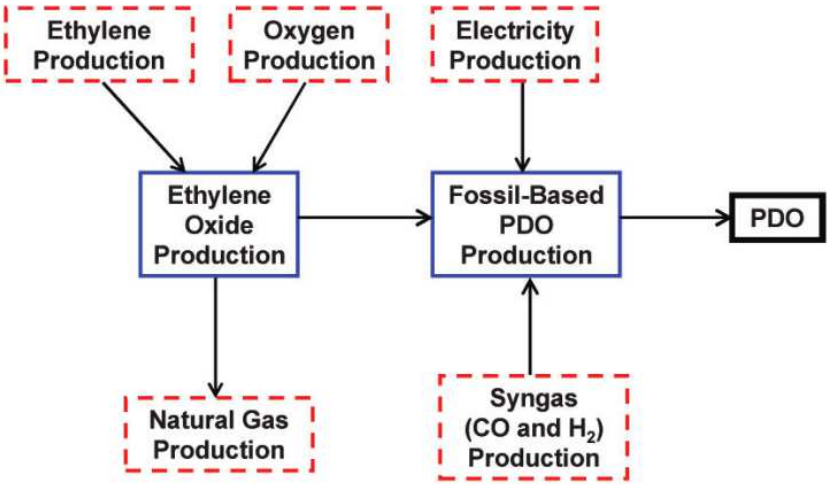

FIGURE 15: SYSTEM BOUNDARIES OF THE FOSSIL PDO PRODUCTION ASSESSED BY URBAN & BAKSHI (2009)

For the PDO production the production of the necessary catalyst was not included. But catalysts for the upstream syngas & ethylene oxide production were included and demonstrated just a very minor impact. An important aspect is furthermore that Urban & Bakshi assumed a credit in form of natural gas for the excess steam that was generated by some processes. Also for the fossil PDO production transport was excluded from the assessment.

As in the study of DuPont the biobased benefit of CO_2-sequestration was not specifically mentioned. Hence, it has to be assumed that its advantage was excluded in the comparison biobased / fossil PDO production, as the limitation to a cradle-to-gate analysis implies.

5.4 SUMMARY

Besides laying the ground for the discussion of the benchmarking in chapter 7, the aim of this literature review was to provide input for the design of the LCA study conducted in this paper. To enable an at least rough comparison between the study results it is important that the methodologies and system boundaries of the studies are as similar as possible. Therefore the design of the LCA will be adapted as much as possible to the analyzed studies. A first step is to identify what the studies have in common and where they differ. Table 1 gives an overview of the previously analyzed studies.

TABLE 1: COMPARISON OF THE REVIEWED LCA STUDIES ON PDO PRODUCTION

	DuPont study (2005)	Anex & Ogletree (2006)	Urban & Bakshi (2009)
Methodology			
Goal	Benchmarking, process development, marketing	Preliminary benchmark of performance of the biobased process	1. Verifying Anex&Ogletree-Study and complementing it with additonal data; 2. Extend conventional LC thinking by also including ecological resources;
LCA-Type	Unspecified	process based	process based + hybrid LCA
Functional Unit	Unspecified	1kg of PDO	1kg of PDO
LCIA-Method	Unspecified; midpoint indicators	Unclear, probably based on GREET-model; midpoint Indicators	CML Baseline method; Midpoint indicators
Allocation	Unspecified	mass-based	mass- & market-based
Scope			
System boundaries	cradle to gate	cradle to gate	cradle to gate
Location	unspecified (probably USA)	Midwest USA	USA
Transport	included, but not clear to which extent	included (except glucose to PDO facility)	Not included
Manufacture of facilities & equipment	Unspecified	Not included	Not included
Biobased production	Fermentation of glucose (yield 0,51 kg PDO / kg glucose)	Fermentation of glucose (yield 0,51 kg PDO / kg glucose)	Fermentation of glucose (yield 0,51 kg PDO / kg glucose)
Fossil production	Acrolein pathway	Ethylene oxide pathway	Ethylene oxide pathway

As the level of transparency differs a lot between the studies, it is difficult to identify all similarities and differences. While Urban & Bakshi offer a great level of detail, Anex & Ogletree did not publish the underlying data of their study. DuPont on the other hand releases almost no information about the methodology of their study. However, the three studies are related to each other, as they all refer to the production process developed by DuPont. It can therefore be expected that the studies are alike concerning the most important aspects.

The process design and simulations done by Anex & Ogletree aimed at matching the performance of the DuPont process by adapting the fermentation process to the data that was publicly available (Nakamura & Whited 2003) and by receiving some guidance by DuPont for the downstream processes (PDO separation and purification) which are based on *"best practice engineering design"* (Anex & Ogletree 2006). As this guidance was received as personal communication no insight was possible on how far the downstream processes are similar to the actual process designed by DuPont.

Urban & Bakshi take both studies as a reference and state the aim of reproducing and verifying the results of Anex & Ogletree. All three studies have the same performance specifications for fermentation (the same yield of 0,51 kg PDO / kg Glucose). Urban & Bakshi furthermore tried to match their process design also to the downstream processes of Anex & Ogletree and assumed the same energy use for the PDO production (fermentation, PDO separation and purification) of 26 MJ.

All three studies conducted a cradle to gate analysis but the papers show differences if it comes to the specific system boundaries. One difference is the inclusion of transport (DuPont and Anex & Ogletree) or respectively the exclusion of transport (Urban & Bakshi). Urban & Bakshi argue however, that the GREET-model has shown that transport only has a minor impact on the total energy consumption.

Anex & Ogletree and Urban & Bakshi seem to go along concerning the plant location and allocation method used as well as concerning the exclusion of the manufacture of production facilities and equipment needed for the production of PDO. As there is just very limited information about the DuPont-study, no statements can be made about those aspects.

For the design of this study's LCA (chapter 6) input from all studies will be considered where possible. But the methodology cannot be adapted to all studies at once. Hence, in case of differences between the studies Urban & Bakshi (2009) will be the main reference. Their study offers the highest level of detail, due to the supporting information they additionally released. A higher level of detail concerning the methodological choices and assumptions made allows a better, critical comparison. Furthermore the study by Urban & Bakshi is the most recent one.

The comparison between the results for the different fossil- and biobased production pathways including the results of this thesis' LCA will be presented and discussed in chapter 7.

6 LIFE CYCLE ASSESSMENT OF THE PDO PRODUCTION FROM GLYCEROL

As described in chapter 2.3 a LCA consists of four different stages which will all be applied to assess the PDO production from glycerol in this chapter. After the goal & scope definition (chapter 6.1) the life cycle inventory is presented (chapter 6.2). In the following contributional analysis (chapter 6.3) the LCIA-results are shown and analysed concerning the specific impacts of different process steps. The subsequent sensitivity analysis furthermore tests the variation of the results when applying different assumptions (chapter 6.4). Finally, the results of the analysis are interpreted in chapter 6.5 and the limitations of the LCA discussed in chapter 6.6.

6.1 GOAL AND SCOPE DEFINITION

6.1.1 GOAL DEFINITION

This LCA represents a preliminary estimate of the environmental performance of the PDO production from glycerol. The results of the study will serve two purposes:

1. Contributional analysis: The processes contributing most to the total environmental impact will be identified. This information might provide guidance where efforts to improve the production process should best be focused on.
2. Benchmarking: The results of the study will be compared to results of LCA studies on other PDO production pathways. To achieve an acceptable degree of comparability the methodology applied will take the methodologies of the benchmarked studies into consideration.

As this study just can be considered as a preliminary assessment, it should probably not be used for decision-making. Hence, the audience this study is dedicated to are scientists that might use the results as basis for further research. Also PDO producers might consider the study as a useful input to minimize the environmental impact of certain process steps.

6.1.2 SCOPE DEFINITION

6.1.2.1 FUNCTIONAL UNIT

To make the results comparable it is essential that the analysed systems serve the same function which eventually has to be broken to a functional unit (FU). The functional unit represents the quantification of the function and is used as a reference to which all inputs and outputs are related to (ISO 14040 2006).

The common function of the different production processes is to provide PDO as a final product. As seen is chapter 5, Anex & Ogletree (2006) and Urban & Bakshi (2009) quantify the function as 1 kg of PDO produced. Even if there is no information given about the functional unit of the study conducted by DuPont, it can be assumed that they chose the same unit since this is common practice for similar assessments (e.g Cok et al. 2014). To make the results of this LCA comparable to the other studies the same functional unit will be defined: 1kg of 1,3-propanediol produced.

6.1.2.2 PRODUCTION SYSTEM

The system analysed can be roughly divided into two overarching processes: The glycerol production, or respectively the biodiesel production, consisting of rape seed cultivation, oil milling (with rape oil and rape meal being the products) and the esterification of the rape oil to glycerol and rape methyl ester (biodiesel) (Jungbluth et al. 2007). This is followed by the PDO production, consisting of glycerol fermentation and of the PDO recovery and purification. Figure 16 displays the production system, focusing on glycerol and PDO but also showing the other system outputs rape meal and biodiesel. To account for those by-products an allocation approach is necessary which will be described in chapter 6.1.2.4.

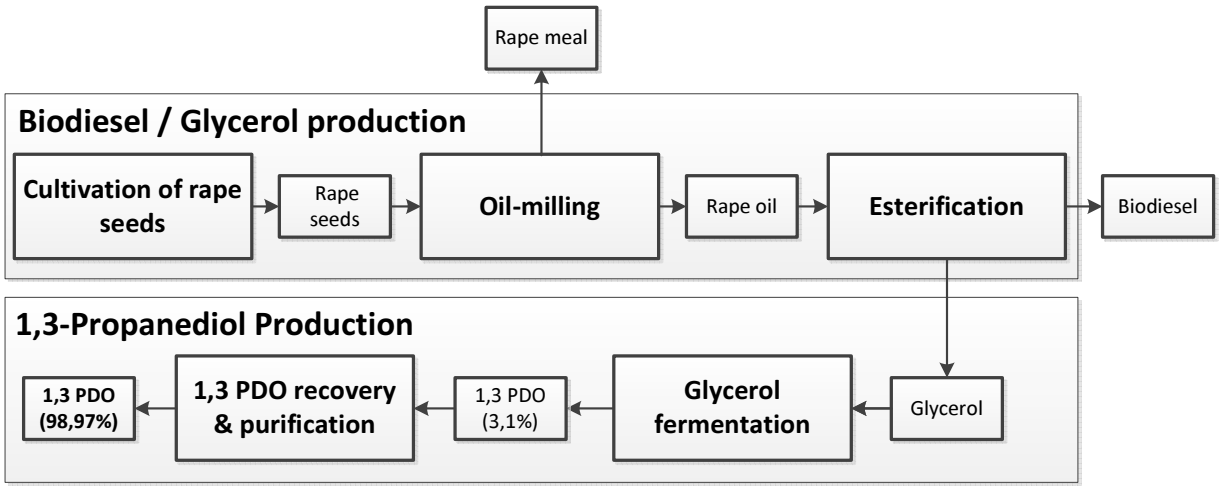

FIGURE 16: SYSTEM DEFINITION OF THE PDO PRODUCTION

6.1.2.3 SYSTEM BOUNDARIES

Like in the other studies on PDO production (DuPont Tate & Lyle 2009; Anex & Ogletree 2006; Urban & Bakshi 2009) a cradle to gate analysis will be conducted, ranging from the crop cultivation until the product PDO at the end of the production process. The function and the possible end-uses of the PDO produced is the same for all production pathways from fossil or biobased sources (Anex & Ogletree 2006; Urban & Bakshi 2009). Hence, the usage and disposal of the product will not be part of the analysis, also due to the large variety in possible further processing steps and uses of PDO (see chapter 1.1).

However, even if not included in the scope of this LCA, for the following benchmarking against fossil pathways (chapter 7.1) additionally a simplified PDO incineration scenario was assumed as disposal. This artificial enhancement of the cradle-to-gate analysis allows a fairer comparison as it includes a big advantage of the biobased PDO production compared to a fossil production route, namely the effect of the CO_2-sequestration during the cultivation phase which balances the CO_2-emissions occurring when PDO is incinerated. For details and for the results please refer to chapter 7.1. The stoichiometric calculation of this scenario can be seen in Appendix 4.

For the glycerol production from rape oil the ecoinvent database has a predefined model which will be used for this analysis using an updated allocation factor (see chapter 6.1.2.4): *glycerine, from rape oil, at esterification plant/kg/RER.* The model includes the production of all necessary inputs like fertilizer, pesticides and energy, but excludes the production of the facilities and machinery used. Of those just the energy demand during their use is considered. Furthermore the transportation of the rape seeds to the oil mill and of the rape oil to the esterification plant is included. But also the transport of the inputs during cultivation (e.g. pesticides, machines, fertilizer) is considered, using standard distances. (Jungbluth et al. 2007)

This goes along with the study by Anex & Ogletree (2006) and probably also to a large extent with the DuPont-study. Urban & Bakshi (2009) on the other hand excluded the transportation from the farm to the production plants, but might have included the transport of pesticides and fertilizers via the ecoinvent process for corn farming.

Figure 17 shows the main processes of the glycerol production process in ecoinvent as described by Jungbluth et al. (2007). For the detailed inputs and outputs used in ecoinvent please refer to Jungbluth et al. (2007). The other system outputs (biodiesel, rape meal) are accounted for in the allocation procedure (see chapter 6.1.2.4).

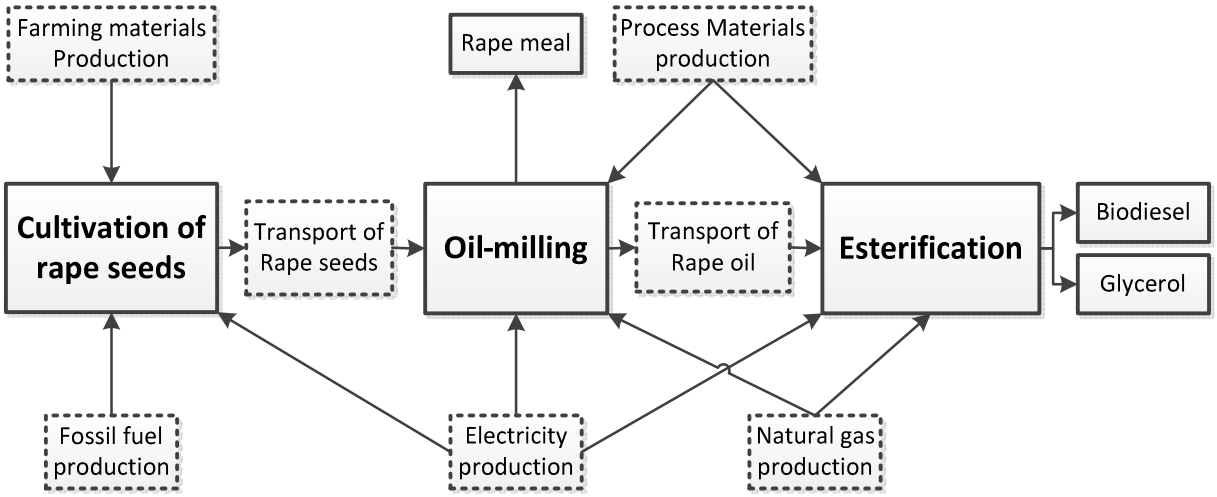

FIGURE 17: MAIN PROCESSES OF THE GLYCEROL PRODUCTION IN THE ECOINVENT DATABASE AS DESCRIBED BY JUNGBLUTH ET AL. (2007)

The PDO production was not readily available in ecoinvent and was therefore set up using the process design reported by Posada (2011). The environmental assessment of this process design includes the production of all necessary inputs like water and energy as well as all emissions coming out of the production process. An exception is the exclusion of the bacteria-input (Klebsiella pneumonia) needed for the fermentation. This exclusion follows Urban & Bakshi (2009) who also omitted the bacteria-production due to its self-sustaining nature (once an initial amount is provided it can be regenerated). Figure 18 shows the PDO production system analysed in the LCA.

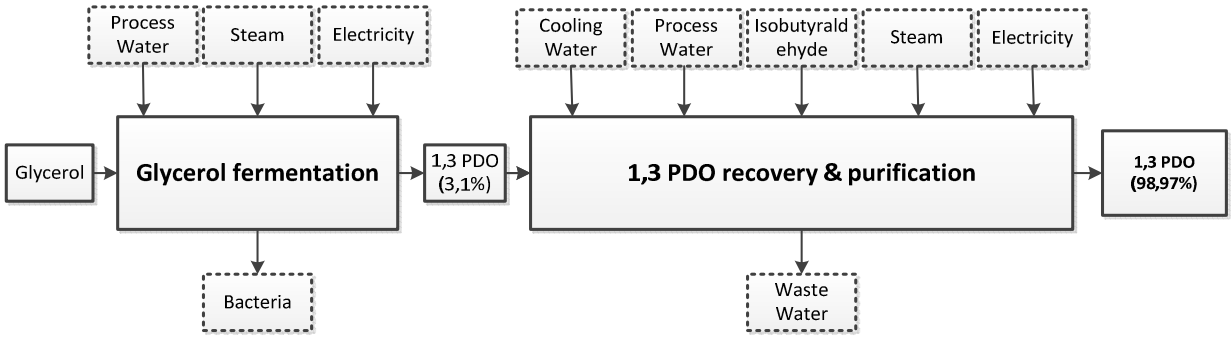

FIGURE 18: THE PDO PRODUCTION SYSTEM ANALYSED

This study will consider the amount of cooling water needed, even if no information about that matter could explicitly be found in the benchmarking studies. The assessment excludes the transportation of the glycerol from the esterification plant to the PDO production plant. It is assumed that they are located in the same area so that the transport is negligible. Furthermore the benchmarking studies (Urban & Bakshi 2009; Anex & Ogletree 2006) did neither include the transport to the last production

stage. Its exclusion therefore also fosters comparability of the results. Furthermore the manufacture of the production facilities is not included in the analysis. Also this goes along with the benchmarking studies and hence allows a better comparison.

6.1.2.4 ALLOCATION PROCEDURE

According to ISO 14040 (2006) allocation is the process of *"partitioning the input or output flows of a process or a product system between the product system under study and one or more other product systems"*. Put in other words: If processes produce several products it is necessary to allocate all inputs and outputs and consequently all impacts among them. In our case the process of oil milling produces besides rape oil also rape meal. Furthermore an allocation is necessary in the esterification process where biodiesel and glycerol are the resulting products (Jungbluth et al. 2007).

There are basically two main ways of dealing with multi-output-processes. One of them is called system expansion and assumes that the by-products would replace the production of those products by other processes and hence avoid a certain environmental load (Goedkoop & Oele 2004; Goedkoop et al. 2013).

The second way is allocation, which raises the question how the environmental load of the inputs and outputs is distributed among the products. Generally it is recommended to avoid allocation by splitting the process in two separate processes with a single output each. Where this is not possible, the next best options would be determining a physical causality for allocation, like a mass or energy based allocation. Another possibility would be economic allocation (market-based allocation), which is regarded as the last option by the ISO standards. However, the benefits of economic allocation are that it allows distinguishing a waste from a product and that it expresses the relative economic importance of a product. A downside of this method is the fluctuation in prices which can have a quite significant effect on the results of the assessment. (Goedkoop et al. 2013; Goedkoop & Oele 2004)

Anex & Ogletree (2006) chose to do a mass-based allocation, Urban & Bakshi (2009) did both, a mass- and market-based allocation but included just mass-based allocation in the results due to the similarity of the factors. DuPont does not provide information on their allocation method. This study will make use of economic allocation but will include mass and energy based allocation in a sensitivity analysis.

The ecoinvent-model used for glycerol production ("*glycerine, from rape oil, at esterification plant/kg/RER")* uses economic allocation for oil-milling with its products rape oil and rape meal, with 74,3% attributed to rape oil. Also for the esterification market based allocation was adopted, resulting in 86,9% for rape methyl ester, 12,9% for glycerol and 0,2% for potassium sulphate. (Jungbluth et al. 2007)

Unfortunately this allocation does not anymore represent recent market prices, which would suggest an allocation of 97% to biodiesel and 2,94% to glycerol[9]. The allocation of the esterification will therefore be updated for this study. The allocation used by ecoinvent for oil-milling will however stay the same.

6.1.2.5 IMPACT ASSESSMENT METHODOLOGY

An elementary question is how the environmental impacts are aggregated and which impact categories are used.

DuPont did not reveal their chosen method and also Anex & Ogletree (2006) are not very specific. Urban & Bakshi (2009) are using the CML Baseline method. What all have in common is the assessment of the midpoint indicators Non Renewable Energy Use (NREU) and Greenhouse Gas Emissions (GHG). Therefore an impact assessment method including those two categories has to be found which is also available in SimaPro.

The method Impact 2002+ (v. 2.10) includes both indicators and seems to be a good choice, which also has been used in other Life-Cycle assessments of chemical productions (e.g. Mendes et al. 2012; Dhaliwal et al. 2011).

This method combines a midpoint indicator approach with an endpoint damage approach (see Figure 19), linking all life cycle inventory results via 14 midpoint indicators to four different damage endpoint categories (Goedkoop et al. 2008).

[9] This new allocation was calculated by using the mass ratio of 1 kg of glycerol per 10 kg of biodiesel and by adapting economic data found in literature (Quispe et al. 2013), from suppliers and from energy agencies (US department of energy).

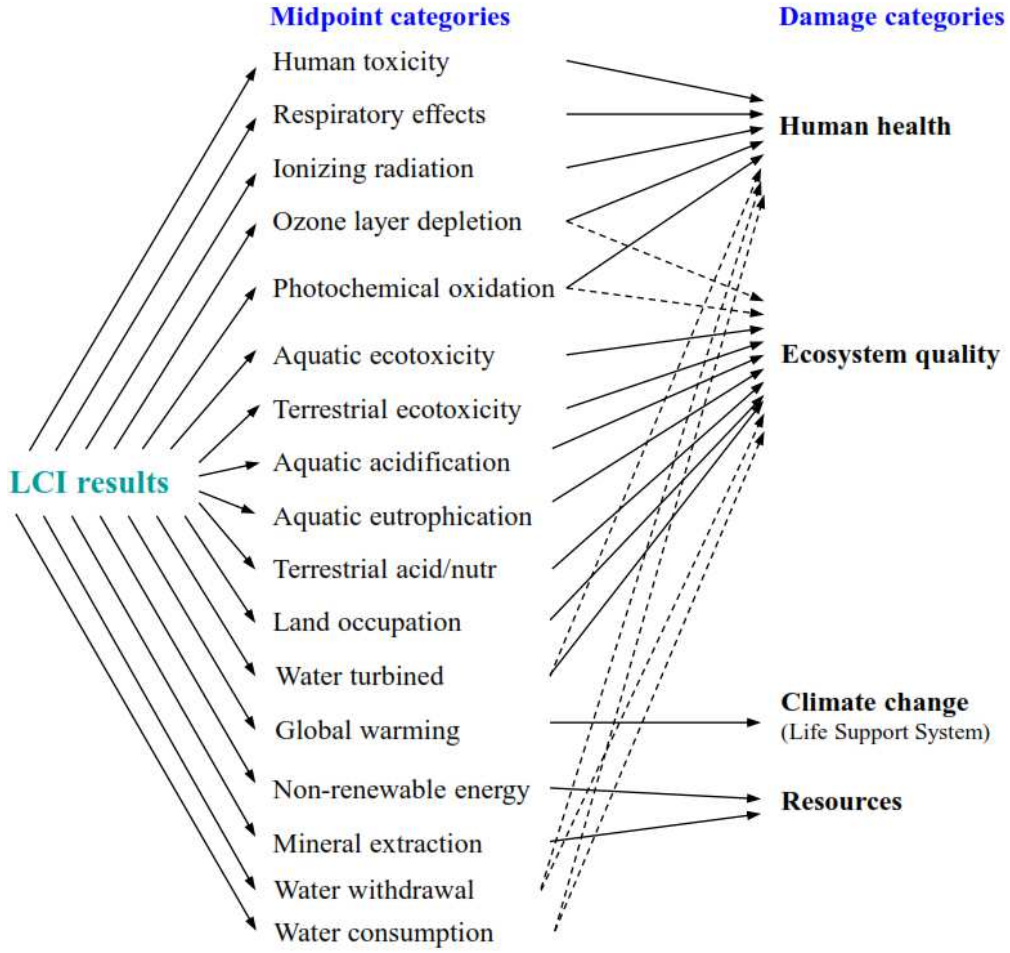

FIGURE 19: IMPACT 2002+ FRAMEWORK (Humbert et al. 2012)

The midpoint indicators include the two categories NREU and GHG-emissions which are the most essential ones for this first screening of the PDO production and for the comparison to existing studies. Most of the other Impact Assessment methods do not have an explicit NREU category.

The Impact 2002+ methodology builds up on the characterization procedure of other methodologies like Eco-indicator 99, CML 2001, IPCC and the Cumulative Energy Demand. Each midpoint indicator is normalized against the respective emissions of one European citizen per year to obtain the four final damage categories. (Goedkoop et al. 2008)

However, this normalization will not be done for this study as midpoint indicators are chosen to display the impacts. Midpoint indicators are situated relatively early in the cause-effect chain, meaning they are closer to the environmental interventions (Finnveden 2000). Endpoint indicators on the other hand are already a further aggregation of midpoint indicators, involving weighting and additional characterization factors (Bare et al. 2000). The major differences between the two categories lie in their relevance and certainty. While endpoint indicators are usually better

understandable for decision makers and thus have a higher relevance they have a lower certainty than midpoint indicators (Bare et al. 2000; Finnveden 2000). Since this study does not address decision makers, the benefit of a higher relevance is of minor importance. Hence, this study will make use of the midpoint indicators to provide a higher certainty of the results.

Being a preliminary screening of the environmental impacts of the PDO production from glycerol, this study focuses on the midpoint-indicators non-renewable energy use (expressed in MJ) and Greenhouse gas emissions (in CO_2 equivalents).

6.1.2.6 DATA REQUIREMENTS

The aim of the study is to analyse the production process in a European context, more specifically in the Netherlands. Therefore the assessment will be based on European data or, where available, Dutch data. If neither of those is available Swiss or global data is used.

If no specifically fitting data is found, similar processes might be used that represent a solid estimate of the process that is to be assessed.

As previously described for the Glycerol production a readily available model from the ecoinvent database (Jungbluth et al. 2007) is taken. For the PDO production the data mainly comes from a process design by Posada (2011) and was complemented by mass balance calculations and additional literature sources where necessary. For the production of the inputs and the treatment of the outputs processes from the ecoinvent database are used.

The following chapter 6.2 (Life Cycle inventory) will reveal for each process step the data used as well as the assumptions and calculations made.

6.2 LIFE CYCLE INVENTORY

6.2.1 DATA COLLECTION

After having defined the scope of the study, the necessary data was determined and searched via a literature review. For many processes readily available datasets from the ecoinvent database were found. For other processes (fermentation, PDO recovery and purification) simulations by Posada (2011) were used. Some inputs and outputs were incorporated by calculating approximation values with the help of available literature.

6.2.2 DATA CALCULATIONS AND ASSUMPTIONS MADE

6.2.2.1 GLYCEROL PRODUCTION

Adapting the results of the fermentation experiments and simulations done by (Posada 2011) to the functional unit (1 kg of PDO) it was calculated that 2,33 kg of Glycerol are needed as input to the fermentation process.

To assess the glycerol production from rape oil (chosen in chapter 4.3) the model *"Glycerine, from rape oil, at esterification plant/kg/RER"* from the ecoinvent database was chosen. This dataset refers to the multioutput-process *"rape oil, in esterification plant"* which produces besides glycerol mainly rape methyl ester but also potassium sulphate. The model uses the economic value to allocate the environmental impacts between the different products. (Jungbluth et al. 2007)

Like mentioned in chapter 6.1.2.4 the economic allocation factors given by the ecoinvent-model were updated using more recent data which suggests an allocation of 2,94% to Glycerol. This new allocation was calculated by using the mass ratio of 1kg of glycerol per 10 kg of biodiesel and by adapting economic data found in literature (Quispe et al. 2013), from suppliers and from energy agencies (US department of energy).

The data used in the model for glycerol production is from different time periods, ranging from 1996 till 2006, depending on the various included processes. The process includes almost only European datasets, just in some cases Swiss or global data is used. (Jungbluth et al. 2007)
The model uses the UCTE-electricity mix which was changed for this study to the Dutch mix for the esterification and oil-milling process.

It is assumed that the ecoinvent process of glycerol production already includes the purification of glycerol. However, the specific purity grade is not given by Jungbluth et al. (2007). Hence, a mismatch

might be possible between the ecoinvent process and the input to the fermentation which is assumed to be glycerol with a purity of 98%.

6.2.2.2 PROVISION OF STEAM

Steam is an important energy input for both, the fermentation and the PDO recovery and purification. Information of Posada (2011) was complemented with mass balance calculations using assumptions from literature to calculate the amount of steam necessary.

The ecoinvent database incorporates a model for steam for chemical processes under European conditions, namely *"Steam, for chemical processes, at plant/kg/RER"*. This model represents a mix of heat generation from heavy oil (24 %) and natural gas (76 %) and also includes the water needed for the production of steam. The data input comes from an average taken from 11 European chemical sites. (Zah & Hischier 2007)

To make use of that model the mass of steam needed has to be calculated. This can be done via the formula:

$$m_{steam} = Q / (h_{e\ (superheated\ steam)} - h_{e\ (saturated\ liquid)})$$

With *"m_{steam}"* being the mass of steam needed, *"Q"* being the heat duty of the process (e.g. distillation) and *"h_e"* the enthalpy for superheated steam and for saturated liquid.

The results of the fermentation experiments and the Aspen Simulations (Posada 2011) of the PDO Recovery and Purification deliver the heat duty and the temperatures of the specific process steps. The steam characteristics were taken from Patel et al. (2006) which assessed the production of bulk chemicals from renewable resources. They mentioned typical values for steam used in the chemical production (see Table 2). Medium-Pressure steam (10 bar) is assumed for all processes, as low-pressure steam will not be able to fulfil the need of distillation column 5 (DC-5, see Figure 47 in Appendix 1) and because medium-pressure steam is used for *"the majority of applications*" in the chemical industry (Patel et al. 2006). Using the information for medium-pressure steam it is possible to look up the specific enthalpies of superheated steam and saturated water.

TABLE 2: TYPICAL CHARACTERISTICS FOR STEAM USED IN CHEMICAL PRODUCTION (Patel et al. 2006)

Type of steam	Pressure in bar	T in °C
Low- Pressure	4	175
Medium-Pressure	10	280
High-Pressure	40	400

With all relevant information at hand the required steam can be calculated using the formula mentioned above. The results are expressed in Table 3, with the first row naming the specific process units which can also be seen in the flow sheet in Figure 47 (see Appendix 1).

TABLE 3: CALCULATION OF THE AMOUNT OF STEAM NEEDED

Unit	Heat duty in MJ/h	T in °C	Steam pressure	Super-heated Steam T in °C	Saturated liquid enthalpy in kJ/kg	Super-heated steam enthalpy in kJ/kg	steam needed in kg/h	Adaption to FU in kg/h
Fermentation								
Fermentation	191,60		10	280	781,43	3005,67	86,14	0,35
PDO Recovery & Purification								
Distillation Column 2 (DC-2)	3404,33	97,64	10	280	781,43	3005,67	1530,56	6,16
Distillation Column 3 (DC-3)	257,34	99,85	10	280	781,43	3005,67	115,70	0,47
Distillation Column 4 (DC-4)	1572,42	138,29	10	280	781,43	3005,67	706,95	2,85
Reactive Distillation Column (RDC)	1693,80	151,58	10	280	781,43	3005,67	761,52	3,07
Distillation Column 5 (DC-5)	86,14	213,82	10	280	781,43	3005,67	38,73	0,16
Total								
							3239,60	13,04

6.2.2.3 ELECTRICITY INPUT

Processes involving mixing, agitation or centrifugation need electricity. The simulations by Posada (2011) do not provide the electricity needed for the process units. Therefore approximation values had to be found via a literature review. Again the study by Patel et al. (2006) can be of help as its literature review offers a variety of electricity values for centrifugation and agitation processes. Seider et al. (1998) was part of their review and provides a heuristic electricity value for the agitation of slurry with an impeller in a baffled tank (2kWh / m^3). No values are given for a mixer. Therefore the value for the fermentation agitation of Seider et al. (1998) was taken as orientation. However, half of that agitation value was assumed for the mixer, as mixing does not require an as high circulation. For the centrifugation Bohlmann (2002) was chosen as a reference. He provides a range of electricity values (9,3 - 12.3 kWh/m^3) for centrifugation processes harvesting E.coli bacteria with a 37kW axial solid ejecting centrifuge. This can be used as estimation for harvesting the Klebsiella pneumonia bacteria at the end of the fermentation process. His average value (10,8 kWh / m^3) will be used for the inventory. Table 4 summarizes those values.

TABLE 4: THE ELECTRICITY VALUES CHOSEN FOR THE LCA

Process	Electricity need in kWh/m³
Centrifugation	10,8
Fermentation Agitation	2
Agitation Mixer	1

To calculate the total electricity use the volumetric flow of the processes had to be determined. For the PDO Recovery and Purification the volumetric flow was given by the Aspen simulations. For the Fermentation process (see Figure 20) just the mass flows and most of the temperatures were given.

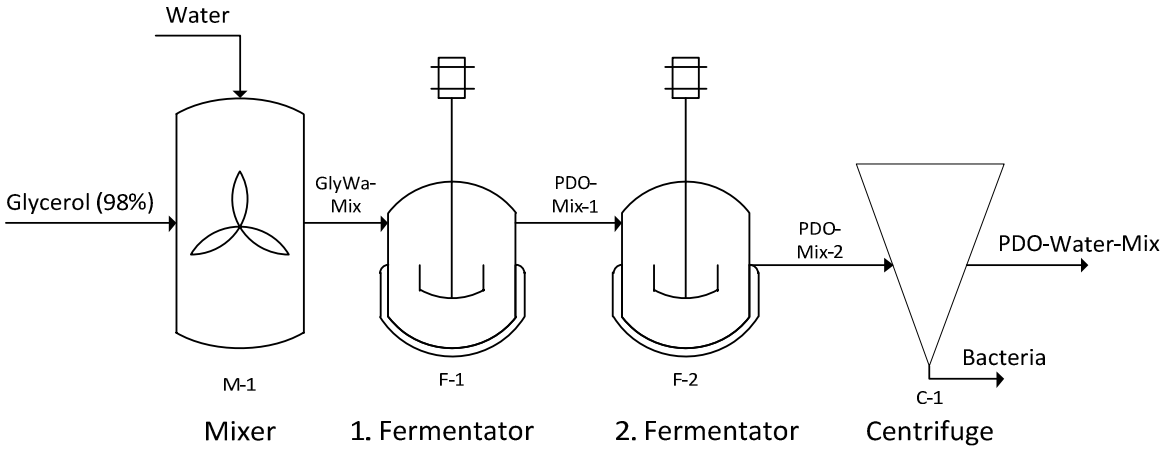

FIGURE 20: FLOWSHEET OF THE FERMENTATION PROCESS

For calculating the volumetric flow the density is needed. The input to the Mixer (Glycerol + Water) consists of 93,2% water and 6,8% Glycerol. The temperature of the mix is assumed to be 20 °C. The density of the Glycerol-Water-Mix at 20°C is 1014,95 kg/m^3 (value taken from table of DOW (n.d.) at 20°C and with a proportion of 7% Glycerol). The temperature within the fermentators of 37 °C is given by Posada (2011). The density of the mix in the fermentators is 998,06 kg/m^3, with some minor differences between the two tanks.

Also the temperature during the centrifugation is assumed to be 37°C. Since the mix entering the centrifugation consists of 95,35% water the water density at 37 °C is taken as an approximation. Having obtained the volumetric flows the electricity use of the processes can be calculated (according to Table 4). The results of those calculations are displayed in Table 5. As for table 3 the process units of the PDO purification & recovery can be seen in the flow sheet in Figure 47 (see Appendix 1) and for the fermentation in Figure 20.

TABLE 5: ELECTRICITY USE OF THE SPECIFIC PROCESSES

Unit	Volumetric flow in m^3/h	Electricity use in kWh	Adaption to FU in kWh
Fermentation			
Centrifugation	8,395	90,665	0,365
Mixer	8,405	8,405	0,034
Agitation 1. Fermentation tank	8,376	16,752	0,067
Agitation 2. Fermentation tank	8,355	16,710	0,067
	TOTAL	132,532	0,534
PDO Recovery & Purification			
Mixer 1 (M-1)	9,752	9,752	0,039
Reactor 1 (Re-1)	9,752	19,504	0,079
Mixer 2 (M-2)	1,002	1,002	0,004
Mixer 3 (M-3)	1,670	1,670	0,007
	TOTAL	31,927	0,129

6.2.2.4 COOLING WATER

Provision of cooling water

For the distillation processes within the PDO Recovery and Purification cooling water is needed. It is assumed that the cooling water is taken from surface waters (Ecoinvent: *"Water, cooling, surface"*). The amount of cooling water needed (m_c) for the distillation columns can be calculated by using the known heat duty (Q) of the condenser:

m_c = Q (Condenser) / (ΔT_c * c_p)

The heat duty is given by the Aspen simulations. The missing variables Temperature change (ΔT_c) and heat capacity (c_p) depend on the specific cooling system used as well as the climate conditions. Having no exact information about those conditions, assumptions have to be made concerning the temperature of the cooling water inflow and the temperature change.

The chemical engineering portal myChemE (2013) describes the cooling systems of chemical plants. According to their article typically a temperature rise of 5-8 °C will be allowed by designers of cooling systems. The temperature varies during the seasons and between regions.

An 8 degree rise in temperature was assumed for our case. Furthermore a Temperature of 20°C was assumed for the water inflow. Water at 20 °C has a heat capacity of 4,183 kJ/kgK and a density of 998,3 kg/m^3 (The Engineering Toolbox n.d.). Those assumptions are listed in the table 6.

TABLE 6: ASSUMPTIONS FOR COOLING WATER STREAM

Assumptions for cooling water stream		
T cooling water inflow	20	°C
Heat capacity c_p	4,183	kJ/(kg*K)
T change	8	°C
water density at 20°C	998,3	kg/m³

With those assumptions and the formula mentioned above the amount of cooling water needed can be calculated (see

Table 7).

TABLE 7: AMOUNT OF COOLING WATER NEEDED

Process Unit	Heat duty Condenser in kJ/h	Cooling water needed in m³/h	Adaption to FU in m³/h
PDO Recovery & Purification			
Distillation Column 2 (DC-2)	-446262,46	13,36	0,05
Distillation Column 3 (DC-3)	-181133,93	5,42	0,02
Distillation Column 4 (DC-4)	-1404395,58	42,04	0,17
Reactive Distillation Column (RDC)	-1556570,11	46,59	0,19
Distillation Column 5 (DC-5)	-44310,73	1,33	0,01
TOTAL		108,74	0,44

This is however just a very rough estimate. To have a more accurate appraisal it would be necessary to simulate a specific cooling system under the respective (climate) conditions. An example for the influence of single factors on the cooling water need is the temperature change between the incoming cooling water and its outflow. A variation of that factor leads to significant changes. For example a system with a 10 °C temperature rise would reduce the water needed by 20 % compared to the 8°C temperature rise assumed in this LCA. If aiming at a low water footprint, several scenarios and measures should be considered that would make the cooling system more efficient (e.g. recirculating systems instead of once through cooling).

Emission of cooling water

No fitting model could be found in the ecoinvent database that simulates the post-treatment of used cooling water. This is probably due to the still on-going debate about how water use should be assessed in LCAs (see Berger & Finkbeiner 2010; Koehler et al. 2010).

Hence, for this assessment it was assumed that the cooling water is emitted back to the surface waters after its use (once-through cooling). The ecoinvent dataset *"Waste Water /m³ to river"* was used for this purpose. This simplification ignores possible negative impacts that could be caused by use of water conditioners or a disturbance of the ecological system by the high temperatures of the cooling

water (Koehler et al. 2010; Bayrisches Landesamt für Umwelt 2012). However, water discharges are regulated by each state (see e.g. Bundesjustitzministerium 2013) to prevent significant harm to the environment. Therefore those impacts are considered as minor if the legal obligations are followed.

The use of alternative cooling systems like a recirculating system with a cooling tower would reduce the amount of water withdrawal and probably reduce negative impacts of the heated cooling water but would on the other hand increase and even double water consumption compared to once-through cooling systems due to the evaporation losses (Macknick et al. 2012). As was indicated, the choice of a cooling system and the assessment of its environmental impacts is a complex topic. Since the cooling water use has little impact on the impact categories NREU and GHG-emissions no further attention was paid to possible variations in cooling water technologies. When focusing on a broader range of impact categories more efforts have to be taken to investigate this issue.

6.2.2.5 PROVISION OF PROCESS WATER

The amount of process water needed is given by the experiments and Aspen simulations done by (Posada 2011). For the distillation deionized water is used (Ecoinvent: *"water, deionised, at plant/CH U"*).

For the fermentation *"Tap Water, at user /RER U"* was considered as sufficient and chosen as input.

6.2.2.6 ISOBUTYRALDEHYDE

In the first step of the PDO recovery Isobutyraldehyde (C_4H_8O) are added to the Mixer. A part of them is assumed to be recovered after the process and reused. A minor part is lost and emitted along with the waste water. The difference between those two streams is the amount of Isobutyraldehyde that has to be freshly added per hour. This amount will be considered as the input to the PDO recovery and purification (see Table 8).

TABLE 8: ISOBUTYRALDEHYDE-STREAMS

Isobutyraldehyde	Mass flow in kg/h
Input to the mixer	1227,35
Recovered part	1221,74
Difference (emitted part)	5,6
Adaption of the emitted part to the FU	0,0226

The stream with the recovered Isobutyraldehyde is however not solely consisting of pure Isobutyraldehyde (see

Table 9)

TABLE 9: CONTENT OF THE RECOVERED ISOBUTYRALDEHYDE-MIX

Content	in kg/h
Water	67,35
Isobutyraldehyde	1221,74
2IP13DOX	5,6
Acetic acid	0,34
Ethanol	2,13
TOTAL	1297,16

Just the pure Isobutyraldehyde (1221,74 kg/h) are included the calculation above (Table 8). The other elements (5,8%) are ignored and not considered in the LCA. As those impurities just account for 0,78 % of the total mass outputs of the PDO recovery and purification their impact can be considered as irrelevant.

Having determined the amount of the Isobutyraldehyde needed as input to the PDO recovery and purification the next problem to solve is how to include them into the LCA.

Isobutyraldehyde are manufactured as a side-product of the propylene hydroformylation (DOW 2013), or alternatively it can be produced using engineered bacteria (Atsumi et al. 2009).

The ecoinvent database does not provide a readily available model for the production of Isobutyraldehyde. But the database includes the production of 1-butanol and Isobutanol which are both resulting from the hydroformylation of propylene and a following hydrogenation. 92,6 % of the impacts resulting from that production process are allocated to 1-butanol and 7,4 % to Isobutanol. (Sutter 2007)

The main production step, the propylene hydroformylation, leads to n-butyraldehyde and isobutyraldehyde. In the following hydrogenation step n-butyraldehyde react to 1-butanol and the isobutyraldehyde to isobutanol. (DOW 2013; Sutter 2007)

Therefore the ecoinvent process *"Isobutanol, at plant/RER"* seems like a reasonable estimate of the isobutyraldehyde production and was thus chosen for this LCA. To account for the additional environmental load caused by the hydrogenisation step, 5% of the environmental load will be deducted from the Isobutanol process.

6.2.2.7 WASTE WATER

During the PDO-recovery and purification three process steps emit waste water. Putting all three waste water streams together they consist of 98,3% waste water and 1,7 % impurities containing Glycerol, Acetic Acid, Ethanol, Propanediol and Isobutyraldehyde.

It is assumed that this waste water stream is brought to and treated in a municipal waste water treatment plant, as ecoinvent does not offer a model that specifies the treatment of waste water from chemical production. In absence of a Dutch or European model in the ecoinvent database the Suisse model *"Treatment, sewage, from residence, to wastewater treatment, class 2/CH U"* was chosen to simulate the waste water treatment.

The mass and volume of the waste water streams are taken from the Aspen simulations (Posada 2011).

6.2.2.8 EMITTED BACTERIA

The centrifugation process following the fermentation (see Figure 20) separates the PDO-Water mix (input for the PDO Recovery and Purification) from the bacterial residues of the Klebsiella pneumoniae strain used during the fermentation process. Those bacterial residues are considered as emissions of the production process.

This LCA classifies those residues as raw sewage sludge which is assumed to be brought to municipal treatment plant where it is incinerated. In absence of a specific disposal-model for Klebsiella pneumonia the ecoinvent model *"Disposal, raw sewage sludge, to municipal incineration/CH"* was chosen to simulate this scenario.

6.2.3 SUMMARY OF THE LIFE CYCLE INVENTORY

Table 10 and Table 11 summarize the inventories for the Fermentation and PDO Recovery and Purification.

TABLE 10: LIFE CYLCE INVENTORY OF THE FERMENTATION

Stream category & name	Amount	Adaption to FU	Unit	Ecoinvent dataset
Material Input				
Glycerol	578,894	2,33065065	kg/h	Glycerine, from rape oil, at esterification plant/kg/RER
Process Water	7951,537	32,0132094	kg/h	Tap Water, at user /RER U
Energy Input				
Steam	86,1397427	0,34680209	kg/h	Steam, for chemical processes, at plant/kg/RER U
Electricity	132,531568	0,53357745	kWh	Electricity, low voltage, at grid/NL U
Emissions				
Bacteria (KPNEUMON)	24,564	0,09889566	kg/h	Disposal, raw sewage sludge, to municipal incineration/CH
Product				
PDO-Water Mix (3,1% PDO)	8337,395	33,5666893	kg/h	

TABLE 11: LIFE CYCLE INVENTORY OF THE PDO RECOVERY AND PURIFICATION

Stream category & name	Amount	Adaption to FU	Unit	Ecoinvent dataset
Material Input				
PDO-Water Mix (3,1% Propanediol)	8337,395	33,5666893	kg/h	(from fermentation process)
Isobutyraldehyde	5,607	0,02257401	kg/h	Isobutanol, at plant/RER U(5% reduction)
Process Water	84,06	0,33842896	kg/h	water, deionised, at plant/CH U
Cooling water	108554,65	437,04541	kg/h	Water, cooling, surface
Energy Input				
Steam	3239,60171	13,0427675	kg/h	Steam, for chemical processes, at plant/kg/RER U
Electricity	31,92726	0,12854044	kWh	Electricity, low voltage, at grid/NL U
Emissions				
Waste Water (Process)	8,103263	0,03262406	m^3/h	Treatment, sewage, from residence, to wastewater treatment, class 2/CH U
Used cooling water	108554,65	437,04541	kg/h	Waste Water /m^3 to river
Product				
1,3-PDO (98,87%)	248,383	1	kg/h	

6.3 LCIA: CONTRIBUTIONAL ANALYSIS

After the Life Cycle Inventory was finalized a Life Cycle Impact Assessment (LCIA) was conducted using the method IMPACT 2002+ (v.2.10) which is explained in chapter 6.1.2.5. According to the scope of the study just the indicators for NREU and GHG-emissions are displayed in this chapter while the further 13 impact categories that are assessed by this method are not considered.

This contributional analysis displays the results of the LCIA and aims at identifying the major contributors to the global LCIA results of the PDO production which are listed in Table 12.

TABLE 12: THE NREU AND GHG-EMISSIONS OF THE PDO PRODUCTION

	Unit	Total	Glycerine production	Glycerol Fermentation	PDO Recovery & Purification
NREU	MJ/kg PDO	**81,89**	18,80	7,50	55,59
GHG	kg CO_2 equ./kg PDO	**4,90**	1,41	0,45	3,04

The total impacts are calculated from the three main processes, namely Glycerol production, Glycerol Fermentation and PDO Recovery and Purification. Figure 21 shows the allocation of impacts between those processes.

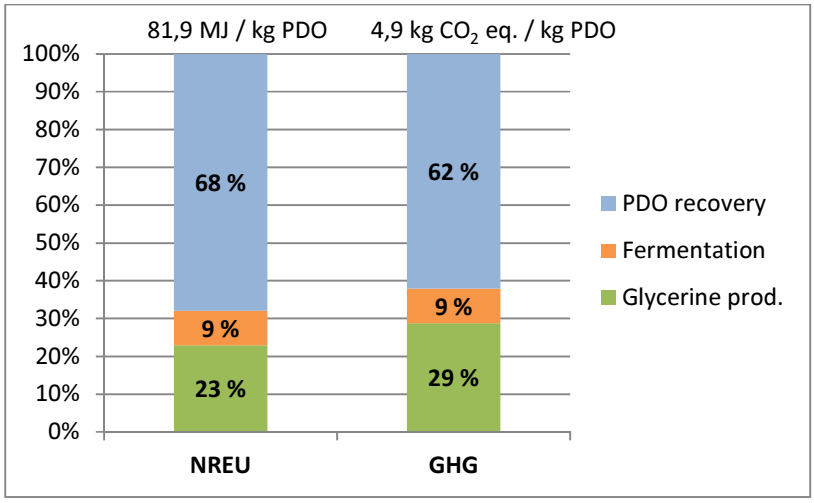

FIGURE 21: CONTRIBUTIONAL ANALYSIS OF THE PDO PRODUCTION

It can be clearly seen that the PDO recovery & purification is clearly the biggest contributor with 62 % to the GHG-emissions and even 68 % to the NREU. This is mainly due to the five distillation processes which consume a large amount of steam from natural gas (28,24 MJ). They alone are responsible for 52,21 MJ NREU and 2,89 kg CO_2-equivalents which equals respectively around 94 % and 95 % of the total emissions of the PDO recovery and purification process (see Figure 22). The

electricity use and the isobutyraldehyde are of minor importance while the impact of the process water and the waste water treatment is with under 0,5 % negligible.

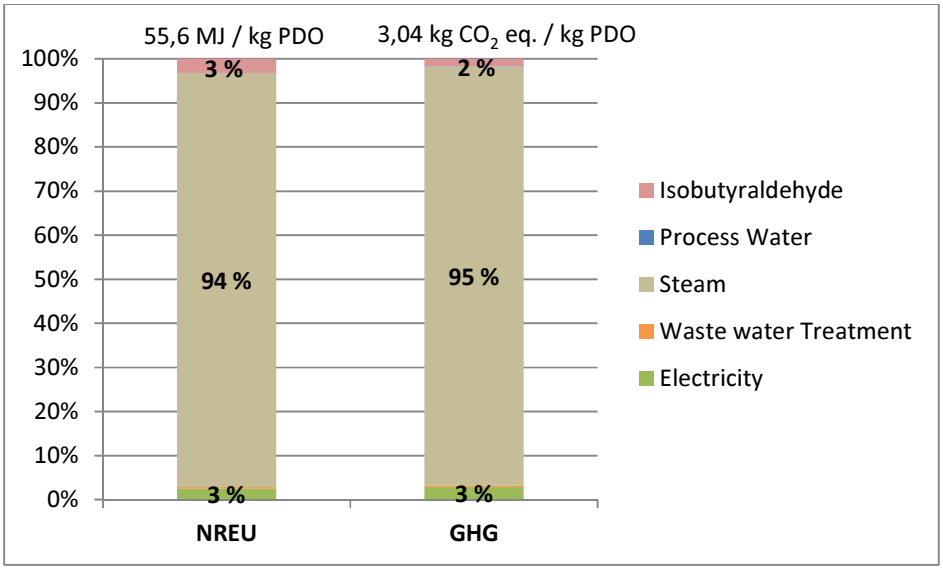

FIGURE 22: CONTRIBUTIONAL ANALYSIS OF THE PDO RECOVERY AND PURIFICATION

The second biggest factor for the global impact of the PDO production is the glycerol production which contributes 29 % to the GHG-emissions and 23 % to the NREU (see Figure 2121). Looking at the contributional analysis of the transesterification process (=glycerol / biodiesel production) in Figure 23 it becomes clear that the input of rape-oil is the by far biggest contributor, followed by methanol and heat.

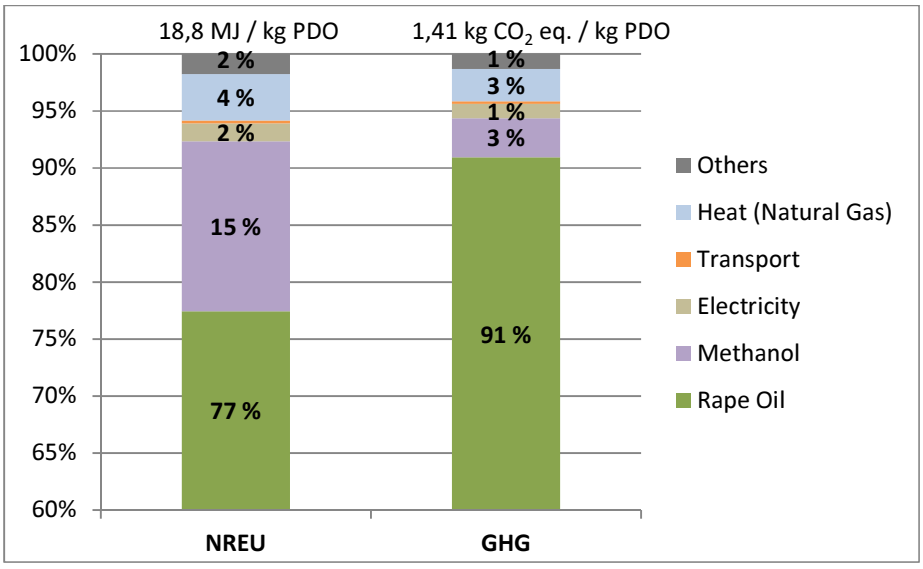

FIGURE 23: CONTRIBUTIONAL ANALYSIS OF THE GLYCEROL PRODUCTION (TRANSESTERIFICATION)

The reason for the substantial impact rape oil has is that its production involves besides the rape oil milling process (see Figure 48 in appendix 2) also the cultivation of rape seeds with the emission-intensive use of fertilizer and agricultural machinery as well as the also not insignificant impacts of grain drying and transport (see Figure 49 in appendix 3).

With circa 9 % to both impact categories the glycerol fermentations has the lowest contribution to the global emissions of the PDO production (see Figure 21). Its relatively low impact is due to the small energy need of the fermentation as the temperature has just to be kept at 37,1 °C, much lower than the temperatures needed for the distillation processes. Therefore the steam use is just responsible for 19 % of the NREU and 18 % of the GHG-emissions resulting from the fermentation (see Figure 24). The main contributor in this sub-process is the electricity use. This is due to the high electricity use of the centrifugation which is needed to separate the PDO-Water-Mix from the Bacterial residues. It amounts to ca. 1,3 MJ which represents over 55% of the total electricity use of the Glycerol fermentation and PDO recovery and purification together.

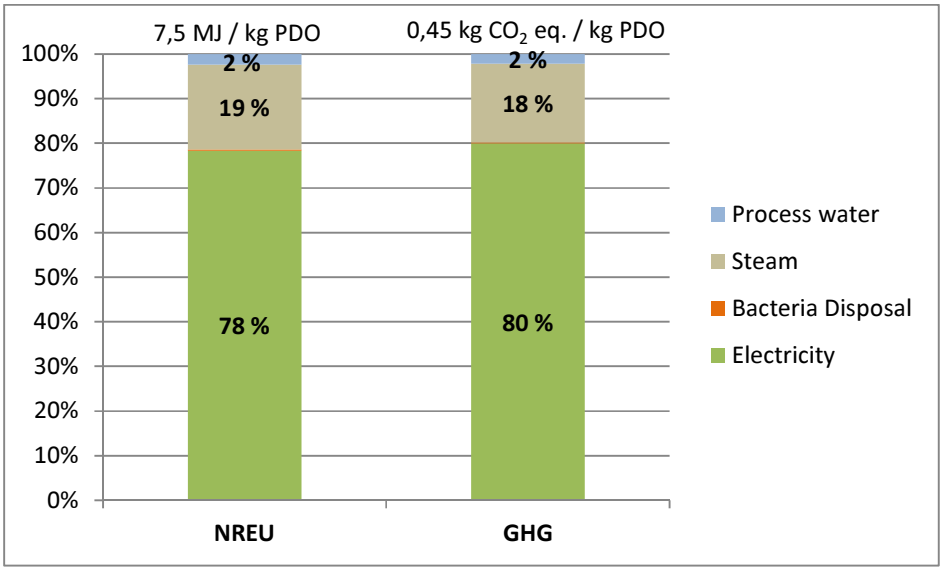

FIGURE 24: CONTRIBUTIONAL ANALYSIS OF THE FERMENTATION

6.4 LCIA: SENSITIVITY ANALYSIS

According to ISO 14044 (2006) the sensitivity analysis is a *"procedure to determine how changes in data and methodological choices affect the results of the LCIA."* The ISO standard recommends a sensitivity analysis especially in *"comparative assertions"* and more importantly if the results are intended to be disclosed to the public. A sensitivity analysis can show how some alterations can significantly change the results obtained and therefore be a helpful tool to highlight the limitations of the LCA and increase the understanding of the mechanisms involved.

Hence, this study also includes a sensitivity analysis, which will not only analyze different input scenarios (e.g. biogas instead of natural gas) but also look at methodological issues (e.g. allocation principles).

6.4.1 VARIATION IN ALLOCATION PRINCIPLES

GOAL & SCOPE

For the simulation of the Glycerol production, economic allocation was chosen to determine the impacts attributed to Glycerol and biodiesel. As described in chapter 6.1.2.4 there is also the possibility to use other allocation methods. To show how the choice of allocation method influences the outcome, the economic allocation within the esterification process will be changed in two scenarios to a) a mass-based allocation and b) an energy-based allocation. The allocation factors for those two scenarios were taken from Jungbluth et al. (2007) and are displayed in table 13 along with the economic allocation used in this LCA (see chapter 6.2.2.1). The allocation of the oil milling process has not been altered and has therefore still the default value given by ecoinvent (economic allocation).

TABLE 13: THE DIFFERENT ALLOCATION FACTORS FOR THE GLYCEROL PRODUCTION

	Economic value	Mass	Energy content
Percentage attributed to Glycerol	2,94%	9,7%	5%

RESULTS

For the production of 1 kg PDO 2,33 kg of Glycerol are needed (see LC Inventory, chapter 6.2). The following two graphs (Figure 25) show the GHG emissions and the NREU for producing 2,33 kg Glycerol according to the three different allocation methods.

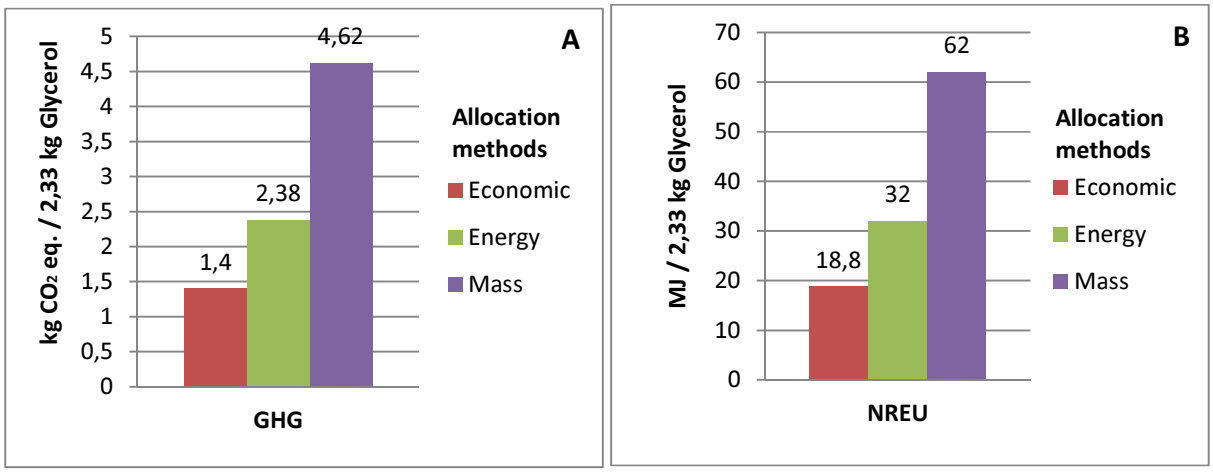

FIGURE 25: GHG EMISSIONS AND NREU OF THE PRODUCTION OF 2,33 KG GLYCEROL ACCORDING TO DIFFERENT ALLOCATION METHODS

Compared to the economic allocation adopted in the main analysis, the use of both alternative methods would imply a significant increase in both impact categories. While the use of energy-based allocation would increase the impacts attributed to glycerol by 70 %, mass-based allocation would increase the impacts by even 230 %.

On the total PDO production (Glycerol production, fermentation, PDO recovery purification) the percentage change is more moderate but the choice of allocation factor has still a strong effect (see Figure 26). Energy-based allocation would raise the impact by 16 % and mass-based allocation by 53 %. That means the results for the PDO production can vary within a range of 4,90 – 8,15 kg CO_2 equivalents (GHG) and 81,9 – 125,1 MJ (NREU), depending on the choice of allocation method.

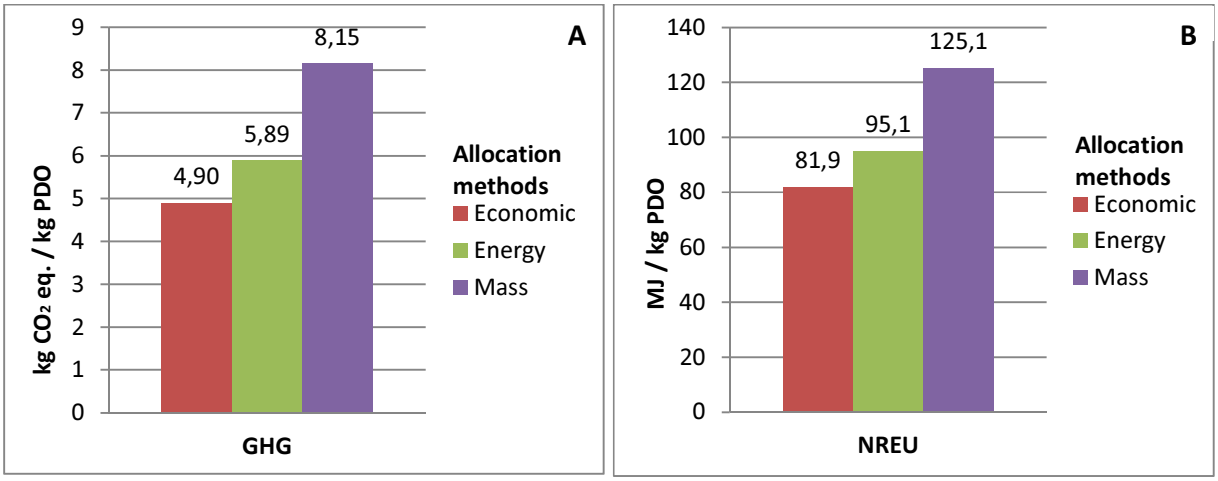

FIGURE 26: GHG EMISSIONS AND NREU OF THE TOTAL PDO PRODUCTION ACCORDING TO DIFFERENT ALLOCATION METHODS

This change also reflects in the role of the glycerol production in the contributional analysis of the total PDO production (see Figure 21), where the contribution to the total NREU would raise from 23 % to 33,6 % (energy-based allocation) till 49,6% (mass-based allocation) and the GHG-emissions from 28,8 % to 40,8 % and 57,2 % respectively.

6.4.2 APPLICATION OF DIFFERENT LCIA-METHODS

GOAL & SCOPE

There exists a great variety of LCIA-methods which have different characterization, aggregation and weighting methods. While many build up on the same methods (e.g. IPCC standards of GHG-calculation) the application of particular methods still can lead to different results.

To highlight the impact of applying different LCIA-methods, the PDO production was not just analyzed by IMPACT 2002+ but also by a couple of other, common methodologies.

RESULTS

For assessing the NREU the methods *Cumulative Energy Demand* and *Cumulative Exergy Demand"* were chosen. Those two methods assess both, renewable and non-renewable energy demand, and differentiate between the specific sources (e.g. nuclear, biomass, water) (Goedkoop et al. 2008). In the comparison (Figure 27) just their results for nonrenewable energy sources were summarized. While both assess the life cycle energy demand in MJ the difference between the two is that the *Cumulative Exergy Demand* also considers the concentration factor and hence the quality of the energy resources (Menoufi 2011). It assesses the potential removal of exergy from nature during the life cycle, which means that it assesses the loss of "useful" energy resources (Goedkoop et al. 2008)[10]. *Cumulative Exergy Demand* is therefore considered to be a more comprehensive energy indicator than *Cumulative Energy Demand* (Menoufi 2011).

[10] *"Exergy is another way to express quality of energy rather than energy content. Both are expressed in MJ. Exergy is a measure for the useful "work" a certain energy carrier can offer. For instance natural gas has a high exergy value, as it can be used to create high temperatures and high pressured steam. If natural gas is used to heat a house in a highly efficient boiler, very little energy content is lost, but the exergy content is almost entirely lost (there is very little one can do with water between 50 and 80 degrees)."* (Goedkoop et al. 2008)

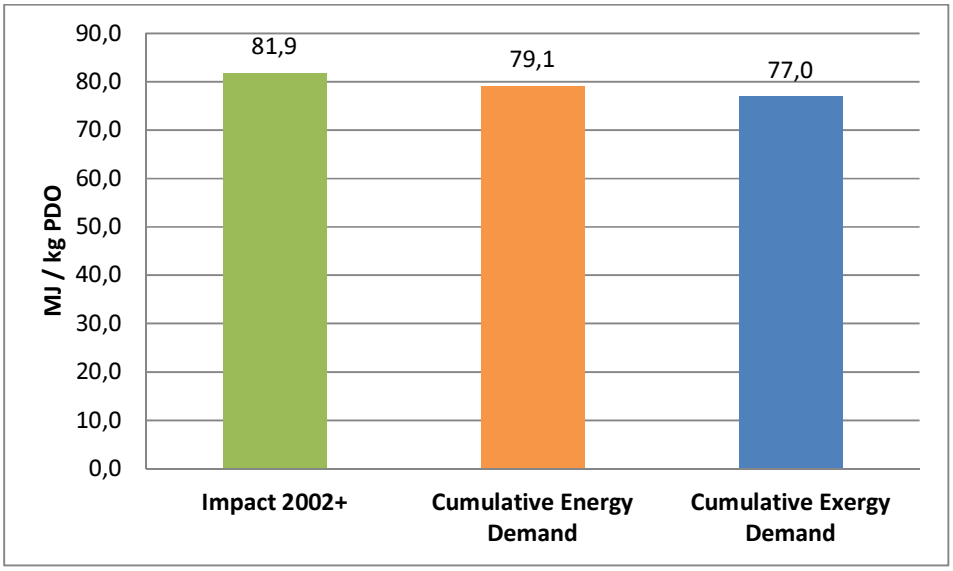

FIGURE 27: COMPARISON OF DIFFERENT LCIA-METHODS FOR ASSESSING NREU

As can be seen applying the different methodologies results in relatively minor changes and provide a range of 77-81,9 MJ. Compared to IMPACT 2002+ applying Cumulative Energy Demand results in 3,4 % lower NREU and applying Cumulative Exergy Demand in roughly 6 % lower NREU.

For the assessment of GHG-emissions four alternatives are presented. Firstly, the CML 2 baseline method was chosen for comparison, which was also used by Urban & Bakshi. Furthermore ReCiPe was applied, which offers three different perspectives (egalitarian, hierarchist and individualist). ReCipe uses the GHG-calculations of IPCC 2007 method (developed by the International panel on climate change), therefore the egalitarian perspective equals the IPCC method for assessing climate change for a 500 year timeframe, the hierarchist equals IPCC with a 100 year time frame and the individualist equals IPCC with a 20 year time frame (Goedkoop et al. 2008). Both other methods, the IMPACT 2002+ and the CML 2 Baseline 2000, apply a 100 year time frame (Humbert et al. 2012; Goedkoop et al. 2008). The results for the different methodologies are contrasted in Figure 28.

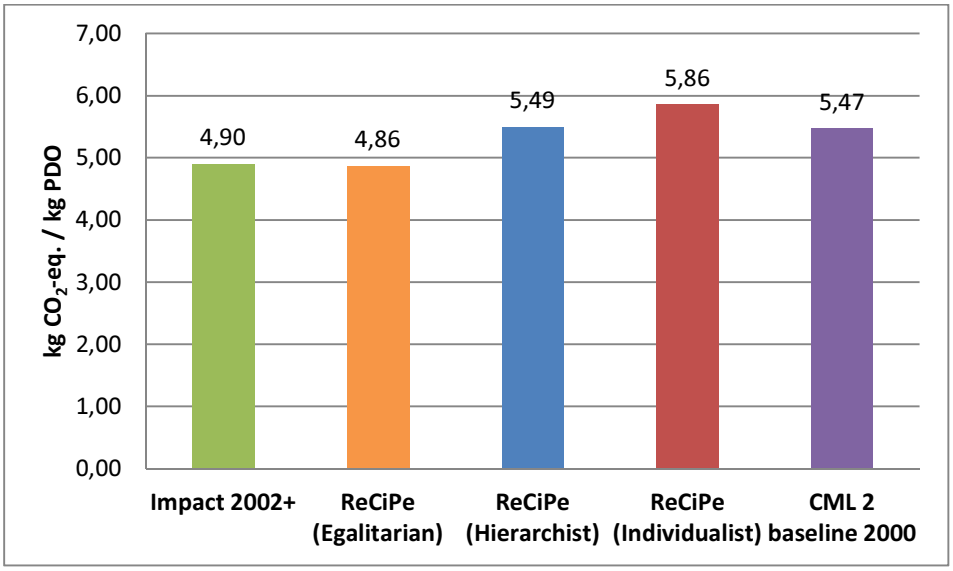

FIGURE 28: COMPARISON OF DIFFERENT LCIA-METHODOLOGIES FOR THE ASSESSMENT OF GHG-EMISSIONS

While for the NREU the alternatives suggest lower values, for the GHG-emissions three of the contrasted methodologies show higher emissions, which can amount up to 5,86 kg CO_2 equivalents (Individualist approach of ReCiPe), meaning 16,4 % higher emissions than with the IMPACT 2002+ method. The only slightly lower value is shown by the egalitarian perspective of ReCiPe, suggesting 3,2 % lower emissions.

As the focus of this paper is not on assessing differences between LCIA-methodologies no further attention will be paid to the reasons behind the discrepancies of the results. Contrasting the different methods just serves the purpose of making the reader aware of the influence the choice of LCIA-methodology can have.

6.4.3 VARIATION OF ELECTRICITY MIX

GOAL & SCOPE

Electricity is a not to be underestimated part of the total emissions of the PDO production, especially in the fermentation where its contribution amounts almost to 80 % in both impact categories. It would therefore be interesting to analyze how the impacts change with different electricity input.

The Dutch electricity mix was used for this LCA. This makes the results more region-specific and complicates drawing general conclusions about the PDO production from glycerol. To minimize at least part of this regional limitation different electricity mixes are assumed for comparison in this sensitivity analysis: The European average *("Electricity, medium voltage, production UCTE, at*

grid/UCTE U") and the electricity mix of the US (*"Electricity, medium voltage, at grid/US U"*). The US mix was chosen to enable a better comparison to the other LCA's on PDO production which are all based on US models.

RESULTS

The first graph (A) in Figure 29 shows the influence of the choice of electricity mix on the GHG-emissions of the PDO production. As can be seen a variation of the electricity mix results in a relatively minor change of emissions. The Dutch mix and the UCTE average are very similar with the UCTE mix performing slightly better by 0,6 % than the Dutch electricity mix. Just choosing the US mix results in a significant change of 2,5 % which would imply an increase of GHG-emissions by 0,12 kg CO_2 equivalents per kg PDO.

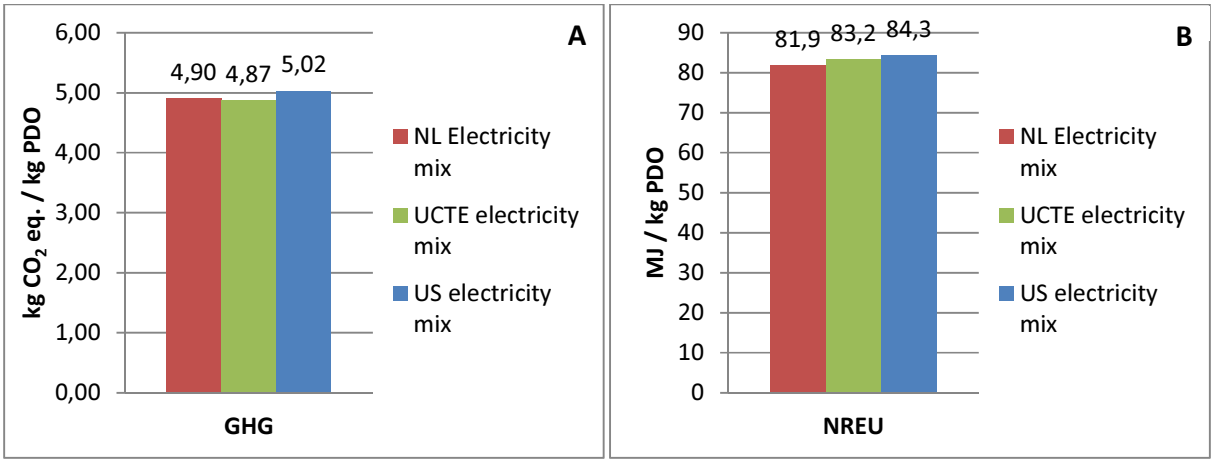

FIGURE 29: THE IMPACT OF THE CHOICE OF ENERGY MIX ON THE GHG-EMISSIONS AND THE NREU OF THE PDO PRODUCTION

Concerning the NREU the picture changes (see second graph B in Figure 29). Here the Dutch electricity mix has the lowest impact as not only the US-mix, which has a 2,9 % higher value, but also the UCTE average has a by 1,6 % bigger NREU. This different performance in the two indicators might be explained by the much higher share of nuclear energy in the UCTE average (29 %; Schakenda & Nyland 2008) which implies fewer CO_2-emissions but a higher NREU. In the Netherlands on the other hand nuclear power is just a minor contributor to the total energy supply (Itten et al. 2014). The high results for the US mix can be explained by the very extensive fossil fuel use in their energy production of around 70 % (Itten et al. 2014).

6.4.4 REDUCING THE NEED OF STEAM: PROCESS OPTIMIZATION AND HEAT INTEGRATION

GOAL & SCOPE

As can be seen in chapter 6.3, steam is a main contributor to the total emissions of the PDO production. Especially in the PDO recovery and purification it is clearly the dominant factor as its contribution amounts to around 94 % in both impact categories. Considering possible scenarios in which less steam is needed should therefore be part of the sensitivity analysis.

Therefore two scenarios for the PDO recovery & purification are considered:

- A very realistic reduction of steam use by 30 % which can be reached by process optimization.
- A reduction by 50 % which still seems within the range of possible improvements if process optimization is combined with heat integration.

RESULTS

Figure 30 compares the impact of those two scenarios on the GHG-emissions of the PDO-production with the base case displayed in chapter 6.3. The variation of steam has a quite strong impact on the total emissions and reduces them respectively by 17,7 % and 29,5 %.

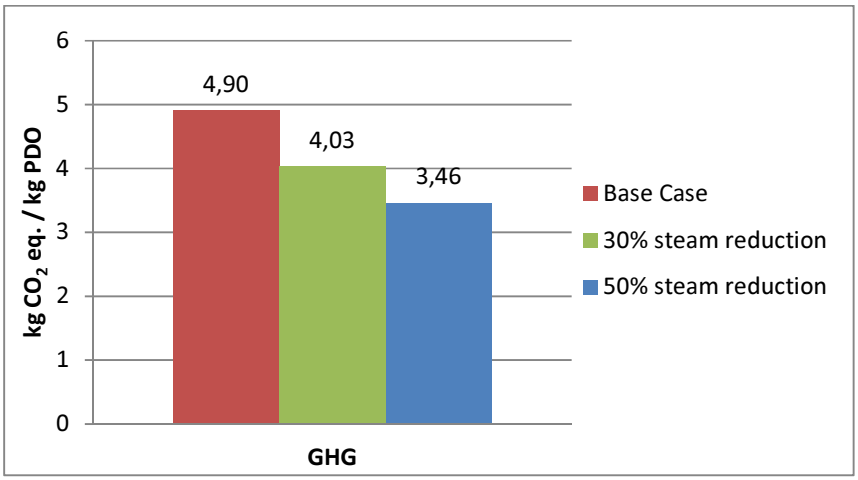

FIGURE 30: THE IMPACT OF STEAM REDUCTION ON THE GHG-EMISSIONS OF THE PDO PRODUCTION

Even stronger reduction possibilities can be observed in NREU (see Figure 31), where the impacts are reduced by 19,1 % and by 31,9 %.

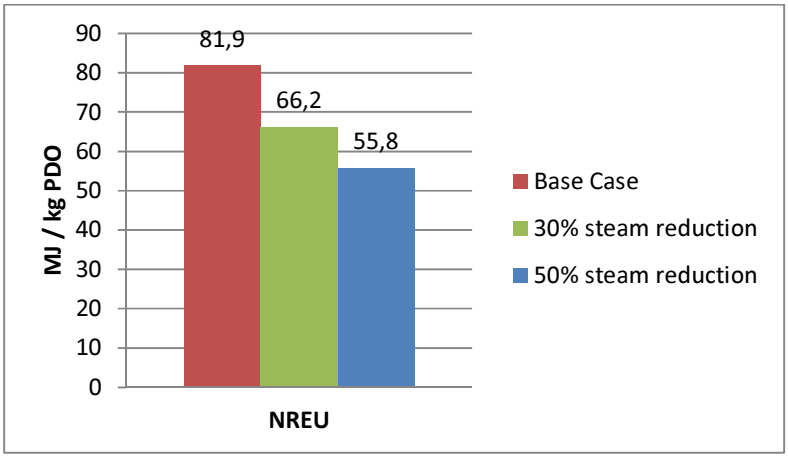

FIGURE 31: THE IMPACT OF STEAM REDUCTION ON THE NREU OF THE PDO PRODUCTION

6.4.5 BIOGAS AS SUBSTITUTE FOR NATURAL GAS

GOAL & SCOPE

The use of natural gas is the input with the largest influence on the NREU and the GHG-emissions of the PDO production. It is burned to produce heat and steam for the different processes involved in the production. Besides its dominating role in PDO recovery (see chapter 6.3) it is also the second biggest contributor as steam in fermentation. But also in the upstream processes natural gas plays a significant role to produce heat. In Glycerol production it is the third biggest contributor with 4,1 % (NREU) and 2,8 % (GHG), in the rape oil production even the second biggest with 7,9 % (NREU) and 4,7 % (GHG) (see Figure 49 in Appendix 2).

The DBFZ (Majer & Oehmichen 2010) examined possibilities to optimize the GHG-balance of the biodiesel production from rape. Replacing heat from natural gas with heat from biogas coming from a combined heat and power plant for steam supply was thereby proven to lead to a significant reduction of the GHG emissions in the rape oil production and the esterification process. According to them the CO_2 emissions resulting from the steam production could be reduced by 76,5 % for rape oil production when using biogas as a substitute to fossil fuels[11].

The DBFZ study does however just focus on CO_2 emissions and does not include other impact categories like NREU. Therefore a simulation via ecoinvent models was conducted for this study. The model "*Steam, for chemical processes, at plant/kg/RER*" was used for this LCA (see chapter 6.2.2.2). It consists of the sub-models *"natural gas, burned in industrial furnace > 100 kW"* and *"heavy fuel oil, burned in industrial furnace 1MW, non modulating"* as well as the water needed for the steam

[11] Calculation based on Majer & Oehmichen (2010): Reduction of CO_2-emissions from 3,4 kg CO_2-eq. to 0,8 kg CO_2-eq. per GJ Biodiesel.

production. Those two heat sources (natural gas, heavy oil) were replaced by the ecoinvent-model *"Heat, at cogen, biogas agricultural mix, allocation exergy/CH U"* to form a biobased model for steam production. This model represents the Suisse mix of heat production from biogas originating from sewage sludge and biowaste for the year 2006. It incorporates a mix of both – biogas engines and ignition gas engines and a production with and without covered stock (higher methane emissions)[12]. (Jungbluth et al. 2007)

For the sensitivity analysis the biogas model for steam production replaced the fossil one within the processes fermentation, PDO recovery & purification but also within the upstream esterification and the rape oil production.

RESULTS

One kg of the biobased model for steam has 93,1 % lower GHG-emissions than one kg of the fossil steam-model from natural gas and heavy oil. This surpasses the already quite impressive reduction of 76,5 % suggested by Majer & Oehmichen (2010), whose fossil reference was however solely based on natural gas and did not include heavy oil.

Replacing the steam from natural gas and heavy oil with steam from biogas in the rape oil production, the esterification, the fermentation and the PDO recovery & purification leads in total to a tremendous decrease of NREU (by 66 %) and GHG-emissions (by 58 %). Figure 32 shows how the total GHG-emissions of the PDO production are reduced to 2,04 kg CO_2 equivalents (graph A) and the NREU to 28 MJ (graph B).

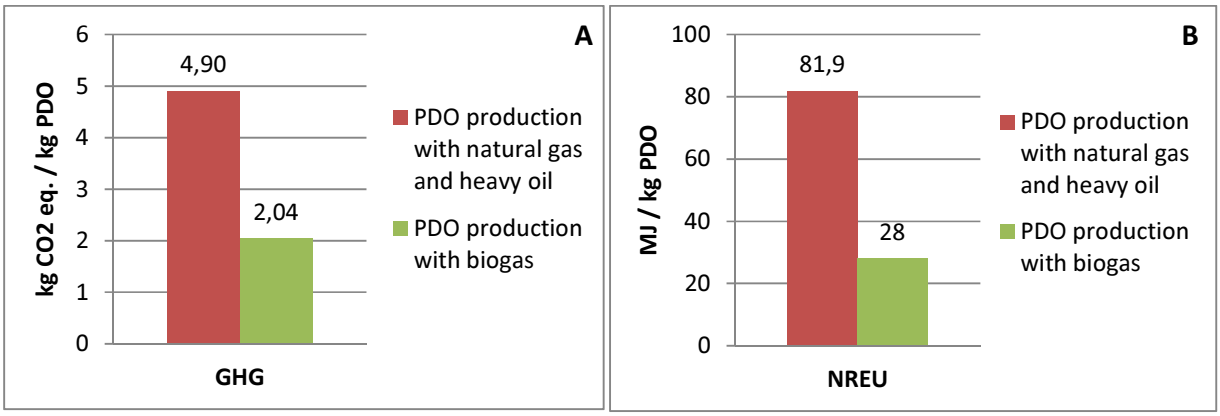

FIGURE 32: THE IMPACT OF THE SUBSTITUTION OF FOSSIL SOURCES WITH BIOGAS ON THE GHG-EMISSIONS AND NREU OF THE PDO PRODUCTION

[12] Exact share: 55,03 % gas engine and covered stock, 28,32 % ignition engine and no covered stock, 8,5 % gas engine and no covered stock, 8,15 % ignition engine with covered stock. (Jungbluth et al. 2007)

6.4.6 VARIATION IN ELECTRICITY USE

GOAL & SCOPE

In chapter 6.4.3 different electricity mixes were analyzed. This simulated input from different electricity production combinations but did not change the amount of electricity used in the PDO production.

The electricity values used in the main analysis (described as Base values in Table 14: Electricity values used in the sensitivity analysisTable 144) were based on values found in the literature review of Patel et al. (2006) (see the Life Cycle Inventory, chapter 6.2.2.3). They were considered as most fitting for this process design. But in the literature there is a wider range of electricity values given. In absence of an observed value for the PDO production there is no certainty about which of the electricity values identified as approximation are most realistic. Therefore it is helpful to look at different electricity values and how they influence the results. In this sensitivity analysis higher and lower electricity values were chosen from literature to assess their impact on the PDO production (see Table 144).

TABLE 14: ELECTRICITY VALUES USED IN THE SENSITIVITY ANALYSIS

Process	Unit	Higher values	Base values	Lower values
Centrifugation	kwh/m³	12,3	10,8	7
Agitation	kwh/m³	5	2	0,5
Agitation Mixer	kwh/m³	2,5	1	0,25

The lower values are taken from Patel et al. (2006), who combined an analysis of white biotechnology processes with an extensive literature review on energy uses of chemical processes. The values displayed in Table 144 for lower values are the ones Patel et al. chose, based on their judgment of the gathered data, as main reference values for their assessment.

Bohlmann (2002) was also part of the literature review conducted by Patel et al. His average electricity value for centrifugation was already used in the main analysis (base value). His upper boundary of the range given for electricity use (12,3 kwh/m^3) was chosen for this sensitivity analysis as the higher value.

Also for the agitation processes another source than in the main analysis was used, namely Petrides et al. (1989) which is also part of the literature review of Patel et al. (2006). In the book the authors present inter alia a range of electricity use for agitation processes for yeast production. Their upper boundary (5kwh/m^3) of their range 3,5 – 5 kWh / m^3 was chosen as the higher value for agitation. Again, half of this value was assumed for the mixing processes.

RESULTS

For both impact categories the higher electricity values lead to an increase of the impacts by almost 7%. The lower electricity values on the other hand reduce both impact categories by almost 5 % (see Figure 33).

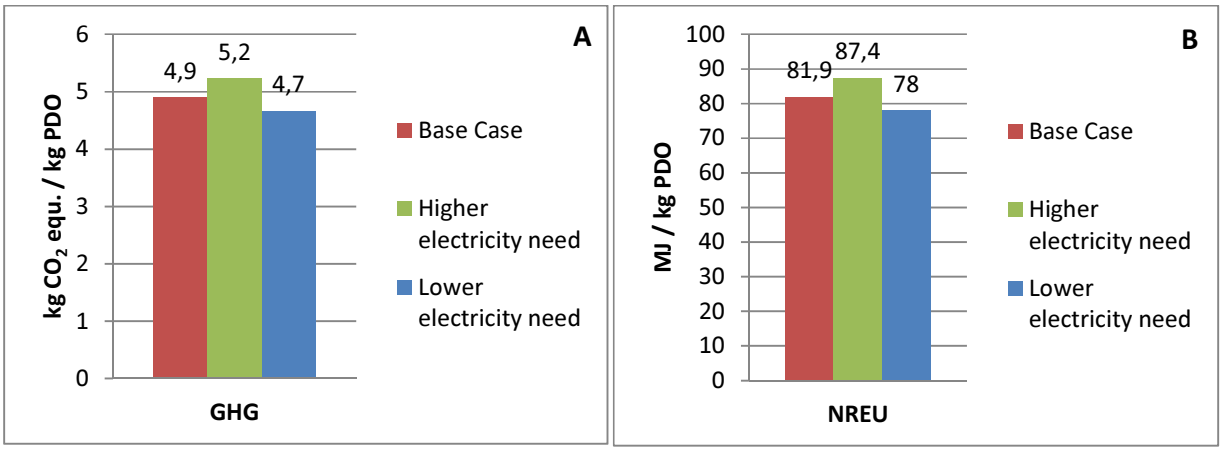

FIGURE 33: THE IMPACT OF VARIATIONS IN ELECTRICITY USE ON THE GHG-EMISSIONS AND NREU OF THE PDO PRODUCTION

6.4.7 HIGHER FERMENTATION YIELDS

GOAL & SCOPE

The glycerol fermentation as adopted for the base case has a relatively low molar yield of 0,542 mol PDO / mol Glycerol. In literature better molar yields can be found for the glycerol fermentation to PDO. Jolly et al. (2014) present values as high as 0,71 mol PDO / mol Glycerol and da Silva et al. (2014) speak of a fermentation yield of 0,75 mol PDO / mol Glycerol. Looking at fermentation processes of other products one might even expect higher fermentation yields for glycerol in the future. For lactic acid for example, Datta et al. (1995) present a fermentation efficiency of 95 % from starch.

In this sensitivity analysis it will be checked how a variation of the fermentation yield affects the NREU and GHG-emissions of the PDO-production. For that purpose two additional fermentation scenarios are presented:

- A higher fermentation efficiency of 62 % (0,75 mol PDO / mol Glycerol).
- A very optimistic fermentation efficiency of 95 %.

This analysis disregards the concentrations achieved by those fermentation processes. The concentrations in the fermentation outflow affect the amount of energy needed for the following centrifugation and mixing processes. A higher yield could also come along with a less favorable

concentration which might increase the energy use for downstream processes. Neglecting them is therefore a simplification that does not consider all relevant factors influencing the environmental impacts.

RESULTS

Concerning the GHG-emissions a higher fermentation yield of 62 % would reduce the emissions by 9 % and a very optimistic fermentation yield of 95 % would lead to a reduction by 16 % (see Figure 34).

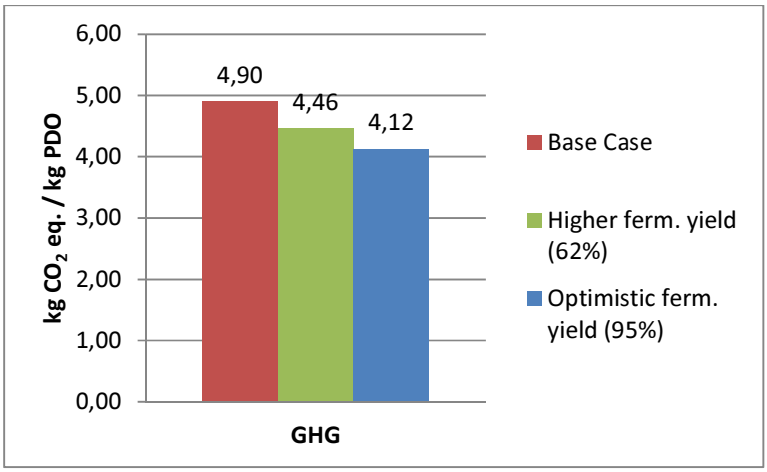

FIGURE 34: THE IMPACT OF VARIATIONS IN FERMENTATION YIELD ON THE GHG-EMISSIONS OF THE PDO PRODUCTION

Similar but a bit lower changes can be observed for the NREU. Here higher fermentation yields would reduce the NREU by 7 % and 13 % respectively (see Figure 35).

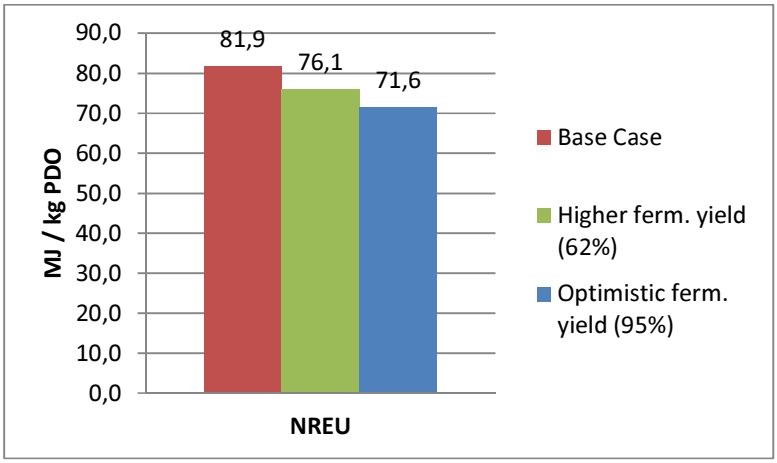

FIGURE 35: THE IMPACT OF VARIATIONS IN FERMENTATION YIELD ON THE NREU OF THE PDO PRODUCTION

One might expect a bigger impact when increasing the fermentation yield as dramatically as done here (by 19 and 52 %). But since the Glycerol production just accounts for 23 % (GHG) and 28,8 % (NREU) of the total emissions of the PDO production (see chapter 6.3) its effect is not as major but still significant. This might however change if the prices of Glycerol rise again (as expected in chapter 4.2) and consequently also increase the economic allocation factor.

An increase in fermentation yield would not just improve the GHG-emissions and NREU of the PDO production by 7 to almost 16 % but also significantly decrease the need for Glycerol and thus slightly lower the impact of price fluctuations and scarcity of this resource.

6.4.8 USE OF BIOBASED METHANOL IN ESTERIFICATION

GOAL & SCOPE

Within the esterification Methanol is, besides the dominating rape oil, the input with the second biggest impact, cumulating 14,9 % (NREU) or respective 3,5 % (GHG) of the impacts of the esterification (see Figure 49 in Appendix 2).

A study by the DBFZ (Majer & Oehmichen 2010) analysed different methanol production pathways and concluded that the use of biomethanol on the basis of synthetic gas from residual woods can decrease the CO_2 emissions of the esterification process by 56,8 % [13].

It might therefore be interesting to consider such a scenario in this study as well. The DBFZ study does however just focus on CO_2 emissions and does not include other impact categories like NREU. Therefore an own simulation using ecoinvent data was conducted for this study. The default ecoinvent-model *"Methanol, at plant/GLO"* produced from natural gas was substituted by *"Methanol, from synthetic gas, at plant/kg/CH"* which is produced from wood. The data for the biobased methanol is however coming from demonstration and pilot plants as this production pathway is according to Jungbluth et al. (2007) not yet commercially applied.

RESULTS

Figure 36 contrasts the GHG-emissions and NREU of 0,071 kg fossil-based methanol with the impacts of 0,071 kg biobased methanol. The results are related to 0,071 kg as this is the amount of methanol needed to produce 2,33 kg Gycerol which are necessary for the production of 1kg PDO. As can be seen the biobased methanol has substantially lower GHG-emissions (by 61,5 %) and NREU (by 80,8 %)

[13] Calculation based on Majer & Oehmichen (2010): Reduction of CO_2-emissions resulting from methanol use from 3,7 kg CO_2-eq. to 1,6 kg CO_2-eq. per GJ Biodiesel.

than the fossil-based methanol. The simulated decrease of the GHG-emissions goes along with the result of the DBFZ-study which predicted with 56,67 % a fairly similar reduction for the methanol use in the esterification (Majer & Oehmichen 2010).

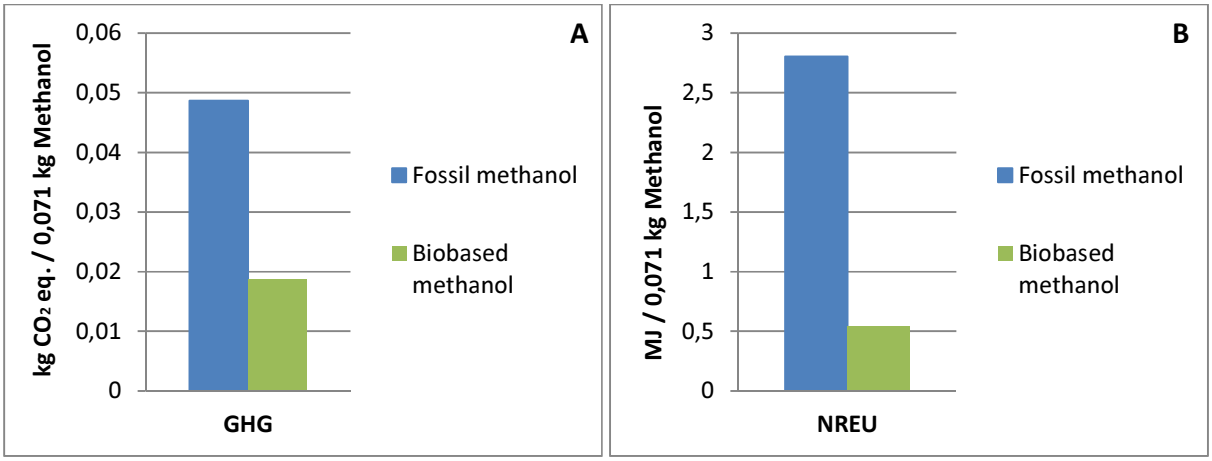

FIGURE 36: GHG-EMISSIONS AND NREU OF THE FOSSIL AND THE BIOBASED PRODUCTION OF 0,071 KG METHANOL (ADAPTED TO FU)

Looking at how the substitution of fossil methanol with biobased methanol influences the NREU of the total PDO production (see Figure 37) it can be seen that it leads to a decrease by 2,8 %.

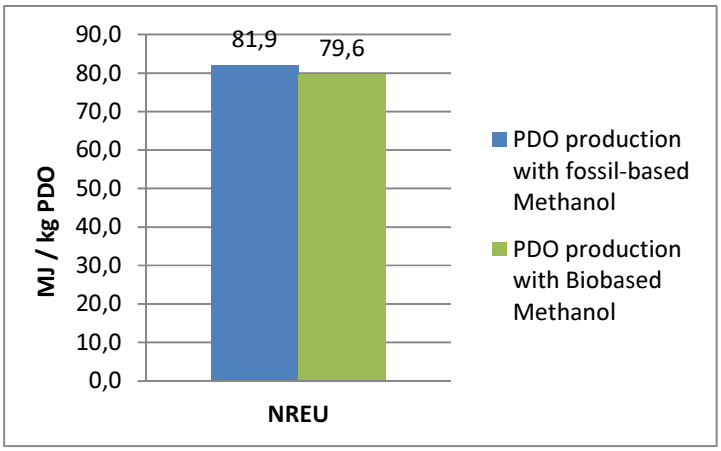

FIGURE 37: THE IMPACT OF THE SUBTITUTION OF FOSSIL METHANOL WITH BIOBASED METHANOL ON THE NREU OF THE PDO PRODUCTION

For the GHG-emissions (see Figure 38) on the other hand just a minor decrease by 0,6 % can be observed.

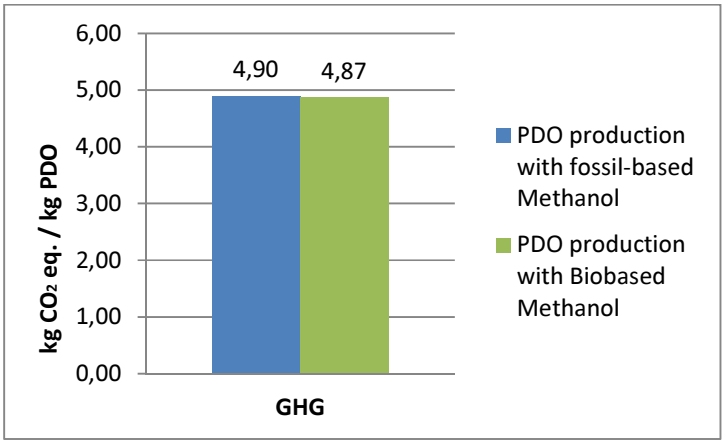

FIGURE 38: THE IMPACT OF THE SUBTITUTION OF FOSSIL METHANOL WITH BIOBASED METHANOL ON THE GHG-EMISSIONS OF THE PDO PRODUCTION

6.4.9 ORGANIC UREA AS N-FERTILIZER TO SUBSTITUTE CONVENTIONAL N-FERTILIZER

GOAL & SCOPE

As can be seen in Figure 49 (Appendix 3) the Nitrogen fertilizer is the biggest contributor to both impact categories in the rape seed cultivation (37,7% to GHG-emissions, 43,5% to NREU). It would therefore be interesting to see how the total values for both impact categories change if the Nitrogen fertilizer input is altered.

Majer & Oehmichen (2010) also assessed the optimization potential of rape seed cultivation and came up with the proposition to substitute the conventional Nitrogen-fertilizer mix with organic Urea as Nitrogen-fertilizer. Their results suggest that such a substitution would decrease the GHG-emissions of the nitrogen fertilizer production by 52,6 % [14]. As Ecoinvent does not provide a dataset for organic urea, the value used by Majer & Oehmichen (2010) will be taken to simulate such a substitution also for this study.

RESULTS

With this modification measure, the total GHG-emissions of the cultivation phase can be reduced by 19,9 % from 1,15 to 0,92 kg CO_2-equivalents. On the PDO production in total the substitution of the nitrogen fertilizer means a 4,7 % decrease of the GHG-emissions (see Figure 39).

[14] Calculation based on Majer & Oehmichen (2010): Reduction of CO_2-emissions resulting from nitrogen production from 21,47 kg CO_2-eq. to 10,17 kg CO_2-eq. per GJ Biodiesel.

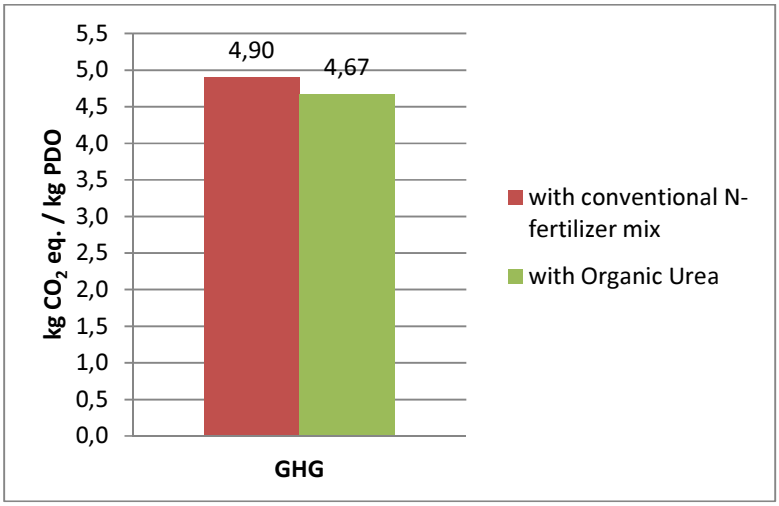

FIGURE 39: THE IMPACT OF THE SUBSTITUTION OF THE CONVENTIONAL FERTILIZER MIX WITH ORGANIC UREA ON THE GHG-EMISSIONS OF THE PDO PRODUCTION

The DBFZ-study did not include the impact category NREU in their analysis. Therefore no specific numbers of how the substitution of N-fertilizer influences this category are available. But to have a rough estimate, the same reduction as Majer & Oehmichen (2010) obtained for the GHG-emissions (53,6 %) was assumed. The results, which can be seen in Figure 40 have to be used with caution as this simplification cannot display the real impact of the fertilizer substitution on NREU. This simulation would suggest a reduction of the total NREU by 3,4 %.

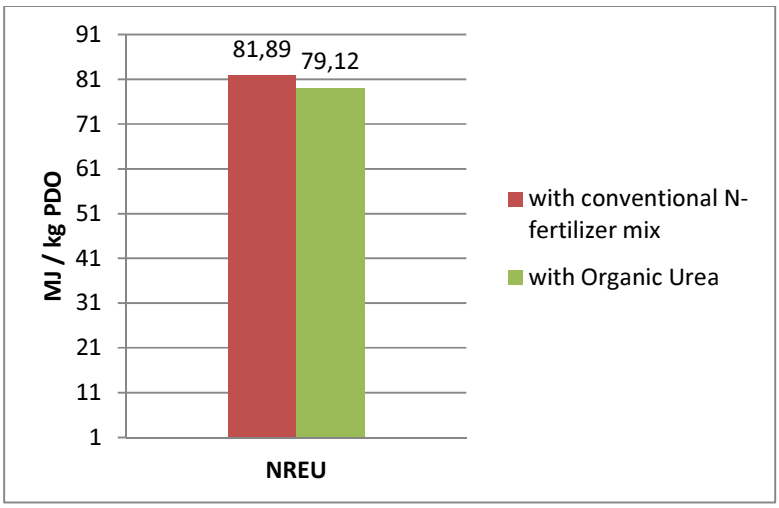

FIGURE 40: THE IMPACT OF THE SUBSTITUTION OF THE CONVENTIONAL FERTILIZER MIX WITH ORGANIC UREA ON THE NREU OF THE PDO PRODUCTION

There is also more optimization potential in the cultivation phase (e.g. fossil diesel use for machinery). However, as the focus of this paper is the PDO production to which the cultivation of rape seeds is just

one contributor of many, the substitution of Nitrogen-fertilizer will be the only modification measure implemented in this sensitivity analysis for the cultivation phase.

6.4.10 SCENARIO DEVELOPMENT

Adding up the different optimization and modification measures displayed in the sensitivity analysis to scenarios can offer an interesting view on what level of environmental impact can be achieved with optimized production systems.

Next to the base case (displayed in chapter 6.3) two further scenarios were developed:

- An *optimization scenario:* This scenario includes a 30% reduction in steam use for the PDO recovery & purification achieved by process optimization (see chapter 6.4.4). Furthermore a higher fermentation yield of 62% is assumed (see chapter 6.4.7) and lower electricity valued are taken (see chapter 6.4.6). This scenario can be considered as fairly realistic as steam reduction and a higher fermentation yield are relatively easy possible with current technology improvements. The lower electricity values can be found in literature and are therefore also a realistic scenario. Furthermore all three modifications can be realized directly by the PDO producer as it involves just the fermentation process and the PDO recovery and purification.
- An *ideal scenario*: This scenario involves further, more optimistic improvement measures that also affect the glycerol production, which normally is not directly controlled by the PDO producer. It can therefore be considered as a very optimistic scenario which might be possible in a more distant future. Besides a 50% reduction in steam use and lower electricity use it furthermore includes the substitution of fossil methanol by biobased methanol and of conventional fertilizer by organic urea fertilizer. Also a very high fermentation efficiency of 95% is assumed and the very influential substitution of natural gas and heavy oil by biogas (see chapter 6.4.5).

Figure 41 compares the GHG-emissions and Figure 42 the NREU of the optimization and the ideal scenario with the base case of chapter 6.3.

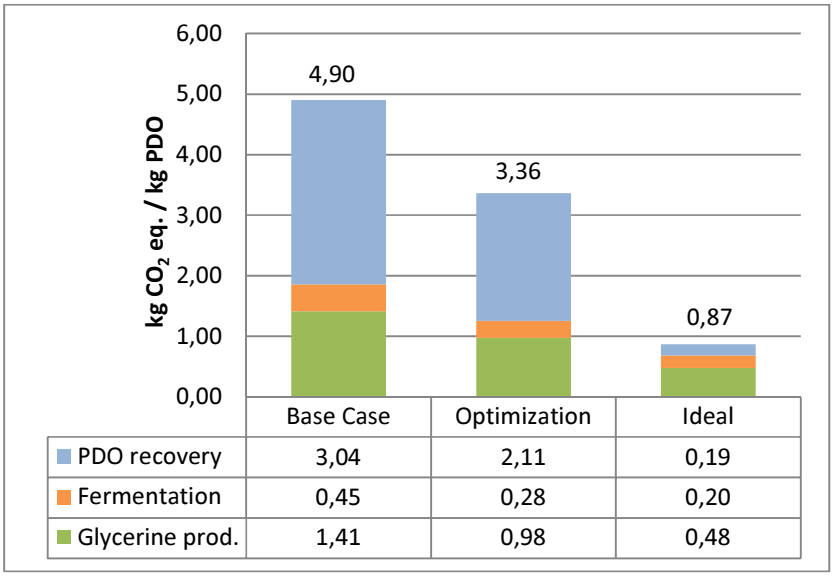

FIGURE 41: COMPARISON OF THE THREE SCENARIOS CONCERNING THEIR GHG-EMISSIONS

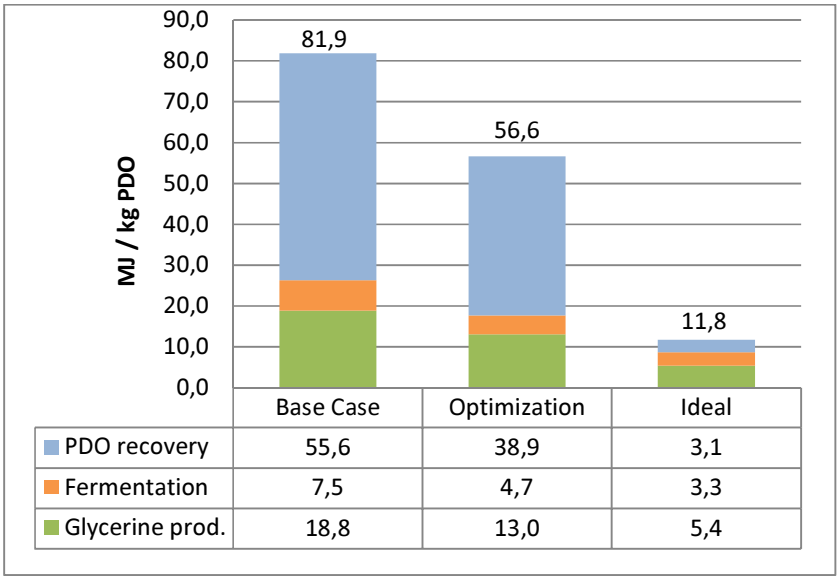

FIGURE 42: COMPARISON OF THE THREE SCENARIOS CONCERNING THEIR NREU

The results of the optimization scenario show a quite impressive drop by 31,3 % from 4,9 kg to 3,36 kg CO_2 equivalents. The reduction realized in NREU is almost the same (30,9 %) and leads to a drop from 81,9 MJ to 56,6 MJ. This is mainly due to the reduction of steam use in the PDO recovery and purification where together with the lower electricity use a reduction of just above 30 % in both categories could be realized.

The ideal scenario suggests a drastic reduction of GHG-emissions by 82,3 % to 0,87 kg CO_2-eq. and for NREU an even steeper drop by 85,6 % to 11,8 MJ. Again, this is mainly due to reductions in the PDO-

recovery and purification (by around 94 % in both categories) where the impact of the steam use is even more reduced by the substitution of natural gas by biogas. But also in the glycerol production reductions of 66,2 % (GHG-emissions) and 71,5 % (NREU) are realized due to the substitution of fossil based methanol, nitrogen fertilizer, natural gas and because of the much higher fermentation yield of 95 %. The fermentation does not show an as dramatic improvement potential but still experiences a fall in GHG-emissions and NREU by around 55 %.

In the ideal scenario the distribution of impacts between the three process steps glycerol production, fermentation and PDO recovery and purification changes drastically. The dominating role of the PDO recovery and purification vanishes due to large improvements in steam use so that now the Glycerol production is the process step with the biggest impact while fermentation and PDO recovery are fairly similar.

6.5 INTERPRETATION: CONCLUSIONS FOR THE RESULTS OF THE CONTRIBUTIONAL & SENSITIVITY ANALYSIS

The biggest influence on the impact categories is the consumption of natural gas and heavy oil. It is most dominating for steam production in the PDO recovery and purification but also significantly present in the fermentation and glycerol production. As demonstrated in the sensitivity analysis, working on this consumption of natural gas and heavy oil would promise the highest reduction possibilities. Process optimization, heat integration or even substitution of fossil heat sources with biogas are all measures that would lead to a substantial reduction of the total NREU and GHG-emissions (around 30% with process optimization + heat integration and 58-66 % with biogas).

Working on the efficiency of the fermentation process (increasing fermentation yield) is also a promising but not as influential approach for reducing the impacts. Here quite realistic improvements between 7 (NREU) and 9 % (GHG) or very optimistic optimization potentials between 13 (NREU) – 16 % (GHG) seem possible. Such increases in fermentation yield would not just improve both impact categories of the PDO production but also significantly decrease the need for glycerol and thus lower the impact of price fluctuations and scarcity of this resource, which might become a factor according to chapter 4.2.

Reducing the electricity input results in a not negligible but comparably lower improvement in both impact categories (almost 5 %). Here, improvements of the biggest contributor to electricity use, the centrifugation, are most desirable.

Other optimization possibilities upstream (transesterification, oil wet milling and cultivation of rape seeds) can also decrease the environmental impacts but to a lower extent. Using biobased methanol in the transesterification would lead to improvements by 0,6 % (GHG) – 2,8 % (NREU), using organic fertilizer in the cultivation would reduce the impacts by 3,4 % (NREU) - 4,7 % (GHG). However, if the allocation factor for glycerol rises (e.g. rising glycerol prices or choosing another allocation method, see chapter 6.4.1) improvements in those upstream processes gain in importance, as the glycerol production would then be a comparably bigger contributor to the total emissions.

However, it has to be considered that the upstream processes are more difficult to influence for a PDO producer. Hence, the focus should clearly be on making the downstream processes (fermentation and most importantly PDO recovery & purification) more efficient, especially concerning the use of fossil sources for heating.

The scenarios developed in chapter 6.4.10 show how much the improvement measures can lower the environmental impacts of the PDO production. The optimization scenario suggest a reduction by around 31 % for both impact categories which can be considered as very realistic as it is technically feasible via optimization measures and as it just involves modifications in the fermentation and PDO recovery and purification, which are directly under the influence of the PDO producer.

The ideal scenario goes even further by suggesting reduction possibilities of over 80 %. This can however just be considered as a very optimistic, future scenario. Some measures of this scenario are not yet existent (e.g. 95% fermentation efficiency) and others very difficult to implement (substitution with biogas on all levels). Furthermore it involves more actors as the included measures also address many upstream processes (esterification, oil milling, cultivation). However, this scenario can still be regarded as a future path the PDO production should aim at.

Concerning methodological choices the sensitivity analysis revealed that they have an influence which should not be underestimated. While the choice of LCIA-methodology has a significant but not dramatic influence on the results (see chapter 6.4.2) the choice of allocation method has a very strong effect on the results in this case (see chapter 6.4.1).

6.6 LIMITATIONS OF THE LCA

A general problem LCA faces is that it is very difficult if not impossible to link impacts observed in the world to the emissions of one specific product using an experimental method. One cannot specifically track the emissions of the production of one particular mobile phone, for example, throughout the cause-effect-chain to a specific final impact observed in nature. Hence, instead of using empirical studies we have to rely on general models that are only valid within certain contexts. (Finnveden 2000)

Furthermore a LCA just displays a single observation, based on certain data and system boundaries. It is therefore difficult to come from a single observation to a universal statement like *"Product A is better than Product B"*. A LCA can be easily challenged by simulating a new situation with different properties. Like in this study this flaw can be reduced by including different scenarios (see sensitivity analysis) but it can never be completely eliminated. (Finnveden 2000)

METHODOLOGY

Concerning the LCIA methodologies one of the biggest points of criticism is the element of weighting. Weighting involves ideological, political and ethical values which are not objectively determined but influenced by perceptions and world views (Finnveden 2000). Since this study chose midpoint indicators to display the results weighting was avoided. Endpoint indicators are more subjective and uncertain as they require weighting and additional characterization steps (see chapter 6.1.2.5).

Also the choice of the time period analysed is a value choice with a significant impact on the results. It is for example related to the ethical choice of how to include the impact on future generations (Finnveden 2000). The sensitivity analysis showed how different time frames can influence the results (see results for different ReCiPe methods in chapter 6.4.2).

The differences in methodologies concerning classification, characterisation, weighting and other choices leads to varying results when applying different methodologies. The sensitivity analysis (chapter 6.4.2) proves such variations also for this case. The other methodologies did not completely change the trends observed with the original methodology applied but still had a significant impact on the results.

Another important point can be the choice of allocation method. As shown in the sensitivity analysis (chapter 6.4.1) it would have a remarkable effect on the results. In other studies the effect might be minor (see Urban & Bakshi 2009) but it is still a subjective choice that can have a big impact in many cases.

DATA INPUT

A LCA stands and falls with the quality of the data it uses for the assessment. In general there is the danger that *"theoretical process descriptions from open sources may not correspond to actual practice"* (Ayres 1995).

This LCA used a variety of data sources which consequently have their specificities concerning geographical scope, date, technology and many more aspects. Many of the models used are simulations that may not display the reality (e.g. Aspen or CHEMCAD simulations). Most data is from European sources (average or specific countries), but even within Europe a variety of technologies and practices exist. Examples of this paper are that data for waste water treatment from Switzerland was used and that data for rape seed cultivation came from Germany. Consequently the results do not display a specific production path at a specific place and time. Or like Haes et al. (2004) put it: The results *"have a low spatial and temporal resolution".*

For some inputs approximation values were applied, based on assumptions. For example the amount of cooling water used was calculated from assumed conditions that do not represent a real observation (chapter 6.2.2.4). This should be improved by assessing a specific cooling system used in the chemical production under certain local climate conditions. To obtain an approximation of the environmental impact of isobutyraldehyde, data of the isobutanol-production was used (chapter 6.2.2.6). The uncertainties arising from those approximations have to be considered when using the results of the study.

TRANSPARENCY

A common criticism of LCAs is the lack of transparency which hinders the reproduction of results (Ayres 1995; Finnveden 2000). By presenting an extensive chapter on the calculation of the inventory data and by using a widely accepted LCIA methodology this study tried to address the transparency issue. Furthermore data models of the common and publicly available ecoinvent database where used wherever possible. However, not all used data models could be analysed in detail concerning the methodology and scope applied. In those cases this study relies on the credible work of the respective authors, which can be expected especially for the models coming from ecoinvent as they are reviewed before entering the database.

SCOPE

An important limitation of this study is the scope applied. With the focus on NREU and GHG-emissions many other important impact categories have been ignored (e.g. eutrophication and land use). In the

sensitivity analysis many improvement measures where proposed to lower the NREU and GHG-emissions. But those improvement measures could have a negative impact on other categories which would counterbalance the benefits achieved in NREU and GHG-emissions. For example biogas and bio-methanol both require growth of biomass which could lead to higher eutrophication and land use as additional land is needed for the cultivation of their feedstock (Cherubini et al. 2009).

To achieve a sounder appraisal about the environmental impact of the biobased PDO production from glycerol, a more encompassing LCA considering all relevant impact categories would be necessary. The focus should especially be on impact categories related to the cultivation of the feedstock (here: rape seed), for example land use and eutrophication. In those impact categories the biobased products usually show their biggest drawbacks compared to their fossil references (Cherubini et al. 2009).

As for many impact categories there is still no consent about valid assessment methods[15] a fully encompassing LCA will not be reached in near future or might even continue to stay just an ideal situation to aim at. Hence, the conclusions have to be limited to the aspects that have been studied and claims that one production pathway is overall environmentally to be preferred to another must be avoided (Finnveden 2000).

Furthermore a LCA just assesses the environmental impacts and ignores economic and social dimensions of the analysed process (Haes et al. 2004). To address all *"three pillars of sustainability"* (Gibson 2006) additional tools like Life Cycle Costing (LCC) or a Social LCA would be necessary. A Social LCA aims at *"providing information about the potential social impacts on people caused by the activities in the life cycle of a product"* (Dreyer et al. 2006). Compared to an environmental LCA and also LCC the concept is still in its infancy but is receiving more and more attention (Hunkeler & Rebitzer 2005).

[15] e.g. indirect land use (Cherubini et al. 2009) or water use (see chapter 6.2.2.4; Koehler et al. 2010; Berger & Finkbeiner 2010)

7 BENCHMARKING TO OTHER STUDIES ON PDO PRODUCTION

In chapter 5 the methodological similarities and differences of the three benchmarking papers have already been analyzed and the results were included as far as possible in the design of this LCA. This was done to enable a better comparison between the LCAs and to provide a basis for the discussion of the results.

Chapter 5 has shown that at least the rough frame of the LCA seems to be the same (Functional Unit, cradle to gate analysis with similar exclusions like manufacture of facilities & machinery) but also revealed high differences in transparency which makes a well-funded comparison very difficult.

This chapter first benchmarks the three scenarios developed in this paper to the fossil production pathways and then to the biobased production routes of the other studies. Subsequently the differences between the results of the three studies are explained where possible. The final part of the chapter then discusses the conclusions for the relative performance of the PDO production from glycerol.

7.1 BENCHMARKING AGAINST FOSSIL PRODUCTION ROUTES

NON-RENEWABLE ENERGY USE

Figure 43 contrasts the NREU of the different glycerol-based bio-scenarios of this paper with the results of the other papers for fossil production pathways.

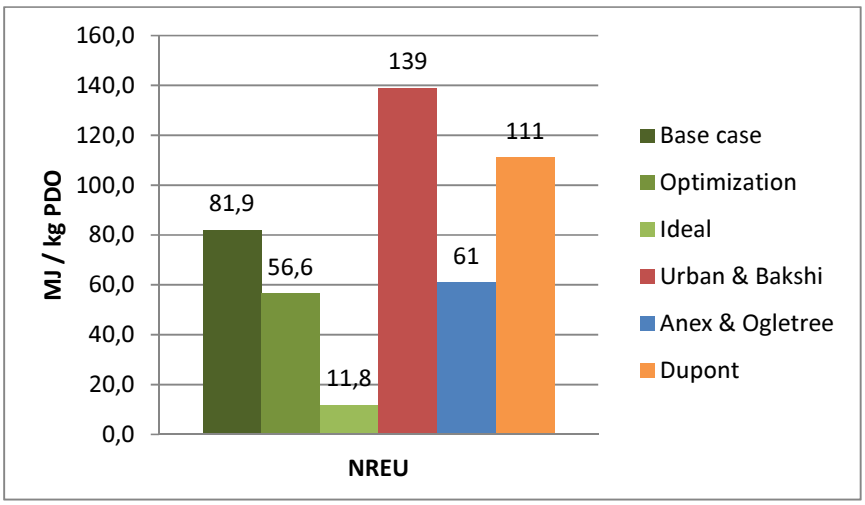

FIGURE 43: COMPARISON OF THE NREU OF THE GLYCEROL-BASED BIO-SCENARIOS WITH RESULTS FOR FOSSIL PRODUCTION PATHWAYS

It can be seen that the base case performs significantly better in NREU than the fossil pathways analyzed by DuPont and Urban & Bakshi. The results for fossil PDO of Anex-Ogletree however show a better performance by 25,5 % than the PDO production from glycerol. The optimization scenario on the other hand is already lower than Anex & Ogletree's result and the ideal scenario clearly outperforms all fossil routes.

GREENHOUSE GAS EMISSIONS

Like for this study the system boundaries of the benchmarked papers were set to from cradle to gate and therefore omitted the disposal of PDO (see chapter 5). Without considering the disposal phase we however ignore an important advantage of biobased PDO compared to fossil based PDO. When choosing e.g. incineration as a way to dispose PDO at the end of its life cycle, one has to consider the CO_2 emission resulting from that process. Assuming that the biobased and the fossil based PDO have the same quality one can conclude that the same amount of CO_2 will be emitted. The difference is however that biobased PDO embodies CO_2 during the cultivation of the feedstock. The CO_2 emitted in the incineration is therefore, at ideal conditions, the same amount of CO_2 which was binded earlier in the life cycle and consequently concludes a circle of uptake and emission of CO_2. Fossil based PDO, on the other hand, will add additional CO_2 to the atmosphere.

Assessing this additional CO_2 would allow a more encompassing and fairer comparison of biobased and fossil based PDO. Hence, a simplified disposal scenario (incineration of PDO) was considered for the comparison of the GHG-emissions (Figure 44). The stoichiometric calculation of this scenario is explained in Appendix 4. The scenario suggests the emission of 1,73 kg CO_2.

This amount was added to the results of the fossil pathways in Figure 44, as illustrated by the shaded areas. The fully colored areas show the results like they are originally communicated by the studies.

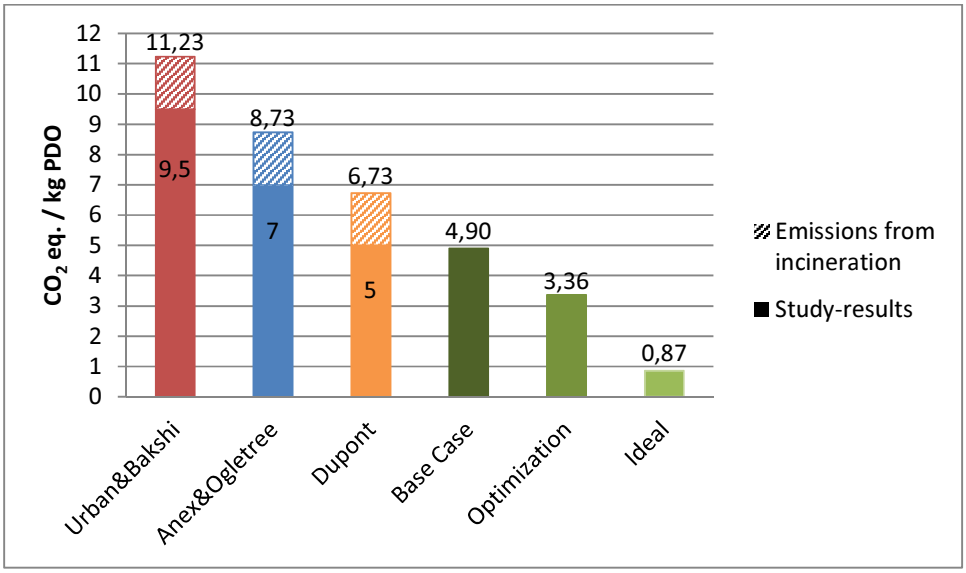

FIGURE 44: COMPARISON OF THE GHG-EMISSIONS OF THE GLYCEROL-BASED BIO-SCENARIOS WITH RESULTS FOR FOSSIL PRODUCTION PATHWAYS

Just considering the original results for the fossil routes, none of the analyzed fossil pathways has a lower value than the base case developed in this paper, even if the results of DuPont almost equal the base case. The two other scenarios on the other hand clearly outperform the fossil alternatives. Including the GHG-emissions resulting from the incineration (shaded areas) leads to an even clearer picture in favor of the PDO production from glycerol.

ANALYSIS

Comparing the different scenarios (base case, optimization and ideal scenario) with the results for fossil based PDO of the other papers we see a quite complex picture. There is however a relatively clear trend that according to this comparison all three scenarios of biobased PDO production from glycerol perform generally better in both impact categories than the fossil equivalents. Just the result of Anex & Ogletree shows a result for NREU that is significantly better than the base case. Concerning GHG-emissions none of the benchmarked fossil results perform better. This becomes even more evident if the CO_2-emissions of the incineration of PDO are taken into account.

Surprising is that the results of DuPont show an almost equivalent result in GHG-emission like the base case (a variation of just about 2 %) while the NREU is clearly higher (by 26,2 %). The reasons for this discrepancy cannot be found due to the very limited information that is available about the LCA of DuPont. However, including the incineration of PDO the GHG-emissions of the fossil DuPont-process is 27,2 % higher than the base case.

An almost reverse situation we have in the case of Anex & Ogletree which show a very low NREU, much lower than the results of DuPont and Urban & Bakshi which have respectively a by 45,1 % and 56,1 % higher value. But on the other hand Anex & Ogletree have the highest GHG-emissions of all benchmarked results.

This is an example for the big differences that can be observed between the results for the fossil PDO production of the three reference papers. This can be partly explained by the fact that Anex & Ogletree as well as Urban & Bakshi analyzed the fossil PDO production based on ethylene oxide while DuPont probably (see chapter 5.1.2) used the acrolein-pathway as fossil reference.

But also Anex & Ogletree and Urban & Bakshi show significant differences between each other, despite the fact that they analyze the same production pathway. Here a possible explanation is that they use a different process design and inventory data to model the fossil pathway.

Anex & Ogletree use input of a private consulting firm for process design and then use the information of a SimaPro database (not specified) for hydrogen production and another literature source for syngas production. Urban & Bakshi on the other hand used a simulation by the CHEMCAD software for their process model and complemented it with process level information for ethylene production and syngas production from a literature review (see chapter 5).

Hence, variations between the results of Anex & Ogletree and Urban & Bakshi were expectable but differences to such an extent (over 56% in NREU and over 26 % in GHG-emissions) are quite surprising, considering that both analyzed the same production pathway and showed a fairly similar scope (see table 1, chapter 5.4). Due to the lack of transparency of DuPont and Anex & Ogletree also Urban & Bakshi were not able to explain these discrepancies (Urban & Bakshi 2009).

7.2 BENCHMARKING AGAINST OTHER BIOBASED PRODUCTION PATHWAYS

NON-RENEWABLE ENERGY USE

Figure 45 shows the NREU of the three glycerol-based scenarios along with the NREU of the other assessments on bio-pathways using glucose for PDO production.

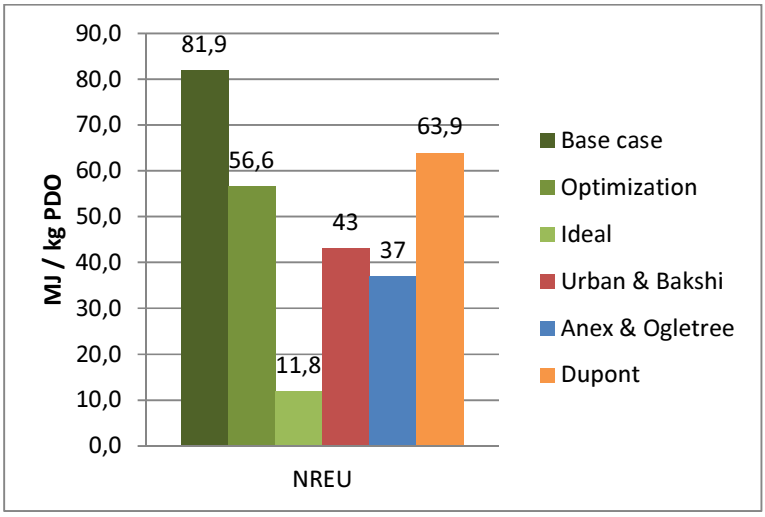

FIGURE 45: COMPARISON OF THE NREU OF THE GLYCEROL-BASED BIO-SCENARIOS WITH RESULTS FOR BIO-ROUTES BASED ON GLUCOSE

According to this comparison the base case has the highest NREU, followed by the DuPont results. The optimization scenario shows the third highest NREU, followed by Urban & Bakshi and Anex & Ogletree. The by far lowest value is achieved by the ideal scenario.

GREENHOUSE GAS EMISSIONS

Looking at the GHG-emissions (Figure 46) we see a different order. While the base case still has a comparably high impact it is now the previously second best Anex & Ogletree which shows the highest GHG-emissions. After the optimization scenario and Urban & Bakshi it is now the DuPont assessment that shows the second-lowest emissions. The ideal scenario stays the clearly best option.

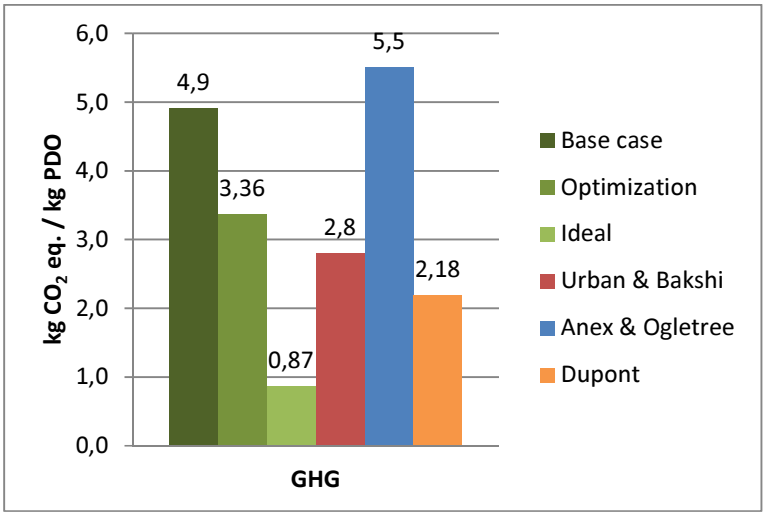

FIGURE 46: COMPARISON OF THE GHG-EMISSIONS OF THE GLYCEROL-BASED BIO-SCENARIOS WITH RESULTS FOR BIO-ROUTES BASED ON GLUCOSE

As all results are from biobased processes they share the same benefit of the CO_2-uptake. The emissions from incineration do therefore not influence the comparison and are thus not included in the graph. This just holds true if it is correct that all benchmarked studies did indeed not include the benefits of CO_2-sequestration in any way (see chapter 5).

ANALYSIS

As already shown in chapter 5, all three LCA-studies chosen for comparison roughly relate to the same biobased PDO production process from glucose. Concerning the fermentation Anex & Ogletree tried to match the performance of the DuPont process and also the further downstream processes separation and purification of PDO where predicted based on *"best practice engineering design"* and *"some guidance"* of DuPont.

Urban & Bakshi on the other hand used the process design provided by Anex & Ogletree to simulate the biobased PDO production process. Therefore they not just share the same fermentation yield but also the same energy use for the fermentation and PDO recovery and purification (26 MJ). Considering those similarities it comes as a surprise that their results are quite different.

Since also the scope of the LCA is similar in many aspects (see chapter 5, with restriction concerning DuPont who provide too limited information) one might expect a fairly similar result. This might be partly true for NREU (with an already quite big difference of DuPont) but is definitely not the case for GHG-emissions where Anex & Ogletree present an extraordinarily high result compared to DuPont and Urban & Bakshi. The specific reasons for those discrepancies are very difficult to find as Anex & Ogletree and especially DuPont provide too little information.

Since those great differences are present in both results - for fossil and biobased PDO (which was much more adapted to each other) – one might assume that the reasons for those discrepancies can be found mainly in differences in methodology than in differences in specific data used or scope applied. DuPont and Anex & Ogletree did not reveal their methodology used for the Life Cycle Impact Assessment. But it is a quite probable scenario that not the same methodology was applied. Those differences might be an important reason for the present discrepancies. But like Urban & Bakshi also this paper is not able to explain why the results differ to the two other studies.

The performance of the glycerol-based PDO production in relation to the one based on glucose will be more closely discussed in the following chapter 7.3.

7.3 LIMITATIONS AND CONCLUSIONS: THE RELATIVE PERFORMANCE OF THE BIOBASED PDO PRODUCTION FROM GLYCEROL

Finnveden (2000) stated that *"the complexity of LCAs makes it hard to identify the reasons behind [...] observed discrepancies".* This statement also holds true when looking at the benchmarking conducted in this paper. The comparison between the three other LCA studies (chapter 7.1 and 7.2) already showed how limited the use of benchmarking LCA studies can be. All three studies aimed at analyzing the same production pathway of DuPont, but came up with very different results. Those differences could be caused by methodological choices, use of different technologies and the presence of various knowledge gaps (Finnveden 2000). As those variations in results could just be explained to a limited extent many questions remained open. The reasons for the inability to comprehend those differences can be mainly tracked back to the lack of transparency concerning the assumptions and data used for the analysis, which is also widely claimed in literature as a major problem of benchmarking LCAs (Ayres 1995; Finnveden 2000).

The comparison between the three studies (DuPont, Anex & Ogletree, Urban & Bakshi) revealed that even if many factors are the same or at least similar, the results can still vary to a large extent. It can therefore be expected that it will be even more difficult to come to sound conclusions about the relative performance of the three scenarios developed in this paper.

Besides the environmental quality of a production process many other factors influence the result of a LCA. Methodological choices (Functional Unit, Methodology for LCIA etc.) and the Scope of the analysis (e.g. inclusion of the use or disposal phase, geographical scope and the inclusion / exclusion of specific processes) have a more than substantial influence. In the review of the benchmarked papers (chapter 5) it was tried to identify differences in those factors and – if possible – to eliminate some of them by adapting the design of this LCA study accordingly.

Since many factors could not be eliminated, the differences in results cannot be solely tracked back to the actual environmental quality of the production process. Additionally, the lack of transparency makes it almost impossible to find out if differences in some influential factors are present (e.g. Methodology for LCIA).

At least for some factors basic information was available. Both papers – Anex & Ogletree and Urban & Bakshi – used mass-based allocation, while this paper focused on economic allocation. The sensitivity analysis (chapter 6.4.1) showed that the choice of allocation method can have a quite

significant impact. Urban & Bakshi, however, concluded that in case of the PDO production from glucose the results are almost the same for economic and mass-allocation (see chapter 5.3.1).

Furthermore, all three benchmarked papers analyzed the PDO production under US conditions (not specifically mentioned by DuPont, but very probable), while this paper situated the production in Europe and used Dutch data where possible (electricity mix). The sensitivity analysis (see chapter 6.4.3) demonstrated the effect the location has on the environmental impact of the electricity use. According to those results a production based in the US would have around 3% higher NREU and GHG emissions. Further possible geographical differences (e.g. fertilizer & pesticide use in cultivation) were not investigated.

Other factors concern specific assumptions for the production processes. Anex & Ogletree for example assumed that all distillation columns operate under vacuum, what could reduce the operation heat and consequentially the energy use for the distillation processes, if the electricity need for keeping the vacuum does not exceed those heat savings. Urban & Bakshi on the other hand included a credit for the excess steam produced during the production of fossil based PDO, which could have a significant impact. Assumptions like that could have an effect on the study results which should not be underrated. But many more assumptions are very likely not even known, as there is no full transparency of the different LCA-studies.

To allow a sound interpretation of the results the full process design and choices made have to be publicly available and would need a very detailed investigation. Since both is lacking in this comparison just very general conclusions can be drawn.

Taking just the base case as reference to the production pathways analyzed by the other studies, the conclusion is that the glycerol production pathway is most likely beneficial compared to fossil production, but might not be better performing than the biobased production based on glucose. The optimization scenario on the other hand shows a fairly similar performance in NREU and GHG-emissions like the biobased references. The ideal scenario would be clearly the best option. But as previously explained, this benchmarking has to be used with caution as many uncertainties are involved.

Besides highlighting the flaws of LCAs and comparisons between them, some general and still uncertain "take-home messages" concerning the relative performances of the different PDO production pathways are:

- The results indicate that the biobased production of PDO from glycerol has lower NREU and GHG-emissions than the production based on fossil fuels. This result fits well into the general trend that biobased production pathways usual perform better in those impact categories (see among others: Cok et al. 2014; Bos et al. 2011; OECD 2011; Dornburg, B. G. Hermann, et al. 2008; Cherubini et al. 2009). This is also backed by the results of the other three papers on the biobased PDO production from glucose which shows significant improvements compared to the respective fossil pathways (see Table 15).

  TABLE 15: REDUCTIONS IN NREU AND GHG-EMISSIONS OF THE BIOBASED PDO PRODUCTION COMPARED TO THE RESPECTIVE FOSSIL BASED PDO PRODUCTION (Expressed in "Improved by X %")

	Unit	DuPont	Anex & Ogletree	Urban & Bakshi
NREU	%	42,4	39,3	69,1
GHG	%	56,4	21,4	70,5

- The comparison to biobased production pathways from glucose seems to indicate that the PDO production from glycerol might not be the best solution, but could be environmentally competitive to existing technologies if further process improvements are made.
- While fossil based production processes are relatively more mature and may have a lower potential for improvements, biopolymer production technologies are still in their infancy and might have a more dramatic optimization potential (Anex & Ogletree 2006). Assuming optimization measures like indicated in the sensitivity analysis and believing in the positive long term effects of learning curves one might conclude that the biobased production from glycerol is environmentally desirable (at least concerning NREU and GHG-emissions) if it substitutes the production based on fossil fuels.
- Considering the future scenarios for biodiesel production (chapter 4.2) rising glycerol prices (along with a rise of the economic allocation factor) might change this picture in favor of the competing production pathways. Hence, from a long-term perspective the production from glucose (given its stable supply) could be the more desirable option.

8 CONCLUSIONS AND DISCUSSION

As stated in the introduction (chapter 1) the markets are currently facing a high supply of glycerol, which raised the question about its value-added use. Several authors therefore looked at the possible use of glycerol for the PDO production. However, so far scientific literature did not address the environmental impacts of a glycerol-based PDO production compared to conventional production pathways. To fill this knowledge gap this paper aimed at answering the following research question:

> *What are the environmental impacts of the production of biobased 1,3-propanediol from glycerol and how do the results relate to existing studies of the petro-chemical production of propanediol as well as the biobased production from corn?*

To answer this main research question a LCA screening of the environmental impact of the biobased PDO production from glycerol was conducted, which was limited to the midpoint indicators NREU and GHG - emissions. Additionally, the results were benchmarked to alternative production pathways that have been assessed by other studies. During that process the six subquestions formulated in chapter 1.2 have been addressed.

This closing chapter presents the findings and answers each of those sub-questions and ends with some final conclusions and recommendations for further research.

1. *What are the energy and material inputs and outputs throughout the production of 1,3 propanediol from glycerol?*

The LC inventory (chapter 6.2.3) provides an overview of all the relevant inputs and outputs of the PDO production process. The energy inputs are steam for heating and electricity for mixing, agitation and centrifugation processes. Relevant material inputs include glycerol, isobutyraldehyde and water, either as process water or for cooling processes. Emissions of the production are waste water, used cooling water and Bacterial residues.

2. *What are the most contributing sub-processes in the production of 1,3-propanediol from glycerol?*

The PDO production has been structured in three sub-processes. Of those PDO recovery and purification is the process with the biggest contribution to the total environmental impact (62 % in GHG, 68 % in NREU). It is followed by the glycerol production (29 % in GHG, 23 % in NREU) and the fermentation, which has the smallest impact (around 9 % in both categories). The use of natural gas and heavy oil is a crucial contributor to the environmental impact and explains the influential role of

the PDO recovery and purification which requires large amounts of steam from those fossil energy sources (see chapter 6.3).

3. *What are predominant biodiesel / glycerol production pathways in Europe and how is their relative environmental performance?*
4. *How do the environmental impacts of the 1,3 propanediol production from glycerol relate to the initial glycerol production?*
5. *What are future trends in the European biodiesel / glycerol production and how could they influence the glycerol-based 1,3-propanediol production?*

A literature review showed that rapeseeds and sunflower are the only oil-based crops with a substantial contribution to the total energy crop production in Europe, with rapeseeds having the major share. The analysed studies had partly contradicting results and could thus not reveal a clear preference for one of the two concerning their environmental performance. Hence, the scale of production and the data availability were finally the decisive factors that spoke in favour of choosing glycerol from rapeseeds as input for this assessment.

Glycerol production is with 23 % (NREU) and 29 % (GHG) the second biggest contributor to the impacts of the total PDO production (see chapter 6.3). As the sensitivity analysis suggested (see chapter 6.4.1) this contribution significantly increases when applying energy- or mass-based allocation. Due to changes in biofuel policy it is expected that the supply of glycerol will decrease in the coming years which might lead to a rise in glycerol prices (see chapter 4.2). Consequentially the economic allocation factor would increase and thus lead to a more significant contribution of glycerol production to the total environmental impact of PDO production.

6. *How do the aggregated results (GHG-emissions & NREU) of the 1,3-propanediol production from glycerol relate to the propanediol production from corn and fossil oil?*

Three scenarios (base case, optimization, ideal) have been developed in this paper and benchmarked to results of three other LCA-studies on PDO production (DuPont Tate & Lyle 2009; Anex & Ogletree 2006; Urban & Bakshi 2009). The comparison (see chapter 7) indicates that the biobased PDO production from glycerol has fewer GHG-emissions and a lower NREU than fossil production pathways from acrolein or ethylene oxide.

The comparison to biobased alternatives from glucose does not provide an as clear trend, but suggests that although the glycerol-based PDO production might currently not be the best option, it could still be environmentally competitive (concerning NREU and GHG-emissions) if further process improvements are made (as indicated by the optimization and ideal scenario). However, future

projections (see chapter 4.2) predict a diminishing supply of glycerol which could hamper the market implementation compared to the existing technologies.

7. *What are the limitations of such an analysis and comparison?*

Since many impact categories have not been assessed in this study it was clear from the start that the results will not display the full picture of the environmental impacts of the glycerol-based production pathway, but will provide an initial screening of chosen categories. Besides the restrictions in scope further limitations that are frequently mentioned in literature apply to this study. To those belong the inconsistency of the data, which often depends on simulations, the subjectivity of choices and the inability to make universal statements about the environmental performance of products. To address the often criticized lack of transparency of LCA studies, all calculations and choices made have been revealed and publicly available data was used where possible. Also the limited time frame available for conducting this research has to be considered as an influential limitation. While all assumptions were based on the best available information the author had at hand, a more encompassing literature review might have provided more accurate numbers and assumptions.

Benchmarking the studies prove to be difficult due to the different methodologies applied and choices made. Especially the lack of transparency of the DuPont- and Anex & Ogletree study made it difficult to explain the observed differences. Therefore only uncertain trends and conclusions have been obtained which have to be used with caution.

However, this study was able to answer the research questions by providing a first screening of the environmental performance of biobased PDO production from glycerol and gave - via a contributional and a sensitivity analysis – an indication which sub-processes have potential for improvement. The benchmarking to other production pathways indicated that the glycerol-based production pathway is environmentally preferable compared to fossil alternatives and might be competitive with biobased PDO from glucose, if the production process is further optimized. Moreover, the study gave an insight to the future development of the biodiesel market which might negatively influence the prospects of a glycerol-based PDO production on long term. Nevertheless, on the short and medium term it could be beneficial to induce a value-added usage of the abundant glycerol supply for which the PDO production would be one example.

This analysis can be the basis for further, more encompassing assessments which do not just consider GHG- emissions and NREU, but include more environmental impact categories. To obtain a more complete picture of the sustainability of the production process also economic and social aspects are worth considering. Furthermore, a direct comparison to the other production pathways within one

study, using the exact same methodology and system boundaries, would be valuable as it reduces the limitations of benchmarking results based on different methodologies and scopes. Future assessments might moreover benefit from data input of by then existing pioneer-plants (see chapter 1.1) that produce PDO from glycerol and not anymore solely depend on models and assumptions.

The difficulties that occurred within the benchmarking of the different LCA studies should be a further incentive to increase the efforts in harmonizing LCA methodologies and foster transparency, which would not just increase the acceptability of LCAs (Finnveden 2000) but also simplify future comparisons to achieve sounder results.

As an environmental assessment of glycerol-based PDO production has not been conducted so far, this study provided some valuable new insights on its performance and could therefore be of guidance for future efforts in research or product development with regard to a possible market implementation.

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APPENDICES

APPENDIX 1: FLOWSHEET FOR THE PDO RECOVERY AND PURIFICATION

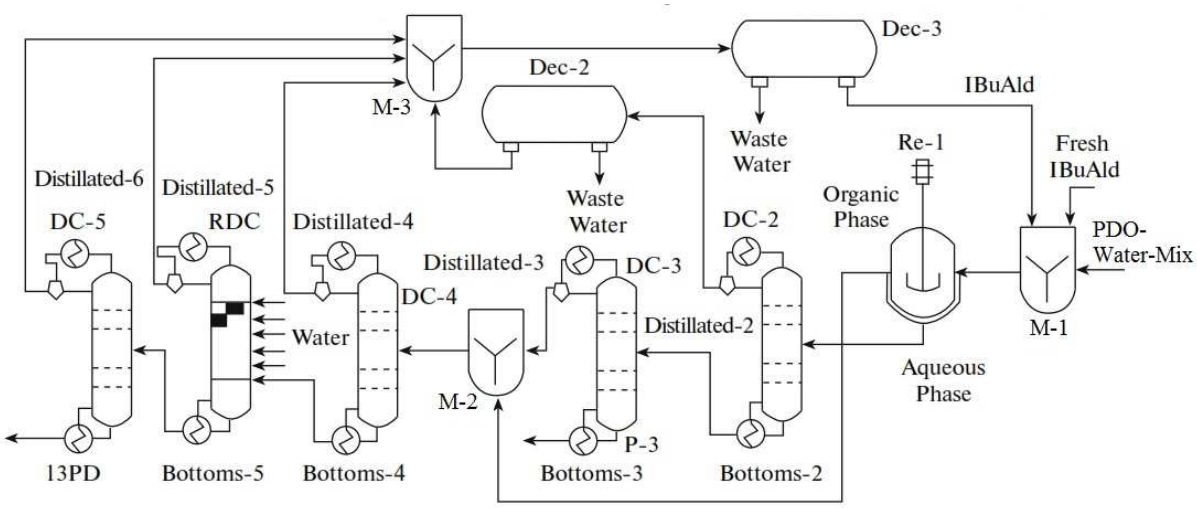

FIGURE 47: FLOWSHEET FOR THE PDO RECOVERY AND PURIFICATION

Read from right to left.
M = Mixer, Re = Reactor, DC = Distillation Column, RDC = Reactive Distillation Column, Dec = Decanter

APPENDIX 2: CONTRIBUTIONAL ANALYSIS OF THE RAPE OIL PRODUCTION

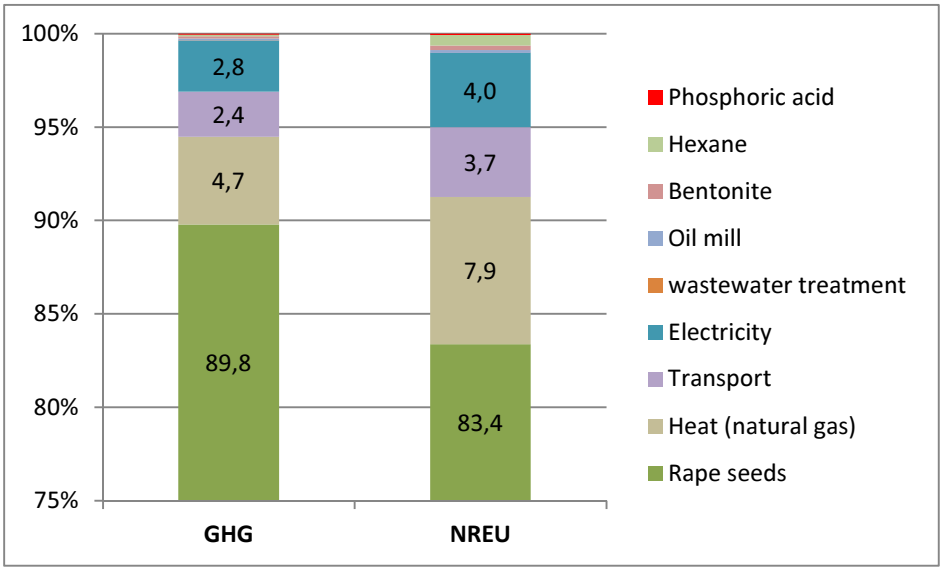

FIGURE 48: CONTRIBUTIONAL ANALYSIS OF THE RAPE OIL PRODUCTION

APPENDIX 3: CONTRIBUTIONAL ANALYSIS OF THE RAPE SEED CULTIVATION

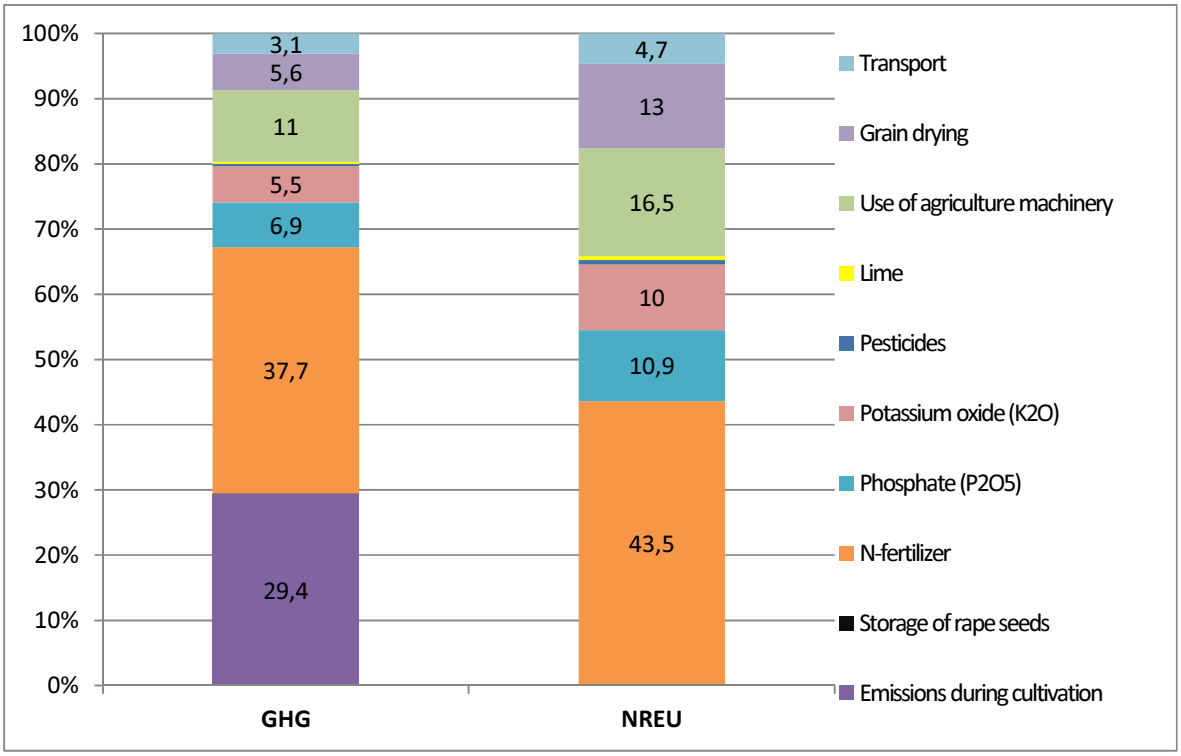

FIGURE 49: CONTRIBUTIONAL ANALYSIS OF THE RAPE SEED CULTIVATION

APPENDIX 4: CALCULATION OF THE CO_2-EMISSIONS RESULTING FROM THE INCINERATION OF PDO

As PDO is processed, used and disposed in many different ways it is not possible to determine one disposal pathway with all its details. Therefore a very simplified scenario was chosen: The incineration of 1kg PDO. A complete incineration without leftovers is assumed. All infrastructure necessary for that incineration will be ignored as it is the same for both versions of PDO and will therefore not affect the relative comparison. The same is true for the energy gained from incineration.

The formula of PDO is $C_3H_8O_2$, its structure is shown in Figure 50.

FIGURE 50: CHEMICAL STRUCTURE OF PDO

The equation for a complete incineration is as follows:

$C_3H_8O_2 + 4O_2 \rightarrow 3\,CO_2 + 4H_2O$ + Combustion heat

Three molecules of CO_2 result from the incineration of PDO. The next step is to calculate the mass of those CO_2 emissions.

According to the functional unit the analyzed mass of PDO is 1 kg = 1000 g. The molar mass of PDO is 76,09 g/mol. With this information we can calculate the Mole of 1 kg PDO: mass / molar mass = 1000g / 76,09 g/mol = 13,14 mol.

From one molecule PDO result 3 molecules CO_2. Hence, the Mole of the created CO_2 are 3 x 13,14 mol = 39,42 mol.

The molar weight of CO_2 is 44,01 g/mol. Knowing the Mole and the molar weight, the mass of CO_2 can be calculated: m_{CO2} = 39,42 mol x 44,01 g/mol = 1,734 kg

The combustion heat resulting from the incineration can be calculated by looking up the specific combustion heat of PDO (1843 kj/mol; Chemical Book n.d.) and multiplying it with the mole per kg PDO:

Combustion heat for 1kg PDO = 13,14 mol * 1843 kj/mol = 24217,02 kJ = 24,21702 MJ

To conclude, 1,734 kg CO_2 are emitted during the complete incineration of 1 kg PDO. The incineration produces 24,2 MJ combustion heat. The results are summarized in the table below

TABLE 16: RESULTS FOR THE INCINERATION SCENARIO

Equation	$C_3H_8O_2$ + $4O_2$ →	$3CO_2$ + $4H_2O$ + 24,2 MJ
Masse	1 kg	1,734 kg
Molar weight	76,09 g/mol	44,01 g/mol
Mole / kg PDO	13,14 mol	39,42 mol