RIGA TECHNICAL UNIVERSITY

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LIFE CYCLE ASSESSMENT OF POLYOL MONOMERS FOR POLYURETHANE PRODUCTION

Doctoral Thesis

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DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Sciences (*Ph. D.*) is my own. I confirm that this Doctoral Thesis had not been submitted to any other university for the promotion to a scientific degree.

Anda Fridrihsone ……………………………. (signature)
Date: ………………………

The Doctoral Thesis has been written in English. It consists of an Introduction; 3 Chapters; Conclusion; 43 figures; 21 tables; the total number of pages is 115. The Bibliography contains 229 titles.

ANNOTATION

The development of advanced new materials and technologies from bio-based products is immensely needed as the world is facing an ever-increasing variety of challenges due to increasing public concern about global sustainability. Polyurethane polymers present a broad spectrum of materials that are produced to meet the needs for various applications, from the automotive industry, building and construction to appliances, furnishing, marine and medicine.

The general objective of the Thesis is to carry out comprehensive cradle-to-gate Life Cycle Assessment of rapeseed oil-based polyols suitable for polyurethane material production. The thesis is dived in three parts. Literature review (chapter I) aims to introduce the reader briefly with sustainability challenges, plastics with focus on polyurethane and state-of-the-art in natural oil-based polyurethanes and their environmental assessment. The methodological chapter (chapter II) aims to provide the reader with a description of the main Life Cycle assessment methodologies applied for rapeseed oil bio-polyol analysis. The results and discussion (chapter III) of this thesis are divided into four parts.

Chapter III Part I presents Life Cycle Inventory of winter and spring rapeseed production in Latvia as a case study country in Northern Europe. In-depth and up-to-date agricultural practices used in the region under study data were provided by a large agricultural company located in Zemgale region in Latvia.

Chapter III Part II presents an inventory of rapeseed oil mill stage with data provided by operation oil mill in Zemgale region. Different allocation methods are applied to further investigate the effect of different allocation methods on the environmental profiles of rapeseed oil-based bio-polyols and the consequences of applying these methods considering the main aims of the study.

Chapter III Part III presents Life Cycle Impact Assessment of winter and spring rapeseed production and rapeseed oil production. Environmental performance is analyzed with Cumulative energy demand impact indicator along with the ReCiPe impact assessment methodology. The main environmental hotspots were identified. Sensitivity analysis was performed.

Chapter III Part IV presents results of the Life Cycle Assessment of two rapeseed oil-based bio-polyols. Life Cycle Inventories were built on experimental data for polyol synthesis that were performed in a pilot-scale (50 L reactor). Bio-based polyols were compared with the petrochemical counterpart. The two developed rapeseed oil-based polyols were analyzed with three different modelling approaches for the bio-based feedstock stage. Sensitivity analysis was performed.

ANOTĀCIJA

Progresīvu jaunu materiālu un tehnoloģiju izstrāde no atjaunojamām izejvielām ir ārkārtīgi nepieciešama, jo, pieaugot sabiedrības rūpēm par globālo ilgtspēju, pasaule saskaras ar aizvien pieaugošu izaicinājumu dažādību. No poliuretāna polimēriem tiek ražots plašs materiālu klāsts, apmierinot vajadzības dažādās pielietojuma jomās: sākot no automobiļu rūpniecības, celtniecības, sadzīves iekārtām un līdz pat mēbeļu, jūras un medicīnas industrijām.

Promocijas darba vispārīgais mērķis ir veikt visaptverošu "no šūpuļa līdz vārtiem" Aprites cikla novērtējumu rapšu eļļas polioliem, kas piemēroti poliuretāna materiālu ražošanai. Promocijas darbs ir sadalīts trīs daļās. Literatūras apskata (1. nodaļa) mērķis ir sniegt lasītājam īsu ievadu par ilgtspējības izaicinājumiem un par polimēriem uzsverot poliuretānus, kā arī par jaunākajiem sasniegumiem par poliuretāniem no dabas eļļām, un to vides novērtējumu.

Literatūras apskats (1. nodaļa) īsumā izskaidro lasītājam ilgtspējības izaicinājumus, sniedz ievadu par plastmasām, īpaši poliuretāniem, un iepazīstina ar jaunākajiem sasniegumiem un vides novērtējumu poliuretānu, kas iegūti no dabīgām eļļām, jomā.

Metodiskās daļas (2. nodaļa) mērķis ir sniegt lasītājam aprakstu par galveno Aprites cikla novērtējuma metodoloģiju rapšu eļļas biopoliolu analīzei.

Disertācijas rezultāti un diskusija (3. nodaļa) ir sadalīta četrās daļās.

3. nodaļas 1. apakšnodaļā sniegta detalizēta Aprites cikla inventarizācija ziemas un vasaras rapša sēklu audzēšanai Latvijā kā gadījuma izpētes valstij Ziemeļeiropā. Detalizēta un padziļināta informācija par lauksaimniecības praksi pētāmajā reģionā, tika iegūta no liela lauksaimniecības uzņēmuma, kas atrodas Latvijas Zemgales reģionā.

3. nodaļas 2. apakšnodaļā sniegta Aprites cikla inventarizācija rapšu eļļas spiestuves posmam ar datiem no rapšu eļļas spiestuves Zemgales reģionā. Tika izmantotas dažādas sadales metodes, lai novērtētu to ietekmi uz rapšu eļļas biopoliolu ekoloģiskajiem raksturlielumiem un šo metožu piemērošanas sekām, ņemot vērā galvenos pētījuma mērķus.

3. nodaļas 3. apakšnodaļā veikts Aprites cikla ietekmes novērtējums ziemas un vasaras rapšu sēklu ražošanai un rapšu eļļas ieguvei. Ekoloģiskie raksturlielumi analizēti, izmantojot Kumulatīvo enerģijas pieprasījuma ietekmes rādītāju kopā ar ReCiPe ietekmes novērtēšanas metodi. Tika noteikti galvenie vides karstie punkti un veikta jutības pārbaude.

3. nodaļas 4. apakšnodaļā prezentēti divu rapšu eļļas biopoliolu aprites cikla novērtējuma rezultāti. Aprites cikla inventarizācijas pamatā ir eksperimentāli dati par poliolu sintēzi pilot-reaktorā (50 L). Aprites cikla inventarizācija dati tika ievākti no eksperimentāliem datiem no poliolu sintēzes pilot-mēroga (50 L) reaktorā. No atjaunojamām izejvielām iegūtie polioli tika salīdzināti ar ekvivalentu no naftas ķīmijas. Divi izstrādātie rapšu eļļas biopolioli tika analizēti izmantojot trīs dažādas sadales sistēmas atjaunojamās izejvielas ieguves posmam. Tika veikta jutības pārbaude.

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The last few years have been a wild ride with having a baby and trying to complete my PhD degree.

The last few years can be expressed with this quote by Angela Schwindt:

"While we try to teach our children all about life,
Our children teach us what life is all about"

I would like to thank my fantastic son, who reminded me to enjoy life, see the sunshine, smell the strawberries, jump from joy seeing first snowfall and just see, feel and embrace the little things in life. He offers me endless happiness, joy, challenges and motivation in my life, and I wish I could have his never-ending energy. I could never have accomplished this if it were not for the support, unconditional love and encouragement that I have received from my wonderful Fridrihsoni family with a very special thank you for my mom. Thank you for all the hours you have put into looking after my kid. Huge thanks go out to my family in Denver, who have supported and believed in me. Inta, thank you for all the proofreading.

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My sincere gratitude for helping me to stay sane during this PhD thesis writing process goes out to my friends.

TABLE OF CONTENTS

LIST OF ACRONYMS AND ABBREVIATIONS

CED	Cumulative Energy Demand
DEA	Diethanolamine
EA	Energy allocation
EC	European Commission
EPD	Environmental Product Declaration
EU	European Union
FAOSTAT	Statistics database of Food and Agriculture Organization of the United Nations
FU	Functional unit
GHG	Greenhouse gas
GNOC	Global Nitrous Oxide Calculator
GWP	Global warming potential
ILUC	Indirect land use change
IPCC	Intergovernmental Panel on Climate Change
ISO	International Organization of Standardization
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LIBRA	Latvian Bioeconomy Strategy 2030
LSIWC	Latvian State Institute of Wood Chemistry
MA	Mass allocation
MVA	Market value allocations
NIPU	Non-isocyanate polyurethane
NOP	Natural oil polyol
NRCED	Non-Renewable Cumulative Energy Demand
PPDB	Pesticide Properties Database
PU	Polyurethane
RO	Rapeseed oil
SDGs	Sustainable Development Goals
SE	System expansion
TEA	Triethanolamine
UN	United Nations

INTRODUCTION

Research Scope

The renaissance of bio-based materials has been initiated over the last few decades due to limited fossil resources and environmental issues, with global warming, and its effect on climate, being one the most pressing issues. Today, the European Union (EU) acknowledges that bio-based materials play a key role in the transition from a fossil to a bio-based economy, and they are essential to the development of a more circular and decarbonized economy. Bio-based materials have received support and are promoted by policymakers and different advisory bodies at the national level, for example, Latvian Bioeconomy Strategy 2030 (LIBRA) [1] and supranational levels, EU with its original Bioeconomy strategy (2012) [2] and updated Bioeconomy strategy (2018) [3] and the United Nations (UN) "Transforming our World: The 2030 Agenda for Sustainable Development" [4]. Thus, the development of sustainable bio-based materials is one of the cornerstones to achieve the transition towards sustainable development and to build a carbon-neutral future in line with the climate objectives of the Paris Agreement [5].

A lot of research is carried out to replace a variety of petrochemical building blocks with bio-based building blocks that can be produced via many different chemical pathways. For a long time, the claimed environmental benefits of bio-based materials were not justified. However, given the urgency of environmental issues the world is facing, with climate change being one of the most urgent, the claimed environmental benefits of the materials have to be justified. This can be done using the Life Cycle Assessment (LCA), which is a state-of-the-art methodology to assess the environmental impacts of products and processes towards a holistic cradle-to-grave approach. According to the International Organization of Standardization (ISO), the LCA is defined as "compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle" [6]. LCA implementation is a complex process due to many factors – from system boundary establishment to accurate data obtainment and interpretation of the results. LCA will give the most consistent results when applied to existing production systems due to the data quality, however, it can also be used during the research and development stage to identify the environmental hotspots and try to reduce them.

EU and Latvia have set out a key role for the bioeconomy in the upcoming decades. Two of the LIBRA`s main objectives are to increase the added value of bioeconomy products and to increase the value of bioeconomy production exports. As to the author's knowledge, the results presented in this Thesis will be the first bio-based product developed in Latvia that will also be assessed from the environmental viewpoint.

Thus, the subject of the Thesis is topical. The Thesis aims to assess the environmental performance of a bio-based material developed in Latvia from the locally available feedstock, namely, rapeseed oil-based polyols for subsequent use in polyurethane (PU) production. All these aspects have determined the choice of objectives and content of the Thesis.

Objectives of the Research

The main objective of the Thesis is to carry out a comprehensive cradle-to-gate LCA of rapeseed oil-based polyols suitable for PU material production.

To achieve the general objective, specific objectives have been formulated:

- to review the relevant scientific literature on LCA evaluation of natural oil polyols (NOPs);
- to carry out a detailed Life Cycle Inventory (LCI) of rapeseed and its oil production in Latvia as a case study country in Northern Europe;
- to evaluate environmental burdens associated with the rapeseed oil-based polyol production based on developed and up-scaled synthesis method.

To reach the objectives of the research, the Thesis has to answer the following research questions.

Research question 1

What agricultural practices are used in Latvia? What is the up-to-date LCI for rapeseed, winter and spring, produced in Latvia that is used as a case study for the Northern European region? What is the regionalized inventory of rapeseed oil production taking into account specific yields and used technologies of the case study? Are there any issues with LCI and harmonization with the ecoinvent database?

The answer to the first question will build an in-depth up-to-date regionalized LCI for the growing phase of rapeseed and production phase of rapeseed oil. Critical and week points in harmonization might be identified during this stage. The answer to Research question 1 is a crucial input for Research question 2 as LCI is generally the base of the LCA study and the quality of the available data determines the quality of LCA to some extent.

Research *question 2*

What is the environmental characterization of rapeseed and rapeseed oil production in Latvia? What are the environmental hotspots? What are the most essential options for improving the environmental performance of these products? Rapeseed oil production yields two products – oil and cake. What is the impact of a co-product allocation in the LCA results of rapeseed oil production?

The answer to Research question 2 will identify the environmental impacts of rapeseed and rapeseed oil production in Latvia. The impact of different co-product allocation will be explored and will be also used in Research question 3.

Research *question 3*

Are bio-based feedstock-based polyols better than the petrochemical alternative? Are there savings of greenhouse gas emissions (GHG) during bio-polyol production? Are there savings of non-renewable energy in a bio-based polyol production system? What are the hotspots? What are the impacts of rapeseed oil co-product allocation in the environmental impact of bio-polyol? What is the impact of the Latvian electricity mix in comparison to other countries on the polyol environmental performance?

Research question 3 can be answered by performing LCA of the developed bio-polyols based on up-to-date regionalized LCI dataset for the agricultural feedstock combined with detailed LCI of up-scales polyol synthesis that is based on experimental results.

Research Methodology

The research methodology is based on the methodological framework of an LCA governed by the international standard ISO 14040-44. The research methodology is based on primary data – information from in-depth interviews carried out with representatives of rapeseed and rapeseed oil production companies, producers and distributors of plant protection products and fertilizers. The primary data was also gathered for up-scaled rapeseed oil-based polyol synthesis and characterization; the data was based on experiments carried out in a chemical laboratory. Also, secondary data were used for the research, such as the database of the Central Statistical Bureau of Latvia, Eurostat database and publications, the Statistics database of Food and Agriculture Organization of the UN (FAOSTAT), Pesticide Properties Database and scientific publications and official reports. The approbation of the methodology has been made toward the specific case study for the Latvian context.

The LCA software SimaPro 9.0 by Pré Consultants and LCI database ecoinvent v3.5 were used to create the LCA model and undertake the impact assessment calculations.

The research is designed in key sections to avoid black box unit processes and provide transparent results, as without transparency the LCA results mean very little. The key research stages are as follows:

- detailed LCI of rapeseed production in Northern Europe with Latvia as a case study country;
- LCI of rapeseed oil production;
- LCA of rapeseed and rapeseed oil production;
- LCA of rapeseed oil-based polyol production.

Separated unit processes will allow these results to have a larger scientific and practical significance which will be described in the following sections of the Thesis.

The Dissertation is composed of five sections – Introduction, Literature Review, Methodology, Results and Discussion, Conclusions and Recommendations for future work. The Introduction provides an introduction to the research scope of the Thesis. The main goals and tasks of the study are presented. The methodology and structure of the Dissertation are indicated at the end of the first section.

Literature Review provides a brief introduction into sustainability challenges, plastics with focus on PU and state-of-the-art in natural oil-based PU and their environmental assessment.

Chapter Methodology concerns the LCA methodology and presents a short introduction of LCA. The four phases of the LCA methodology are described according to the ISO 14040-44 series. A short description of software and databases is given. Finally, a short description of rapeseed oil-based polyol synthesis is presented.

The Results and Discussion chapter provides detailed results on LCI of rapeseed agricultural phase and harmonization with ecoinvent databases, followed by LCA of rapeseed. Afterwards, LCA of rapeseed oil is performed where the impact on different allocation approaches is demonstrated and finally LCA of two rapeseed oil derived polyols is presented. To verify the plausibility of the LCA study, the results are compared with international research studies.

The Conclusions and Recommendations chapter finalizes the work, summarizing conclusions and further research perspectives.

Scientific Significance and Contribution

The results of the LCA can vary significantly from product to product, depending on the feedstock type and production, the chemical transformation technology, means of transport, and other factors, there is no "*one LCA fits all*" concept.

This research provides science-based results on the environmental impacts of the specific bio-based product – rapeseed oil diethanolamide and rapeseed oil triethanolamine ester polyols – produced in Latvia from the locally available feedstock. The inventory for rapeseed oil-based polyol production is based on the experimental data at a laboratory where the polyol synthesis process has been validated at pilot-scale production. Moreover, the developed rapeseed oil-based polyols have been demonstrated and validated for spray-applied PU coating production and rigid PU foam thermal insulation, which is an important aspect in the bio-based product development as not all technological approaches yield successful up-scaling and demonstration in the end application. The research offers a complete and accurate identification and quantification of the environmental performance of the rapeseed oil-based polyols. It will contribute to filling the lack of information on the environmental performance of NOPs. Moreover, the NOPs LCI can be used in other research studies to compare different bio-based polyols, their technological production approach and resulting environmental impact.

The LCA results conclude that for analysed bio-polyols, a cradle-to-gate LCA showed environmental benefits for bio-based polyols produced from rapeseed oil compared to petrochemicals polyols. The savings in cumulative energy demand, including non-renewable cumulative energy demand, were demonstrated. The claimed environmental benefits in lower GHG emissions for bio-polyol production have been justified.

The results will contribute to supporting the future bioeconomy policies and decision-making at the EU level.

The Thesis presents a detailed quantitative and qualitative LCI analysis for rapeseed, rapeseed oil production and rapeseed oil polyol production that is based on valuable primary data. The outcomes from the presented study both in terms of LCI and LCA will be essential on one hand to provide outcomes at local conditions (i.e. Northern European country Latvia) and on the other hand to better compare the overall sustainability of the process with the actual state of knowledge at EU and in the worldwide context.

The main findings and outputs from the research work have been discussed in international conferences and presented in peer-reviewed scientific papers supporting the novelty and importance of the research work.

Practical Significance

The results and outcomes presented in the Thesis can be used to enhance the practical applicability and usefulness of the findings to other LCA researchers, in terms of:

- LCI of rapeseed agricultural stage results can be implemented in the LCI databases, such as ecoinvent, where at the moment there are no respective data sets for Latvia, Baltic States or Northern Europe. It will contribute to the regionalization of LCI. Moreover, the results can be used in other research studies where a fully developed bio-based economy is studied. The results would be regionalized rather than based on a data set taken from a database. The data about feedstock production would be built on up-to-date agricultural practices used in a specified region.
- LCI of rapeseed oil results can be implemented in the LCI databases, such as ecoinvent, where at the moment there are no respective data sets for Latvia, Baltic States or Northern Europe. The results for rapeseed oil can be used in future LCA studies where bio-based polyols have been synthesized employing new synthesis approaches, such as enzymatic catalysis or other. Moreover, the results can be used to study biodiesel production in Latvia and for comparison of different scenarios – the bio-based feedstock for fuel vs. chemical production. The results would be regionalized rather than based on a data set taken from a database.
- LCI for rapeseed oil-based polyol results can be implemented in the above-mentioned ecoinvent, as at the moment there are only datasets for petrochemical polyol representing industry average and soy-based polyol from U.S. LCI Database. The results can be used to prepare the Environmental Product Declaration (EPD), which is an independently verified and registered document that communicates transparent and comparable information about the life-cycle environmental impact of products. A bio-based product, namely in this case rapeseed oil-based polyol, with an EPD could encourage the demand for the product that causes less stress on the environment.
- It is a contribution to the integration process of Latvia into an interconnected European research area in regards to bio-based materials and their environmental assessment.

Approbation of the Research Results

The results of the research have been published in scientific journals that are indexed in Scopus and Web of Science databases and have been presented at international scientific conferences.

1. **Anda Fridrihsone**, Francesco Romagnoli, Ugis Cabulis. Environmental Life Cycle Assessment of rapeseed and rapeseed oil produced in Northern Europe: a Latvian case study. Sustainability 2020, 12(14), 5699; https://doi.org/10.3390/su12145699
2. **Anda Fridrihsone,** Francesco Romagnoli, Vladimirs Kirsanovs, Ugis Cabulis. Life Cycle Assessment of Vegetable Oil Based Polyols for Polyurethane Production. Journal of Cleaner Production 266 (2020) 121403. https://doi.org/10.1016/j.jclepro.2020.121403

3. **Anda Fridrihsone**, Francesco Romagnoli, Ugis Cabulis. Life Cycle Inventory for winter and spring rapeseed production in Northern Europe. Journal of Cleaner Production 177 (2018) 79–88. DOI: https://doi.org/10.1016/j.jclepro.2017.12.214
4. **Anda Fridrihsone-Girone**. Preliminary Life Cycle Inventory of Rapeseed Oil Polyols for Polyurethane Production. Journal of Renewable Materials, Volume 3, Number 1, March 2015, pp. 28–33(6), DOI*:* http://dx.doi.org/10.7569/JRM.2014.634136
5. U. Stirna, **A. Fridrihsone**, B. Lazdiņa, M. Misāne. Dz. Vilsone. Biobased Polyurethanes from Rapeseed Oil Polyols: Structure, Mechanical and Thermal Properties. Journal of Polymers and the Environment 21 (4) 2013, pp. 952–962. DOI: https://doi.org/10.1007/s10924-012-0560-0

In addition to the five papers that form the main body of the Thesis, the following publications dealing with the validation and demonstration of the developed rapeseed oil-based polyols in spray-applied polyurethane coatings were also developed and published during the PhD studies.

1. **Fridrihsone-Girone, A**., Stirna, U., Misane, M., Lazdiņa, B., Deme, L. Spray-applied 100% volatile organic compounds free two component polyurethane coatings based on rapeseed oil polyols. Progress in Organic Coatings, 2016, 94, 90–97. DOI: https://doi.org/10.1016/j.porgcoat.2015.11.022
2. EU patent. U. Stirna, M. Misane, **A. Fridrihsone-Girone**, U. Cabulis, S. Gaidukovs, V. Tupureina. Method for producing spray-applied polyurethane coatings on metal constructions. EP2865724 (A1). 29.04.2015.
3. **A. Fridrihsone-Girone,** U. Stirna. Characterization of polyurethane networks based on rapeseed oil derived polyol. Polimery/Polymers, Volume 59, Issue 4, 2014, pp. 333–338. DOI: dx.doi.org/10.14314/polimery.2014.333
4. U. Stirna, **A. Fridrihsone-Girone**, V. Yakushin, D. Vilsone. Processing and properties of spray-applied, 100% solids polyurethane coatings from rapeseed oil polyols. Journal of Coatings Technology Research. 11 (3) 409–420, 2014. DOI: https://doi.org/10.1007/s11998-013-9545-8
5. **Fridrihsone, A**., Stirna, U., Lazdiņa, B., Misāne, M., Vilsone, Dz. Characterization of Polyurethane Networks Structure and Properties Based on Rapeseed Oil Derived Polyol. European Polymer Journal 49 (2013) pp. 1204–1214. DOI: http://dx.doi.org/10.1016/j.eurpolymj.2013.03.012

Results of the Thesis are published in the proceedings of the following international scientific conferences.

6. **A. Fridrihsone**, F. Romagnoli, U. Cabulis. Life Cycle Assessment of Polyurethane Materials from Biobased Feedstock. Sixth International Conference on Natural Polymers (ICNP 2018), 07–09 December 2018, India. SIL 15, p. 49 (*oral communication, short invited lecture*)

7. **A. Fridrihsone**, F. Romagnoli, U. Cabulis. Rapeseed Oil as a Feedstock for Polyols and Polyurethane Materials from the Life Cycle Perspective. SETAC Europe 24th LCA Symposium, 24–26 September 2018, Vienna, Austria. Abstract book. MO002, p. 22. (poster)
8. **Anda Fridrihsone**, Francesco Romagnoli, Vladimirs Kirsanovs. Rapeseed oil based polyols from the perspective of environmental footprint. International Conference on Bio-based Polymers and Composites 2018 (BiPoCo), September 2–6, 2018, Hungary. Abstract book. P40, p. 292. (*poster*)
9. **Anda Fridrihsone**, U. Cabulis, Francesco Romagnoli. Life cycle assessment of rapeseed oil based polyols for biobased polyurethane. Conference "The 6th International Conference on Biobased and Biodegradable Polymers (BIOPOL-2017)" proceedings in a flash drive (pp. 1–47). Mons (Belgium), 11–13 September 2017. (*poster*)
10. Urethanes Technology international. February/March 2014. Vol 31, No.1
11. **A. Fridrihsone-Girone**. Preliminary LCA of Rapeseed oil Polyols synthesized by transesterification with triethanolamine. In 5th Workshop Green Chemistry and Nanotechnologies in Polymer Chemistry, ECLIPSE Workshop, BIOPURFIL Workshop. Spain, Donostia – San Sebastian, 9–11 July 2014, in flash drive p. 19. (*poster*)
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1. LITERATURE REVIEW

1.1. Sustainable Development and Its challenges

The 20th century was the age of black gold or petroleum. During a little over 100 years, mankind enjoyed the prosperity of the petroleum-based economy. However, the unblemished optimism about the petroleum-based economy did not last [1]. The drawbacks of the petroleum-based economy were felt across the globe, as the environmental, geopolitical, and socioeconomic situation started to worsen. There was a need for a change in the economic model, it was clear that economic development issues are closely and directly related to environmental issues [2]. For example, it is estimated that when the country`s economy doubles, the emissions rise for 80 % [3].

The concept of sustainable development was first introduced to the public in the report "Our Common Future". The report, also known as the Brundtland Report, was published in 1987 by the World Commission on Environment and Development [4]. In the Brundtland report, Sustainable development was defined as follows (Fig. 1.1):

"Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs"

Fig. 1.1. Sustainable development definition, Brundtland definition, 1987 [4].

The goal of Sustainable development is to achieve balance/harmony between environmental sustainability, economic sustainability and socio-political sustainability. The typical representation of sustainability as three intersecting circles is depicted in

Fig. 1.2, it seems that this diagram was first introduced by Barbier et al. 1987 [5].

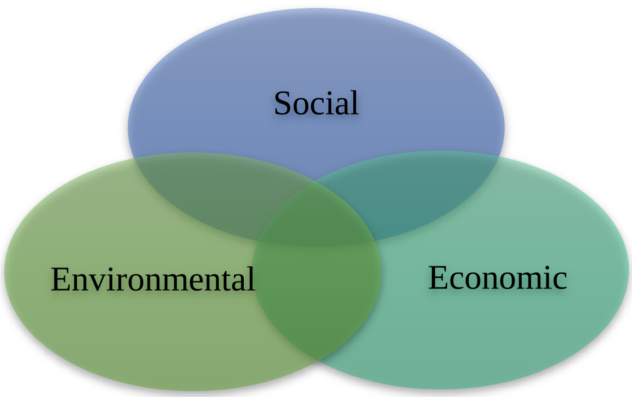

Fig. 1.2. Three pillars of sustainable development (adapted from Barbier et al. 1987 [5]).

Over the next decades, there have been several global initiatives to improve different aspects of key sustainability issues [6], [7]. The landmark initiatives embedding the sustainable development principles have been the Earth Summit in 1992 [8]. In 2000, the UN held a Millenium Summit in New York, where eight Millennium Development Goals were set for 2015 [9]. In 2005, the Kyoto protocol (signed 1997) came into force. Kyoto protocol has legally binding targets that require industrialized countries to reduce their greenhouse gas emissions by at least 5 % below 1990 levels and establishing the Clean Development Mechanism for developing countries [10]. The Doha Amendment was adopted, launching a second commitment period of the Kyoto Protocol [6]. In 2012, The Rio+20 Conference on Sustainable Development was held, where the focus was on green economy in the context of sustainable development [11]. In 2016, the Paris Agreement on climate change was signed. It aims to limit greenhouse gas emissions that would prevent global temperatures from increasing more than 2 °C above pre-industrial levels [12].

The latest landmark initiative is the Sustainable Development Goals by the UN. At the UN Sustainable Development Summit in 2015, world leaders adopted the agenda "Transforming our World: the 2030 Agenda for Sustainable Development", which includes a set of 17 Sustainable Development Goals (SDGs) aimed at ending poverty, fighting inequality and injustice, and tackling climate change by 2030. These 17 SDGs (Fig. 1.3. UN`s Agenda 2030: 17 SDGs, listed below, are all accompanied by specific targets – 169 in total. At the heart of UN agenda is the same principle as in Brundtland`s report to implement these 17 goals as follows: "They are integrated and indivisible and balance the three dimensions of sustainable development: the economic, social and environmental" [13].

Fig. 1.3. UN`s Agenda 2030: 17 SDGs [14].

Without doubt, greenhouse gas emissions and global climate change are one of the most central aspects of sustainability challenges the humankind is facing today. The reduction of fossil fuel use in energy production and transportation, new technologies and also improvement in the efficiency of already existing technologies are few of the most visible actions to tackle the global climate change. However, today humankind is also completely dependent on petroleum products for materials – plastics. Petroleum derived products are nearly in every product we use daily. Traditional materials, wood, metal, glass, leather, paper and rubber, are often replaced by plastics as they can offer better properties and are also cheaper than the traditional materials. The plastics along its life cycle also contribute to the global climate change as fossil resources are used. British Plastics Federation estimates that in Europe 4–6 % of oil and gas is used for the production of plastics, while 87 % is used for transport, electricity and heating (thus being the largest contributor to carbon emissions) [15]. Due to climate change and finite fossil resources, bioplastics have been in the focus of research [16]. New pathways to produce plastics can be directly related to achieving the SDG 7 and SDG 13 (Fig. 1.3) and substantially contribute to achieving other SDGs. However, to reach that the focus has to be interdisciplinary, where economic, social and environmental aspects are taken into account.

1.2. Bio-Based Europe

By the end of the 20th century, it was clear that an alternative economic model has to be proposed to repair mistakes of the past and ensure that further development is carried out in a sustainable manner. The bio-based feedstock used for the production of energy, chemicals and materials is an essential part of a sustainably sound transition. With this paradigm shift, the use of biomass as a feedstock for the production of chemicals is perceived as a means of “going green” [17].

The issue of sustainable development has been high on the EU`s list of priorities. For the last decades, with special focus during the last 10–15 years, the EU has been striving towards more innovative, resource-efficient, competitive and sustainable Europe and away from being petroleum-based society. There has been a number of policies, strategies, action plans and partnerships to support, foster and push bioeconomy vision [18], [19].

The bioeconomy concept was introduced in the first decade of the 21st century. In 2012, the European Commission (EC) adopted the strategy "Innovating for Sustainable Growth: A Bioeconomy for Europe", where bioeconomy was defined as “the production of renewable biological resources and the conversion of these resources and waste streams into value-added products, such as food, feed, bio-based products and bioenergy” [20]. In 2018, the Bioeconomy strategy was updated and refocused. The updated Bioeconomy strategy aims to accelerate the deployment of a sustainable European bioeconomy to maximize its contribution towards the 2030 Agenda and its SDGs, as well as the Paris Agreement [21]. The EU is taking an active role to implement the SDGs. The EU is fully committed to being a frontrunner and leader in implementing the global Agenda 2030, as outlined in its Communication on “Next steps for a sustainable European future” [22].

Moreover, Bioeconomy has gained and continues to gain further momentum globally. 21st is the Bioeconomy century where a great deal of effort, research and investment will be put on the transition from a fossil-fuelled to the renewables-driven economy. At the beginning of 2018, 49 countries were pursuing bioeconomy development in their policy strategies, however, the scope and depth, objectives, actors and focus of each policy varies greatly depending on the country [23]. However, the EU continues to be a trendsetter for the Bioeconomy worldwide.

The EU bioeconomy strategy is the foundation for Member State bioeconomy/bioeconomy related policy development. Strategies and other policy initiatives dedicated to the bioeconomy in the EU Member States are presented in Figure 1.4.

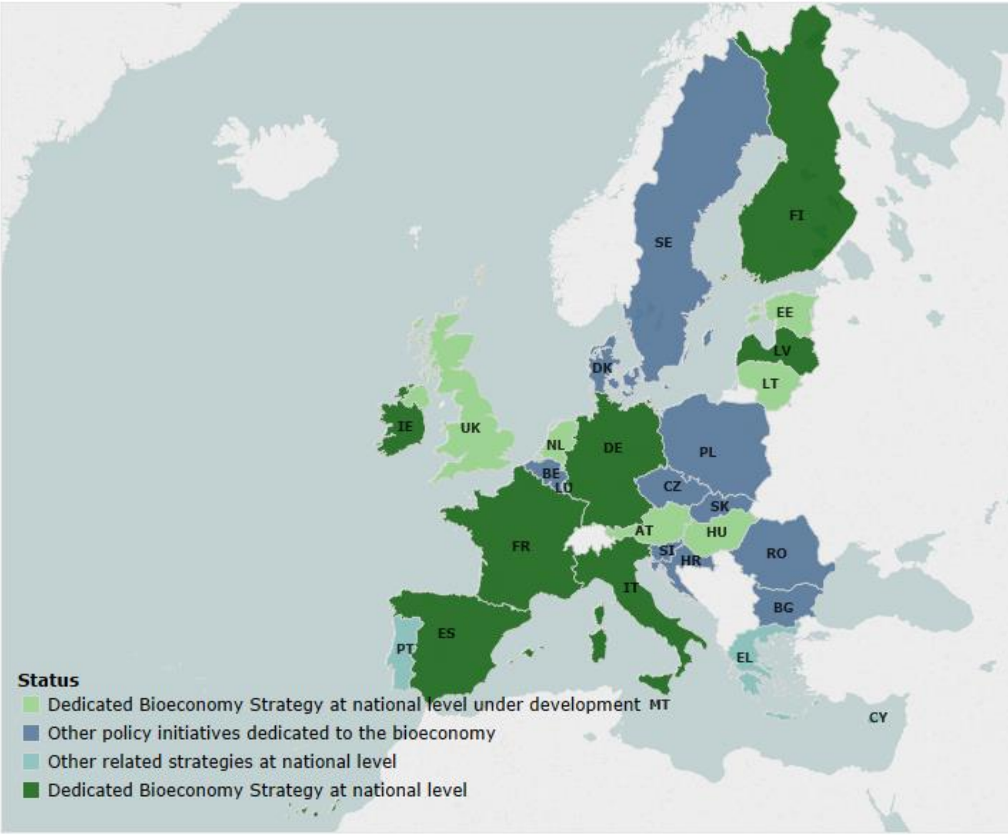

Figure 1.4. Strategies and other policy initiatives dedicated to the bioeconomy in the EU Member States. Status: March 2018 [24].

Latvia is one of the EU member states that have a dedicated Bioeconomy strategy at a national level. LIBRA 2030 was published at the end of 2017 [25]. Now, Latvia is the only country in Baltics, also in the Central-Eastern and South-Eastern European regions to have a dedicated Bioeconomy strategy. LIBRA is a long-term strategy for one of the priority directions of economic development of Latvia “Strategies for Smart Specialisation” (RIS3 direction “Knowledge-intensive bioeconomy”). Two of the LIBRA`s main objectives are to increase the added value of bioeconomy products and to increase the value of bioeconomy export production, the third objective is to promote and preserve employment in bioeconomy sectors by 2030 [25].

1.3. Vegetable Oils

One of the sectors that Bioeconomy covers is the conversion of produced, renewable biological resources into chemical products [21]. Among the others, the use of vegetable oils in the production of polymers and other chemicals is well integrated within the framework of the Bioeconomy concept. The production scheme would follow the cascade principle for which biomass should be used firstly for production of high-value applications, such as biomaterials and biochemicals, and afterwards leftovers and remains can be used for lower value applications – i.e. biofuels, bioenergy, biogas [26]. According to the published Sustainability Report by the European Chemical Industry Council in 2017, renewables comprise 10 % (7.8 million tonnes (t)) of total organic raw materials – material (feedstock) use only. Among the renewable components, Vegetable oils comprise 18 % (1.42 million t) of total renewables in the European Chemical Industry [27].

Against the background of biofuels and bio-plastics to replacing fossil fuels and petroleum-based feedstock for the polymer industry, the global oilseeds production has been steadily growing due to food, feed, fuel and industrial applications in the last 20 years. Crushing oilseeds provide vegetable oil and meal. Vegetable oil is further used in food applications, for production of biodiesel and other industrial applications, such as lubricants and in paints and coatings [28], [29]. The by-product of vegetable oil production is oilseed meals that are an important protein-rich animal feed ingredient [29] or eventually transformed in energy carries trough drying and palletization processes [30]. A historical outline of global major vegetable oil (includes coconut, cottonseed, olive, palm, palm kernel, peanut, canola, soybean and sunflower seed oil) production is depicted in Fig. 1.5.

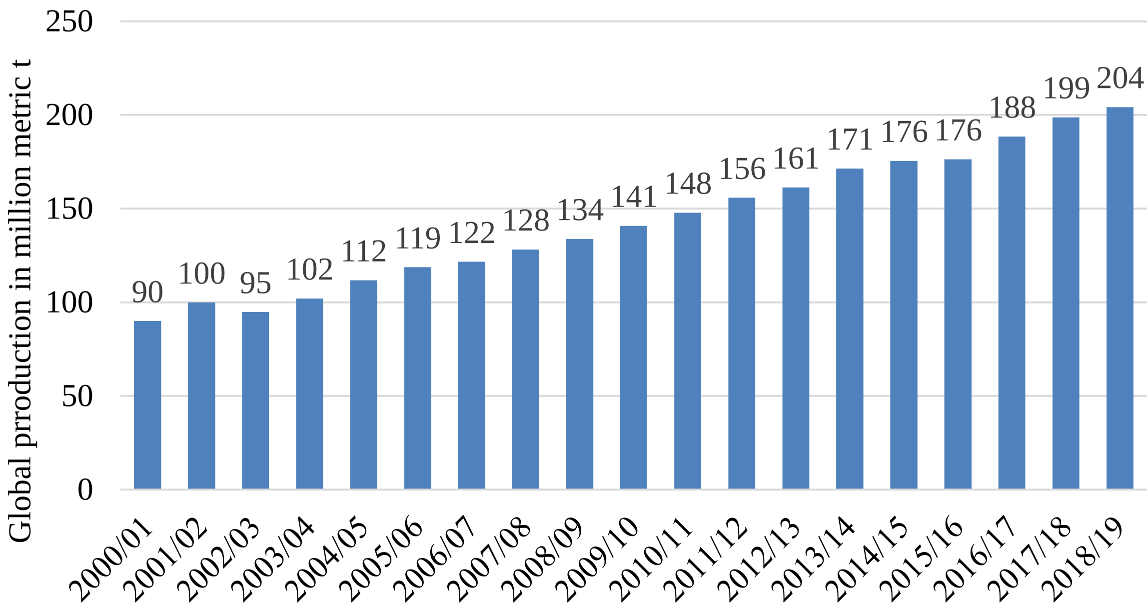

Fig. 1.5. Global production of vegetable oils from 2000/01 to 2018/19 [31].

The global increase in vegetable oil production was mainly due to the biodiesel industry in Europe and the development of the palm oil industry in Southeast Asia. It is estimated that oil consumption was shared between food, feed and industrial use in the ratio 80:6:14, but with demand for biodiesel and other industrial uses it has shifted to 74:6:20 [32]. In European and in Latvian context, rapeseed oil is the one with significant industrial importance.

Moreover, vegetable oils are considered platform chemicals and one of the most important classes of bio-based feedstock for polymer production due to the wide range of possible chemical transformations and modifications, universal availability, and low price and meantime representing a preferred alternative by the chemical industry. By modifying plant oils, it is possible to obtain a large variety of monomers and polymers [32]–[35]. Oils are composed of triglycerides, which are esters composed of three fatty acid units linked to glycerol (Fig. 1.6).

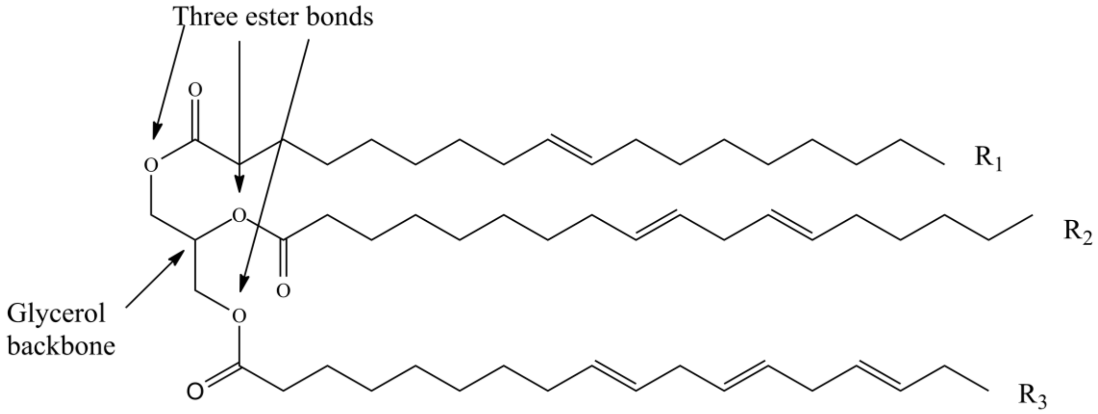

Fig. 1.6. Triglyceride structure of vegetable oils, where R_1, R_2, R_3 represent fatty acid chains.

The total weight of triglycerides is composed of mainly fatty acids (95 %). The composition of fatty acids is specific and individual for each plant oil. There are several highly reactive sites, double bonds, allylic positions and the ester groups, present in triglycerides from which a great variety of polymers with different structures and functionalities can be prepared [32], [35]–[37]. Moreover, they are much easier to process than the second-generation lignocellulose based feedstock [36], [38].

1.3.1. Rapeseed

Rapeseed (Brassica napus), belonging to the Brassicaceae family, is a widely cultivated crop around the world due mainly to its oil-rich seeds (>40 %) (Fig. 1.7).

Fig. 1.7. Flowering rapeseed field in Zemgale, Latvia. Photo by A.Fridrihsone in May 2019.

It is one of the few oilseeds that are adapted to cooler temperate agricultural zones and winter production. Members of the Brassicaceae were among the first plants domesticated by a man several thousand years ago. Rapeseed was cultivated in India 3000–4000 years ago, in China 2000–2500 years ago, in Japan, Greece and Italy 2000–2500 years ago, in Europe 800 years ago and only 60 years ago in North America [39].

The EU-28 is amongst the largest rapeseed producers in the world, with Canada and China being also large players. Germany, France and Poland are the largest rapeseed producers in the EU, producing ~50 % of the EU-28 production [40]. In comparison, countries in Northern Europe (defined according to the UN geoscheme [41]) produced much less rapeseed only 6 % of worldwide rapeseed production in 2017 [42]. In the EU-28, in 2017/2018, the production of rapeseed oilseed came to 22 175 thousand t and 4007 thousand t of rapeseed oilseeds were imported.

Rapeseed is a widely cultivated oil crop also in Latvia Since 2000, the amount of land devoted to rapeseed cultivation has increased vastly (Fig. 1.8).

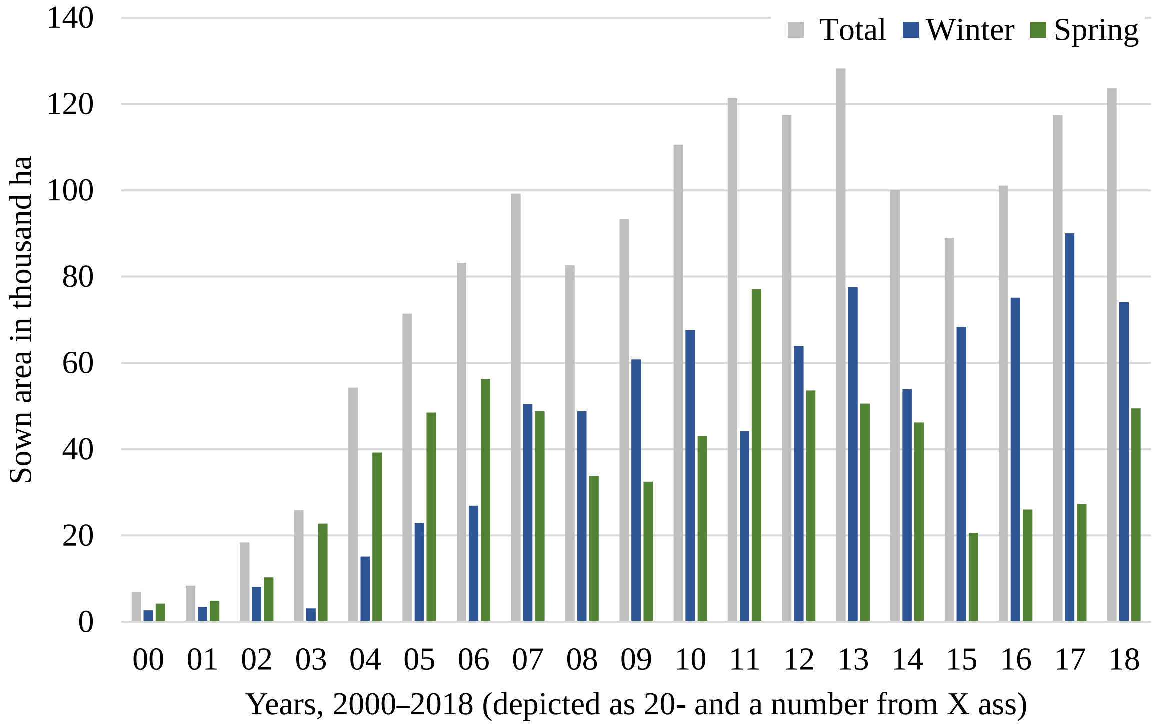

Fig. 1.8. The sown area of rapeseed in Latvia, 2000–2018 [43].

In 2000, 6900 ha were used for rapeseed cultivation; by 2018 it reached 123 600 ha from which 74 100 ha (60 %) was winter rapeseed and 49 500 ha (40 %) was spring rapeseed. Land used for rapeseed cultivation was 10 % of the total sown area of crops (1 208 700 thousand ha) in Latvia in 2018 [44]. One of the reasons for this rise is rapeseed cultivation was the EU's Sugar policy which began in 2006. As a result of major reforms, two Latvian sugar refineries – the Liepaja Sugar Refinery in western Latvia and the Jelgava Sugar Refinery in central Latvia – were closed in 2007 [45]. Approximately 14 000 ha were used for sugar beet cultivation in 2000–2006. Another reason for the increase in rapeseed cultivation was increased demand for rapeseed due to increase in biodiesel production.

Rapeseed oil mainly contains oleic acid (18:1), linoleic (18:2) and linolenic (18:3) fatty acids. The iodine value is 94–120 mg per 100 g of vegetable oil [35], [46]. The iodine value represents the amount of iodine (mg) that reacts with the carbon-carbon double bonds in 100 g of vegetable oil; the larger iodine value indicates more carbon-carbon double bonds per vegetable oil triglyceride. In comparison, palm oil has an iodine value of 44–58 mg per 100 g of vegetable oil and an iodine value of soybean oil is 117–143 mg per 100 g of vegetable oil [46]. The use of vegetable oil largely depends on its degree of unsaturation.

Rapeseed is the third-largest source of vegetable oil in the world with production of 28.09 million metric t; the first largest source is palm oil with 70.61 million t followed by soybean with 55.17 million t in 2017/2018. Of other major vegetable oils, only the sunflower reaches double digits, with production volume around ~15-18 million t annually in the last five years [47]. Domestic consumption of rapeseed oil reached 10 100 thousand t, from which 69.8 % is for industrial (biodiesel, lubricants, other), 29.7 % for food consumption (cooking, frying, as an ingredient), and 0.5 % as a feed. Breakout of industrial use is as follows: 89 % biodiesel and 11 % other industrial use [40].

In the last 15 years, the EU has promoted the use of vegetable oil due to the targets set out in the Renewable Energy Directive (2009/28/EC) requires to fulfil at least 20 % of its total energy needs with renewables by 2020 [48]. Biodiesel is the most important biofuel in the EU and, on an energy basis, represents 80.7 % of the total transport biofuels market in 2017 [49]. Rapeseed oil is the main feedstock for biodiesel production in the EU, accounting for 45 % of total production in 2017, in comparison to 72 % in 2008. However, rapeseed oil has lost its share over the last 10 years due to the higher share of palm oil and used cooking oil for biodiesel production [50]. Previously all the EU countries were obligated to ensure that at least 10 % of their transport fuels come from renewable sources by 2020. Since 2015, due to the ILUC Directive (EU) 2015/1513 which amended Directive 2009/28/EC on the promotion of the use of energy from renewable sources, the contribution of biofuels produced from “food” crops (to the 10 % renewables in transport target) is capped at 7 % (leaving 3 % to be covered by non-food crop-based biofuels) [51]. In December 2018, the revised Renewable Energy Directive (known as RED II) (2018/2001/EU) entered into force, where the overall the EU target for Renewable Energy Sources consumption by 2030 has been raised to 32 % [52]. Most likely, it is expected that a further expansion of first-generation biofuels will not take place due to the cap on food crop-based biofuels. However, this does not limit to use of oilseeds in various other industrial applications. As mentioned above, oil crops, including rapeseed, are also attractive sources of feedstock for the polymer industry to produce more added value products as a potential replacement for petroleum-based products.

1.4. Plastics

As discussed, today our daily life seems unimaginable without the presence of plastics or synthetic organic polymers, however, their large-scale production and use only dates back to ~1950 [7], [55, 56]. Almost all products contain some part of plastic and/or are packaged in the plastics.

Given the insight in the previous chapters, environmental considerations have been and will continue to be an important motivation to develop and introduce bio-based polymers, however, a dependence on fossil resources that are diminishing along with high fossil fuel prices have also contributed to the renaissance of bio-based materials, including bioplastics [55]–[57].

Plastics industry play a major role in achieving more sustainable development as the production volumes of plastics are major. In 2017, the total production of fossil-based plastics reached 348 million t, in EU28+Norway/Switzerland 65 million t of fossil-based plastics were produced [58]. The total production volume of bio-based plastics reached 7.2 million t. However, the total production of bioplastics remains insignificant (2 %) in comparison to the total produced volume of plastics worldwide [58]. Thus, the polymer industry continues to be under pressure to be more sustainable towards finding innovative solutions from an environmental and sustainability perspective [56], [59].

What are bioplastics? Although there has been heightened interest in bioplastics or biopolymers, there is no clear definition. Generally, bioplastics can be defined as bio-based and/or biodegradable polymers. Bio-based polymers are polymers in which at least a part is derived from biomass (i.e. plants, animals, fungi or bacteria) [60], [61]. According to the European bioplastics association, currently, 57 % of produced bioplastics was bio-based/non-degradable plastics and the remaining 43 % were biodegradable plastics [62]. A synthetic challenge for the bio-renewable industry is to make materials with properties that match those of chemicals currently in use. There is a need to think about the low cost, high volume, high-mass materials as commodity polymers and how to prepare these kinds of polymers from renewable resources [37].

The next chapter will give a concise insight in polyurethane (PU) which is one of the most important plastic families, others being polyolefins (polyethylene, polypropylene, polyvinyl chloride, polystyrene and polyethylene terephthalate [61].

1.5. Polyurethane in Brief

It was first invented by Professor Dr Otto Bayer in the year 1930, from the reaction between a polyester diol and a diisocyanate. PU was first developed as an alternative for rubber during World War II. In the late 1950s, PU gained its importance by being used as adhesives, elastomers & rigid foams and also as flexible cushioning foams [33], [61], [63].

Millions of t of PUs are produced annually for use in widespread applications (Fig. 1.9), it is the sixth most used polymers on a global scale [61], [63]. PU industry is also an important industrial sector in the EU economy. In 2016, PU comprised 7.5 % of used plastics in Europe [64]. In 2014, it was estimated that there are 240 000 companies involved throughout Europe, contributing EUR 207 billion annually to the European economy [65].

Fig. 1.9. Worldwide PU production and an estimated forecast up to 2020 [63].

The urethane group is the major repeating unit in PU. It is synthesized in a reaction between isocyanate moiety containing isocyanate groups (-N=C=O) and polyhydroxylated (-OH) containing co-reactant (polyol). The generic reaction is depicted in Fig. 1.10 [33], [63], [66]–[68]. The length and the chemical nature of the moieties R_1 and R_2 depicted in Fig. 1.10 play the most significant role in the properties of the final material [68].

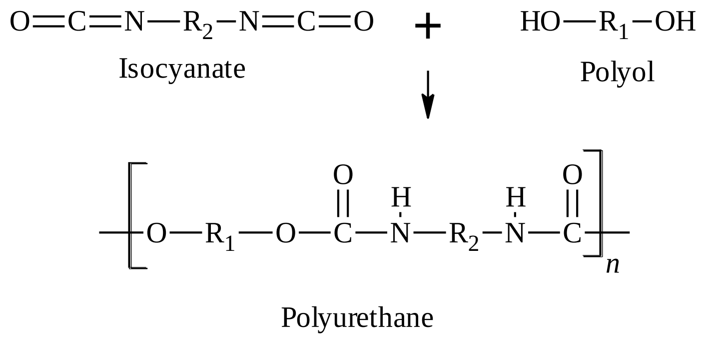

Fig. 1.10. Generic urethane linkage reaction [68].

By a careful selection of different polyols and isocyanates (and other components), a variety of PUs with specific properties can be developed for a broad range of industrial applications like foams, paints, thermoplastics, fibres and adhesives. Depending on the chosen reactants, PU can be tailored to a broad spectrum of materials (foams, coatings, sealants, elastomers etc.) that are produced to meet the needs for various applications, from the automotive industry, building and construction, appliances, furnishing, marine, medicine, and others, the breadth of PU applications is remarkable. The possible PU applications are depicted in Fig. 1.11. As mentioned, PU plastics are available in different forms with different uses for a countless number of applications. PU consumption in different application areas is depicted in Fig. 1.12. Over 50 % of PU application is dedicated to foams: flexible foams with 31 % market being widely used in mattresses, cushions, car seats and others; rigid foams with 25 % market share, commonly used for insulation purpose in the construction sector.

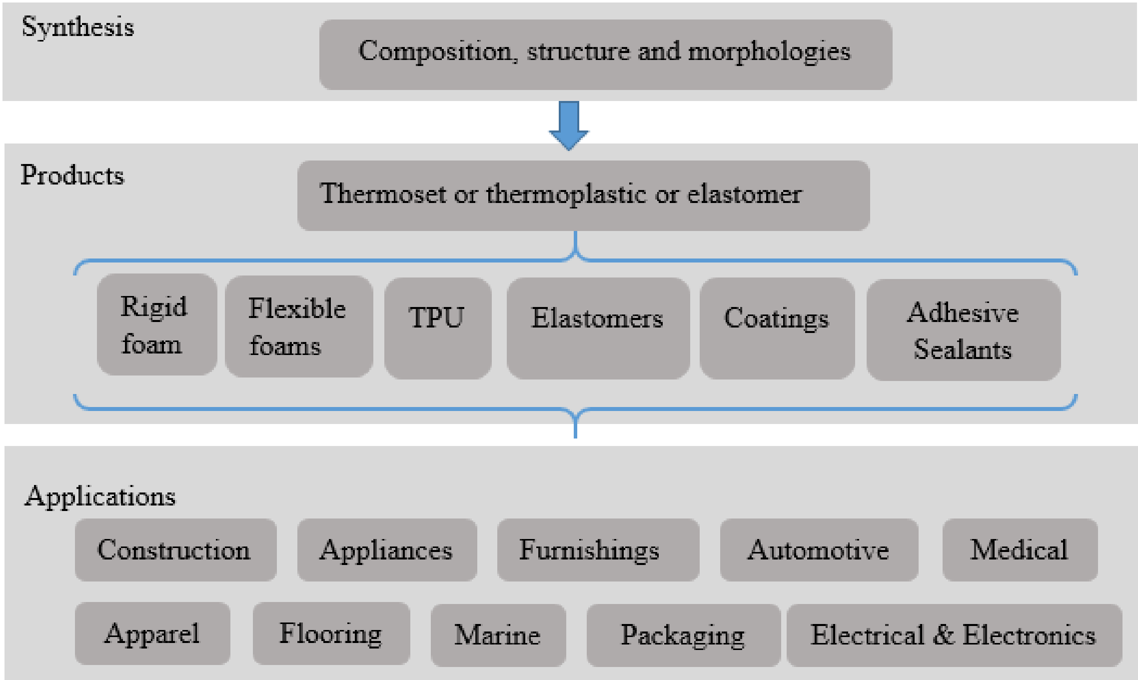

Fig. 1.11. Polyurethane applications, adapted from Lu et al. 2017 [69].

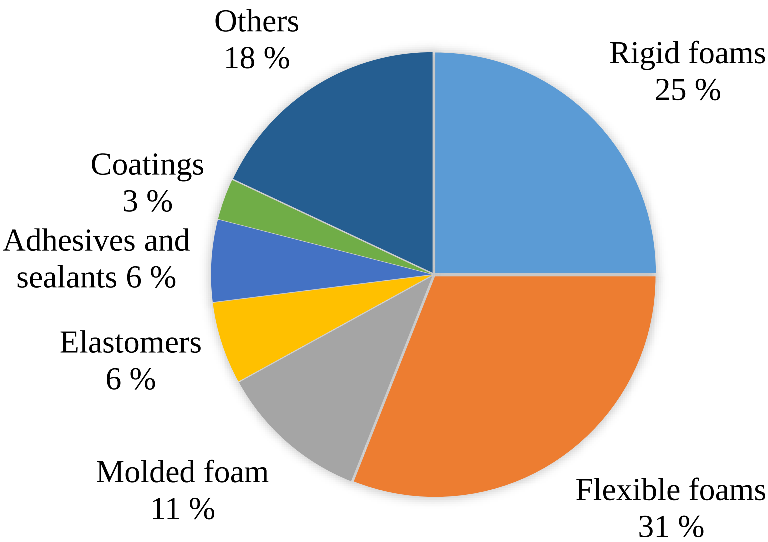

Fig. 1.12. Polyurethane consumption for different applications, data from 2016 [70].

Research and developments in the field of PU have always been linked with the sustainability issues from manufacturing to the final disposal of materials. Research groups, from an academic and industrial background, around the globe have been actively exploring the options to make PU more “green”. One of the most studied and developed research directions if the use of bio-based building blocks for the production of PU. This research direction focuses on the use of bio-based feedstock to develop polyol component or so-called soft segment, while the hard segments or the di-isocyanate part are still made from petroleum.

There are also researches in Non-isocyanate PU (NIPU) that is a promising way to develop "green" PU. NIPU is a novel kind of PU prepared by the synthesis of cyclic carbonates, followed by their reaction with amines or polyamine compounds, without the use of toxic isocyanates [71]. However, NIPU is in their infancy. Furtwengler et al. 2018 reported that only three foaming systems are being developed and described [61].

1.5.1. Polyurethanes Formulated From Natural Oil Polyols

It is hard to estimate to production capacities of PU that are partially formulated from bio-based feedstock. In 2016, The European bioplastics association estimated that bio-based PU formulated from renewable feedstock production represents 41.2 % of the global production capacities of bioplastics [72]. However, European bioplastics association did not include the produced PU formulated with bio-polyols in their yearly market data reports for 2017 and 2018 due to lack of data as the available data shows the amount of biomass used to produce bio-polyols [62], [73]. Despite abstaining to estimate production volume for PU formulated with bio-polyols, European bioplastics association considers that "Bio-based PU are another important group of polymers that have huge production capacities with a well-established market and are expected to grow faster than the conventional PU market due to their versatility" [62], [73].

In 2018, the German nova-Institute proudly released their annual market and trend report "Bio-based Building Blocks and Polymers" where production data were presented for all bio-based polymers. In the released report, estimates of the bio-based polymer production in 2018 were presented and forecast for 2023 was given (Fig. 1.13) [58]. The production of PU formulated with bio-polyols comprises around half of the total bio-based polymer production.

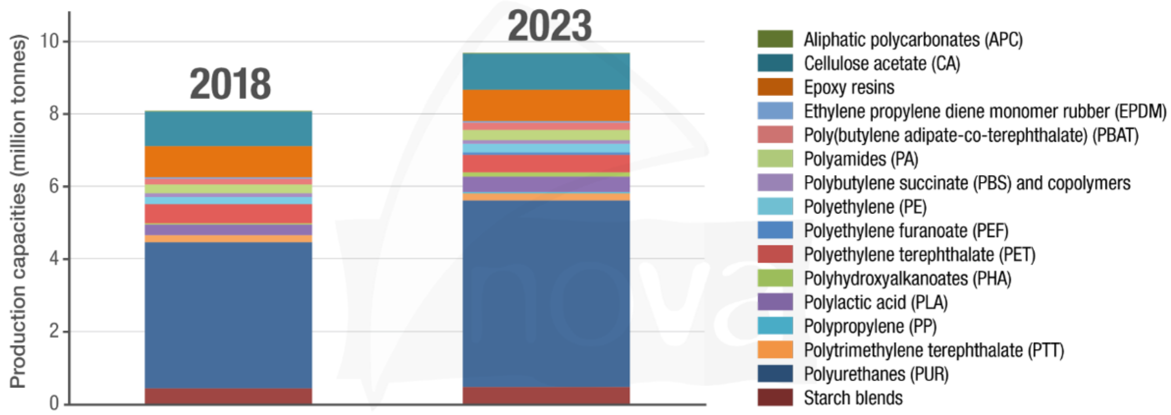

Fig. 1.13. Bio-based polymers production capacities in 2018 and 2023 [58].

Dedicated bio-based polymers mean that these chemical have new properties and functionalities that petrochemistry does not provide (Fig. 1.14). Both have their advantages and disadvantages from a production and market perspective.

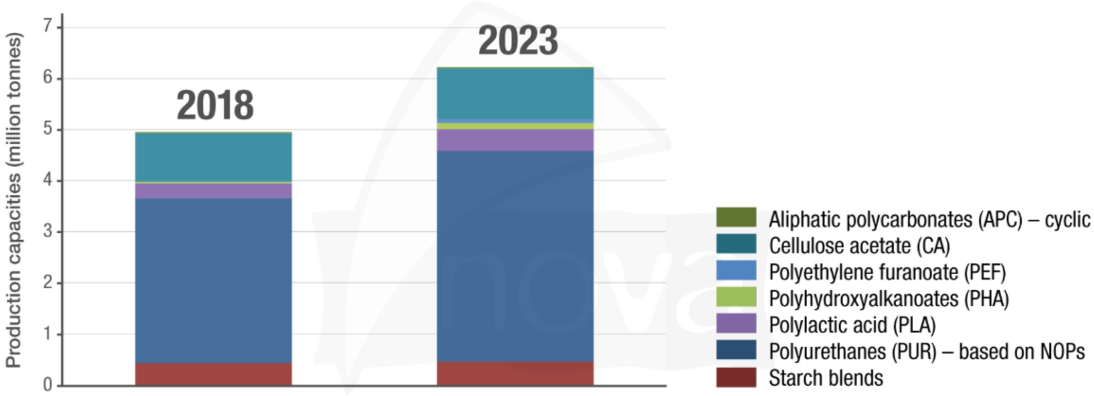

Fig. 1.14. Dedicated bio-based polymers production capacities in 2018 and 2023 [58].

As can be seen from Fig. 1.14, the largest capacity of bio-based polymers will be dedicated PU- based on NOPs, which means natural oil polyols. NOPs are bio-polyols derived from vegetable oils by several different techniques, meaning that in these PU materials, petrochemical polyol component fully or partially is replaced by bio-based (renewable) content polyols. In the next chapter, a closer look at NOPs will be taken.

There is also research direction dedicated to new bio-based di-/ poly-isocyanates, however, these technologies are also in their infancy [74].

1.6. Bio-Based Polyols

Oil crops are an attractive raw material for the polymer industry and have been studied intensively by both, academia and industry, to find more sustainable feedstock for the industry. Vegetable oil is mentioned as having the largest potential for application in polymers, specifically in polyols production to be further used in PU production [28], [75]–[77].

As discussed previously, to synthesize PU, there is a need for -OH groups containing reactant. The structure of natural oil was presented in Fig. 1.6 and as can be seen, there are no -OH groups present in the structure. Thus, natural oils have to be chemically modified to introduce -OH groups in their structure for them to be used in PU material production. The exception of this is castor oil that has naturally occurring hydroxyl groups. Different natural oils, such as castor [78]–[83], soybean oil [84]–[87], palm [88]–[90], jatropha [91], [92], wild safflower [93], sunflower [94], rapeseed [95]–[100] and others (linseed, coconut, tung oil [61]) have been studied as a bio-based feedstock for PU materials. The properties of the developed polyols vary significantly depending on the chosen feedstock and its fatty acid composition to the chemical route chosen for the synthesis. For example, viscosity can be from 150 mPa·s to 35 000 mPa·s at 25 °C, while hydroxyl value can vary from 71 mg KOH/g to 465 mg KOH/g. [61], [75]–[77], [101]. There are several processes to convert vegetable oils to polyols, which include epoxidation and ring-opening, transesterification, amidization, hydroformylation, ozonolysis, and others [101].

For a new bio-based product to reach the market, not only the quality of the end product is important, but also other factors, such as – biomass availability, volume and price. Different oil-bearing crops are the main oil crop in different regions depending on the geographical location and agricultural production in this area. Soybean is the dominant oil crop in the USA, while rapeseed is extensively cultivated in Europe, palm oil is dominant in the Asian region [102]. Pricewise, soybean oil, palm oil, and rapeseed oil are the most attractive for large-scale industrial products [76]. For European context, oil is not relevant feedstock [102] as its production volume remains minor with an expected production of ~3000 thousand Mt in 2019/2020 [40]. Palm oil has an especially high concentration of saturated fatty acids, that in PU material will act as dangling chains and thus lower the performance of end material [76], thus industrial production of palm oil polyols is not existing. Moreover, RED II also puts in place freeze on the use of high-risk indirect land use change (ILUC) biofuels at the 2019 levels to phase them out completely by 2030, palm oil falls under this. It is expected that any large scale production of bio-based material from this kind of feedstock will not be supported.

Castor oil has a unique chemical structure with naturally occurring hydroxyl functionality in its fatty acid chain, which means there is no need for chemical modification and can be directly used for PU synthesis; it is mainly produced in India [81], [103]. In castor oil, approximately 90 % of fatty acids are ricinoleic acid (C18:1), which have a hydroxyl functional group at the 12th carbon [75], [104]. However, castor oil has secondary hydroxyl groups that result in low functionality and low reactivity that sets a challenge for PU production [105].

NOPs are drop-in replacements for their petrochemical counterpart. By developing bio-based drop-in replacements, there is no need to adjust or develop new processing conditions as it is with new polymers, such as, polylactic acid, polyhydroxyalkanoates and others which is an important advantage to ensure faster uptake by the industry [57]. No economic model will be able to take it over if it is not, at least, as efficient as the current one. Moreover, bio-based polyols will take market place only if they offer overall benefits in terms of a unique and better set of properties and performance compared to existing commercial petrochemical counterparts. Moreover, developed bio-based plastics or buildings blocks for plastics, have to ensure better environmental performance in comparison to the petrochemical counterpart. Although PU based on NOPs represented more than 50 % of the total dedicated bio-based polymers production capacity in 2018 (Fig. 1.14), there still is fairly little information on their environmental performance.

1.6.1. Commercial Bio-polyols

The majority of PU formulated partially from sustainable feedstock use NOPs that are based on natural oils as only these technologies are commercially developed and matured (Fig. 1.14). Up till now, major progress has been made concerning the production of bio-based polyols at industrial scale, and it is expected that green and bio polyols market will reach USD 4.71 Billion by 2021, at a compound annual growth rate of 9.5 % from 2016 to 2021 [106].

There are several bio-based polyol plants up and running in Europe. Nivapol Technology Aps, located in Denmark, is producing castor oil-based polyether and polyester polyols under the tradename Polem® for different PU applications [107]. In Germany, Altropol Kunststoff GmbH produces Neukopol® from rape oil, sunflower oil, soya bean oil and castor oil [108].

Another company Vanderputte, located in Belgium, produces polyfunctional polyester polyols under the trade name Veopur® from castor oil [109]. Polycin® bio-based castor oil polyols have been developed by Vertellus Holdings LLC, a US company with several locations in the United Kingdom [110]. Cognis (now BASF) is using different epoxidized vegetable oils to produce their bio-polyols under the name Sovermol® [39], [111], [112]. Latvian State Institute of Wood Chemistry (LS IWC) has developed rapeseed oil-based polyols [95], [96] and spin-off company PolyLabs Ltd. is commercializing them [113].

In the USA, Cargill has a series of soy-based polyols, under tradename BiOH® that are used in the production of flexible PU foam for upholstered furniture, mattresses, mattress toppers, pillows, carpet cushion, and automotive seats [114]. In 2007, Europe's largest flexible foam manufacturer, Recticel, launched a line of foams that contain Cargill's soybean-oil-based polyols rather than petro-polyols. Cargill estimates that replacing ~455 kt of traditional polyols with its BiOH® brand polyols will save 350 m^3 of crude oil [115]. In 2017, Cargill purchased another company producing soy-based polyols under trade name Agrol® [116].

2017 was a 10-year mark since Ford first used soybean-based foam in the 2008 Mustang. Since 2011, it’s been a key material used in the seat cushions, seat backs and headrests of every vehicle we build in North America. It is claimed that the company has saved more than 228 million pounds of carbon dioxide from entering the atmosphere. This is the same amount that would be consumed by 4 million trees per year, according to North Carolina State University [117].

In 2016, Mitsui Chemicals & SKC Polyurethanes Inc. (MCNS) opened castor oil-based bio-polyol producing company in India, Vithal Castor Polyols Pvt. Ltd [118]. In 2019, a bio-polyol from MCNS is being used in the Robo self-driving cars [119]. Feihang Industry plans to start up a 50 kt epoxidized soybean oil polyol facility by the end of 2019 [120]. BASF has developed castor oil-based polyol Lupranol® BALANCE 50 [111], [121]. Dow Chemicals Co. have a bio-polyol using functionalized vegetable oils (soybean) under brand name Renuva™ [122]. A longer list of commercially available polyols derived from natural resources for the production of PU is presented by Desroches et al. 2012 [101].

Barriers to entry are high for the bio-polyol market. The newcomers require innovative products and processes at a comparative price to enter the market. The price for commercial bio-polyols on the market at the moment is 1.8 – 2.2 EUR/kg, the price of fossil-based polyols are in the range from 1.3 – 1.9 EUR/kg for rigid PU foam applications. It is possible to purchase petroleum-based polyols from China for 0.9 EUR/kg. More specific niche polyol price is around 3 EUR/kg. In the soft PU foam segment, the price for polyols could even reach 10 EUR/kg [123].

In future more efforts are expected from researches, to develop commercially viable polyols from the second and the third-generation feedstock, but there is a long way before these bio-polyols will be introduced in the market.

Although there are already several commercial production sites across the globe, there still is a lack of environmental assessment for NOPs. There are few papers in regards to bio-based polyol environmental assessment, but feedstock is limited to soybean and/or castor oil [124], [125] and palm oil [126].

1.7. LCA as a Tool for Environmental Evaluation

Due to the fact, that the bio-based industrial sector has been recognized by the EU, including Latvia as its member state, as a priority area toward sustainability, it is crucial to evaluate the environmental performance of bio-based products. Important environmental concerns have emerged regarding the intensive cultivation of bio-based feedstock, especially oil crops, including rapeseed. Using an LCA method and its holistic approach, the environmental sustainability and the overall impacts, bottlenecks and benefits from the use of a bio-based feedstock can be better evaluated and understood.

LCA is a science-based technique to assess resource consumption and potential environmental impacts associated with a product or service throughout its whole life cycle, from extraction via manufacturing and use to end-of-life by compiling an inventory of relevant energy, material, water and land inputs, and releases to the environment. The idea for the LCA was conceived in the 1970s, however, at the time there were no unified methods. The methodology was originally developed by the Society of Environmental Toxicology and Chemistry in the early 1990s. During mid-90s ISO 14040–14043 series was released for product-oriented environmental impact assessment and [127]–[129].

Today, according to the ISO, the LCA is defined as "compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle" [130]. LCA is an established decision tool for assessing both environmental and social impact of system products and processes.

LCA may be used for a broad spectrum of applications, such as, compare alternative choices, identify points for environmental enhancement, count on a more global perspective of environmental issues, to avoid problem shifting, contribute to the understanding of the environmental consequences of human activities, establish a picture of the interactions between a product or activity and the environment as quickly as possible, provide support information so that decision-makers can identify opportunities for environmental improvements. More particular examples of LCA use are: to define the environmental performance of a product during its entire life-cycle, to identify the most relevant steps in the manufacturing process related to a given environmental impact, to compare the environmental performance of a product with that of other concurrent [129].

To stress the importance of LCA, there are two examples. During the 2000s there was a renewed interest in biofuels due to several reasons, from economical to environmental. Early on it was considered that biofuels are better than fossil fuels in regards to the climate change due to the biogenic carbon cycle. However, LCA studies have shown that it was a mistake to consider that biofuels are climate neutral. It is wrong to look only at the use stage of the fuel and ignore the previous industrial and agricultural steps to produce this biofuel. Moreover, LCA showed it is wrong to disregard potential increases in environmental problems other than climate change from a transition from fossil fuels to biofuels. Accordingly, EC amended its legislation on biofuels by introducing a set of sustainability criteria [127], [128].

The second example is related to investments for new bio-based product and technology development. Previous chapters explained the importance of sustainable development globally and also expressed that the EU is the frontrunner in implementing sustainable development and growth. During 2014-2020, EU has invested EUR 3.7 billion in the Bio-Based Industries Joint Undertaking, operation under Horizon 2020, to foster a strong European bio-based industrial sector. All proposals submitted under Bio-Based Industries Joint Undertaking must include an environmental assessment using LCA methodologies based on available standards, certification and accepted and validated approaches [131].

Above mentioned examples show that although bio-based feedstock is used, the environmental advantage is not guaranteed. Thus, LCA is necessary to fully understand the advantages and trade-offs of bio-based materials, and to understand more completely the sustainability value of a renewable feedstock [128].

1.7.1. LCA on Natural Oil Polyols

Even though NOPs and bio-PUs have been extensively studied the over last two decades and high industrial interest and development, only a few papers are available in the open literature about the environmental performance of NOPs. As there are several available feedstocks for NOPs development, along with different chemical routes, it is important to assess each case on its own.

The amount of peer-reviewed papers in the literature in regards to NOPs is very limited, it narrows down to a few papers. Dow published a comparative LCA to understand the sustainability performance of the NOPs (Fig. 1.15).

The research studied the impact of different farming and co-product allocation assumptions for soybean oil and castor oil feedstocks, considering seven total NOP scenarios. In all of the scenarios, less fossil energy was required and a smaller amount of GHGs was emitted compared to the European average fossil-based polyol. Overall, the NOP performance ranged from 33 % to 64 % of the fossil energy and -13 % to 46 % of the GHG emissions of the fossil-based polyol [124]. This LCA research noted the significant changes depending on the farming model applied. The difference in the GWP of soy and castor oil-based polyols is depicted in (Fig. 1.15). For a full and detailed description refer to the study by Helling and Russel (2009) [124].

Also, palm oil polyols were studied using two different scenarios, where the source of electricity is changed. The amount of GHG emitted from the palm polyol system "cradle-to-gate" using national electricity grid was found to be 1.31 kg CO_2 eq per kg palm polyol and 0.49 kg CO_2 eq per kg palm polyol if energy from biomass as an alternative source is used.

A study was carried out where bio-based products from oil crops, biodiesel, polyol and bioresin were studied. The research concluded that a higher reduction in non-renewable energy use per t of product is possible when replacing the chemical with a bio-based feedstock than when replacing the fuel. It was noted that results of the research are an important outcome also for policymakers as in many countries the replacement of fossil fuels by biofuels is stimulated, whereas far less attention is paid to the replacement of chemicals by biomass [132], [133].

Omni Tech International published a peer-reviewed study where they assessed the environmental performance of the soy-based industrial products, including polyol. It was found that overall soy-based polyol showed better results than fossil-based polyol. In the study, sequestration of carbon was taken into account, which resulted in negative GWP for the soy-based polyol [134].

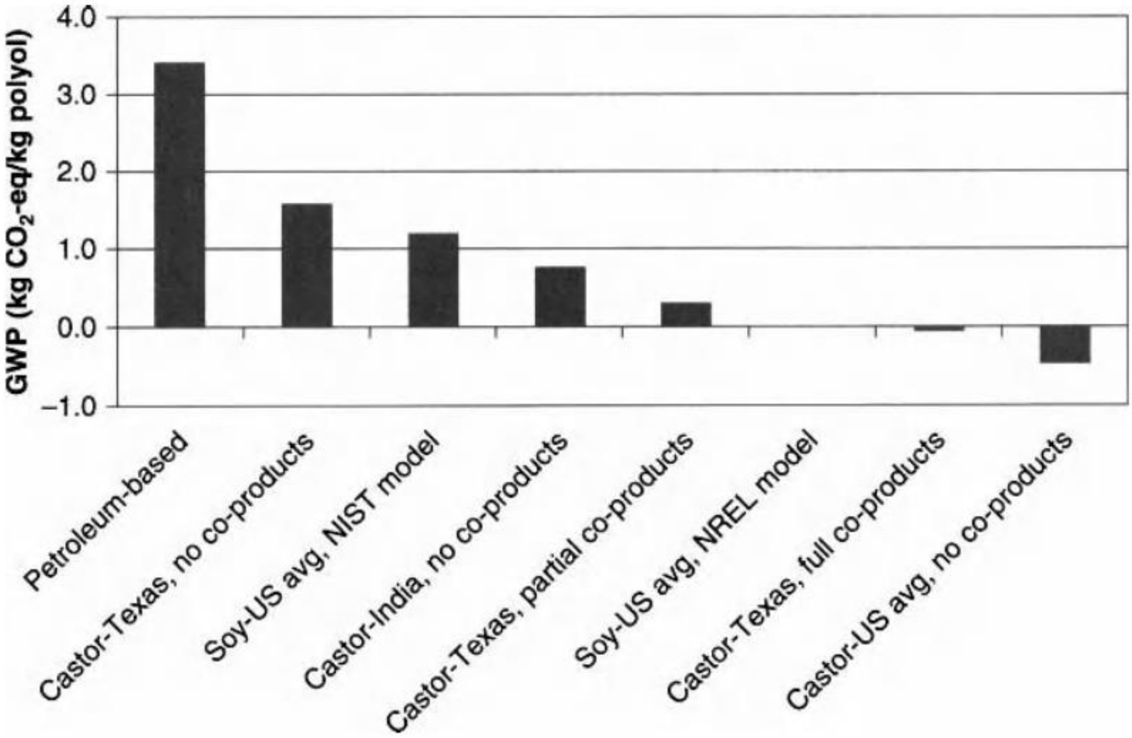

Fig. 1.15. Impact of feedstock, farming model, and co-product allocation assumptions on GWP for cradle-to-gate production of polyols [128].

Although not a peer-reviewed study but a rather commercial statement, preliminary LCI data for Cargill`s soy-based polyols report that their BiOH® polyols (suitable for flexible foams) have 23 % less total energy demand, 61 % less non-renewable energy and 36 % less global warming emissions than traditional petrochemical polyols [125].

2. METHODOLOGY

2.1. LCA Methodology

According to the ISO, the LCA is defined as "compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle" [130]. The general principles and framework for LCA are described in the international standards ISO 14040 [130], requirements and guidelines are described in ISO 14044 [135].

There are two main modes of LCA – attributional LCA and consequential LCA. Both approaches are defined as follows:

- Attributional LCA – assesses the environmental impacts associated with all stages in the life cycle of a product, a process or a system, from cradle to grave (i.e. from raw material extraction through processing, manufacture, distribution, use, etc.).
- Consequential LCA – identifies the consequences of a decision within the relevant system on other systems and processes of the economy [136].

This thesis does not attempt to explain in detail the differences between the two LCA modes. ILCD handbook recommends using the consequential approach for analyses that will inform policymaking, while the attributional approach only in contexts where no decision is to be made based on the results of the analysis [137].

For this thesis Attributional-LCA mode was used. In the next subchapters, the key methodological aspects will be shortly explained.

2.2. Phases of the LCA

The LCA framework includes four separate phases: The goal and scope definition, inventory analysis, Impact assessment and Interpretation of results [130], [135]. The relationship between the four phases is illustrated in Fig. 2.1.

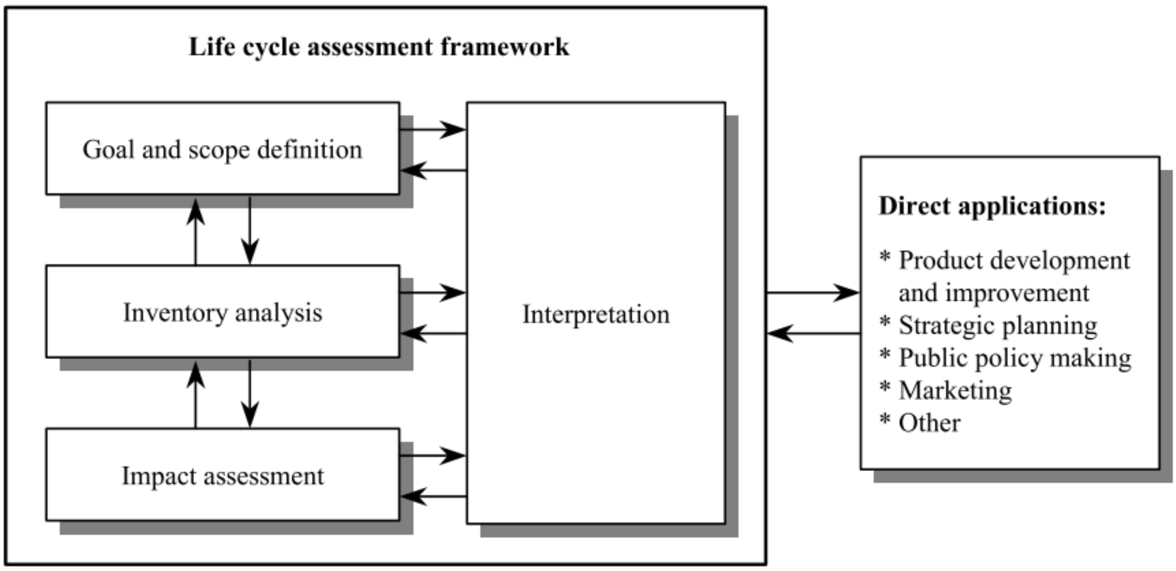

Fig. 2.1. The framework of LCA phases, modified from the ISO 14040 standard [130].

The Fig. 2.1 is well recognized and captures the "essence" of LCA study – that LCA is an iterative process, i.e. the interpretation of the preliminary results helps refine the first three phases towards the final results. ISO standard states that "LCA is an iterative technique. The individual phases of an LCA use results of the other phases. The iterative approach within and between the phases contributes to the comprehensiveness and consistency of the study and the reported results" [130]. As an LCA case study progresses, various aspects may require modification for the performed LCA to be solid and sound research study.

2.3. Goal and Scope Definition

The goal definition is the first phase of an LCA study, where the purpose of the study is defined and described [127].

According to the ISO standard, the goal is defined with four main aspects:

- The intended application;
- The reasons for carrying out the study;
- The intended audience, i.e. to whom the results of the study are intended to be communicated;
- Whether the results are intended to be used in comparative assertions intended to be disclosed to the public [130].

According to ISO standard, the scope includes the following items:

- The product system to be studied;
- The functions of the product system or, in the case of comparative studies, the systems;
- The functional unit (FU);
- The system boundary;
- The allocation procedures;
- Impact categories selected and methodology of impact assessment, and subsequent interpretation to be used;
- Data requirements;
- Assumptions;
- Limitations;
- Initial data quality requirements;
- Type of critical review, if any;
- Type and format of the report required for the study.

ISO standard defines FU as follows "FU quantified performance of a product system for use as a reference unit" [130]. The defined FU provides a reference to which the input and output data are normalized. The FU must be defined quantitatively, clearly and consistently with the goal of the study [127]. After the FU is defined, a reference flow can be defined. ISO definition for the reference flow – "reference flow measure of the outputs from processes in a given product system required to fulfil the function expressed by the FU" [130]. To put it more simply, reference flow is the amount of product that is needed to realize the FU.

Another important step is to define the system boundary of the system under study. ISO defines system boundary as ‘set of criteria specifying which unit processes are part of a product system” [130].

2.4. Life Cycle Inventory

LCI is a key aspect dealing with the quantification, definition and gathering of a specific in- and out data set for the system under study. According to the ISO 14040, LCI is a “phase of life cycle assessment involving the compilation and quantification of inputs and outputs for a product throughout its life cycle” [130]. Developing the LCI part is the most difficult and time-consuming aspect of the whole LCA study. The LCI must be in line with the goal and scope definition. However not always it is possible and/or necessary to collect the highest quality data for all the involved steps in a product system due to several factors, such as data availability, confidentiality issues and high costs. Essentially the result of LCI is an inventory table, where input and output flows have been quantified according to the chosen FU. The LCI analysis result is used as an input to the subsequent Life Cycle Impact Assessment (LCIA) [127], [128], [138], [139].

2.4.1. Data types in LCI

As LCA is a very data-intensive methodology, it is important to focus the data gathering activities on the data that are specific to the chosen product system – foreground system, which is modelled by the LCA practitioner, and for the background process use LCI databases, where data can be selected and adapted if needed [127], [140], [141].

Frischknecht et al. 1998 defined foreground and background system as follows:

- The foreground system consists of processes which are under the control of the decision-maker for which an LCA is carried out. They are called foreground processes;
- Background system: The background system consists of processes on which no or, at best, indirect influence may be exercised by the decision-maker for which an LCA is carried out. Such processes are called background processes [141].

2.4.2. Quality of LCI Data

The quality of the available data will largely also determine the quality and accuracy of LCA. ISO defines data quality as “characteristics of data that relate to their ability to satisfy stated requirements” [130]. Understanding and communicating data quality is essential to the scientific integrity of LCA.

ISO also states the data quality requirements:

- Data quality requirements shall be specified to enable the goal and scope of the LCA to be met;
- The data quality requirements should address the following: time-related coverage, geographical coverage, technology coverage, precision, completeness,

representativeness, consistency, reproducibility, sources of the data, the uncertainty of the information [135].

For LCI data sources, primary and secondary sources can be differentiated (Table 2.1).

Table 2.1

Types of Primary and Secondary Data [130, 138]

Data type	Includes	Guiding principle
Primary data	Interviews Questionnaires or surveys Bookkeeping or enterprise resource planning system Data collection tools (online/offline) On-site measurements.	The guiding principle should be the availability and quality of the most appropriate data
Secondary data	Databases Statistics Open literature	

Moreover, data also can be classified by their creation type:

- Site-specific (directly measured or sampled).
- Modelled, calculated or estimated.
- Non-site specific (i.e., surrogate data).
- Non-LCI data (i.e., data not originally intended for use in an LCI).
- Vendor data [128].

2.5. Allocation

If a system under study has different co-products, then it is necessary to decide how the environmental burdens of the unit process will be treated (allocated) among the co-products. The term "co-product" is defined as "any of two or more products coming from the same unit process or product system" by ISO [130], [135]. Allocation procedure is one of the most controversial issues in LCA.

ISO defines allocation as follows: "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" [130], [135].

According to ISO 14044, the allocation is a stepwise procedure which is explained below:

- Step 1: Wherever possible, the allocation should be avoided by
  1) Dividing the unit process to be allocated into two or more sub-processes and collecting the input and output data related to these sub-processes, or
  2) Expanding the product system to include the additional functions related to the co-products, taking into account the requirements of Section 4.2.3.3 of ISO 14044.
- Step 2: Where allocation cannot be avoided, the inputs and outputs of the system should be partitioned between its different products or functions in a way that reflects the underlying physical relationships between them; i.e. they should reflect the way in which

the inputs and outputs are changed by quantitative changes in the products or functions delivered by the system.

- Step 3: Where physical relationship alone cannot be established or used as the basis for allocation, the inputs should be allocated between the products and functions in a way that reflects other relationships between them. For example, input and output data might be allocated between co-products in proportion to the economic value of the products [135].

2.6. Life Cycle Impact Assessment

According to the ISO standards, LCIA is defined as "phase of life cycle assessment aimed at understanding and evaluating the magnitude and significance of the potential environmental impacts for a product system throughout the life cycle of the product" [130]. It is the third out of four inter-related phases in an LCA study (Fig. 2.10). During the LCIA phase of LCA, an elementary flow from the inventory is transformed into its potential impacts on the environment.

According to ISO standards, the LCIA step includes mandatory and optional steps. Mandatory steps are:

- Selection of impact categories, category indicators and characterization models (in practice typically done by choosing an already existing LCIA method);
- Classification (assigning LCI results to impact categories according to their known potential effects, i.e. in practice typically done automatically by LCI databases and LCA software);
- Characterization (calculating category indicator results quantifying contributions from the inventory flows to the different impact categories, i.e. typically done automatically by LCA software) [127], [128], [130], [135].

Optional steps include:

- Normalization (expressing LCIA results relative to those of a reference system);
- Weighting (prioritizing or assigning weights to each impact category);
- Grouping (aggregating several impact indicator results in a group) [127], [130], [135].

The LCIA methods used in this thesis are shortly described below.

2.6.1. Cumulative Energy Demand

Cumulative Energy Demand (CED) is an LCIA methodology quantifying the direct and indirect energy use in units of MJ throughout the life cycle of a product or a process. The CED method is structured in eight different impact categories, as shown in Table 2.2 [142]. The idea of CED is that all technical processes require energy, providing this energy is related to environmental issues, as a result, the needed energy amount for a given process or product reflects the environmental impact of a system under study. CED is often used as a complementary assessment method especially for analysing the energy perspective for the system under study. CED takes into account primary energy use, both renewable and non-renewable, and energy flows intended for both energy and material purposes [143]. Moreover, energy use indicators have been shown to be good proxy indicators for environmental impacts in general [144] and are useful to get a general view of the energy-related environmental impacts [145]. A CED V1.11 was used for this Thesis.

Table 2.2

The Subcategories in LCIA Method: CED

Impact category group	Subcategory	Includes
Non-renewable resources	Fossil	Hard coal, lignite, crude oil, natural gas, coal mining off-gas, peat
	Nuclear	Uranium
	Primary forest	Wood and biomass from primary forests
Renewable resources	Biomass	Wood, food products, biomass from agriculture, e.g. straw
	Wind	Wind energy
	Solar	Solar energy (used for heat & electricity)
	Geothermal	Geothermal energy (shallow: 100-300m)
	Water	Run-of-river hydropower, reservoir hydropower

2.6.2. ReCiPe Method

The most recent and harmonized indicator approach, that being the ReCiPe method [146], was proposed for the LCIA for this study. A recent review paper in regards to green chemical processes and synthesis design highly recommended using the ReCiPe method along with the latest ecoinvent dataset to improve the actuality, comparability and consistency of LCA studies [147].

In the ReCiPe method, there are 18 midpoint indicators and 3 endpoint indicators. The relationships between midpoint and endpoint methods are depicted in Fig. 2.2. In general midpoint indicators focus on a single environmental issue. In the ReCiPe endpoint level (damage-oriented), the environmental impacts are aggregated into three types of damage: human health, ecosystem quality and resources. The aggregated environmental impact is expressed as the ReCiPe score, written in normalized and weighted millipoints (mPt). Although the drawback of endpoint level is that the statistical uncertainties are higher, the results are easier to understand and interpret by decision-makers [148].

There are three perspectives in the ReCiPe2016 method:

1. The individualistic perspective is based on the short-term interest, impact types that are undisputed, and technological optimism with regard to human adaptation.

2. The hierarchist perspective is based on scientific consensus with regard to the time frame and plausibility of impact mechanisms.

3. The egalitarian perspective is the most precautionary, taking into account the longest time frame and all impact pathways for which data is available [149].

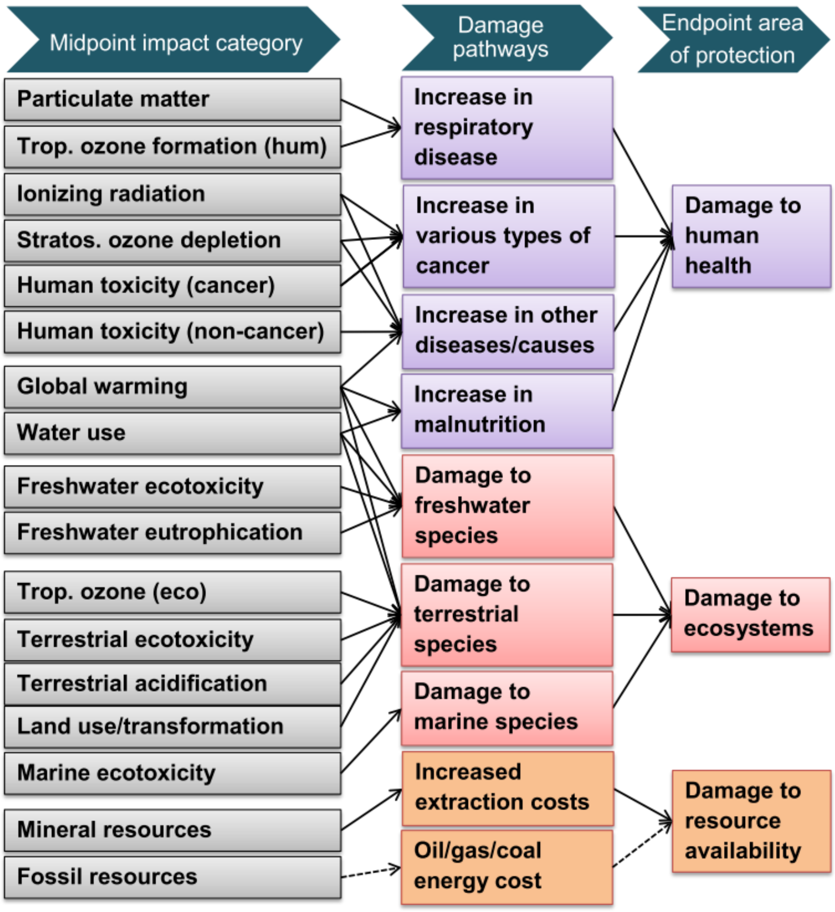

Fig. 2.2. Overview of the midpoint and endpoint impact categories and their relationships that are covered in the ReCiPe2016 methodology [149].

2.7. Interpretation

The concluding part of the LCA study is interpretation. Interpretation is a "phase of life cycle assessment in which the findings of either the inventory analysis or the impact assessment, or both, are evaluated in relation to the defined goat and scope to reach conclusions and recommendations" [130]. During this step, all the data are analysed and conclusions are made what are the impacts of the product system under study over its lifecycle. Also, during this phase, the LCI model can be improved to meet the goal and scope of the study, if not possible to reconsider the goal and scope of the study [127].

The interpretation phase of LCA includes:

- Identification of significant issues from other LCA phases, such as key processes and assumptions, most important elementary flows that have the potential to impact the results;
- Evaluation by completeness, sensitivity and consistency checks – which aims to establishes the basis for the conclusions and recommendations and is needed to determine the reliability and stability of the results;

- Formulation of conclusions and recommendations from the study – this is the final step of the interpretation phase where conclusions and recommendations are drawn to answer questions posed in the goal definition [127], [139].

2.7.1. Sensitivity Analysis

To ensure that the LCA results are robust, a sensitivity analysis can be performed. ISO standards define sensitivity analysis as follows: systematic procedures for estimating the effects of the choices made regarding methods and data on the outcome of a study [130]. The essence of sensitivity analysis is to determine how sensitive results are to the assumptions made during the study. Observing the change in the results will help determine how important the assumptions are with respect to the results [128].

2.8. Software and Databases

LCA rely on – data and software – as the two main pillars. Although LCA results can also be calculated without specific LCA software, for example, with Excel or MatLab, the computation of LCA becomes quite elaborate. A typical LCA case study requires hundreds or even thousands of processes that are characterized by input and output flows, which need to be connected, so the common practice is to use LCA software.

There are different commercial software products for LCA. The world`s leading LCA software is SimaPro®. Other widely used commercial software for performing LCA are GaBi® [150] and Umberto® [151]. Also, there are many commercial and free tools for LCA that are provided by different institutions. OpenLCA by GreenDelta is free and open-source software for modelling the life cycle [152]. CMLCA, developed by Leiden University, Institute of Environmental Sciences (CML), is another free software that allows calculating the LCA [153].

As mentioned before not always it is possible and/or necessary to collect LCI data about all the involved process. Most often LCI databases are used to source data for the background systems (for example, electricity generation, machinery production and others), however, there are case-specific situations where databases also are used for the foreground system [127], [128].

In the last decades, there has been a growing number of LCA databases as a response to increasing academic, industrial interest in LCA. Ecoinvent is recognized as the world`s leading supplier of consistent and transparent LCI data. Ecoinvent has been continuously expanded since 2003 and currently contains over 16 000 unique datasets (ecoinvent Version 3.5 was released on the 23rd August 2018) [154]. Other LCI databases are Gabi datasets by Thinkstep [155], Agri-footprint, database for the agriculture and food sector, developed by Blonk Consultants [156], U.S. LCI database developed by National Renewable Energy Laboratory (USA) [157] among others. A detailed list of the available LCI databases can be found in sources by Curran et al. 2012 [128] and Hauschild et al. 2018 [127].

2.8.1. Software and Database for the Present Study

The LCA software SimaPro 9.0 by Pré Consultants and ecoinvent v3.5 database were used to create the LCA models and undertake the impact assessment calculations.

2.8.2. Ecoinvent System Models

There are several system models available in ecoinvent v3 depending on the needs and goal of the study. The system models in ecoinvent v3 along with short description are depicted in Table 2.3. For this study, ecoinvent v3 model Cut-off system model was used.

Table 2.3

System Models Present in Ecoivent v3 [139, 159]

System model	Short explanation	Other remarks
Allocation, cut-off by classification	Primary (first) production of materials is always allocated to the primary user of a material. Secondary materials thus bear only the burden of the recycling process and no burdens from the primary production of the material.	Simply known as Cut-off system model
Allocation at the point of substitution	Follows the attributional approach in which burdens are attributed proportionally to specific processes	Simply known as APOS system model
Substitution, Consequential, Long-Term	Follows a substitution-based approach and is intended to serve as a background database in consequential LCA studies. A reference product for an activity is always burdened with the full impacts of all inputs and emissions but is credited with benefits for any by-products it produces that can substitute other productions	Simply known as Consequential system model

2.9. Land Transformation

Land use was modelled as follows: transformation (land-use change) and occupation (land use), which are defined as follows:

- For land occupation: square meter × years, land use type i, and region k;
- For land transformation: square meter, initial land-use type i→ final land-use type j, and region k [159].

2.10. Field Emissions

2.10.1. Emissions from Plant Protection Products

Pesticide emissions shall be modelled as specific active ingredients. Emissions data related to the application of plant protection products were estimated according to the method proposed by the EMEP/EEA air pollutant emission inventory guidebook. To calculate emissions, it is necessary to know the applied quantity and pesticide vapour pressure. The emissions factors are derived from the vapour pressure of the pesticides [160]. Vapour pressure of pesticides was taken from PPDB [161]. The emissions to surface water and soil were estimated as 0.50 % and 50 %, respectively, of the applied plant protection product amount [162].

2.10.2. Emissions Related to Phosphorus

Emissions related to the phosphorus cycle were calculated according to Schmidt et al. 2007 [163]. Phosphorus emissions contain no emissions to air. Phosphor binds tightly to soil particles, phosphate leaching was specified as 2.9 % of the surplus of phosphorus. The remaining was accumulated into the soil. To recalculate from oxide to element, a coefficient of 0.436 was multiplied with the applied amount of P_2O_5 [164].

2.10.3. Release of Fossil CO_2 After Urea Applications

For fertilizers containing urea, CO_2 emissions must be calculated, as during the urea production process CO_2 is used, which is chemically bound in the urea molecule. After application and transformation processes in the soil, this CO_2 is released to the atmosphere. The worst-case approach was used so that the total amount of CO_2 is considered as released to the air. For urea, 1.57 kg CO_2 is released per kg urea-N [165], [166].

2.10.4. Emissions of Ammonia to Air

The NH_3 emissions from applied mineral fertilizers are calculated by constant emission factors for each group of fertilizer, which can be found in ecoinvent documentation [165].

2.10.5. Emissions of N_2O to Air

Nitrous oxide emissions from the cultivation of rapeseed were calculated using the Global Nitrous Oxide Calculator (GNOC) – an online tool to estimate soil N_2O emissions from the cultivation of biofuel crops [167]. The emissions calculations are based on the Intergovernmental Panel on Climate Change (IPCC) 2006 combining TIER1 and TIER2. Soil organic matter content, pH and other environmental conditions (provided by the agricultural company) were taken into account and parameters were adjusted accordingly in GNOC online tool. Environmental parameters and crop residue parameters were adjusted to this specific case.

2.10.6. Emissions of NO_x to Air

During denitrification processes in soils, nitrous oxide (NO_x) may also be produced. These emissions were estimated from the emissions of N_2O by multiplying it by 0.21. Since this process is not one of conversion from N_2O to NO_x, but a parallel process, no correction of the N_2O emissions is required [165].

2.10.7. Nitrate Leaching to Groundwater

IPCC 2006 methodology was followed to calculate nitrate leaching, for each applied kg of nitrogen fertilizer, 1.33 kg of nitrate is leached [168].

2.11. Bio-Polyol Syntheses

Rapeseed oil-based polyols were synthesized using transesterification of rapeseed oil with triethanolamine (TEA), as well as amidization with diethanolamine (DEA). The synthesis of rapeseed oil polyols was carried out in a pilot-scale reactor with a volume of 50 L, according to more detailed description and properties analysis methods of rapeseed oil-based polyol synthesis as given in the published paper by the author [96].

2.12. Energy Consumption for Polyol Synthesis

To determine energy consumption for polyol synthesis Hobo Onset data logger U12-006 with CTV-A sensors was used. The sensors were installed at a reactor power supply cable for each of the three phases. The sensors measured AC in the range from 2 amps to 20 amps. The measured current was converted to power according to equation (1):

$$P = (U_1 \cdot I_1 \cdot \cos(\varphi_1) + U_2 \cdot I_2 \cdot \cos(\varphi_2) + U_3 \cdot I_3 \cdot \cos(\varphi_3)) / 1000 \quad (2.1)$$

where,

P - power, kW

U_1, U_2, U_3 – voltage for each phase, V;

I_1, I_2, I_3 – current for each phase, A;

φ_1, φ_2, φ_3 – power factor for each phase, A.

Since the electricity power factor is taken with a phase of 90^o (thus cos $(\varphi_{1,2,3}) = 1$ and voltage is 220 V for all phases for the measuring system, it is reasonable to simplify equation:

$$P=220 \cdot (I_1+I_2+I_3)/1000 \quad (2.2)$$

Total energy consumption for polyol synthesis depends on the synthesis duration, according to the equation:

$$Q=P \cdot t \quad (2.3)$$

where,

Q – energy consumption, kWh;

t – test time, h [169].

Additionally, the energy consumption for 0.55 kW vacuum pump was calculated according to the equation (2.3) and added to the polyol synthesis energy.

3. RESULTS AND DISCUSSION

The contents of the papers, figures and tables have been extracted literally from the versions of the papers submitted and published to the international peer-reviewed scientific journals, and adapted, if necessary, to the format of this thesis.

The thesis was designed to show comprehensively inputs and outputs for all major steps and to avoid black box unit processes and provide transparent, reproducible results. The visual representation of research design and phases is depicted in Fig. 3.1.

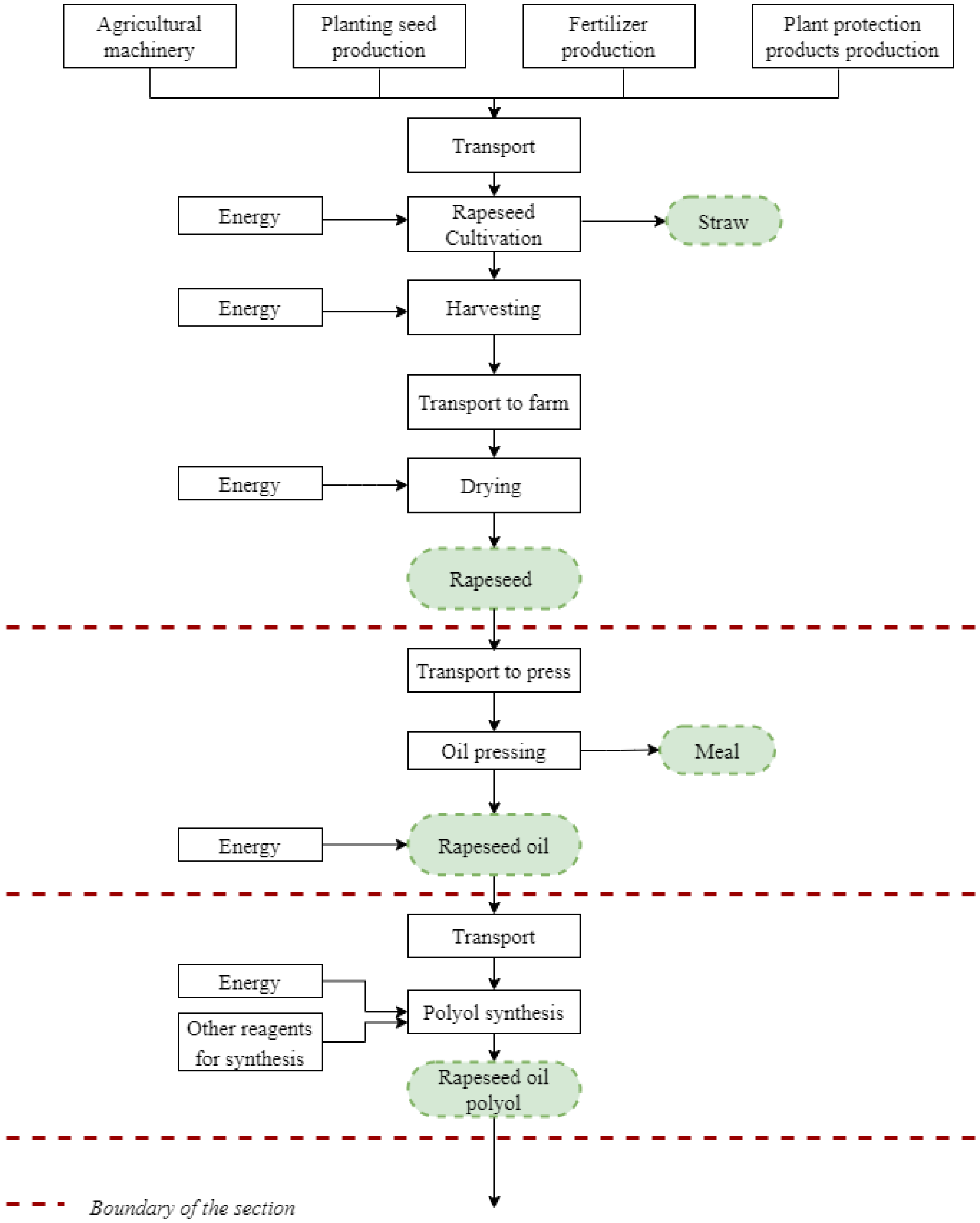

Fig. 3.1. Research design and system boundaries for each of the steps for renewable polyol monomers for polyurethane production.

The results are reported in three large sections:

- Detailed LCI of rapeseed production in Northern Europe with Latvia as a case study, published by author Fridrihsone et al. 2018 [170].
- LCI of rapeseed oil production [171].
- LCA of rapeseed and rapeseed oil production [171].
- LCA of rapeseed oil-based polyol production, published by author Fridrihsone et al. 2020 [172]

3.1. LCI of Rapeseed Agricultural Stage

3.1.1. Goal and Scope Definition, Functional Unit

The goal was to carry out a cradle-to-gate LCI of rapeseed (both spring and winter) production in Northern European country Latvia, to be further involved in an LCA for bio-based polyols for PU production. The starting point is the cradle-to-gate perspective – from raw materials production to seed harvesting and drying. The inventory has been carried out to identify and quantify the inputs and outputs associated with the production of oilseed rape in Zemgale region of Latvia.

The FU was set as 1 t of rapeseed. The reference flow selected was 1 ha. It should be considered that on average, 1 ha produces 3.5 t of winter rapeseed and 2.5 t of spring rapeseed (refer to Section 3.1.5).

3.1.2. System Boundaries

3.1.2.1. Geographical Boundary

Oilseed rape is grown in Zemgale region in a cereal and oilseeds production company. Zemgale region is located in the central part of Latvia to the south from Riga and it has a long land border with Lithuania. Zemgale region is in the central part of the Zemgale plain (Fig. 3.2).

Fig. 3.2. The location of Zemgale (Latvia) in Europe.

Zemgale has a very high proportion of arable land and the most fertile agricultural land of Latvia [173]; it also has a developed agriculture and agricultural processing industry. Zemgale is commonly recognized as the granary of Latvia. All of the components needed for rapeseed production are produced outside Latvia and are imported.

3.1.2.2. Time Horizon

Data about spring oilseed rape production is from 2008 to 2014. For winter oilseed rape, the data is from the period of 2008 to 2016. The taken data horizon is enough to level out differences in crop yields related to fluctuations in growing conditions over the years such as climate, pests and diseases.

3.1.2.3. Data Requirements

The goal was to be as accurate as possible and avoid assumptions as much as possible. The LCI data for the foreground system (data about yield, use of plant protection products, fertilizers, seeds, the kind of agriculture machinery used and other data related to agricultural practices used) were collected from the lead agronomist at one of the largest agricultural companies in Latvia. Data about fertilizers, plant protection products and the seed supply chain – from factory/warehouse to farming company were collected from distributors/importers in Latvia. If data about the complete supply chain or a specific element was not available, a consistent assumption was made. Assumptions will be discussed in sections where the LCI data will be described.

3.1.3. General Description of Rapeseed Production and Data Provider

In the region under study, Zemgale region, Latvia, spring rapeseed is usually sown in April and harvested from August 20th to 28th. Winter rapeseed is sown between August 5th and 25th and harvested from July 28th to August 10th [174].

The interviewed Latvian company practices intensive farming implementing a low-tillage method for winter rapeseed with the adoption of a soil disc cultivation within a depth of a 10 – 12 cm. After that, the company uses agricultural machinery that carries out soil loosening and sowing in one-step. In the case of spring rapeseed, tillage is used, followed by disc cultivation, drag harrowing, followed by soil loosening and sowing in one-step [174].

The agricultural company providing the data is one of the largest crop farming companies in Latvia. In 2015, the company had 5742 ha of land 18.9 % (1083 ha) of which was used for winter rapeseed cultivation in [174]. In 2015, the average total land area per agricultural holding was 35.9 ha, of which agricultural area was 24.3 ha. In 2016, Latvia had 82 400 agricultural holdings [175].

3.1.4. Land

The lead agronomist reported that the average organic matter content of the soil is 3.4 % and the pH is 7.4. The soil has a normal humidity regime being sandy loam or loam sodcalcareous soil. The soil is not limed [174]. No artificial irrigation is applied to rapeseed fields, only natural irrigation (rain) [174].

It was assumed that direct land use did not occur as there had not been any cropland management activities for more than 20 years [176]. Rapeseed has been cultivated in croplands that have been used for intensive agriculture over the last 50 years [174]. The land occupation was recorded as Occupation, annual crop, non-irrigated. The assessment of ILUC was beyond the scope of this study.

3.1.5. Winter and Spring Rapeseed Yields

The yields of winter and spring rapeseed (Fig. 3.3) produced in Zemgale, Latvia are depicted in Fig. 3.4 and Fig. 3.5, respectively.

Fig. 3.3. Harvested rapeseed in Zemgale, Latvia. Photo taken by J.Butkus in July 2019.

The average yield for winter rapeseed was 3.5 t/ha during the period 2008–2016. The average yield for spring rapeseed was 2.5 t/ha during the period 2008–2014. In 2014, harsh winter and unusual freezing conditions caused a large acreage of winter rapeseed to freeze, and the company was forced to plant spring rapeseed in spring and that resulted in an increase in spring rapeseed cultivation. After 2014, the company discontinued spring rapeseed cultivation due to attacks of flea beetles. Spring oilseed rapeseeds can't be treated because of bees, and thus crop fields have to be sprayed all the time [174].

In Europe, rapeseed is mainly grown as a winter crop as it generates the highest seed and oil yield of oilseed crops [177]. The average yield of rape and turnip rape yield of EU-28 is 3.2 t/ha as reported by Eurostat during 2008–2016 [178]. According to the Central Statistical Bureau of Latvia, the average winter rapeseed yield was 2.7 t/ha during 2008–2016. The average spring rapeseed yield was 1.7 t/ha during 2008–2014 [43]. The yield rapeseed yield varies across Europe depending on soil type, climatic conditions, agricultural management practices, time of planting and other factors and also yield information differs from source to source. The highest yields typically are harvested in Central and Eastern Europe [177]. However, according to the latest data, the average yield in Western Europe was 3.6 t/ha, while in Eastern and Southern Europe it was below 2.5 t/ha. According to FAOSTAT, from 2008 through 2016, the average yield for Northern Europe was 3.0 t/ha, the best performer was Ireland with 3.8 t/ha, followed by Denmark with 3.7 t/ha, the United Kingdom with 3.4 t/ha The yield below 2.5 t/ha was for remaining countries in the region – Estonia, Lithuania, Finland, Latvia and Norway [42].

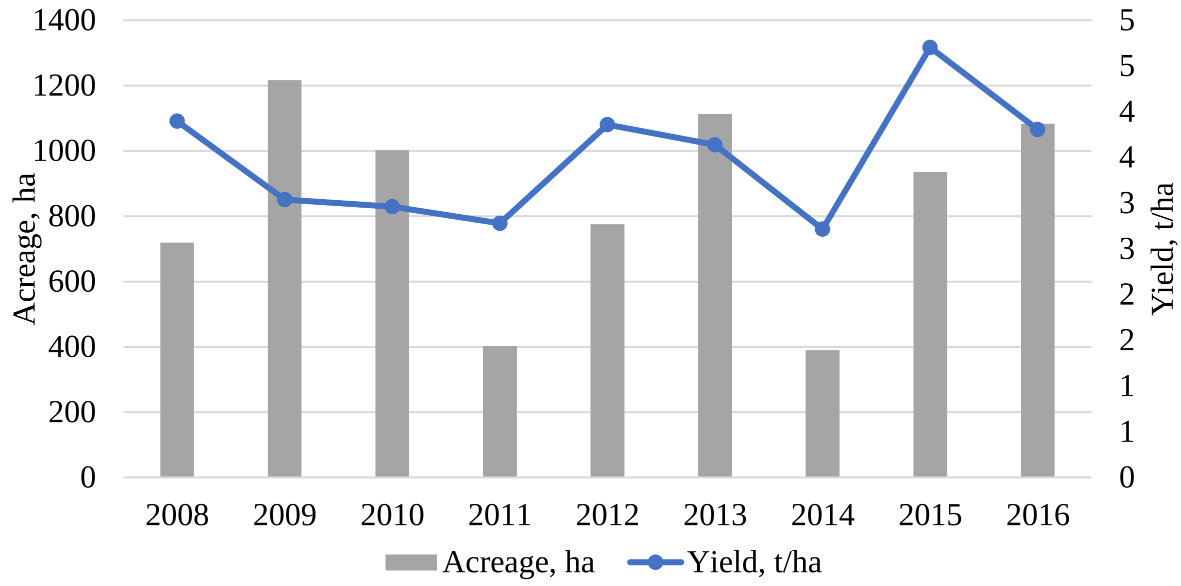

Fig. 3.4. Yield (barn weight cleaned, dried with a water content of 8 %) of winter rapeseed produced in Zemgale, Latvia, from 2008–2016.

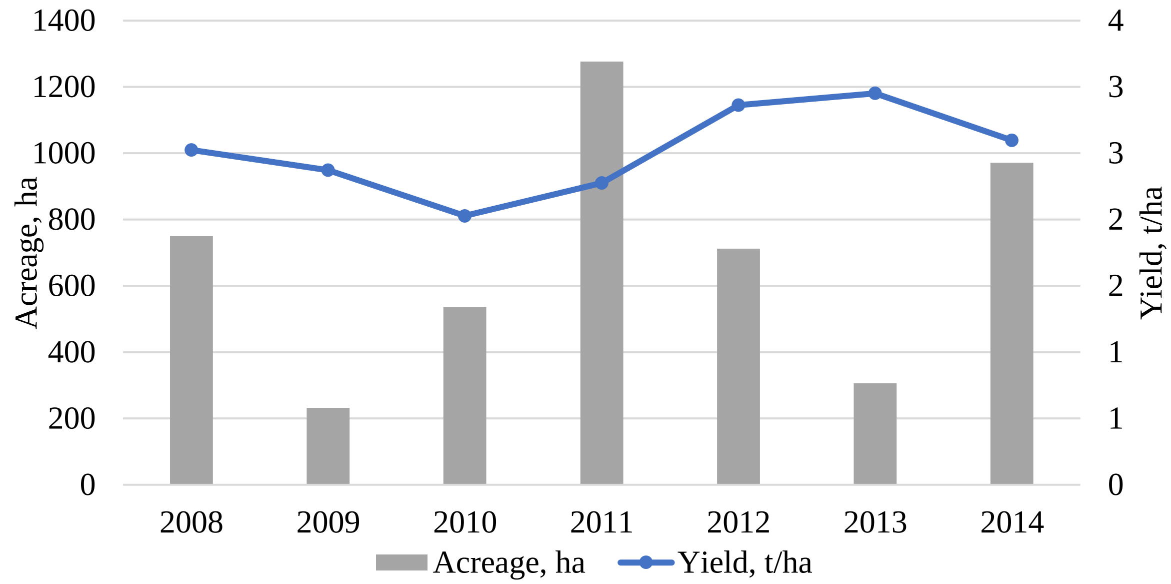

Fig. 3.5. Yield (barn weight cleaned, dried with a water content of 8 %) of spring rapeseed produced in Zemgale, Latvia, from 2008–2014.

3.1.6. Materials

Materials for rapeseed production include planting seed, plant protection products and fertilizers and micronutrients. The summary of material input is in Table 3.12, however, each input is explained in detail in the following sections.

3.1.6.1. Planting Seed Material

The agricultural company in Zemgale region in Latvia is effectively using only hybrid seeds for rapeseed breeding and production. Hybrid varieties can be used only for one year without changes in the properties because the next generation of plants from those hybrids will not have the uniform characteristics of their parental lines. Rape plants are not uniform, they ripen unevenly and are unevenly prolific [174]. Thus, the agricultural company buys new seeds every year.

Other papers mostly do not report and specify what kind of seed is used - hybrid or open-pollinated seeds. However, in terms of cultivation, there is a trend towards increased use of hybrids in all major canola and oilseed rape-growing areas worldwide. In Germany, Great Britain and France, from 50 % up to 70 % of rapeseed acreage uses hybrid seeds [177], [179]. The agricultural company uses several winter rapeseed breeds from different breed selectors with planting seed input ranging from 3.6 kg/ha to 6 kg/ha to achieve the desired plant density. Seeds are delivered from Sweden, Germany and Denmark. Germany was chosen as a country of origin as it is the farthest point from Latvia to model the worst possible scenario for transportation impact. For spring rapeseed, the company used two different breeds from a company located in Sweden. The average planting seed input needed for rapeseed is presented in Table 3.1.

Table 3.1

Planting Seed Input for 1 t of Winter and Spring Rapeseed With Reference Flow of 1 ha

Type	**Average planting seed input**	
	kg/ha	**kg/t**
Winter rapeseed	4.8	1.4
Spring rapeseed	4.0	1.6

3.1.6.2. Fertilizers

Fertilizers used for rapeseed cultivation include nitrogen, potassium, sulphur and phosphorus. The need for fertilizers depends on whether the crop is winter or spring rapeseed, as well as on soil type and climate, the previous crop [163]; thus fertilizer use differs for rapeseed cultivation in different countries.

The lead agronomist reported a standard fertilizing scheme the company uses for winter and spring rapeseed (Table 3.2). The yearly dosage can change ±10 % depending on various factors. The company does not take into account nutrients from the previous crop and the standard fertilizing scheme is not adjusted to this factor. At times, the company also uses pig slurry; however since the amount and area applied varies significantly, this factor was not taken into account in the LCI. The difference between dosage and applied nutrient is due to other compounds/additives present in the fertilizer to make it mechanically and chemically stable. Most of the additive is calcium sulphate.

Table 3.2

Fertilizer Application Rates for Winter and Spring Rapeseed

Applied fertilizer product	**Dosage /nutrient**	**Value, kg/ha**		**% of total applied N**	
		Winter	**Spring**	**Winter**	**Spring**
NPKS 4-16-34-2S	Dosage	380.0	380.0		
	Nitrogen	15.2	15.2	6.9	8.1
	P_2O_5	60.8	60.8		
	K_2O	129.2	129.2		
	Sulphur	7.6	7.6		
Ammonium nitrate N34.4	Dosage	300.0	220.0		
	Nitrogen	103.2	75.7	46.7	40.5
Ammonium sulphate N21+S24	Dosage	180.0	160		
	Nitrogen	37.8	33.6	17.1	18.0
	Sulphur	43.2	38.4		
KAS N25+S3	Dosage	260.0	250.0		
	Nitrogen	65.0	62.5	29.4	33.4
	Sulphur	7.8	7.5		
Total	Nitrogen	221.2	187.0		
	Sulphur	58.6	53.5		
	P_2O_5	60.8	60.8		
	K_2O	129.2	129.2		

The total nitrogen fertilizer application rate reached 221.2 kg N/ha for winter rapeseed and 187 kg N/ha for spring rapeseed. Schmidt et al. 2007 reported N-norm of 171 kg N/ha with 3.6 t/ha yield for winter rapeseed on mixed sand and clay soil (52 % of Denmark`s agricultural soil) [163]. The nitrogen level for winter rape recommended in Germany is up to 250 kg N/ha; for spring rape the recommended level is up to 180 kg N/ha [180]. Dutch cultivation practices give an application of 200–250 kg N/ha for rapeseed cultivation representing two case studies with a yield of 3.9 t/ha and 4.0 t/ha [181]. The total P_2O_5 application reached 60.8 kg/ha. The recommended P_2O_5 level for winter and spring rape cultivated in Germany is 80–100 kg/ha, respectively [180]. Marinussen et al. 2012 give a value of 55 kg P_2O_5 and 70 kg P_2O_5 for the two case studies, representing a rapeseed yield of 3.9 t/ha and 4.0 t/ha [181]. Concerning potassium, K_2O fertilizer 129.2 kg/ha is applied for both winter and spring rape. German standards report up to 120 kg/ha for spring rapeseed and 180–220 kg/ha for winter rapeseed [180]. The average use of K_2O for rapeseed cultivated in France and Germany was 82 kg/ha [181]. The total amount of N, P and K fertilizers equals 117.5 kg/t for winter rapeseed, while for spring rapeseed this amount rises to 150.8 kg/t. The total amount of applied nitrogen reached 63.2 kg N/t and 74.8 kg N/t for winter and spring species, respectively, and was satisfied with 4 different fertilizers. In Latvia, many fertilizers are imported from Belorussia and Russia and Lithuania and for many of them there are no inventories present in ecoinvent v3.5 database, so the assumption has to be made or the closest general data from the inventory has to be selected. Moreover, different fertilizers present a different share of NPK values and at times contain a portion of sulphur – i.e. NPKS 4-16-34-2S and KAS N25+S3 under trade name Lyderis© 25+S3 which is urea ammonium nitrate mixture with additional sulphur.

The in-depth LCI data about fertilizers also have to be harmonized with datasets available in the ecoinvent v3.5 database. To model fertilizers, the data from the State Plant Protection Service about the volume of imported fertilizers in Latvia was used. Fertilizers from Table 3.2 were modelled as the largest produced and imported fertilizer in corresponding fertilizer type [182]. Within present LCA model, NPKS 4-16-34-2S fertilizer satisfied phosphorus and potassium requirements, the input of potassium oxide (K_2O) was modelled as the input of potassium chloride, while the input of phosphorus pentoxide (P_2O_5) was modelled as the input of diammonium phosphate. Nitrogen in NPKS 4-16-34-2S fertilizer was modelled as the input of ammonium sulphate. Fertilizer KAS N25+S3 is urea ammonium nitrate mixture that contains 25 % of nitrogen and was modelled as urea ammonium nitrate with N content 32 %. The amount was recalculated to correspond to nitrogen content in fertilizer KAS N25+S3.

3.1.6.3. Plant Protection Products

During the cultivation of rapeseed, plant protection products, commonly referred to as pesticides, are used to destroy pests and prevent diseases. Data about the quantity and active ingredients in plant protection products used for rapeseed production is given in Table 3.3.

Table 3.3

Plant Protection Products Used for Winter and Spring Rapeseed, Reference Flow 1 ha

Plant protection product type	**Active ingredient/ CAS#**	**Dosage, L/ha**	**Active ingredient**	
			content, g/L	**per ha, g/ha**
Herbicide-1	Metazachlor 67129-08-2	2.5	333	832.5
	Quinmerac 90717-03-6		83	207.5
Herbicide-2 (Winter rape only)	Propaquizafop 111479-05-1	1.0	100	100
Insecticide*	λ-Cyhalothrin 91465-08-6	0.2	50	10
Fungicide-1*	Deltamethrin 52918-63-5	0.1	50	5
Fungicide-2*	Cyproconazo 94361-06-5	0.6	80	48
	Azoxystrobin 131860-33-8		200	120
Fungicide-3**	Metconazole 125116-23-6	0.7	90	63
Desiccant (Spring rape only)	Diquat dibromide 85-00-7	2.5	150	375

* – plant protection product applied together with micro-elements reported in Table 3.5.
** – applied as a growth regulator.

The formulas and active ingredients in plant protection products were obtained from the State Plant Protection Service that publishes the List of Registered Plant Protection products in the Republic of Latvia every year [183]. Plant protection products are sprayed on the fields and thus they are diluted with water. Plant protection products without active ingredients also contain other ingredients. Water for dilution and other ingredients present in plant protection products was negligible.

The total of plant protection products used reached 5.0 L/ha for winter rapeseed and 6.6 L/ha for spring rapeseed. Overall data about plant protection product use and their representation is a “grey zone” in LCA papers. Other authors report total pesticide use per hectare without giving details about specific pesticides or their active ingredients, yet others report kg of active ingredients per hectare.

The input of plant protection products was aggregated according to their chemical class (Table 3.4) in the ecoinvent v3.5 database [184].

Table 3.4

Aggregated Plant Protection Products According to Their Class

Chemical class of plant protection product	**Active ingredients**	**The applied amount, g/ha**	
		Winter rape	**Spring rape**
Acetamide-anillide-compound	Metazachlor	832.5	832.5
Pesticides, unspecific	Azoxystrobin, Quinmerac	327.5	327.5
Diphenyl ether compounds	Propaquizafop	100	–
Pyrethroid compound	λ-Cyhalothrin, Deltamethrin	15	15
Cyclic N-compound (triazole)	Cyproconazo, Metconazole	111	111
Bipyridylium compounds	Diquat dibromide	–	375

3.1.6.4. Micronutrients

Other fertilizers, such as sulphur and micronutrients, are also used for rapeseed cultivation. Sulphur is reported in Table 3.2 as it is applied in complex fertilizer together with macro-nutrients (N, P, K). The agricultural company also uses micronutrients as reported in Table 3.5.

If a micronutrient producer has allowed making the mixtures, few of the plant protection products are applied together with micronutrients, mixtures are made. The company uses this practice to save time and fuel.

Table 3.5

Micronutrient Application Rate

Type	**Micro-nutrient**	**Dosage, L/ha**	**Active ingredient content in micro-element, g/L**	**Active ingredient applied, g/ha**
Micro-element-1	Nitrogen	2.0	80	160
	Magnesium		90	180
	Sulphur		80	160
	Boron		50	100
	Manganese		90	180
	Molybdenum		4	8
Micro-element-2	Nitrogen	3.0	350	1050
	Magnesium oxide		47	141

With reference to 1 t of produced rapeseed, these amounts are equal to 16.7 kg/t and 21.4 kg/t of applied Sulphur for winter and spring rapeseed, respectively. For both rapeseed species, micronutrient mixtures in a total of 5.0 L/ha were also applied, which equals to 1.4 L/t and 2.0 L/t for winter and spring rapeseed, respectively. Micronutrients and sulphur constitute approximately 14.0 % and 14.1 % of the application of the total fertilizers for winter and spring rapeseed, respectively. These figures are in line with the outcomes by Schmidt et al. 2007 that shows a share of 13 % of the total application of fertilizers not including sulphur, boron, magnesium [163]. Unfortunately, no LCI have been identified for these fertilizers. Therefore, sulphur and micronutrient mixtures are not included in the final LCI (Table 3.12) used for the modelling of rapeseed production in Latvia. Other authors also reported that for several fertilizers, such as multi-nutrient compounds sulphur, boron, magnesium, and others, there are no LCI [163], [185]. These fertilizers have not been comprehensively assessed and thus these inputs have to be excluded from the LCA or adapted with a generalization of the type of fertilizer used. It was identified that other studies do not report the use of micronutrients for rapeseed production and thus this aspect has not been comprehensively assessed in rapeseed cultivation. Moreover, it is not clear do crop companies in other countries use micronutrients because in the vast majority of papers micronutrient input flow is not reported. According to leading agronomist of data providing company, most likely all farmers use micronutrients [174]. In Latvia, also Lithuania, agricultural companies choose to use micronutrients that are foliarly-applied nutrients because they are directly absorbed through the leaves. This uncertainty highlights the need to improve and expand the database of fertilizer inventories.

3.1.7. Rapeseed Straw

Rapeseed straw is a co-product of rapeseed production. There is a large amount of rapeseed straw generated from the harvest of rapeseed. Different residue to crop ratios are reported, it varies depending on the soil, agricultural practices, rain, fertilizers, geographical location and other factors. Residue to crop ratio for rapeseed varies from 1.4–2.0 [186]. The agricultural company reported that on average straw (fresh matter) is collected twice as much as rapeseed [174].

The agricultural company located in Zemgale implements the type of an agricultural management practice where the remaining biomass generated (stalks, pods and leaves) is left on the field and incorporated back into the soil. Rapeseed straw was incorporated back into the soil at a depth of 10–12 mm using disc cultivators. Also, according to official data, 0 % of the rapeseed straw is removed from the field in Latvia [187]. The above mentioned agricultural management practice presents several benefits, namely enhances the organic content of the soil, which is beneficial for the next crop as a soil nutrient, and improves the structure of the soil and prevents soil erosion [185], [188], [189].

Consequently, no value was allocated to the straw and 100 % of the impact was allocated to the oilseed. Moreover, the company would not be willing to remove the straw as it requires additional agricultural machinery, in the end, it wouldn't be economically viable for the company [174]. Also, energy production from straw is not yet economically feasible [133].

3.1.8. Agricultural Machinery and Transport

The transport of input materials, planting seeds, fertilizers and plant protection products, has been defined as accurately as possible, in terms of mode and distance (Table 3.6). Information was gathered from the producers and/or distributors of the products. The origin is specified: some distribution chains start at the producer, some at the distributor. In the case of the latter, most often local distributors were able to give information only about the last distribution chain link. The transported amount of input materials needed for the production of rapeseed in regards to the reference flow is considered. For plant protection products and micro-elements, to calculate mass instead of volume per ha, the density provided in safety data sheets was taken. The type of the ship is not known, so an assumption will have to be made. It was not possible to obtain more detailed information about the transportation of micro-nutrient 2 other than it is delivered from Poland. The average distance from the company`s storage to the field and from fields to the regional processing centre, where the grain drying takes place, is 15 km.

Table 3.6

Transport of Goods Related to the Agricultural Stage for Rapeseed per ha

Input material	Type* W or S	Amount, kg/ha	From	To	Distance, km	Mode, size	From	To	Distance, km	Mode, size
Seed	W	5.8	Producer in DE	Storage in LV	1600	Truck, 24 t	Storage in LV	Company warehouse	65	Truck, 10 t
	S	4.0	Producer in SE	Port in Riga	900	Ship, no info	Port in Riga - Storage in LV	Company warehouse	120	Truck, 10 t
Fertilizer NPKS 4-16-34-2S	W, S	380	Producer in BY	Storage in LV	600	Truck, 24 t	Storage in LV	Company warehouse	70	Truck, 24 t
Fertilizer – Ammonium nitrate	W S	300 220	Producer in LT	Storage in LV	210	Truck, 24 t	Storage in LV	Company warehouse	45	Truck, 24 t
Fertilizer – Ammonium sulphate	W S	180 160	Producer in LT	Company warehouse	280	Truck, 24 t	–	–	–	–
Fertilizer-KAS N25+S3	W S	260 250	Producer in LT	Storage in LV	210	Truck, 24 t	Storage in LV	Company warehouse	45	Truck, 24 t
Herbicide-1	W, S	2.8	Port in DK	Port in LV	1100	Ship, no info	Port in LV	Company warehouse	80	Van
Herbicide-2	W	1.0	Producer in IL	Storage in LT		Truck, 24 t	Storage in LT	Company warehouse	–	–
Insecticide	W, S	0.2	Storage in PL	Company warehouse	600	Truck, 24 t	–	–	–	–
Fungicide as a growth regulator	W, S	0.7	Port in DK	Riga port	1000	Ship, no info	Port in LV	Company warehouse	80	Van
Fungicide-1	W, S	0.1	Port in DK	Riga port	1000	Ship, no info	Port in LV	Company warehouse	80	Van
Fungicide-2	W, S	0.7	Storage in PL	Company warehouse	600	Truck, 24 t	–	–	–	–
Desiccant	S	2.9	Storage in PL	Company warehouse	600	Truck, 24 t	–	–	–	–

Input material	Type* W or S	Amount, kg/ha	From	To	Distance, km	Mode, size	From	To	Distance, km	Mode, size
Micro-element-1	W, S	3.1	Port in the UK	Port in LT	2500	Ship, no info	Port in LT	Company warehouse	270	Van
Micro-element-2	W, S	3.0	Producer in PL	Company warehouse	600	Truck, 24 t	–	–	–	–
Seed and plant protection product transportation from company storage to the field	W S	0.01 0.01	Company storage	Field	15	Truck, 25 t	–	–	–	–
Fertilizer transportation from company storage to the field	W S	1.1 1.1	Company storage	Field	15	Tractor and trailer, 10 t	–	–	–	–
Rapeseed from field to farm	W S	3.5 2.5	Field	Company storage	15	Truck, 25 t	–	–	–	–

*Type: Winter rapeseed – W; Spring rapeseed – S.

DE – Germany, LT-Lithuania, LV – Latvia; DK – Denmark; UK – United Kingdom; PL – Poland; IL – Israel; BY – Belorussia; Sweden – SE.

Fuel consumption for each fieldwork process has been well documented by the lead agronomist of the company. The agricultural machinery (Fig. 3.6), diesel consumption related to the cultivation of rapeseed and operations per year is shown in Table 3.7.

Table 3.7

Diesel Consumption for Different Fieldwork Process

Fieldwork process		**Diesel consumption, L/ha**		**Operations per year**
		Winter	**Spring**	
Tilling	Tilling – turn over the soil	0	27.0	1
	Disc cultivation	7.5	7.5	1
	Drag harrowing	0	8.6	1
Sowing	Sowing	16.2	9.6	1
Fertilizing	Application of fertilizer	1.1	1.1	2–3*
Spraying	Application of plant protection products	0.8	0.8	4–7*
Harvesting	Combine harvesting	20.0	20.0	1
	$Total_{min}$	49.2	78.2	
	$Total_{max}$	52.8	81.8	

* depending on the need.

Fig. 3.6. Harvesting of rapeseed in Zemgale, Latvia. Photo taken by J. Butkus in July 2019.

The data from Table 3.6 was aggregated by transport mode and expressed as a tonne-kilometre (tkm), which is a unit of measure of freight transport which represents the transport of one t of goods by a given transport mode over a distance of one km (Table 3.8).

The summary of transport and agricultural machinery inputs is depicted in Table 3.8. For the application of fertilizers and plant protection products amount of operations vary from year to year, so an average was taken to determine the final consumption of fuel. Moreover, it is meaningless to compare diesel consumption for different countries, as it varies depending on the soil type and the condition of the agricultural machinery, its age, model type and horsepower.

Table 3.8

Diesel Used for Winter and Spring Rapeseed Agricultural Machinery and Transport per FU

Input flows	Unit	Rapeseed	
		Winter	**Spring**
Agricultural operations			
Tilling – turn-over of the soil	L/t	–	10.8
Disc cultivation	L/t	2.1	3.0
Drag harrowing	L/t	–	3.4
Sowing	L/t	4.6	3.8
Application of fertilizer	L/t	0.8	0.9
Application of plant protection products	L/t	1.3	1.8
Combine harvesting	L/t	5.7	8.0
Transport			
Lorry 7.5–16 t	tkm	0.1	0.2
Lorry 16–32 t	tkm	146.7	183.7
Transoceanic freight ship	tkm	1.1	3.0
Lorry 3.5–7.5 t	tkm	0.1	0.1
Tractor	tkm	4.8	6.1

Despite having high-quality primary data from the company, it was very challenging to model the agricultural machinery inputs because the ecoinvent database did not contain the specific machinery datasets. It was especially challenging for the soil tillage operations, namely, disc cultivation, drag harrowing and sowing together with soil loosening, as there were no such datasets. Agricultural equipment is infinitely more complicated and proprietary today than available in the databases. The most relevant datasets in the ecoinvent v3.5 were modified so the diesel consumption (and associated emissions) correspond with the information provided by the agricultural company.

3.1.9. Drying

After harvesting rapeseeds are transported to drying and purification. Drying kiln heated by gas with drying capacity 60 t/h is used. Purification takes place through a sieve using gravity and wind power [174]. Drying of rapeseed is requested by industry players to avoid spoilage by fungi and mites during storage [190]. The agricultural company provided data about the necessary gas amount needed for drying 1 t of grain crops (including rapeseed). In this case, it was not divided more finely as the company does not collect such type of data. Depending on the year and amount of precipitation, rapeseed contains a different amount of moisture and gas amount needed for drying varies significantly. For example, in 2016 during harvesting there was a lot of rain, the grains had high moisture content and the needed gas amount was 9.1 m^3/t. In 2015, the weather was dryer and the natural gas consumption for seed drying was only 1.2 m^3/t [174]. On average during 2013–2016, the natural gas consumption for drying of 1 t of grain crops was 5.9 m^3/t. The lower heating value of 31.82 MJ/m^3 was taken from official data provided by the natural gas provider in Latvia [191], which resulted in 189.2 MJ per t of rapeseed. Other studies report various values for grain drying in terms of MJ, for example, French researchers report 147.9 MJ/t provided with electricity [192], for rapeseed cultivated in Poland only 17.1 MJ/t is reported for grain drying [193] provided with fuel oil. German study provided a value of 420 MJ/t provided with electricity and fuel oil [194]. The amount of evaporated water is calculated according to the methodology described by Nemecek and Kagi, 2007 [184]. Rapeseed is dried till moisture content of 8 %, moisture content after harvest on average is 12 % [174].

3.1.10. Emissions

The summary of emissions during the agricultural state is presented in Section 3.1.12, however below all inputs are explained in detail.

3.1.10.1. Emissions of Fossil CO_2 After Urea Application

Fertilizer KAS N25+S3 is urea ammonium nitrate mixture that contains 25 % of nitrogen and was modelled as urea ammonium nitrate with N content 32 %. Respectively, 14.5 kg and 19.5 kg of urea ammonium nitrate were applied for winter and spring rape, per FU. Urea ammonium nitrate contains 32 % N, which results in 8.0 kg CO_2/t and 10.7 kg CO_2/t for winter and spring rape.

3.1.10.2. Emissions of Ammonia to Air

During 2008-2016, the average ammonia emissions from agriculture comprised 82.3 % of total emissions. In 2016, ammonia emissions from agriculture was 85.7 % (14 kt), while for EU-28 it was 92.0 % (3623 kt) [195], [196]. In 2016, ammonia emissions reached 20.3 kg NH_3/ha in EU-28, in Latvia 7.2 kg NH_3/ha, which was the lowest number in EU-28 [196]

For rapeseed cultivated in Latvia, Zemgale region, the total ammonia emissions were 9.4 kg NH_3/ha and 8.4 kg NH_3/ha for winter and spring rapeseed, respectively.

3.1.10.3. Emissions of the Application of Plant Protection Products

Due to the increased use of pesticides over the last decades and due to their toxic nature and potentially adverse health effects, the use of plant protection products and emissions have caused great public concern [197].

Pesticide emissions occur during and after the application of plant protection products in agriculture. The rate and extent of emissions are affected by many factors, including the properties of the pesticides, soil and crop type, application method and environmental variables (wind, temperature, soil moisture content, soil type and structure).

The amount of active ingredients applied is given in Table 3.3 and recalculated to the FU. The emission factors for the used plant protection products can be found in a previously published paper by the author [170]. The emissions of plant protection products are presented in Table 3.9.

Table 3.9

Emissions of Plant Protection Products for Winter Rape and Spring Rape

Plant protection product type	**Active ingredient**	**The applied amount, kg/t**	**Emission to the compartment, kg/t**			**Difference, kg/t**
			Soil	**Surface water**	**Air**	
Winter rape						
Herbicide-1	Metazahlor	0.24	0.12	0.0012	0.012	0.11
	Quinmerac	0.059	0.030	0.00030	0.00059	0.029
Herbicide-2	Propaquizafop	0.029	0.014	0.00014	0.00029	0.014
Fungicide-1	Deltametrin	0.0014	0.00071	0.000007	0.000014	0.00069
Fungicide-2	Cyproconazo	0.014	0.0069	0.000069	0.00069	0.0061
	Azoxystrobin	0.034	0.017	0.00017	0.00034	0.017
Insecticide	λ-Cyhalothrin	0.0028	0.0014	0.000014	0.000029	0.0014
Fungicide-3	Metconazole	0.018	0.0090	0.000090	0.00018	0.0087
Spring rape						
Herbicide-1	Metazahlor	0.33	0.17	0.0017	0.017	0.15
	Quinmerac	0.080	0.040	0.00040	0.00083	0.039
Fungicide-1	Deltametrin	0.0020	0.010	0.000010	0.000020	0.0010
Fungicide-2	Cyproconazo	0.019	0.010	0.00010	0.00096	0.0085
	Azoxystrobin	0.048	0.024	0.00024	0.00048	0.023
Insecticide	λ-Cyhalothrin	0.0040	0.0020	0.000020	0.000040	0.0019
Fungicide-3	Metconazole	0.025	0.013	0.00013	0.00025	0.012
Desiccant	Diquat dibromide	0.15	0.075	0.00075	0.023	0.052

For all plant protection products, there was an existing emission in ecoinvent v3.5 database with exception of Metconazole, which is a Triazole class fungicide and was replaced by another fungicide in this class, namely, Epoxiconazole [198].

3.1.10.4. Nitrous Oxide Emissions

Nitrous oxide emissions are produced from natural and human sources. The use of synthetic fertilizer in agriculture is a major source of nitrous oxide emissions and is of great concern [199]. The use of nitrogen-containing fertilizers creates direct emissions that come from fertilized agricultural soils and manure and indirect emissions from runoff and leaching of fertilizers. Cultivation of rapeseed is characterized by high greenhouse gas emissions, which is associated with high nitrogen demands for plant growth [185].

Nitrous oxide emissions from the cultivation of winter and spring rapeseed were calculated using the GNOC [167]. The calculated N_2O emissions are shown in Table 3.10.

Table 3.10

Nitrous Oxide Emissions Calculated by GNOC

Type	**Value, kg N_2O/ha**	
	Winter	**Spring**
Direct N_2O emissions from fertilizer application N_2O	3.40	2.67
Indirect N_2O emissions produced from leaching and runoff from fertilizer application N_2O	0.78	0.66
Indirect N_2O emissions produced from atmospheric deposition of N volatilised N_2O	0.35	0.29
Direct N_2O emissions from N in crop residues N_2O	1.24	0.89
Indirect N_2O emissions produced from leaching and runoff from N in crop residues N_2O	0.28	0.20
Total soil N_2O emissions	**6.05**	**4.71**

3.1.10.5. Emissions Related to Phosphorus

Phosphorus emissions contain no emissions to air. Phosphor binds tightly to soil particles, phosphate leaching was specified as 2.9 % of the surplus of phosphorus. The remaining is accumulated into the soil. The content of phosphorus in the harvested crop is 6.2 g per kg of rapeseed and 0.77 g per kg of straw (fresh weight basis) [163]. The applied amount of fertilizer P_2O_5 is 60.8 kg/ha for winter and spring rapeseed (Table 3.2), which corresponds to 26.5 kg of phosphorus. The phosphorus surplus can be calculated by applying the reported yield of rapeseed (spring – 2.5 t/ha, winter 3.5 t/ha), straw production with a straw to seed ratio of 2:1 (all the straw remains on the field) and planting seed input as reported in Table 3.11.

Table 3.11

Phosphorus Field Balance and Leaching Calculation

Input, kg P/ha	**Winter**	**Spring**
Seed	0.036	0.025
Fertilizer	26.51	26.51
Total P input	26.54	26.53
Output, kg P/ha		
Harvested rapeseed	21.70	15.50
Straw	remains on the field	remains on the field
Total P output	21.70	15.50
Balance, kg P/ha		
P surplus	4.84	11.03
P leaching, kg/ha	0.14	0.32
P leaching, kg/t	0.040	0.13

3.1.10.6. Nitrate Leaching to Groundwater

The nitrate leaching, calculated according to IPCC 2006 Tier 1, resulted in 84.06 kg NO_3^- and 99.48 kg NO_3^- per t of winter and spring rapeseed, respectively.

3.1.11. Not Included

Elemental contaminants, known as heavy metals, are present in the fertilizers. Heavy metals are toxic elements that may express their pollutant potential directly on soil organisms, due to the availability for plants in phytotoxic levels. They also have the ability to transfer to the food chain through the plants or by contamination of soil and water resources [200]. To date, there is very little reporting on heavy metal content in fertilizers and their impact on oil crops` LCAs. Information about heavy metal content in fertilizers and harvested crops and residues of crops are scattered among sources, in time and locations. Schmidt et al. 2007 reported on heavy metal emissions from rapeseed cultivation and carried out a sensitivity analysis where he found that heavy metals constitute only a minor share (0.065 %) of the total contribution to ecotoxicity [163]. For these reasons, heavy metal emissions from fertilizers are not included.

As discussed, also the input of micronutrients and Sulphur is not included in the final inventory that will be harmonized with ecoinvent v3.5 as there were no data sets available for these.

Capital goods and overhead, which include means of production, i.e. buildings and machinery, electricity and energy for administration buildings, and human labour were not included in the inventory since it was not possible to obtain detailed data of these factors. As noted by Queirós et al. 2015 this approach allows results to be compared with other studies where capital goods are also neglected [185].

3.1.12. LCI of Rapeseed Agricultural Stage, Summary

Table 3.12

Inventory Data for Winter and Spring Rapeseed Production With FU of 1 t of Seeds

Flow	**Unit**	**Winter**	**Spring**	**Comments**
Yield	t/ha	3.5	2.5	
Material use				
Planting seed material	kg/t	1.4	1.6	Imported hybrid seeds, new seeds every year
Fertilizer application rates				
P_2O_5	kg P_2O_5/t	17.4	24.3	Modelled as diammonium phosphate
K_2O	kg K_2O/t	36.9	51.7	Modelled as an input of potassium chloride
Nitrogen in total	kg N/t	63.2	74.8	
(6.9 % as NPKS 4-16-32-2S)	kg N/t	4.3	–	Nitrogen in NPKS fertilizer was modelled as an input of ammonium sulphate
(46.7 % as ammonium nitrate)	kg N/t	29.5	–	
(17.1 % as ammonium sulphate)	kg N/t	10.8	–	
(29.4 % as KAS N25+S3)	kg N/t	18.6	–	14.5 kg of urea ammonium nitrate with N content 32 %*
(8.1 % as NPKS 4-16-32-2S)		–	6.1	
(40.5 % as ammonium nitrate)		–	30.3	
(18.0% as ammonium sulphate)		–	13.4	
(33.4 % as KAS N25+S3)		–	25.0	19.5 kg of urea ammonium nitrate with N content 32 %*
Plant protection product application				
Acetamide-anillide-compound	kg/t	0.24	0.33	
Pesticides, unspecific	kg/t	0.094	0.13	
Diphenylether compounds	kg/t	0.029	–	Winter rape only
Pyrethroid compound	kg/t	0.0043	0.0060	
Cyclic N-compound (triazole)	kg/t	0.032	0.044	
Bipyridylium compounds	kg/t	–	0.15	Spring rape only
Grain drying	MJ/t	189.2	189.2	Provided with natural gas

Flow	Unit	Winter	Spring	Comments
Diesel for agricultural operations				
Tilling – turn-over of the soil	L/t	–	10.8	
Disc cultivation	L/t	2.1	3.0	
Drag harrowing	L/t	–	3.4	
Sowing	L/t	4.6	3.8	
Application of fertilizer	L/t	0.8	0.9	
Application of plant protection products	L/t	1.3	1.8	
Combine harvesting	L/t	5.7	8.0	
Transport				
Lorry 7.5–16 t	tkm	0.1	0.2	
Lorry 16–32 t	tkm	146.7	183.7	
Transoceanic freight ship	tkm	1.1	3.0	
Lorry 3.5–7.5 t	tkm	0.1	0.1	
Tractor	tkm	4.8	6.1	
Emissions				
To water				
Phosphorus	kg P/t	0.04	0.13	
Nitrate	kgNO_3/t	83.97	99.38	
Plant protection products				
Metazachlor	kg/t	0.0012	0.0017	
Quinmerac	kg/t	0.00030	0.00042	
Metconazole	kg/t	0.000090	0.00013	Proxy-Epoxicanozole
λ-Cyhalothrin	kg/t	0.000014	0.000020	
Cyproconazo	kg/t	0.000069	0.00096	
Azoxystrobin	kg/t	0.00017	0.00024	
Deltametrin	kg/t	0.0000071	0.000010	
Propaquizafop	kg/t	0.00014	–	Winter rape only
Diquat dibromide	kg/t	–	0.00075	Spring rape only
To air				
Nitrous oxide in total	kg N_2O/t	1.73	1.88	
Direct N_2O emissions from fertilizer application	kg N_2O/t	0.97	1.07	
Indirect N_2O emissions produced from leaching and runoff from fertilizer application	kg N_2O/t	0.22	0.26	

Flow	Unit	Winter	Spring	Comments
Indirect N_2O emissions produced from atmospheric deposition of N volatilised	kg N_2O/t	0.10	0.12	
Direct N_2O emissions from N in crop residues	kg N_2O/t	0.036	0.34	
Indirect N_2O emissions produced from leaching and runoff from N in crop residues	kg N_2O/t	0.08	0.08	
Plant protection products				
Metazachlor	kg/t	0.012	0.017	
Quinmerac	kg/t	0.00059	0.00083	
Metconazole	kg/t	0.00018	0.00025	Proxy-Epoxicanozole
λ-Cyhalothrin	kg/t	0.000029	0.000040	
Cyproconazo	kg/t	0.00069	0.00096	
Azoxystrobin	kg/t	0.00034	0.00048	
Deltametrin	kg/t	0.000014	0.000020	
Propaquizafop	kg/t	0.00029	–	Winter rape only
Diquat dibromide	kg/t	–	0.23	Spring rape only
Carbon dioxide, fossil	kg CO_2/t	7.97	10.73	
Nitrogen oxides	kg NO_x/t	0.36	0.40	
Ammonia	kg NH_3/t	2.69	3.35	Emission factor
(6.9 % as NPKS 4-16-32-2S)	kg NH_3/ t	0.17	–	4 %
(46.7 % as ammonium nitrate)	kg NH_3/ t	0.59	–	2 %
(17.1 % as ammonium sulphate)	kg NH_3/ t	0.86	–	8 %
(29.4 % as KAS N25+S3)	kg NH_3/ t	1.06	–	5.7 %
(6.9 % as NPKS 4-16-32-2S)	kg NH_3/ t	–	0.24	4 %
(46.7 % as ammonium nitrate)	kg NH_3/ t	–	0.61	2 %
(17.1 % as ammonium sulphate)	kg NH_3/ t	–	1.08	8 %
(29.4 % as KAS N25+S3)	kg NH_3/ t	–	1.43	5.7 %
Water	kg H_2O/t	45.45	45.45	From seed drying
To soil				
Plant protection products				
Metazachlor	kg/t	0. 12	0.017	
Quinmerac	kg/t	0.030	0.042	
Metconazole	kg/t	0.0090	0.013	Proxy-Epoxicanozole
λ-Cyhalothrin	kg/t	0.0014	0.0020	

Flow	Unit	Winter	Spring	Comments
Cyproconazo	kg/t	0.0069	0.010	
Azoxystrobin	kg/t	0.017	0.024	
Deltametrin	kg/t	0.00071	0.001	
Propaquizafop	kg/t	0.014	–	Winter rape only
Diquat dibromide	kg/t	–	0.075	Spring rape only

*Modelled as urea ammonium nitrate with N content 32 %. The amount was recalculated to correspond to nitrogen content in the fertilizer KAS N25+S3.

3.2. LCI of Rapeseed Oil Production

3.2.1. Goal and Scope Definition, Functional Unit, Data Provider

The purpose of this section is to provide LCI of rapeseed oil production in Latvia as a case study country in Northern Europe, to be further involved in an LCA study aimed to evaluate the overall impact of PU formulated using bio-polyol from rapeseed.

The FU selected was 1 t of edible rapeseed oil, produced using cold-press extraction, at a factory gate. The system boundaries and relevant unit processes for rapeseed oil production are depicted in Fig. 3.1. The rapeseed oil production system includes the following stages: 1) oil crop cultivation, 2) transportation, 3) oil crushing. In the present oil mill, there is no oil refining.

A local company in Zemgale region, located 34 km from the rapeseed producing company, provided primary data about rapeseed oil pressing using cold extraction technique. The company produces ~4000 t of rapeseed oil annually.

3.2.2. Oil Mill Stage

After rapeseeds have been grown, harvested and dried, in detail described in Section 3.1 LCI of Rapeseed Agricultural Stage, they are transported to the oil mill. A tractor is used for transportation and the oil mill is located 35 km from the drying and storage site of the agricultural company. Electricity use comes from oil pressing and pumps. LCI data for the oil mill was provided by the company [201]. Screw type press is used for rapeseed pressing, the technical parameters are as follows: yield 1000 kg/h, power 45 kW. Pumps are used for oil pumping from pressing collection tanks to oil setting tanks with following technical parameters: yield 12.5 m^3/h, power 7.5 kW.

For electricity, the reference was to the Latvian production mix of low voltage electricity available in the ecoinvent v3.5. The LCI data for winter and spring rapeseed oil production systems per 1 t of rapeseed oil is presented in Table 3.13.

Table 3.13

LCI for Oil Mill Stage

Input flow	**Unit**	**Value**	
		Winter	**Spring**
Rapeseeds	kg	2778	3125
Electricity for pressing oil	kWh	125	141
Electricity for pumping oil from pressing tanks to storage	kWh	0.65	0.65
Transport, tractor	tkm	97.2	109.4
Output flow			
Oil	kg	1000	1000
Cake	kg	1722	2063
Loss 2 %	kg	56	63

Oil mill stage involves not only the product of interest (rapeseed oil) but also a co-product (cake/expeller) during oil crushing stage. Another rapeseed oil production process involves a combination of crushing the seeds followed by extracting the remaining oil in solvent. The residue from process is rapeseed meal. Rapeseed expeller or rapeseed cake has a higher lipid content compared with rapeseed meal. The market availability of rapeseed cake is much lower than the rapeseed meal [202]. The above-mentioned product systems that involve more than one product require to apply allocation to determine the proportion of the environmental impacts that will be attributed to the production of each product.

In the LCIA stage impacts are allocated between the oil and cake. Impacts refer to agricultural phase impacts (producing rapeseed oilseed), rapeseed transport impacts, and oilseed crushing-process impacts (energy consumption). Any variation in the yield between the oil and the cake, as any variation in energy content, economic value, can have a significant (non-negligible) effect on the results.

ISO standard states that physical allocation can be carried out when allocation cannot be avoided through subdivision or system expansion. Physical allocation can be conducted based on the physical flow of mass or energy. Four different allocation methods are applied for the study: allocation with a system expansion was applied to avoid allocation, and it was assumed that the use of protein residues as animal food would offset the production of an equivalent amount of soy meal in regular animal feed production; mass allocation (MA); energy allocation (EA); market value allocation (MVA) (allocation abbreviations will be used in Figures, not in text).

The determination of allocation factors is shown in Table 3.14. The market value allocation is based on the data given by the oil-mill company for 2016. However, a sensitivity analysis will be performed on market value allocation because in 2017 the price for rapeseed oil increased by 17 % in comparison to 2016, while in 2018, the price dropped and was the same as in 2016. The price of rape cake has remained the same.

Table 3.14

Allocation Factors Considered in Oil Mill

Flow	**Mass allocation, %**		**Price, EUR/t** [201]	**Market value allocation, % for 2016**		**Energy LHV, MJ/kg** [203]	**Energy allocation, %**	
	Winter	**Spring**		**Winter**	**Spring**		**Winter**	**Spring**
Oil	36.7	32.6	715.0	63.9	59.6	36.0	53.7	49.2
Cake	63.3	67.4	235.0	36.1	40.4	18.4	46.3	50.8

Each of the allocation methods has its drawbacks. The advantage of mass and energy allocation is that these factors do not change over time However, mass and energy allocation might be challenging when the co-products have different end uses. Energy allocation is most suitable for systems where the products are energy carriers, such as electricity, biofuels etc. market value allocation normalizes all products to a common base despite their end-use, however, in application market value allocation factors change with time, as change prices for the products.

The rape cake is mainly purchased by poultry and ruminant producers. System expansion (SE) is when the system boundaries of the LCA are expanded to include co-products and what they substitute on the market. In this case study, rapeseed cake is used as protein feeds instead of imported soybean meal. Thereby, from the rapeseed oil production system, the impact of soymeal production has been subtracted. It was assumed that crude protein content (dry matter) in soybean meal is 48 %, while in rapeseed cake is 34 % (dry matter) [204]. Thus, the replacement ratio is – 1.4 kg of rape cake is needed to provide the same amount of protein as 1 kg of soybean meal.

3.3. LCA of Rapeseed Agricultural Stage and Rapeseed Oil Mill Stage

LCIA is the third stage of an LCA that involves calculating the potential environmental burdens associated with specific activities by quantitatively expressing all inputs and emissions tabulated in the LCI stage according to their contributions to relevant impact category.

The results of the present study were analysed according to the scope and goal of the study that is set out in Section 3.1 and Section 3.2, to identify the most important aspects of the rapeseed and rapeseed oil production system and determine which activities cause the most significant environmental impacts in Northern European country Latvia.

3.3.1. Life Cycle Impact Assessment of Rapeseed Production

3.3.1.1. CED Method

CED of a product or process represents the direct and indirect energy use in units of MJ throughout the life cycle [142]. As discussed, CED takes into account primary energy use, both renewable and non-renewable, and energy flows intended for both energy and material purposes, consumed by transport operations [143]. Moreover, energy use indicators are good proxy indicators for environmental impacts in general [144]. CED was chosen as a method for measuring the energy demand of rapeseed agricultural stage (Fig. 3.7).

The production of 1 t of winter and spring rapeseed in Latvia has an overall impact for CED of 6450 MJ and 8809 MJ (22.6 GJ/ha and 22.0 GJ/ha). The comparison of the results shows that CED for spring rapeseed is 36 % higher than for winter rapeseed, which is due to a lower yield of spring rapeseed.

The main inputs into the Latvian rapeseed agricultural production system consist of mineral fertilizers, plant protection products, diesel fuel for agricultural machinery and transportation of materials and drying. Fertilizers accounted for 61.8 % of the total CED for winter rapeseed, followed by agricultural field operations (19.3 %), drying (9.6 %) and transport (6.6 %). Comparatively, the impact of fertilizers for spring rapeseed was approximately 54.8 %, while the contribution of agricultural field operations was higher with 29.3 %. The higher CED for spring rapeseed is largely due to two time’s higher diesel consumption for agricultural machinery (14.5 L/t vs 31.7 L/t for winter and spring rapeseed, respectively). For both rapeseed type, the impact of plant protection products and planting seed material was below 2 %. The CED could be reduced by alternative tillage systems, such as reduced and minimum tillage practices instead of conventional tillage for spring rapeseed, also the reduction of fertilizer use would lead to lower CED and thus lower GHG emissions.

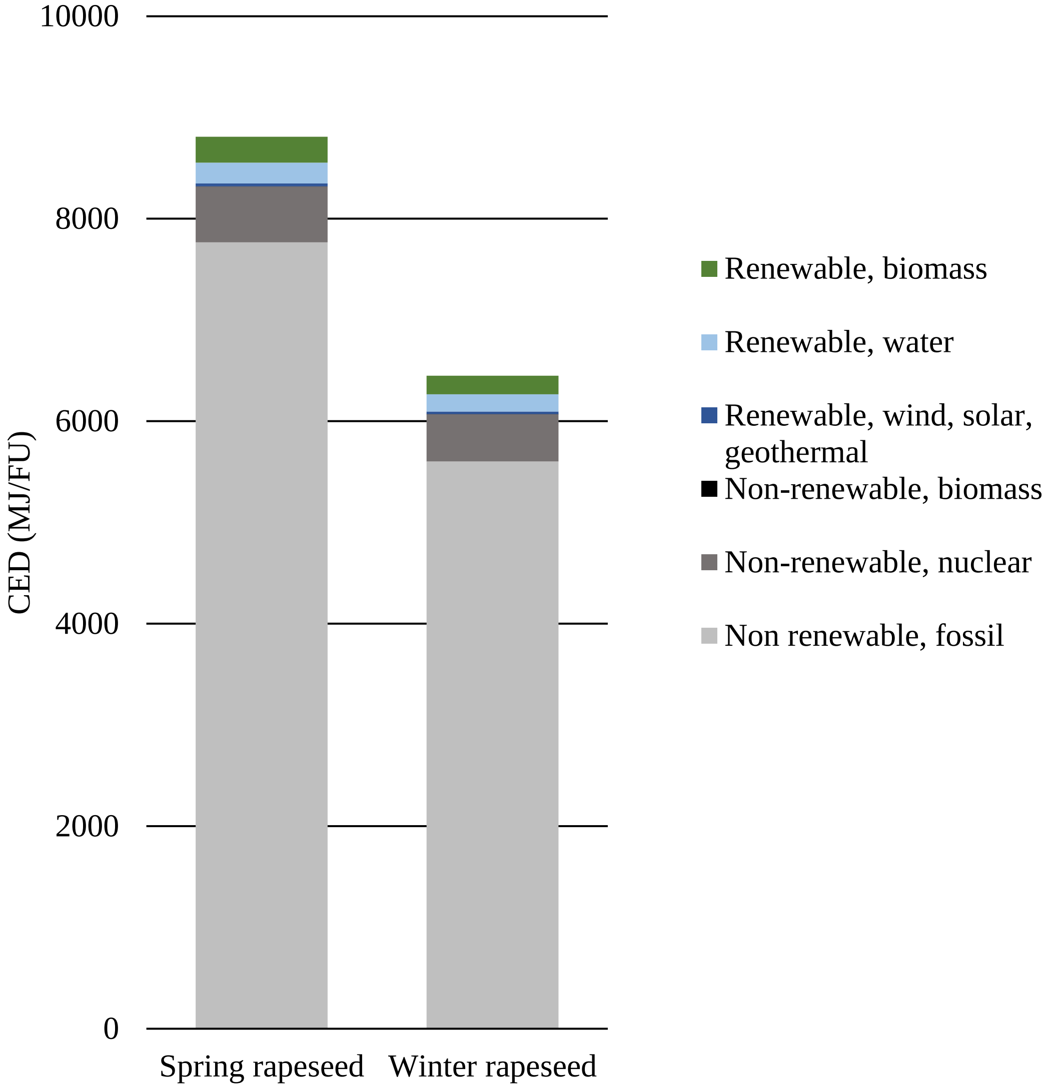

Fig. 3.7. CED characterized impacts calculated for spring and winter rapeseed production per FU.

In "cradle-to-farm gate" study of canola grown in Canada, the CED of 5200 MJ/t was reported, the reported N fertilizer input was 46.1 kg N/t seeds. [205]. A CED of 15.3 GJ/ha was reported for canola cultivated in the USA, with nitrogen input of 77.3 kg N/t seeds [206]. The energy demand of 5.3 GJ per t of rapeseeds was reported for Chilean conditions [207]. A study in Italy reported an energy demand of 3.6 GJ/t to 7.2 GJ/t depending on mechanization input [208]. The input of energy to winter oilseed rape was highly variable ranging from 7.42 GJ/ha to 16.1 GJ/ha, but drying was not included [209]. The CED values depend on the fertilizer and plant protection product application, level of mechanization, type, quality and frequency of agricultural machinery operations, the need for drying and other factors.

It is well known that fossil resources used for energy and material generation are mainly responsible for the depletion of fossil resources and global warming [210], [211]. If CED is analyzed by impact categories as shown in Fig. 3.7., the Non-Renewable Cumulative Energy Demand (NRCED), representing the total of fossil energy and nuclear energy, for winter and spring rapeseed, is 94 % with the majority of that being fossil energy.

3.3.1.2. ReCiPe Method Endpoint Level

In ReCiPe endpoint level (damage-oriented), the environmental impacts are aggregated into three types of damage: human health, ecosystem quality and resources. The aggregated environmental impact is expressed as the ReCiPe score, written in normalized and weighted mPt. Although drawback of endpoint level is that the statistical uncertainties are higher due to the final conversion to a weighted ecological score, the results are easier to understand and interpret by decision-makers [148].

For winter and spring rapeseed, the most impacted category at the endpoint level was human health with 67.2 % (36.0 mPt) and 78.9 % (46.7 mPt) of the impact, followed by ecosystems with 32.2 % (17.2 mPt) and 20.4 % (12.1 mPt), respectively. Less than 1 % of contribution was to resources.

A comparison with France and Denmark was performed using ecoinvent v3.5 datasets for rapeseed which unfortunately do not specify which type of rapeseed, spring or winter, was used. However, over 90 % of total rapeseed production in Europe is winter annual forms (France, UK, Germany and other European countries) [212]. It was assumed that datasets represent winter rapeseed production. In ecoinvent v3.5 dataset for Denmark, the reported yield was 3.5 t/ha, for France the yield was 3.0 t/ha. The average yield for winter rape production in Latvia was 3.5 t/ha as reported in Table 3.12. In all three countries, the inputs of seeds, fertilizers and plant protection products are considered and it is assumed that no organic fertilizers are applied, no land-use change occurs. Rapeseed production ends at the farm gate. In the case of Denmark, also seed drying is taken into account. LCA models of winter rapeseed cultivation in Latvia and Denmark showed similar value, with a score for Denmark being 9 % lower. However, France has a 36.4 % higher environmental impact result, than for the specific case study in Latvia.

3.3.1.3. ReCiPe Method Midpoint level

In ReCipe midpoint level, the environmental impact is translated into 18 environmental issues (midpoint indicators) - global warming (GWP), stratospheric ozone depletion (ODP), ionizing radiation (IRP), ozone formation, human health (HOFP), fine particulate matter formation (PMFP), ozone formation, terrestrial ecosystems (EOFP), terrestrial acidification (TAP), freshwater eutrophication (FEP), marine eutrophication (MEP), terrestrial ecotoxicity (TETP), freshwater ecotoxicity (FETP), marine ecotoxicity (METP), human carcinogenic toxicity (HTPc), human non-carcinogenic toxicity (HTPnc), land use (LOP), mineral resource scarcity (SOP), fossil resource scarcity (FFP), water consumption (WCP).

The relative contribution of the agricultural inputs on environmental impacts of spring and winter rapeseed is presented in Fig. 3.8.

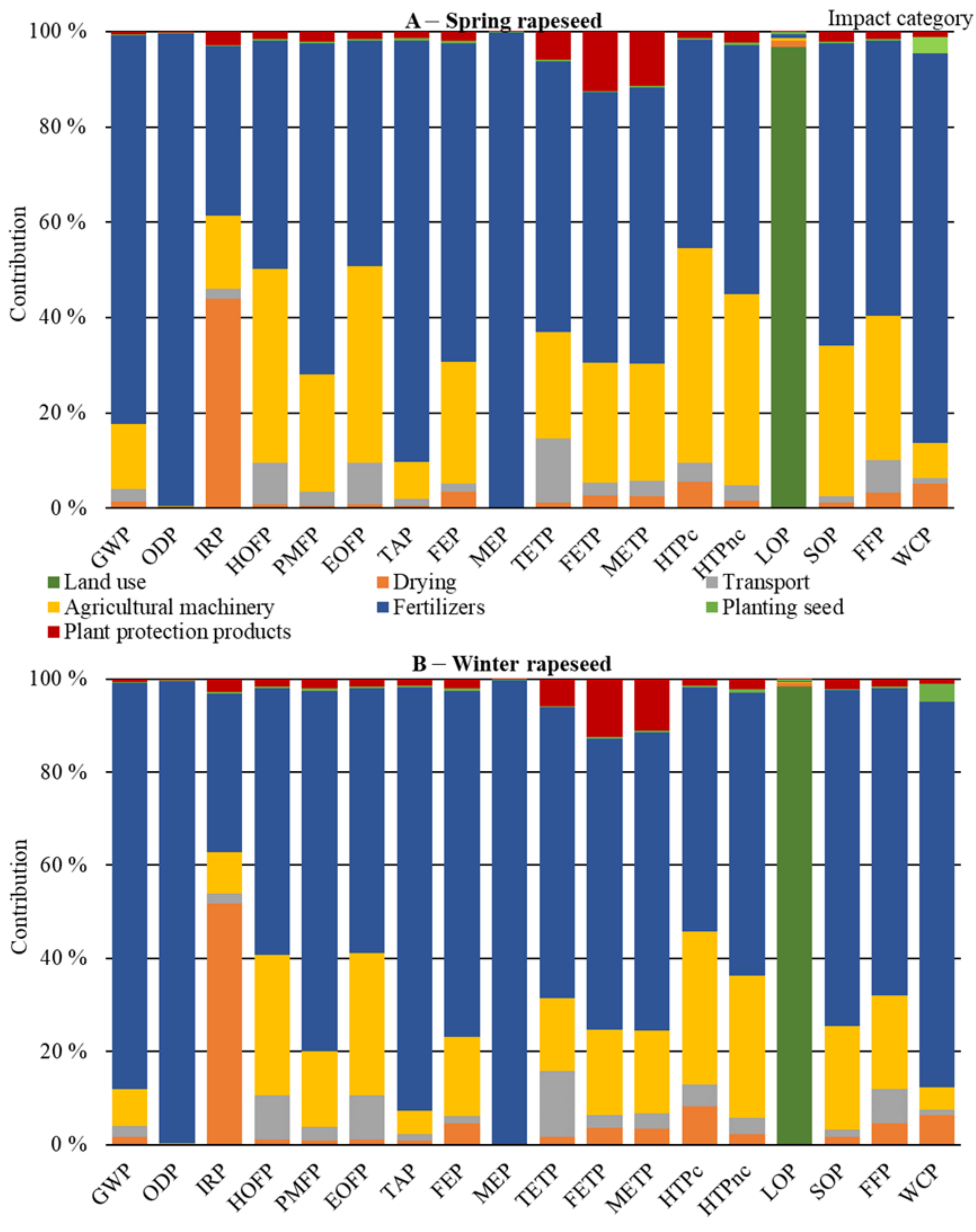

Fig. 3.8. Contribution of agricultural inputs to the environmental impacts of rapeseed production.

For both rape types, mineral fertilizers are the agricultural input with the highest environmental emissions in all impact categories, except the land use. Eutrophication potential is generally associated with the environmental impacts of excessively high nutrients (i.e. N and

P) that lead to shifts in species composition and increased biological productivity (e.g. algal blooms) [213].

In the rapeseed agricultural system, the process that causes the largest GHG emissions is the fertilizers with a contribution of 87.5 % for winter and 81.5 % for spring rapeseed, followed by agricultural machinery with 7.8 % and 13.7 % for winter and spring rapeseed, respectively. All the other processes present a much lower value, with combined contribution below 5 %. A closer look at comparative GHG emissions of rapeseed production depending on rapeseed type is presented in Fig. 3.9.

Another considerable input is the agricultural machinery for different field works. The contribution of agricultural machinery is overall higher for spring rapeseed as the diesel consumption (L/t) is two times higher for spring than winter rapeseed. Transport has an impact below 5 % for 14 impact categories. Only in terrestrial ecotoxicity category, the contribution is above 10 %, which is due to transport and its heavy metal emissions. The use of plant protection products contributes the most for the following midpoint categories in the impact decreasing order: freshwater ecotoxicity (12.4 % for spring rape, 11.7 % for winter rape), marine ecotoxicity (spring – 11.4 %) winter – 8.7 %) and terrestrial ecotoxicity is around 5 % for both. Planting seeds has the lowest contribution to impacts.

The total GHG emissions are 1267.9 kg CO_2 eq/t for spring rapeseed and 1064.1 kg CO_2 eq/t for winter rape. Forleo et al. reviewed different studies of rapeseed LCA and found that GHG emissions vary significantly. For example, a study in Finland reported GHG emissions of 1480 kg CO_2 eq/t, 828.5–5904.2 kg CO_2 eq/t in Italy, 794.2 kg CO_2 eq/t in Poland, 1180 kg CO_2 eq/t in Iran, 203.7–354.7 kg CO_2 eq/t in Slovenia [176]. It is obvious that GHG emissions vary in a wide range, it depends on multiple factors, starting from inputs in the LCI phase to the adopted LCIA method.

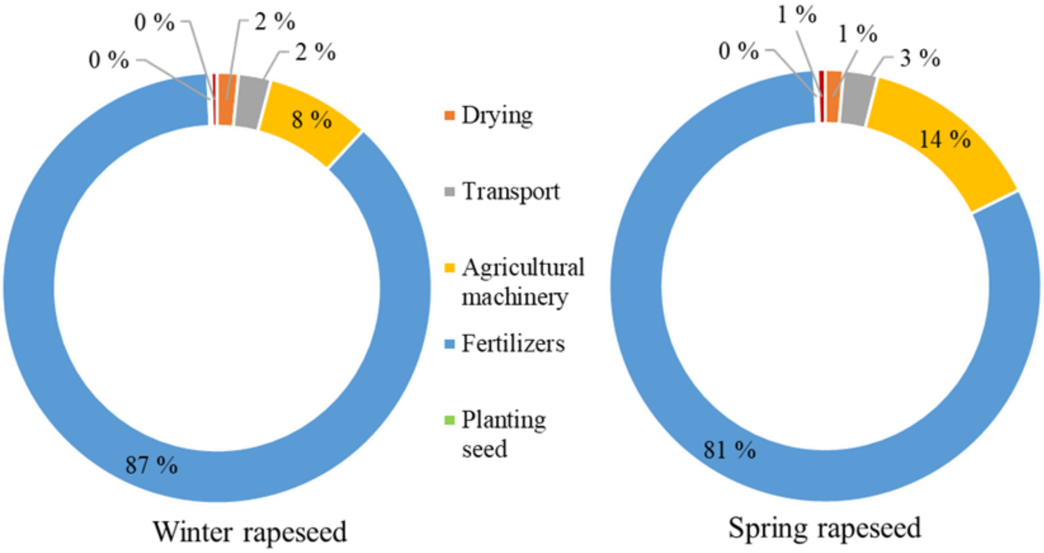

Fig. 3.9. GHG emissions for spring and winter rapeseed per 1 t of rapeseed.

The GHG emissions are primarily driven by the use of mineral fertilizers (87.4 % and 81.5 % for winter and spring rapeseed, respectively), chiefly due to dinitrogen monoxide emissions during fertilizer application (Table 3.12). Spring rapeseed has higher GHG emissions due to several reasons, but the main is higher usage of N-containing fertilizers to produce 1 t of rapeseeds as 74.8 kg of N are applied (from Table 3.12), in comparison 63.2 kg N per t of rapeseeds are applied in the case of winter rape. If N input per ha is compared, then winter rapeseed has considerably higher N input with 221.2 kg N/ha to 187.0 kg N/ha for spring rapeseed as reported in our previous paper by Fridrihsone et al., 2018. However, on average spring rapeseed in Latvia has a much lower yield than winter rapeseed, 2.5 t/ha versus 3.5 t/ha, respectively.

Agricultural machinery is the second-largest contributor to GHG emissions. To cultivate spring rapeseed a larger input of agricultural machinery is used. Using fossil-based diesel in agricultural machinery also generate GHG emissions (CO_2, CH_4, N_2O), therefore agricultural machinery requiring high fuel consumption have a higher impact. As mentioned before, spring rapeseed farming has two times higher (14.5 L/t vs. 31.7 L/t) diesel consumption than winter rapeseed for agricultural machinery. The difference is mainly due to tilling and drag harrowing, land processing steps only used for spring rapeseed. In the present study, it was considered that direct land-use change is null, as rapeseed is cultivated on the existing agricultural land. The contribution of other inputs is minor, below 3 %.

3.3.1.4. Sensitivity Analysis for Rapeseed Production

To validate and give consistency to the results, a sensitivity analysis has been carried out. The major contributor to most of the impact categories is NPK fertilizer. As reported, the fertilizer yearly dosage can change ±10 % depending on various factors. A variation of ±10 % has been considered for the fertilizer contributors to evaluate their effect on the impact categories (Table 3.15).

Table 3.15

Sensitivity Analysis on ReCiPe Midpoint Categories if Fertilizer Yearly Dosage is Changed ±10 %

	Midpoint impact category								
	GWP	**ODP**	**IRP**	**HOFP**	**PMFP**	**EOFP**	**TAP**	**FEP**	**MEP**
Change, %	±8.7	±9.9	±3.4	±5.7	±7.8	±5.7	±9.1	±7.5	±10.0
	TETP	FETP	METP	HTPc	HTPnc	LOP	SOP	FFP	WCP
Change, %	±6.3	±6.3	±6.6	±5.2	±6.2	0.0	±7.3	±6.6	±8.3

Sensitivity analysis showed that overall the results of different midpoint impact categories change within the range of ±10 %. The highest change is for impact category marine eutrophication as the fertilizer use contributes almost 100 % to the impact of this category. Other categories that were impacted more were GWP and ODP and TAP.

The results are also impacted by the chosen LCIA method, to test the robustness of the ReCiPe method IPCC 2013 GWP 100a and EDP (2018) methods are used to compare the GHG emissions (Fig. 3.10).

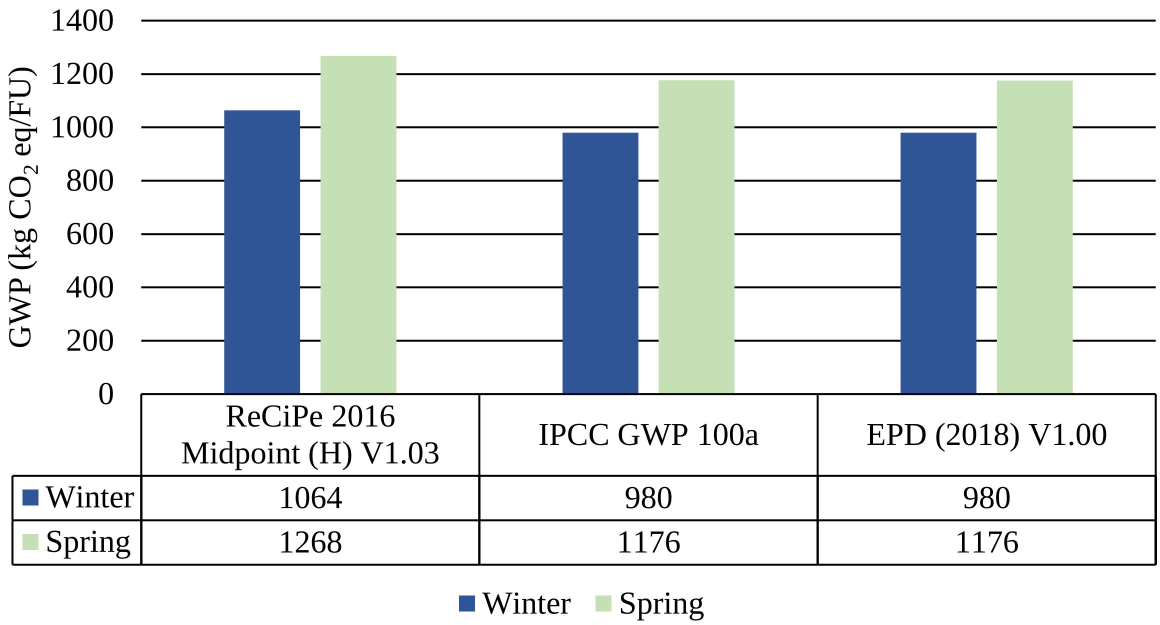

Fig. 3.10. Sensitivity analysis of the impact assessment method.

The results show that the ReCiPe method yielded the highest GWP for rapeseed production. The GWP for other two LCIA methods were identical. For winter rapeseed the GWP with other two LCIA methods other than ReCiPe is 7.9 % lower, for spring rapeseed – 7.2 % lower.

3.3.2. Life Cycle Impact Assessment of Rapeseed Oil Production

Allocation procedure is one of the most controversial issues in LCA, especially in agricultural LCAs. It is a critical aspect of any LCA and can impact the results significantly. Up to date, there is no uniform approach on how to deal with multi-functionality in agricultural systems [162], [214]. Allocation based on mass can generally be considered as appropriate when the economic value of the product and co-product is similar. Allocation based on market value is generally preferable when there is a large difference in the price of product and co-products. Energy allocation is preferred if the energy content of both is important for the goal of LCA [214]. As discussed, system expansion if preferred since according to the ISO standards in this way allocation problems can be partially avoided, at the same time it should be kept in mind that system expansion offers larger freedom of choice mostly in terms on the selection of the avoided impact attributable to the process included in the expanded system.

3.3.2.1. CED Method

The results in this section are calculated according to the allocation scenarios described in Section 3.2.2 Oil mill stage for both, winter and spring rapeseed. The company is predominantly producing cold-pressed rapeseed oil from winter rape due to higher yields in comparison to spring rape [201].

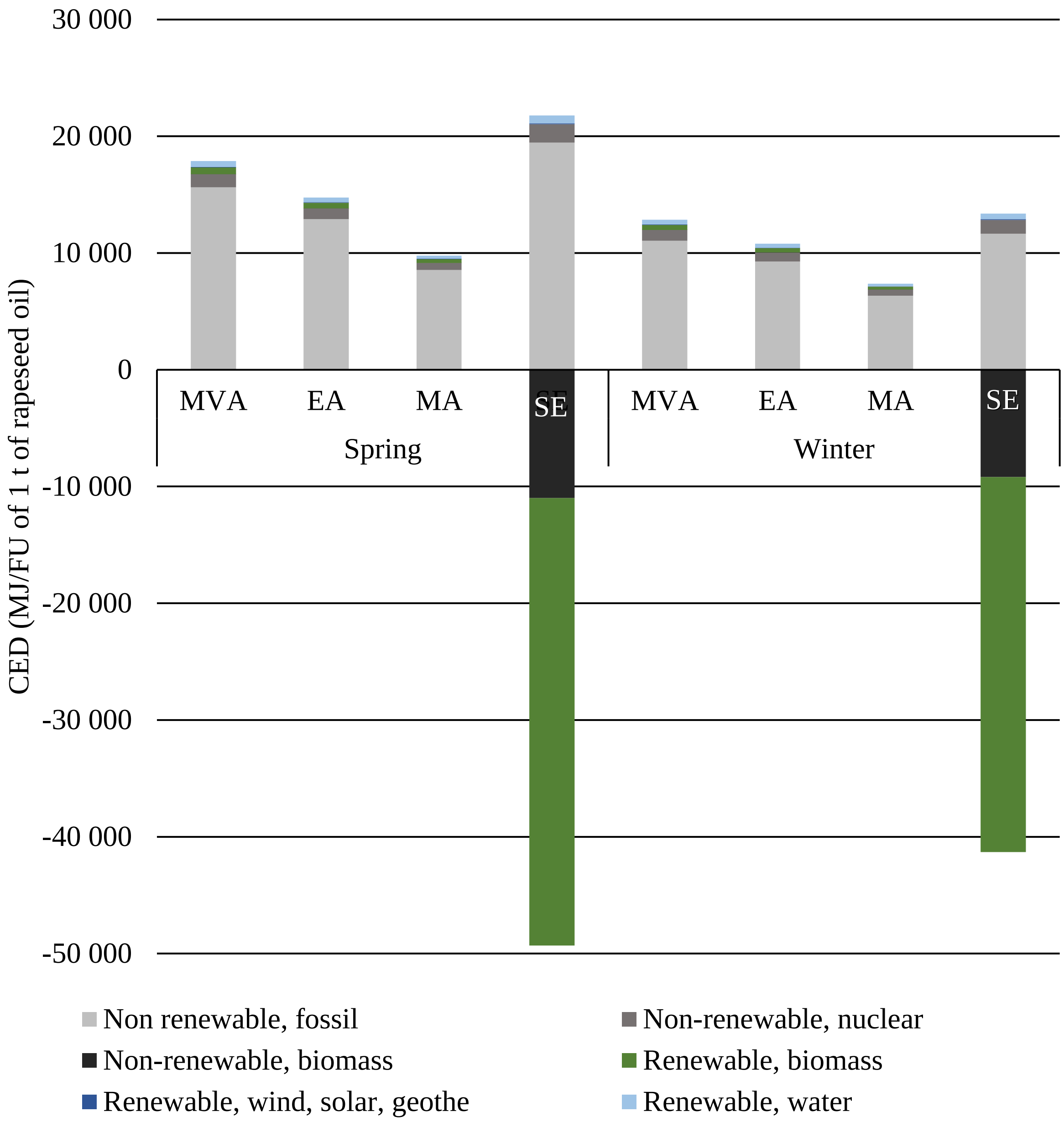

Fig. 3.11. CED for rapeseed oil depending on allocation type applied in mill stage and used rapeseed.

Fig. 3.11 presents CED results grouped according to rapeseed type used to press oil – winter or spring, respectively, and by chosen allocation method for the rapeseed oil in the oil mill stage. In both cases, if system expansion was applied, the final CED value was negative -28 GJ/t of oil produced, meaning that the produced rape cake replaced soybean meal produced. In the ecoinvent v3.5 dataset global soybean production was chosen as an avoided product. Results show that by system expansion, there would be fewer interventions associated with the clear-cutting of primary forest for the provision of arable land tenure, which is translated into Non-renewable, biomass impact category. Also, the need to produce less soybean meal would make a difference in crop expansion into primary forest, secondary forest, grassland, perennial and annual land.

For other allocation types applied, CED was the lowest for mass allocation, followed by energy allocation and the highest score was for market value allocation.

3.3.2.2. ReCiPe Method

ReCiPe’s endpoint damage categories for rapeseed oil produced from winter and spring rapeseed using different allocation in oil mill state are depicted in Fig. 3.12.

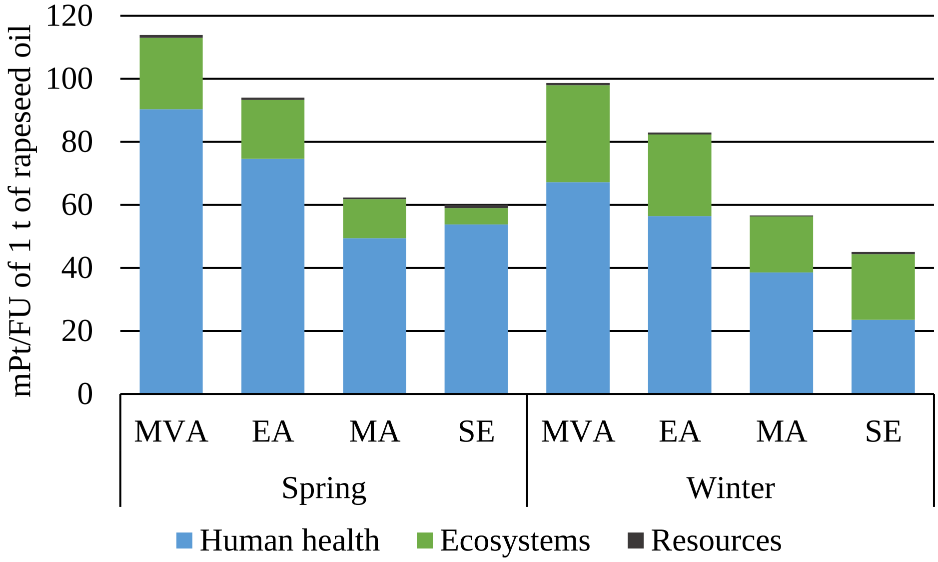

Fig. 3.12. ReCiPe’s endpoint damage categories for rapeseed oil produced in Latvia using different allocation methods.

In the LCIA stage, co-product allocation is avoided by system expansion (it was assumed that the use of protein residues as animal food would offset the production of an equivalent amount of soy meal in regular animal feed production) as described in the Section 3.2.2 Oil Mill Stage. Also, the impacts are allocated between the oil and cake in the case of economic allocation, energy and mass allocation according to allocation factors presented in Table 3.14. The impacts refer to agricultural phase impacts (producing rapeseed oilseed), rapeseed transport impacts, and oilseed crushing-process impacts (energy consumption).

Overall, the rapeseed oil produced from winter rape has slightly lower environmental footprint due to the higher yield of oil from seeds. In both cases, the system expansion yields the lowest potential environmental impact. For winter rapeseed, if system expansion scenario with a value of 45 mPt is set as a baseline, then the total impact of mass allocation is 25.8 % higher, 84.1 % higher for energy allocation and 119.1 % higher for market value allocation. For spring rapeseed, the increase is as follows: 3.7 %, 56.4 % and 89.5 % for mass, energy and market value allocation, respectively.

In the case of rapeseed oil, the results show that rapeseed farming is the production step with the largest impact in all Endpoint categories, with a contribution of 89 % to 99 %. The impacts of rapeseed production contributed the most to the Endpoint category of human health, followed by ecosystems and resources. Overall the significantly largest impact of the rapeseed oil production is to the endpoint category human health due to environmental impacts of rapeseed farming, followed by ecosystems and a minor impact on resources.

Comparative GHG emissions of rapeseed oil production depending on rapeseed type and allocation method are presented in Fig. 3.13.

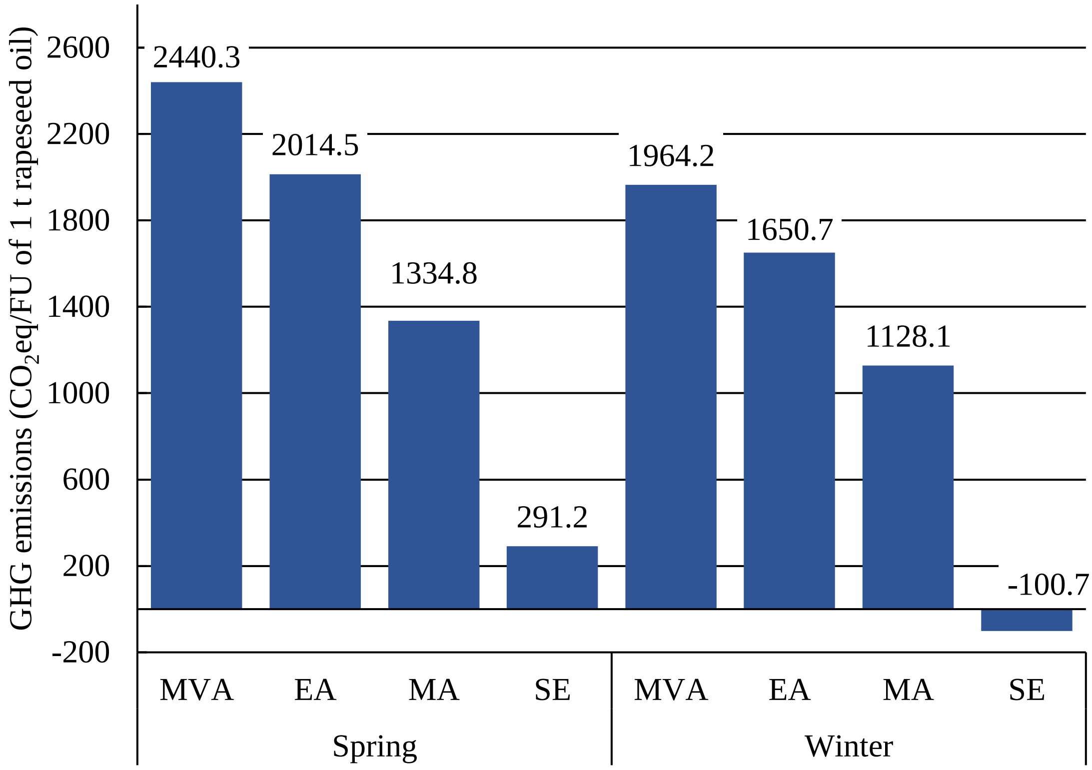

Fig. 3.13. Comparative GHG emissions of rapeseed oil depending on rapeseed type and allocation method.

In the case of oil produced from winter rapeseed when system expansion is applied, it is evident that yielded result is a negative value which means that by substituting soybean meal fed to ruminant and poultry by rape cake it would lead to GHG emissions.

Any variation in the yield between the oil and the cake, as any variation in energy content, economic value, can have a significant (non-negligible) effect on the results as shown in Fig. 3.11 to Fig. 3.13. It is interesting to see how the different allocation provides a different range of variation among winter and spring rapeseed; for example, the difference in market value allocation between the winter and spring scenarios are at a level of 24.2 % while for the mass allocation the difference is lower with 18%. This highlights the importance of allocation in LCA.

Analysis of the present case study confirms that the choice of allocation method has a significant impact on the results of the LCA of oil mill products. Despite being a critical point in LCA, there is a large variance in the applied allocation type (or even allocation is ignored altogether) in other studies as reviewed by Khatri et al. 2017 [162].

3.3.2.3. Sensitivity Analysis for Rapeseed Oil Production

Sensitivity analysis was performed to evaluate to what extent the results are affected by changes in methods, models, or assumptions. Sensitivity check on market value allocation was performed. The impact of market value allocation on the environmental score of the rapeseed oil was evaluated. As discussed, the allocation procedure is one of the most controversial issues in LCA. ISO 14044 gives market value allocation option in step 3 of its allocation procedure [135], i.e. the least preferable allocation under ISO standard, however, others argue that market value allocation method is the most advised for most allocation situations in a detailed LCA [215]. The year 2016 data is chosen as a baseline scenario, but price relations are variating over time, which will affect the environmental performance of the products. Sensitivity was performed by changing the price of oil in the range of ±30 % with a step of 10 %. The sensitivity results on market value allocation are presented in Fig. 3.14.

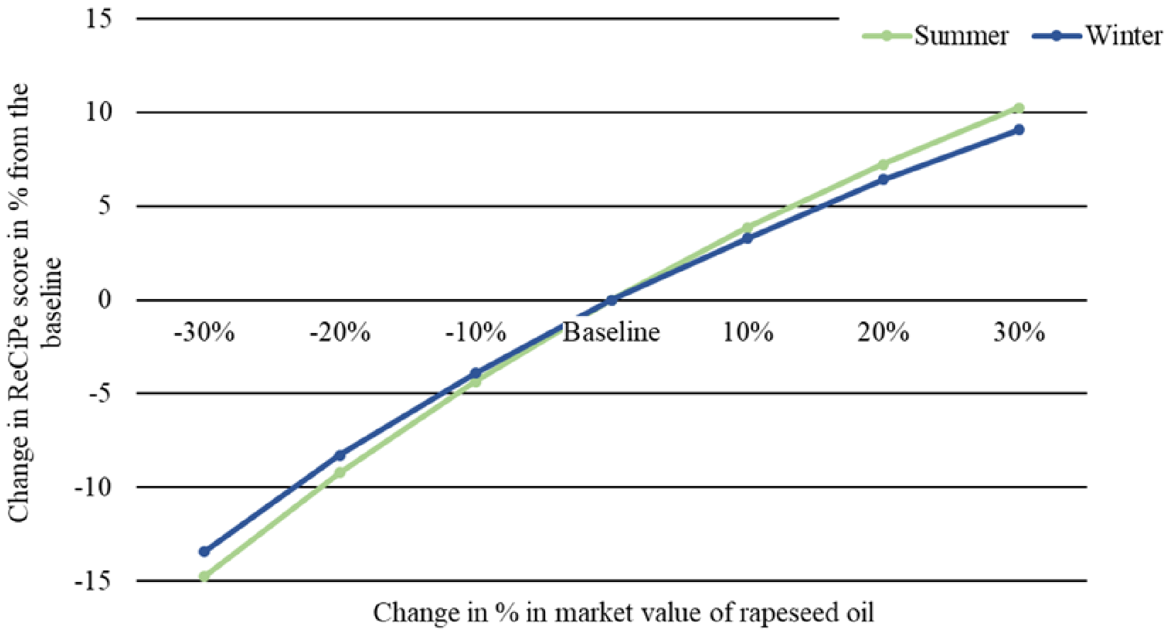

Fig. 3.14. Sensitivity check on allocation rule in rapeseed oil mill stage.

The sensitivity analysis results show that increasing the price of winter rapeseed oil by 30 %, the ReCiPe environmental score increases by 9 %, for spring rapeseed oil the increase is 10 %. When the price is decreased by 30 %, the environmental score decreases by 13 % and 15 %, respectively. There are no clear benchmarks that have to be used to judge the sensitivity. Other authors suggest that if values are within ±15 % of each other the results are considered equivalent [199].

To further test the impact of a single unit process on the overall environmental performance, the potential of transport distance travelled from rapeseeds to oil mill was evaluated. In the baseline scenario, the distance is only 34 km, however not always the distance will be so small. It was modelled that rapeseeds are transported over a distance of 250 km, which equals to the distance from the rapeseed storage site to another large rapeseed oil and biodiesel producer in Latvia. For scenarios where market value, mass and energy allocation were applied, the increase in ReCiPe score was 8.6 % higher than for baseline. The largest increase was for resources endpoint category with 15.2 % increase, followed by human health. In these cases, the increased impact is due to the larger distance travelled and more fossil fuels were burned, thus more fossil fuels were depleted and emissions formed. For system expansion scenario, the increase in ReCiPe end score was 29.4 % higher, if the distance was increased to 500 km, the result was 63.6 % higher. For system expansion scenario, the distance of seed storage site to oil mill is a sensitive input.

3.4. LCA of Rapeseed Oil-Based Polyol Production

3.4.1. Goal and Scope Definition

The purpose of this chapter is to carry out a cradle-to-gate LCA of rapeseed oil-based polyols. The rapeseed oil polyols were analysed with three different modelling approaches for the bio-based feedstock stage – system expansion, mass allocation and market value allocation. The allocation factors employed are discussed in Section 3.2.2.

3.4.2. Functional Unit and System Boundary

The FU selected was 1 kg of rapeseed oil-based polyol, capable of being used to make spray-applied PU coatings and rigid PU thermal insulation foams. The system boundary of rapeseed oil-based polyol production is depicted in Fig. 3.1.

3.4.3. Bio-Polyol Production

Polyols were synthesized using transesterification of rapeseed oil with TEA, as well as amidization with DEA. The synthesis of rapeseed oil polyols was carried out in a pilot-scale reactor with a volume of 50 L, according to a more detailed description of rapeseed oil-based polyol synthesis as given in previous work carried out by the author [96]. Amidization with DEA was carried out at 140 °C ± 5 °C. Transesterification with TEA was carried out at 170 °C ± 5 °C. The given synthesis process does not require purification and/or filtration steps, as glycerol and monoglycerides contain hydroxyl groups in their chemical structure, which are reactive with isocyanates in the PU formation reaction and have no adverse effect on the PU production. The idealized synthesis scheme for rapeseed oil polyol synthesis is given in Fig. 3.15, the characteristics of rapeseed oil polyols are described in Table 3.16.

Table 3.16

Characterization of Rapeseed Oil-based Polyols (Adapted From [96])

Polyol	Hydroxyl value, mg KOH/g	Average functionality f_n	Viscosity, mPa·s at 25°C	Bio-based content, %
RO/DEA	416	2.25	825	74
RO/TEA	374	2.25	156	67

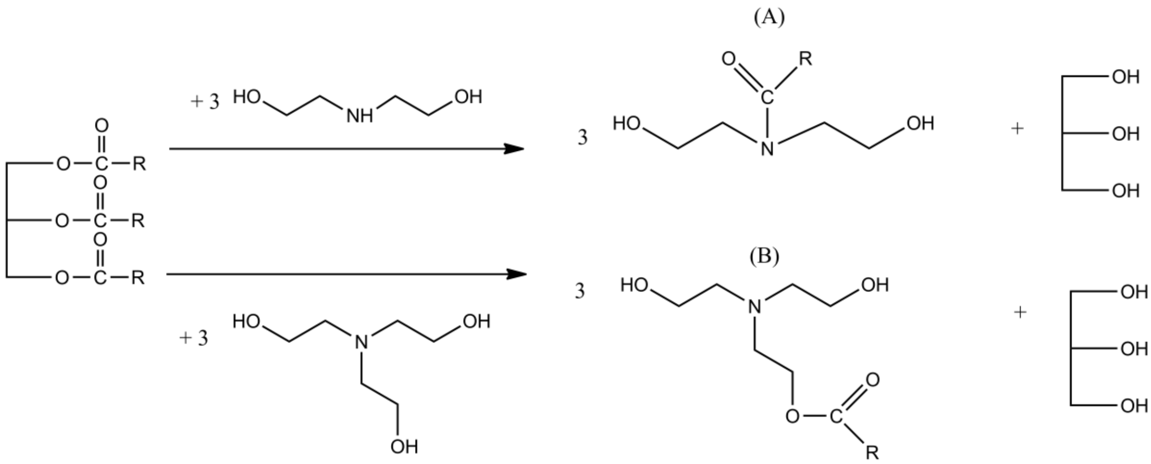

Fig. 3.15. Idealized synthesis scheme for rapeseed oil-based polyols: A – RO/DEA polyol; B – RO/TEA polyol; RO – rapeseed oil [96].

Both rapeseed oil polyols are characterized by high hydroxyl value and low functionality, the viscosity is suitable for industrial application. Moreover, RO/TEA polyol has a built-in catalytic activity as it contains tertiary amine, which acts as a catalyst in urethane-forming reactions; it reduces or eliminates the need to include a conventionally used catalyst in PU chemistry – tertiary amine or organometallic catalysts [216].

Developed rapeseed oil polyols have been demonstrated using industrial PU spraying equipment. Six fast curing, two-component PU coating systems were formulated, bio-based content for end PU product reached 21.7–31.9 % [216]. Rigid PU thermal insulation foams were produced from these polyols by replacing of 70 wt. % of a petrochemical polyol with bio-based rapeseed oil polyols. The bio-based content in final PU foams reached 15.6 % for RO/DEA polyol and 15.1 % for RO/TEA polyol at laboratory scale foaming. When industrial PU spraying equipment was used, the bio-based content in rigid PU foams reached 16.1 % [217], [218].

3.4.4. Material and Energy Input

Data for rapeseed cultivation and rapeseed oil production have been in detail reported in the previous sections of this thesis to provide transparent results.

The production of alkanolamines and inert gas needed for polyol synthesis was taken from ecoinvent v3.5. As there was no inventory for a catalyst, zinc acetate dehydrate (CAS # 5970 - 45-6), an assumption was made. An approach was adopted from chemistry – a "working-backwards" problem-solving technique called retrosynthesis, where the target molecule is recursively analysed and dissected until a set of known building blocks is obtained [219]. In this study, the catalyst was dissected until building blocks available in the ecoinvent v3.5 database were obtained, European averages were used. The catalyst was modelled as a product of the reaction of zinc oxide with acetic acid. The enthalpy of formation was taken as (- 66,02 kJ/mol) – exothermic reaction [220]. This number was multiplied by factor 4.2 as actual industrial scenarios involving potential future scale-up are expected to be more energy-intensive, as in an industrial plant the actual energy consumption is a few times greater than theoretical energy requirements due to heat and energy losses [221].

For electricity use, Latvian electricity grid was chosen from the ecoinvent v3.5 database. The electricity consumption was measured according to the method described in Section 2.12.

3.4.5. Transport

Transport has been adapted to the local situation for a more reliable inventory. The transport of input materials, rapeseed oil and reagents for synthesis, has been defined as accurately as possible, in terms of mode and distance. Alkanolamines and catalyst are imported from Schnelldorf (Germany) using 20 t truck. Rapeseed oil is supplied from a local producer in Latvia.

3.4.6. LCI Summary for the Rapeseed Oil-Based Polyols

The inventory summary for rapeseed oil-based polyol production is depicted in Table 3.17.

Table 3.17

LCI Data for Two Rapeseed Oil-based Polyol Synthesis, FU – 1 kg of Polyol

Inputs	**Unit**	**RO/DEA**	**RO/TEA**	**Comments/data source**
Rapeseed oil	kg	0.74	0.67	Rapeseed inventory modelled by Fridrihsone et al. [170]
DEA CAS # 111-42-2	kg	0.26	–	ecoinvent v3.5
TEA CAS # 102-71-6	kg	–	0.33	ecoinvent v3.5
Catalyst Zinc acetate dihydrate 0.15 wt %	kg	0.0015	0.0015	Retrosynthesis performed. Approximated to 37 % of zinc oxide and 55 % of acetic acid, 8 % of water by weight; ecoinvent v3.5
Inert gas	g	20.80	17.60	ecoinvent v3.5
Electricity	kWh	0.44	0.48	ecoinvent v3.5, low voltage, LV electricity mix
Transport, 20 t truck	tkm	0.43	0.55	ecoinvent v3.5
Transport, 3.5–7.5 t truck	tkm	0.036	0.033	ecoinvent v3.5
Outputs				
Polyol	kg	1.00	1.00	
Condensate	g	0.02	0.02	Negligible

Bio-based rapeseed oil polyols were compared with the petrochemical polyol available in ecoinvent v3.5. Petrochemical polyether polyol is representing a European industry production average with data provided by the European plastics industry (Plastics Europe) [222].

3.4.7. Life Cycle Impact Assessment of Bio-Polyols: ReCiPe Method

ReCiPe impact assessment method version 1.03, a hierarchical (H) perspective with global normalisation factors for the reference year 2010, was used to identify the environmental hotspots and to compare the environmental performances of rapeseed oil-based polyols to a petrochemical polyol at midpoint and endpoint levels.

3.4.7.1. Endpoint Level

The network tree exhibits rapeseed oil-based polyol production inputs in synthesizing the product. The main contributors to the total aggregated environmental impacts of bio-based rapeseed oil polyols with mass allocation in the oil production stage is depicted in Fig. 3.16 and Fig. 3.17.

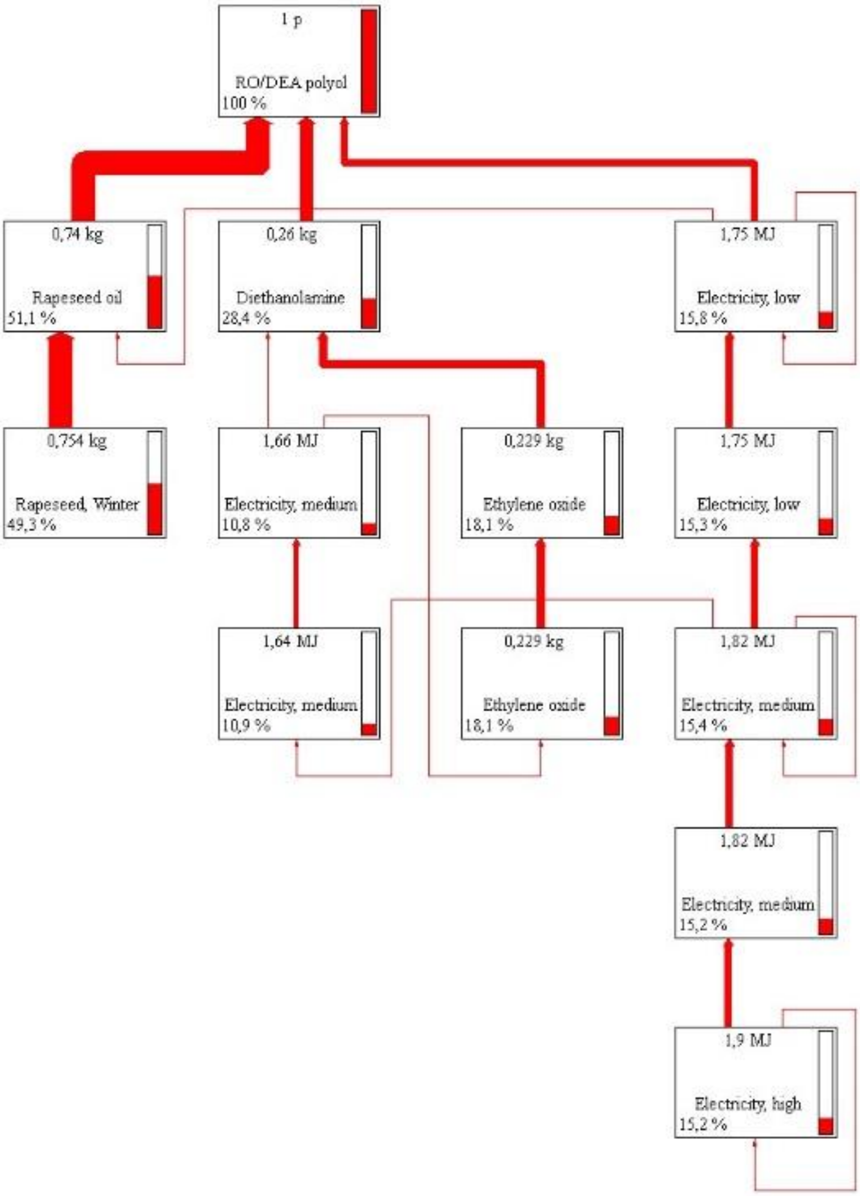

Fig. 3.16. Network tree of the main contributions to environmental impacts for 1 kg of rapeseed oil-based polyols: RO/DEA polyol.

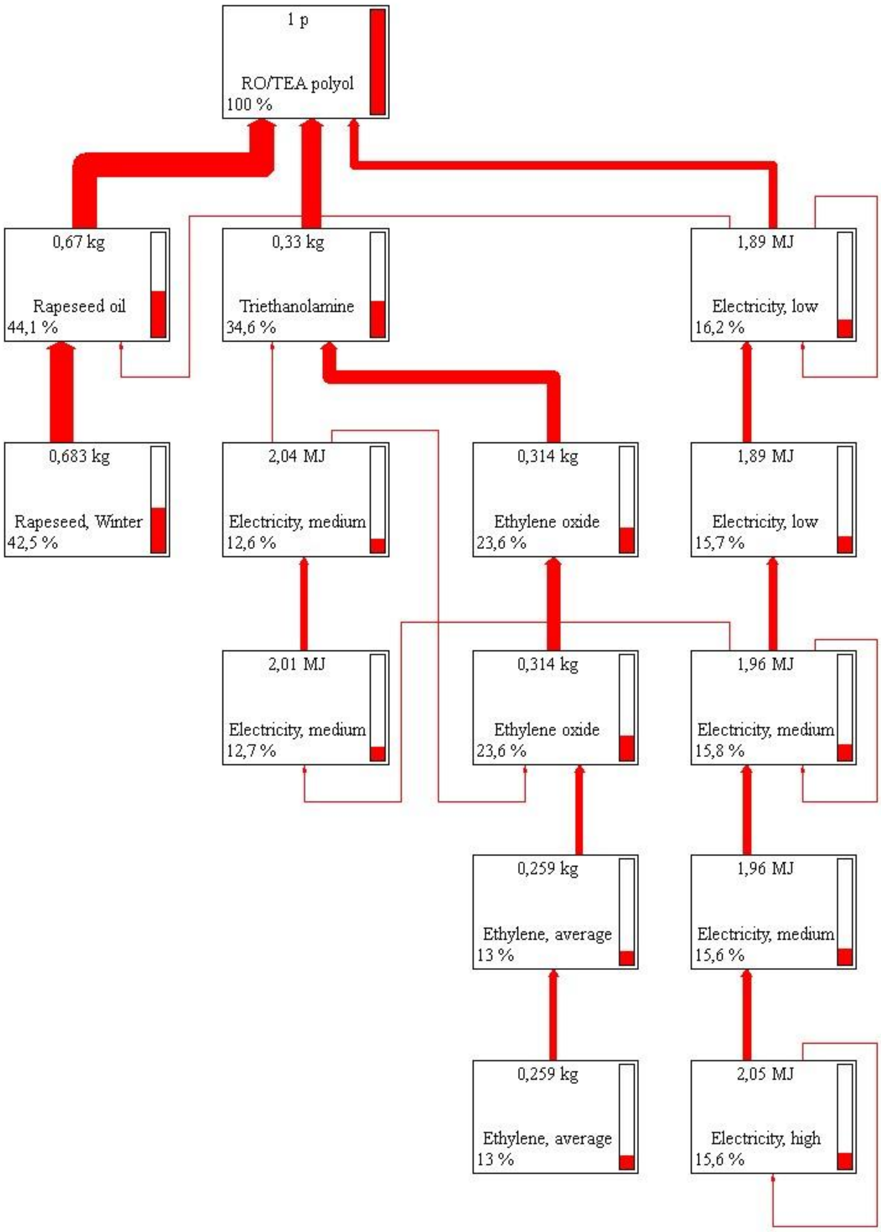

Fig. 3.17. Network tree of the main contributions to environmental impacts for 1 kg of rapeseed oil-based polyols: RO/TEA polyol.

The thicker pathway shows the major contributors and corresponding emissions or environmental impact during the production phase of polyol. The main contributors form 95 % of the total impact. For both rapeseed oil polyols, the main environmental impacts are attributed to rapeseed oil and alkanolamine production, followed by electricity needed for synthesis. Naturally, the rapeseed oil impact is dominated by rapeseed farming. For the alkanolamines, the impact is mainly dominated by the ethylene oxide production.

Fig. 3.18 provides the LCIA results at the ReCiPe endpoint level for RO/DEA and RO/TEA polyol in comparison to petrochemical counterpart when different allocation methods are applied for the oil mill stage. The results are reported in term of ecological performance score (i.e. mPt) per FU.

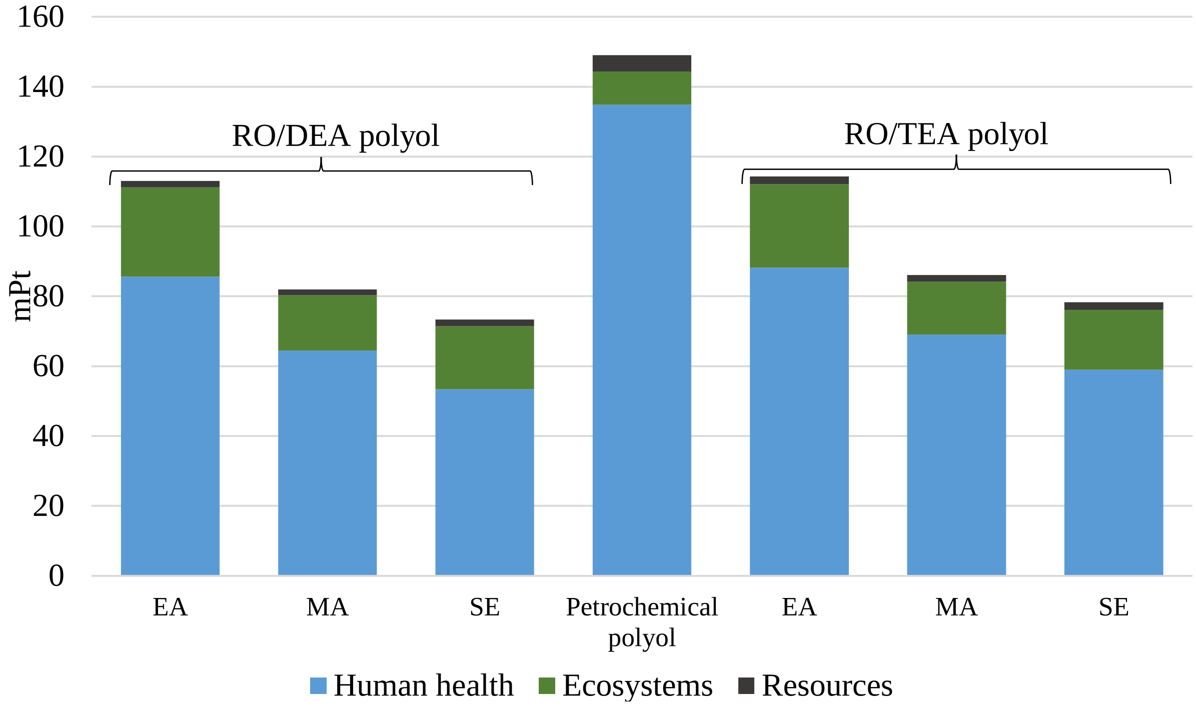

Fig. 3.18. ReCiPe's endpoint damage categories for bio-based rapeseed oil polyols, RO/DEA and RO/TEA, depending on rapeseed oil allocation method and their petrochemical counterpart.

Overall, both bio-based rapeseed oil polyols show lower ecological performance score than the petrochemical polyol. The slight difference between both polyols is due to slightly different inputs in each polyol (Table 3.17).

The overall environmental score for rapeseed oil-based polyols also significantly changes depending on the chosen allocation method in the rapeseed oil mill stage. For RO/DEA polyol for the system expansion case, the Endpoint value was 73.3 mPt, for mass allocation the value was 81.9 mPt (11.7 % higher), the highest value of 113.0 mPt was for the market value allocation, an increase of 54.1 % in comparison to the lowest polluting allocation method. In RO/DEA polyol is compared to end Endpoint value of petrochemical polyol, then the difference depending on the chosen allocation method is significant. If system expansion is applied, the ecological performance score is 50.1 % lower than for petrochemical polyol and 24.2 % lower in the case of market value allocation. The results show that the choice of allocation approach in the bio-based feedstock production stage can have a profound effect on the results of the developed bio-based chemical. From all allocation methods applied in the study, only the market value allocation is sensitive as rapeseed oil and cake price changes year to year.

Regardless of the polyol type, bio-based or petrochemical-based, the highest score was yielded by human health endpoint category. In the case of petrochemical alternative, the contribution was as high as 90.5 % of the total impact. For bio-based RO/DEA polyol, the contribution of human health category to total score decreased from 7.7 % (mass allocation) to 75.8 % (market value allocation), with the lowest value for system expansion scenario with 72.8 %.

However, for the endpoint impact category ecosystems, the results were the opposite. In the category ecosystems, rapeseed oil-based polyols showed worst performance as their contribution to total score was three to four times worse (depending on the chosen allocation) than the petrochemical polyol which is due to the use of bio-based feedstock for polyol production. For ecosystems category, the system expansion scenario contributed the most to total score with 24.7 %, while mass allocation scenario contributed the least with 19.3 %. In mass allocation for rapeseed oil mill stage, a significantly lower percentage of total impacts is contributed to oil than cake, while in market value allocation it is the opposite.

In the case of RO/TEA polyol, the overall trend remained the same as for the RO/DEA polyol across all Endpoint impact categories. The impact of each category varied a few per cent due to the different proportion of rapeseed oil in the polyol. RO/TEA has a lower input of rapeseed oil and higher for alkanolamine than for RO/DEA polyol (Table 3.17), thus the contribution of endpoint category ecosystems was lower and human health was higher to the total score.

Regardless of the polyol type, bio-based or petrochemical-based, the lowest score was yielded by resources endpoint category. For all the scenarios, it was in the range of 2–3 %.

The comparability of LCA results of different bio-based products is often limited, due to the lack of an agreed standard method for the allocation. Svanes et al. 2011 state that for external communication mass allocation might be the preferred method in most cases [223]. Moreover, LCA results are also often used in communication to the market, to show the possible benefits of bio-based alternative and as different allocation methods yield results that could lead to different behaviours by market actors.

A more in-depth analysis of rapeseed oil polyol production system and individual production steps is depicted in Fig. 3.19. The results propose the comparison among all the allocation methods applied in rapeseed oil production stage. The only difference raises due to the chosen allocation for the rapeseed oil production phase, as co-product cake is also produced. In Latvia, rape cake is mainly purchased by poultry and ruminant producers [201]. System expansion is when the system boundaries of the LCA are expanded to include co- or by-products usage pathways involving as well the potential re-using and/or recycling. In this way is possible to include the benefit (in terms of environmental credit to the modelled system) of what type of product or processing they substitute on the market. In this case study, rapeseed cake is used as protein feeds instead of imported soybean meal. Thereby, from the rapeseed oil production system, the impact of soymeal production has been subtracted.

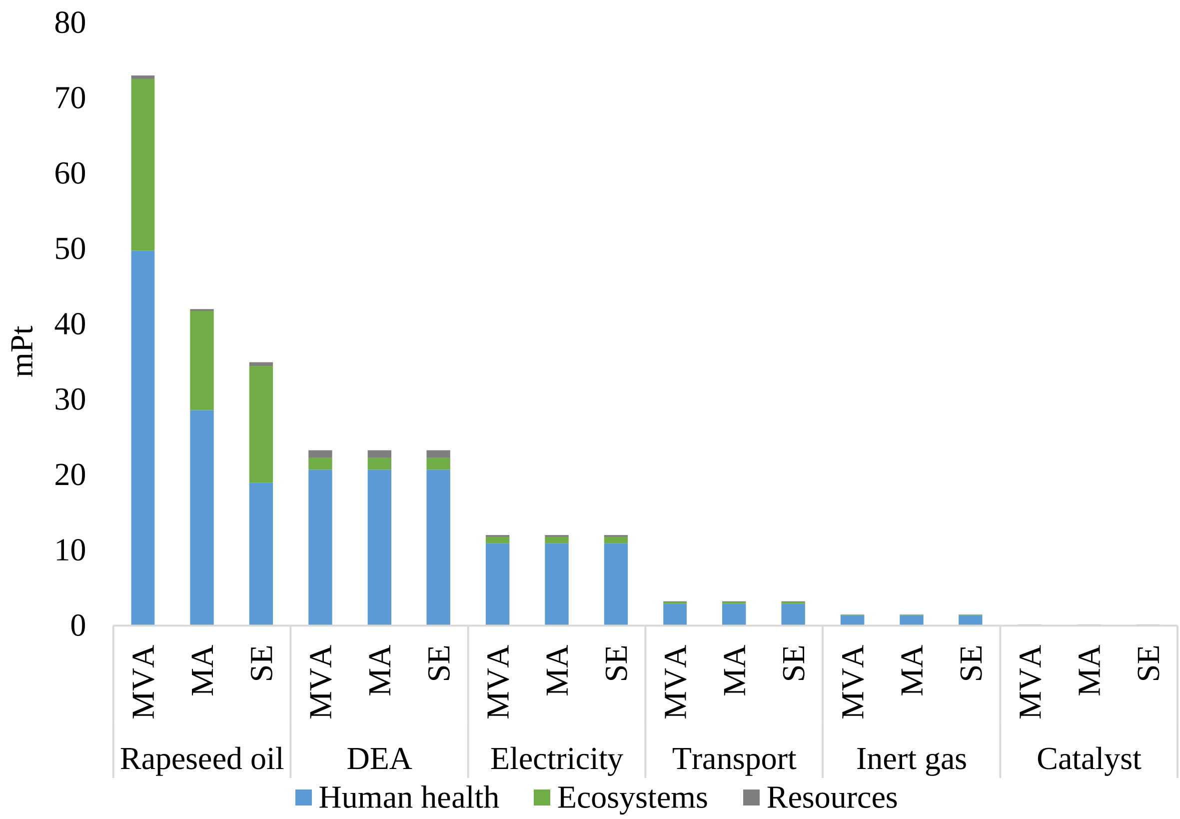

Fig. 3.19. ReCiPe's endpoint damage categories for bio-based rapeseed RO/DEA polyol from the perspective of their production inputs and depending on the allocation type.

Both bio-polyols are analyzed and compared, when mass allocation is applied for rapeseed oil mill stage (Fig. 3.20).

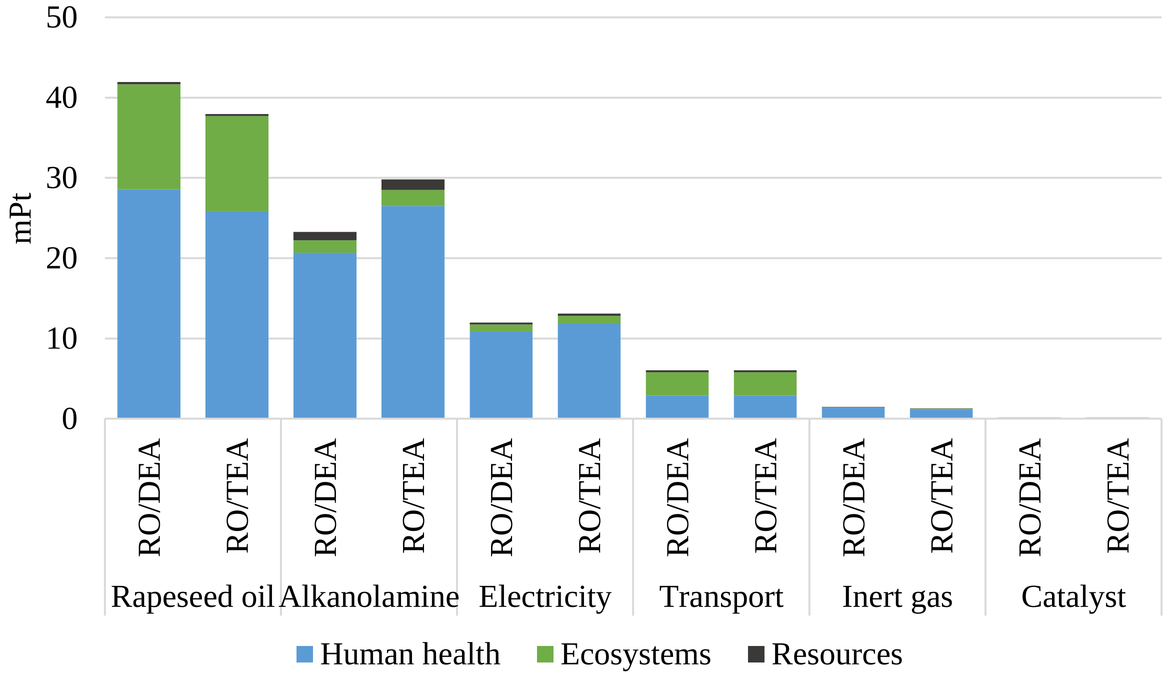

Fig. 3.20. ReCiPe's endpoint damage categories for bio-based rapeseed oil polyols from the perspective of their production inputs, MA for rapeseed oil mill stage.

Fig. 3.20 reveals that the main contributors to the Resource category are the alkanolamines used for the polyol synthesis and rapeseed oil where diesel is used as a fuel for agricultural machinery. The minor differences for this category are due to lower energy requirement for the RO/DEA polyol synthesis and lower input of alkanolamine, a chemical derived from fossil resources (Fig. 3.17). In comparison, taking the petrochemical polyol as the reference, the resources endpoint value for RO/DEA and RO/TEA polyols is 65.1 % and 58.1 % lower than the petrochemical polyol value.

The endpoint category resources contributors are the following midpoint categories – mineral and fossil depletion. In the ReCiPe method, nuclear energy, as depletion of ores for nuclear energy production, is accounted under the mineral resources midpoint indicator, and fossil energy is under fossil resources [149]. As discussed before, the endpoint category resources present the least impact of all endpoint categories. ReCiPe Endpoint category resources is related to the CED as they both depict the use of fossil resources for the production of the given product. However, Stavropoulos et al., 2016 argue that important advantage of CED method is the use of MJ-eq, which is a universally used unit and can be used in general for comparisons while it is challenging to compare the results of other LCIA methods [224]. CED gives more precise outlook and yields robust results on the depletion of non-renewable energy resources. The results of CED will be discussed in Section 3.4.8.

The contributors to the endpoint category human health are climate change, stratospheric ozone depletion, human toxicity, photochemical oxidant formation, particulate matter formation, and ionizing radiation [149]. Damage category human health is primarily affected by rapeseed oil production (44 %) and alkanolamine production (32 %) and electricity (17 %). Rapeseed oil-based polyols yielded around half of the petrochemical polyol impact in the human health category. For all endpoint categories, the contribution of transport, inert gas and catalyst contributed insignificantly to the total endpoint category`s value. However, it must be noted that the contribution of catalyst might be underestimated due to the use of proxy not full dataset from ecoinvent.

The largest contributors to ecosystems category are the production of rapeseed oil and alkanolamines as OH groups containing reactant for polyol synthesis. ecosystems category derives from combining the following endpoint impact categories: climate change ecosystems, terrestrial acidification, freshwater eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, agricultural land occupation, urban land occupation and natural land transformation [149].

3.4.7.2. Midpoint Level

At the midpoint level ReCiPe, the environmental impact is defined through 18 environmental mechanisms expressed as midpoint indicators. The characterization results were compared at the ReCiPe midpoint level (Fig. 3.21). The results were compared to the petrochemical polyol as a ratio petrochemical polyol to bio-based polyol, system expansion and market value allocation was used for rapeseed oil stage. If the value is >1, then rapeseed oil-based polyol performed better than petrochemical polyol, if the value is <1, bio-based polyol shows worse result than the petrochemical counterpart. If values are within ±15 % of each other, the results are considered equivalent [199].

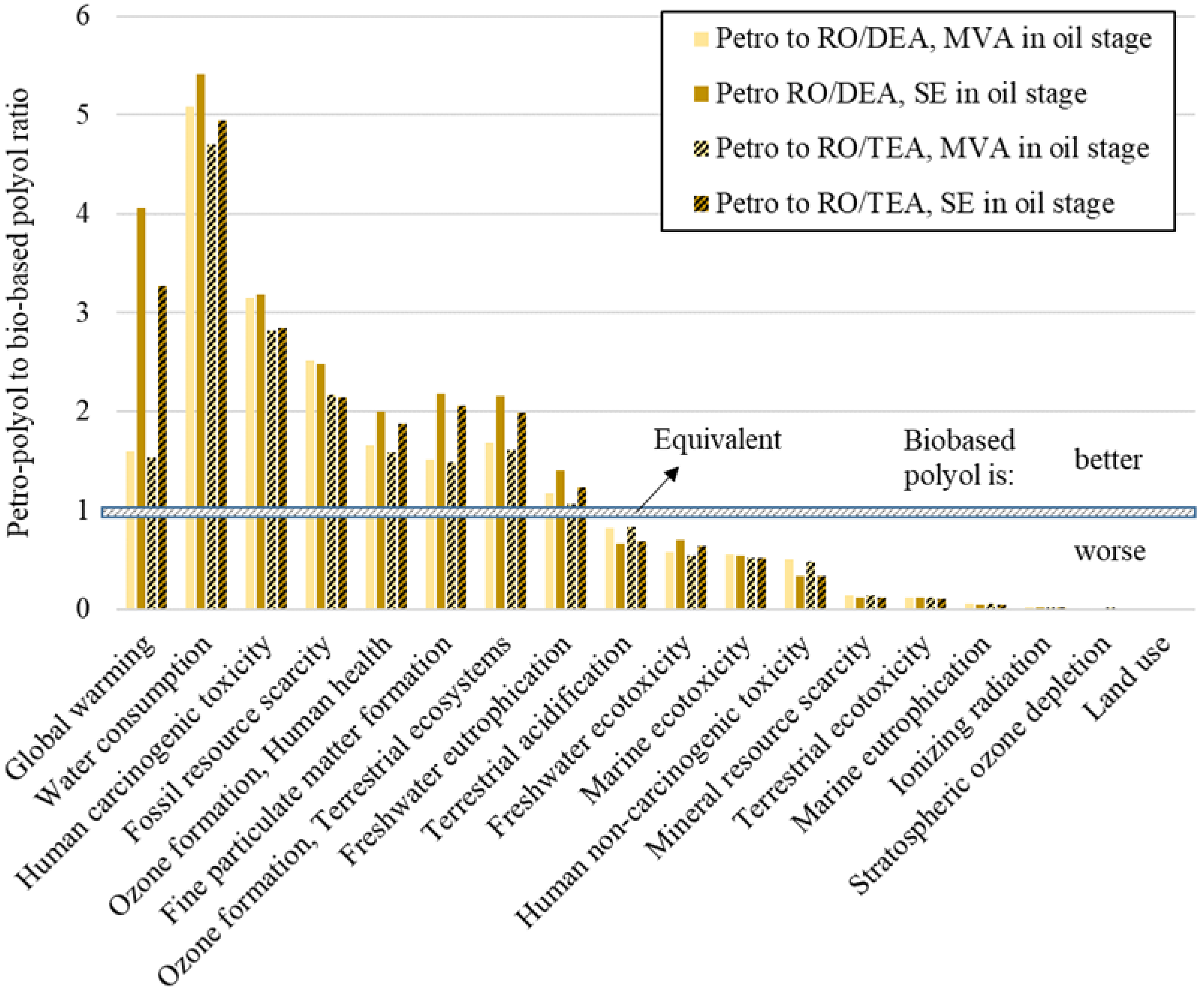

Fig. 3.21. Rapeseed oil-based polyols vs. petrochemical polyol (FU – 1 kg of polyol), LCIA method – ReCiPe Midpoint H impact categories, SE and EA for rapeseed oil stage.

The rapeseed oil-based polyols performed better in the following midpoint categories – global warming, fossil resource scarcity, water consumption, ozone formation, fine particulate matter formation, human carcinogenic toxicity and freshwater eutrophication. Another study reports that water consumption profile is heavily dependent on crop irrigation [225]. The rapeseed farming in Latvia does not use any artificial irrigation, only natural rainwater, also for the oil production there is no steam used as cold extraction technique is used, thus rapeseed oil-based polyols perform significantly better in this midpoint category. A closer look at the climate change midpoint category is presented in Section 3.4.7.2.1.

Bio-based rapeseed oil polyols have the potential to reduce non-renewable energy use, GHG emissions and water consumption, however, they may come at the cost of additional land used and other agricultural activity related impacts [214]. Patel et al., 2005 recommended that a *good practice target for bio-based polymers* is to reduce most other environmental impacts by at least 20 % [55], however, rapeseed oil-based polyols fail to reach this. To better show the rapeseed oil-based polyol drawbacks, the midpoint categories where rapeseed oil polyols performed worse are depicted in the inverse ratio – bio-polyol to petropolyol in Fig. 3.22. For categories related to land use, rapeseed oil-based polyols performed substantially worse than the petrochemical polyol, potential impact was from eight hundredfold to thirteen hundredfold higher. To produce rapeseed oil, agricultural land is needed for rapeseed farming and that results in the agricultural land occupation being the highest contributor for bio-based polyols (Fig. 3.22). Other midpoint impact categories, that are important and directly related to agricultural production, are eutrophication, ecotoxicity and acidification.

In marine eutrophication rapeseed oil bio-polyols performed ~20 times worse than petrochemical polyol, depending on the polyol type and also the chosen allocation method. For terrestrial acidification, both rapeseed oil polyols performed 1.2–1.5 times (market value allocation and system expansion allocation applied, respectively) worse than the petrochemical alternative. For this case study, the major contributor is rapeseed production as it uses mineral fertilizers in crop farming. For marine and freshwater ecotoxicity, bio-based polyols exhibited ~two times worse performance than petrochemical polyol. In arable crop farming, potentially toxic emissions come mineral fertilizer application, pesticide emissions, and use of agricultural machinery [226]. About one-third of the impact comes from the production of alkanolamine in marine and freshwater ecotoxicity category.

Other midpoint impact categories, where rapeseed oil-based polyol performed significantly worse are stratospheric ozone depletion and ionizing radiation.

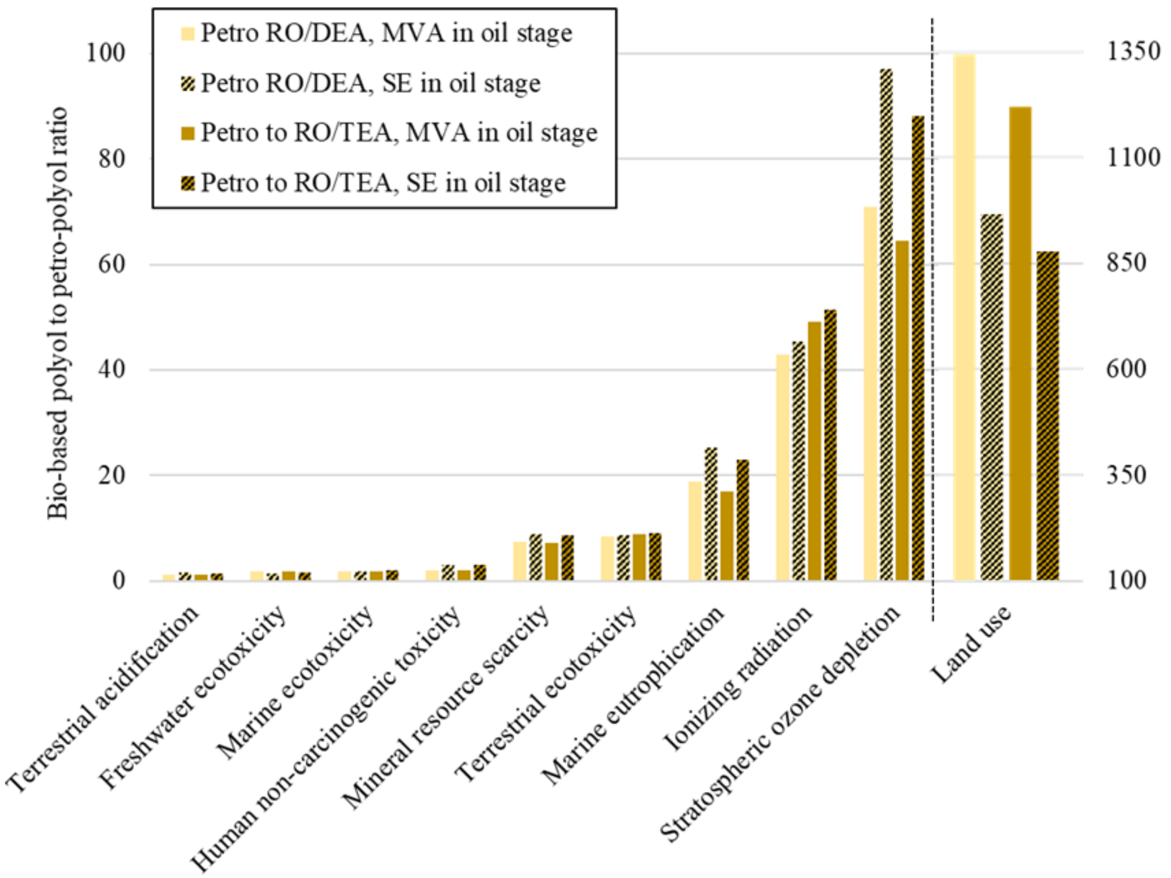

Fig. 3.22. ReCiPe Midpoint H impact categories, where rapeseed oil-based polyol performed worse in inverse ratio.

3.4.7.2.1. GHG Emissions

Climate change is a critical challenge humanity is facing in the 21st century [13]. The midpoint characterization factor for climate change is the Global Warming Potential (GWP) [149]. It is one of the key global life cycle indicators used in LCA.

The GHG emissions over a time horizon results are shown in Fig. 3.23.

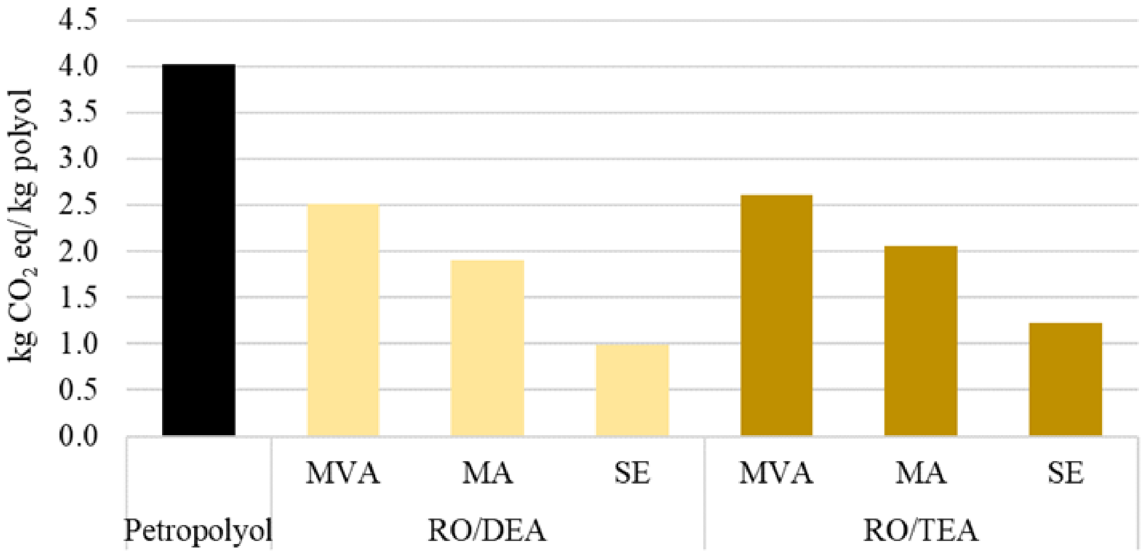

Fig. 3.23. Total GWP for the total rapeseed oil-based polyol production depending on rapeseed oil allocation method and the GWP for petrochemical polyol.

The replacement of petrochemical feedstock by vegetable oil for bio-polyol production leads to a decrease in GHG emissions. The total cradle-to-gate GWP of rapeseed oil bio-polyol is highest if the market value allocation is applied, while the lowest value is when system expansion is applied. The GHG emission savings are 1.50 kg CO_2eq (market value allocation) to 3.02 kg CO_2eq (system expansion) for RO/DEA, for RO/TEA polyol 1.40 kg CO_2eq (market value allocation) to 2.79 kg CO_2eq (system expansion) for 1 kg of produced polyol if compared to petrochemical polyol. Patel et al. recommended that a *good practice target for bio-based polymers* is to avoid at least 1 kg CO_2 per kg polymer [55].

Fig. 3.24 gives a contribution to different production steps in bio-based polyol production system when all three allocation methods are applied in oil mill stage. Depending on the chosen allocation approach in the oil mill stage, the largest GWP contributors also change. If system expansion is used, then the largest contributors to GHG emissions are alkanolamine production and electricity with a considerably lower value. When the expansion was used as the allocation method, the impact of soymeal production has been subtracted from the rapeseed oil production system, thus yielding a negative GWP value for rapeseed production. If mass and market value allocation are applied, then rapeseed oil and alkanolamine production are significant contributors. For market value allocation, rapeseed oil contribution is significantly higher and thus also for the polyol itself. Rapeseed oil is the main raw material as the rapeseed oil-based polyols contain up to 74 % bio-based content (Table 3.16). Rapeseed oil is a large contributor to GWP, and in general to GHG emissions related to the rapeseed oil production are related to the emissions related to (i) the use of fertilizers, (ii) the use of the fossil fuels (agricultural machinery, drying of seed), and (iii) inputs for rapeseed production (seeds, plant protection products, fertilizers). The contribution of transportation of alkanolamines, inert gas for synthesis and catalyst to net GWP is very low. However, it must be noted that for catalyst the contribution might be underestimated, as no specific dataset was available in ecoinvent v3.5.

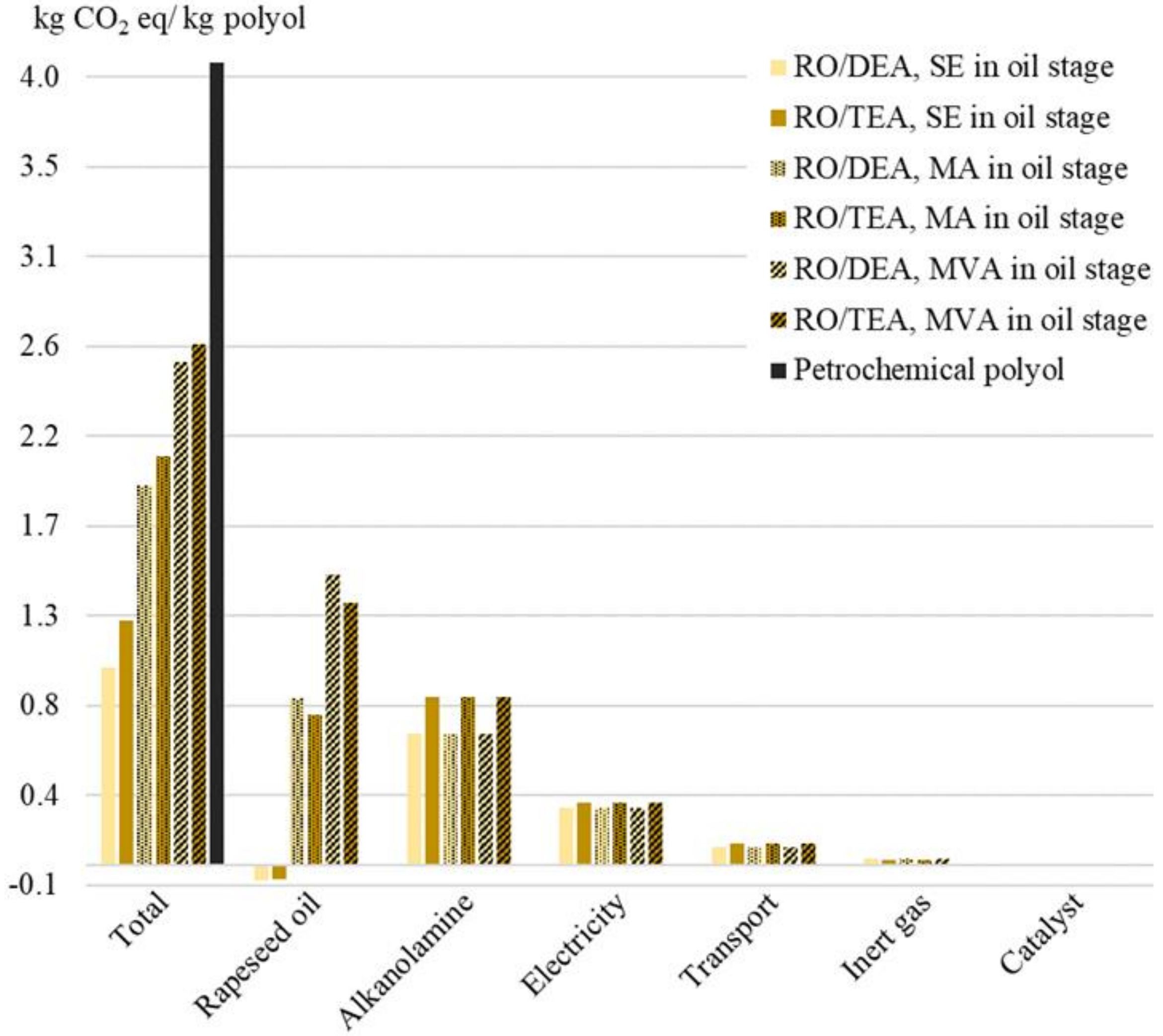

Fig. 3.24. Total GWP for the total rapeseed oil-based polyol production and the GWP per individual production step compared to petrochemical polyol, depending on rapeseed oil allocation method.

For the petrochemical polyol, GHG emission breakdown for production stages is not available.

3.4.8. Life Cycle Impact Assessment of Bio-polyols: CED Method

Concerns about non-renewable energy use along with Greenhouse gas (GHG) emissions have triggered and stimulated the growing interest in bio-based products, thus GHG and non-renewable energy use are important parameters to characterize the performance of a bio-based product in comparison to the petrochemical counterpart [214].

CED of a product or process represents the direct and indirect energy use in units of MJ throughout the life cycle [142]. CED takes into account primary energy use, both renewable and nonrenewable, and energy flows intended for both energy and material purposes [143]. Moreover, energy use indicators have been shown to be good proxy indicators for environmental impacts in general [144].

Fig. 3.25 presents CED results grouped according to rapeseed oil polyol type – RO/DEA and RO/TEA, respectively, and by chosen allocation method for the rapeseed oil in the oil mill stage. CED results are also compared to the CED for the petrochemical polyol available in the ecoinvent v3.5 database.

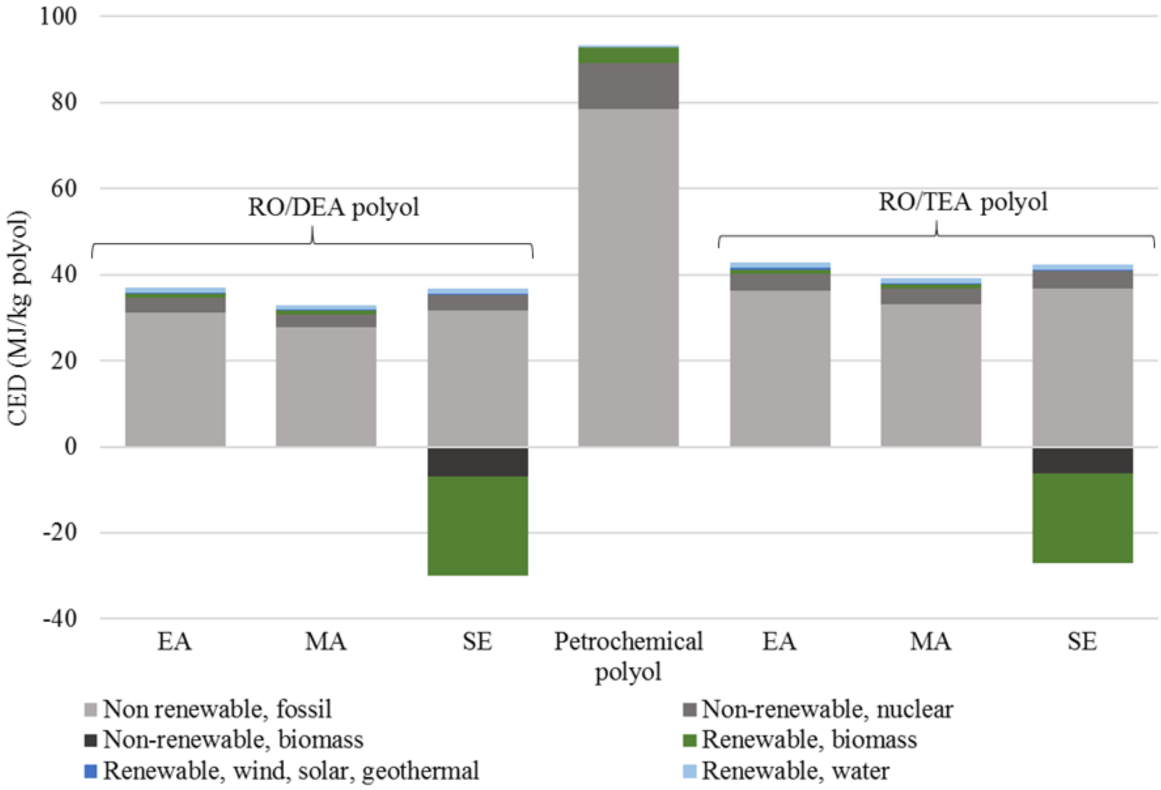

Fig. 3.25. CED for bio-based rapeseed oil polyols depending on rapeseed oil allocation method and their petrochemical counterpart. Method: CED V1.11.

The difference between both polyols is due to the different amount of oil and alkanolamine content in each polyol (Table 3.17) and differences in energy consumption during polyol synthesis. For rapeseed oil-based polyol synthesis, 0.44 and 0.48 kWh of electricity are needed to produce 1 kg of polyol at a pilot-scale reactor (Table 2). The study by Omni tech reports that for soy-based Agrol polyols by BioBased Technologies, LLC, suitable for flexible PU foam production, the energy required for polyol synthesis is 1.04 kWh/ per kg polyol [227]. According to the patent filed by BioBased Technologies, a two-stage process is used to synthesize polyol, which results in higher energy demand [228]. Other reports fail to clearly present their LCI due to confidentiality issues most likely.

Overall, both bio-based rapeseed oil polyols show lower CED in all cases of applied allocation in oil mill stage than the petrochemical polyol with CED of 93.4 MJ/kg. The lowest CED is for the case where system expansion is applied in the rapeseed oil production stage.

CED results are 6.8 MJ/kg (83 % lower) and 15.5 MJ/kg polyol for RO/DEA and RO/TEA (93 % lower) polyols, respectively. The CED decreased to 60 % in the case of market value allocation, 65 % for mass allocation for RO/DEA polyol; for RO/TEA polyol, the percentage is 54 % and 58 %, respectively, if compared to the petrochemical polyol.

Preliminary LCI data for Cargill`s soy-based polyols report that their BiOH® polyols (suitable for flexible foams) have 23 % less total energy demand than traditional petrochemical polyols [125]. However, no information is given on allocation applied for bio-based feedstock agricultural phase. A study carried out by Hilling & Russell showed similar results for bio-based soy and castor oil polyols, capable of being used to make flexible polyurethane foam, in comparison to Plastics Europe petrochemical polyol. Both, soy and castor, oil-based polyols showed lower gross energy intensity (MJ/kg) and lower proportion of fossil fuel energy than the petrochemical counterpart did. Although the authors do not mention exact numbers, the gross energy intensity value for castor oil is ~70 MJ/kg and for the soy-based polyol ~62 MJ/kg. LCI for soybean oil is based on the USA soy farming, for castor oil LCI is based on irrigated castor with fertilizer coproduct (lowest burden on castor oil) [124].

It is well known that fossil fuel energy resources used for energy generation are mainly responsible for the depletion of fossil resources and global warming [210], [211]. If CED is analyzed by impact categories, NRCED is often applied. For bio-based polyols and petrochemical-based polyol, the non-renewable fossil energy is by far the largest contributor to total CED of the systems under study, followed by nuclear energy. In the case of market value allocation, mass allocation and system expansion allocation, there is a decrease of 61.2 %, 65.4 % and 68.1 % in NRCED for RO/DEA polyol, respectively, if bio-based polyol is compared to NRCED of petrochemical polyol. In the case of RO/TEA, the decrease in NRCED is 54.9 %, 58.7% and 61.1 %. Preliminary LCI data for Cargill`s soy-based polyols report that their BiOH® polyols have 61 % less non-renewable energy use than traditional petrochemical polyols [125]. Overall, the percentage of fossil resources savings is significant. Patel et al., 2005 suggested that *good practice targets* for "environmentally correct" bio-based products could be very useful; it was recommended that, relative to their petrochemical counterparts, bio-based polymers should save at least 20 MJ (non-renewable) energy per kg polymer and avoid at least 1 kg CO_2 per kg polymer.

In the scenario, where system expansion is applied in oil mill stage and produced rapeseed cake is used to replace the soybean meal as a feed for animals, the soybean meal with global representation was chosen as a dataset from ecoinvent v3.5 Thereby, from the rapeseed oil production system, the impact of soymeal production has been subtracted. The total CED of both bio-based polyols is offset by the non-renewable biomass and renewable biomass impact categories (Fig. 3.25). A closer insight is given, when CED results are compared for a more in-depth analysis of rapeseed oil polyol production system and individual production steps (Fig. 3.26). The results clearly show that the difference is due to the different allocation for rapeseed oil production, while for other polyol production inputs CED remains the same.

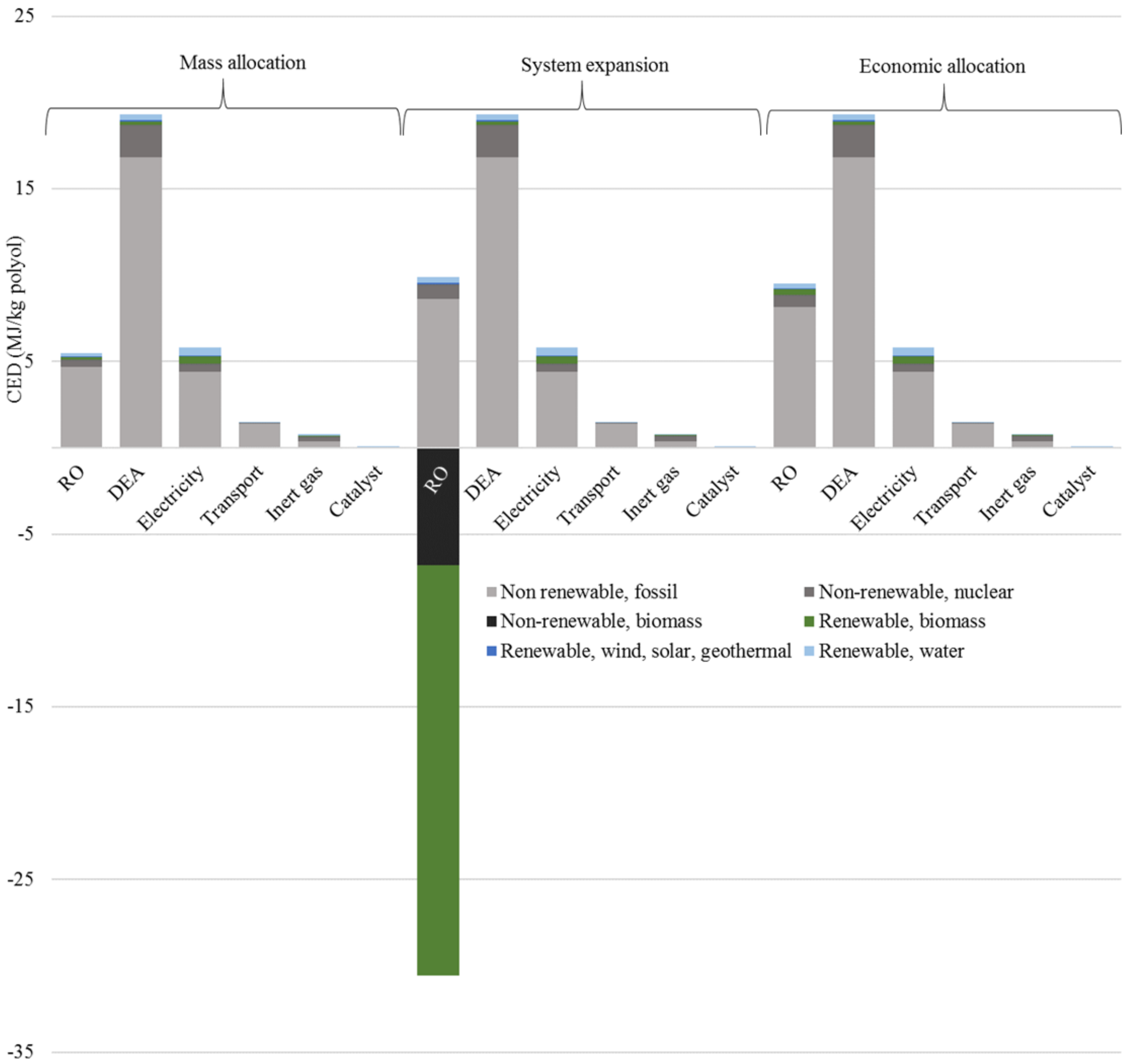

Fig. 3.26. CED results for bio-based RO/DEA polyol from the perspective of their production inputs and based on different allocation approaches.

3.4.9. Sensitivity Analysis for Bio-polyol Production

The purpose of this subsection is to analyse to what electricity mix, the higher or lower per cent point of renewables in the mix, is affecting the final environmental score. Rapeseed oil and alkanolamine input are major contributors to environmental hotspots in the polyol production, the change in quantitative material inputs for polyol synthesis is not desired because developed rapeseed oil-based polyols are already the optimal version of the chemical synthesis route [96]. As electricity is the third-largest environmental hotspot (Fig. 3.17), the sensitivity analysis was checked using electricity mixes of different countries present in the ecoinvent v3.5 database.

In the baseline scenario, rapeseed oil-based polyols were produced in Latvia. For comparison, several other EU countries were chosen. The constituents of electricity mixes for each country is shortly characterized in Table 3.18. Electricity mix was changed for each polyol, the ReCiPe Endpoint total value recalculated, and expressed as a percentage change from the baseline scenario.

Table 3.18

Sensitivity Analysis for Rapeseed Oil-based Polyols Undertaken by Exploring Electricity Sources From Different Countries

Chosen polyol production country	Electricity mix description, according to Itten et al., 2014 [229]	RO/DEA polyol			RO/TEA polyol		
		MA	SE	MVA	SE	MA	MVA
		given country vs baseline					
Baseline scenario – Latvia	Hydropower 32 %, fossil fuels 20 %, renewables 1%, import 48 %* (assumed from Russia with 64 % of fossil fuels in the mix)	-	-		-	-	
Austria	Hydropower 48 %, fossil fuels 20 %	-8 %	-8 %	-6 %	-9 %	-8 %	-6 %
Germany	Fossil fuels 56 %, nuclear 22 %, renewables 10 %	-2 %	-2 %	-1 %	-2 %	-2 %	-2 %
Sweden	Hydropower 43 %, nuclear 38 %, renewables 7 %	-13 %	-14 %	-9%	-15 %	-13 %	-10 %
ENTSO-E	Fossil fuels 50 %, hydropower 17 %, nuclear 27 %, renewables 6 %	-4 %	-4 %	-3 %	-5 %	-4 %	-3 %
Estonia	Fossil fuels 85 %, from that 79 % lignite	8 %	9 %	6 %	10 %	9 %	7 %

It can be seen that the results do not present a change in value by more than ±15 % of the baseline scenario (Table 3.18). Depending on the chosen electricity mix, there is a small improvement or decrease in environmental aspects. Sweden`s electricity mix showed the highest percentage change from the baseline scenario. Using Swedish electricity mix, the total impact reduction would be 9 % to 13 % lower result than in baseline scenario, which is due high share of hydropower and a minor share (2 %) of fossil fuels in the electricity mix [229].

On the other hand, if a fossil- fuel-oriented energy mix, as that in Estonia, is considered, then bio-based polyols will exhibit higher environmental impact than the baseline scenario. When the share of fossil fuels in the electricity mix is lowered, the environmental impact is also reduced as in the case of Germany and Austria. The European Network of Transmission System Operators for electricity (ENTSO-E) electricity mix also showed minor impact reduction in comparison to the baseline scenario.

3.4.10. Data Gaps

Although this LCI was build based on a pilot-scale production of rapeseed oil polyols, LCI data from a larger scale polyol production might be different and thus yield different results in the LCIA. The difference would rise for several reasons, to name a few – the electricity consumption needed for the synthesis, type of chemical plant and transportation depending on the location of the production site, as the molar ratio for the synthesis remain the same.

CONCLUSIONS

The main question to be answered by this Thesis was whether the bio-based rapeseed oil polyols suitable for the production of PU materials had a better environmental performance than that of the petrochemicals polyols.

To meet this aim, an in-depth LCA was performed. In addition to generating the environmental profiles required to fulfil the research objectives, the development of regionalized and up-to-date LCI was required, thus enabling the quantification of customized inputs not been previously reported for Latvia as a country in Northern Europe. To facilitate this, the research was divided into four sections designed to present transparent and consistent results of each major conversion and production stages. To acquire accurate and realistic LCA results, good quality, transparent primary data are crucial for the creation of LCA models. The publication of separate LCI representing the state-of-art in terms of rapeseed cultivation for the Latvian context and bio-polyol synthesis will be one of key findings of this research addressed to other LCA researchers and practitioners, they are relevant to be implemented in any LCA software database.

A regionalized LCI for spring and winter rapeseed cultivation in Latvia was presented. In the LCI stage, a comprehensive primary data collection allowed avoiding the definition of assumptions from literature. The methodology used for the finalization of the LCI resulted in an in-depth inventory resembling as closely as possible the actual agricultural practices used for rapeseed production in Latvia, which is essential for the following LCA. The rapeseed cultivation inventory identified that the average yield of winter and spring rapeseed is 3.5 t/ha and 2.5 t/ha. Rapeseed yield is in line with the average yield of rape and turnip rape yield of the EU-28. The use of fertilizers is similar with respect to other EU member state practices, for winter rapeseed 63.2 kg/N/t of nitrogen was used, while for summer rape – 74.8 kg/N/t. To cultivate spring rapeseed, more field-work is required, which results in higher diesel consumption of 31.7 L/t vs. 14.5 L/t for winter rapeseed. The use of plant protection products was 5.0 L/t for winter and 6.6 L/t for spring rapeseed. This study reported the use of micronutrients for rapeseed cultivation, which has not been fully reported elsewhere. The study was addressed to actual rapeseed cultivation strategy within the analysed region, thus identifying and highlighting a lack of the use of agricultural leftovers. The LCI data harmonization with the ecoinvent database highlighted several areas of alignment challenges, such as lack of inventories for fertilizers and micronutrients and also challenges with the agricultural machinery harmonization.

The CED for winter and spring production in Latvia is 6450 MJ/t and 8809 MJ/t, respectively, the NRCED comprised 94 % of total CED with the majority of that being fossil energy. The comparison of the CED results shows that spring rapeseed cultivation required 36 % more energy than winter rapeseed, which is due to a lower yield of spring rapeseed and higher agricultural inputs. For winter and spring rapeseed, the most impacted category at the ReCiPe H endpoint level was human health with 67.2 %, 78.9 % of the impact, followed by ecosystems with 32.2 % and 20.4 %, respectively. Less than 1 % of contribution was to resources. The mineral fertilizers are the agricultural input with the highest environmental impact for both rapeseed types. Another considerable input is the agricultural machinery for different field works. In contrast, transport and plant protection have minor to some influence, contribution below 15 %. Seeds for sowing have negligible influence in all impact categories, except for water consumption with less than 4 % impact. Research findings have highlighted that oil crop yield is a crucial factor in the environmental analysis as with higher yields the impacts decrease. Winter rapeseed cultivation is less environmentally damaging than spring rapeseed.

LCA analysis for rapeseed oil mill stage shows that the choice of allocation method has a significant impact on the results of LCA of rapeseed oil. Overall, the environmental performance score increased as follows: system expansion < mass allocation < energy allocation < market value allocation. System expansion yielded the lowest score, the CED for 1 t rapeseed oil was −28 GJ for both rapeseed types, while for market value allocation CED was 13 GJ/t for winter and 18 GJ/t for spring rapeseed. The importance of yield was also highlighted as spring rapeseed performed worse than winter rapeseed. LCIA with ReCiPe method showed that system expansion yielded the lowest score with 45 mPt for winter rapeseed, the impact of mass allocation was 25.8 % higher, 84.1 % higher for energy allocation and 119.1 % higher for market value allocation. The trend was the same for spring rapeseed. The sensitivity analysis indicates that increasing or decreasing the price of oil by 30 %, the change in environmental score is below 15 %.

The work models a cradle-to-gate LCA for a pilot-scale bio-based polyol production. LCA results show that the environmental impacts caused by bio-polyol production mainly originate from rapeseed oil and alkanolamine production, with electricity being the third-largest environmental hotspot electricity; other synthesis inputs have a minor impact. Overall, both rapeseed oil-based polyol systems have similar total environmental impacts, the difference being several percentage-points due to different proportion of rapeseed oil and alkanolamine in the polyol.

The CED needed for RO/DEA polyol synthesis was 6.8 MJ/kg polyol and 83 % lower in comparison to petrochemical alternation, for RO/TEA − 15.5 MJ/kg (93 % lower). The fossil energy by far was the largest contributor to total CED. The savings of NRCED were significant if bio-based polyol is compared to NRCED of petrochemical polyol, the NRCED was 54.5 MJ/kg, 58.3 MJ/kg, 60.7 MJ/kg lower in case of market value, mass and system expansion allocation. In the case of RO/TEA, the decrease in NRCED was 54.9 %, 58.7%, and 61.1 %. ReCiPe results for RO/DEA polyol yielded environmental score 73.3 mPt for the system expansion allocation, while the highest value of 113.0 mPt was for the market value allocation. The replacement of petrochemical feedstock by vegetable oil for bio-polyol production leads to a decrease in GHG emissions. The total GHG emissions savings for cradle-to-gate of rapeseed oil bio-polyols are 1.50 kg CO_2eq (market value allocation) to 3.02 kg CO_2eq (system expansion) for RO/DEA, for RO/TEA polyol 1.40 kg CO_2eq (market value allocation) to 2.79 kg CO_2eq (system expansion). Sensitivity analysis for rapeseed oil-based polyols was performed by exploring electricity sources from different countries. Depending on the chosen electricity mix, the improvement or decrease of environmental aspects varies less than 15 %.

The detailed LCA investigations of rapeseed oil-based bio-polyols have given complex answers that are not unidirectional. The results of this study show that the use of rapeseed oil as a bio-based feedstock for polyol production offers a clear impact reduction compared to petrochemical polyols in terms of non-renewable energy use, lower GHG emissions and water consumption. However, LCA results also showed that rapeseed oil-based bio-polyols performed worse in important midpoint categories such as land use, marine eutrophication, terrestrial ecotoxicity, and stratospheric ozone depletion.

FUTURE RESEARCH

The research that has been undertaken for this Thesis has highlighted several questions on which further research would be beneficial.

Further research based on the full implementation of bio and circular economy could be carried out where it is expected that straw co-product will also be fully used to generate energy or derive bio-based chemicals. The use of rapeseed straw for different applications and avoided impact scenarios can be modelled and exploited in further LCA studies aiming to assess the environmental strategies enhancing the overall environmental performances.

This study is an effort to begin evaluating the potential environmental impacts of PU materials that are formulated using bio-based polyols. Further research would also allow determining for what kind of PU end applications rapeseed oil bio-based polyols are most suitable in terms of environmental benefits and drawbacks.

It would be interesting and valuable to assess the effect of bio-polyol synthesis up-scaling to the industrial level on the energy demand. Without doubt, the specific energy demand would change, however, while the energy demand for the synthesis itself might be lower, additional energy demand might arise due to use of additional equipment, such as pumps, etc.

The debate about the effects of land use change and indirect land use change is still ongoing, the effects of these changes were not taken into account in the present study. However, it would be interesting to get insight into the effects of land use questions might have on the results of the present study.

There are also several applications for the work undertaken in this Thesis. The developed LCI for rapeseed, rapeseed oil, and bio-polyols can be implemented in various LCI databases where other researchers and LCA practitioners can use this data for their respective studies. In a context of research carried out at Latvian State Institute of Wood Chemistry, the data can be used to perform other LCA studies in regards to bio-polyols that are synthesized via different chemical route. The impact of the chosen chemical route to the environmental profile of the end product can be assessed.

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