RIGA TECHNICAL UNIVERSITY
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LIFE CYCLE ASSESSMENT OF RENEWABLE POLYOL MONOMERS FOR POLYURETHANE PRODUCTION

Summary of the 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 Science (*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; Conclusions; 43 figures; 21 tables; the total number of pages is 115. The Bibliography contains 229 titles.

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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 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. **<u>Anda Fridrihsone</u>**, 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. **<u>Anda Fridrihsone-Girone</u>**. 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, **<u>A. Fridrihsone</u>**, 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. **<u>Fridrihsone-Girone, A</u>**., 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, **<u>A. Fridrihsone-Girone</u>**, U. Cabulis, S. Gaidukovs, V. Tupureina. Method for producing spray-applied polyurethane coatings on metal constructions. EP2865724 (A1). 29.04.2015.
3. **<u>A. Fridrihsone-Girone,</u>** 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, **<u>A. Fridrihsone-Girone</u>**, 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. **<u>Fridrihsone, A</u>**., 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.

1. **<u>A. Fridrihsone</u>**, 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*)

2. **<u>A. Fridrihsone</u>**, 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)
3. **<u>Anda Fridrihsone</u>**, 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*)
4. **<u>Anda Fridrihsone</u>**, 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*)
5. Urethanes Technology international. February/March 2014. Vol 31, No.1
6. **<u>A. Fridrihsone-Girone</u>**. 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*)
7. **<u>Fridrihsone-Girone, A</u>**., Stirna, U. Post curing kinetics of VOC-free, 100% solids, spray-applied polyurethane coatings from rapeseed oil polyols, 4th Workshop of Green chemistry and nanotechnologies in Polymer Chemistry, Italy, Piza, September 4–6, 2013, pp. 23–24 (*oral presentation*)
8. **<u>A. Fridrihsone</u>**, U. Stirna, L. Deme, V. Zeltins, B. Lazdina, V. Yakushin. Accelerated ageing, chemical resistance and hydrolytic stability of polyurethane coatings based on rapeseed oil polyol. In: Book of abstracts Coatings Science International 2013, The Netherlands, Noordwijk, June 24–28, 2013, pp. 214–217 (*poster*)
9. Zeltins, V., Deme, L., Lazdina, B., **<u>Fridrihsone, A</u>**., Yakushin, V., Stirna, U. Degradation study of rapeseed oil bases polyurethane coatings. In: *Baltic Polymer Symposium 2012, Programme and Proceedings*, Latvia, Liepaja, September 19–22, 2012, p. 103 (*poster*)
10. **<u>Fridrihsone, A</u>**., Stirna, U., Zeltins, V., Mechanical and thermal properties of polyurethanes from biobased rapeseed oil polyols. In: *Baltic Polymer Symposium 2012, Programme and Proceedings*, Latvia, Liepaja, September 19–22, 2012, p. 105 (*poster*)
11. **<u>Fridrihsone, A</u>**., Stirna, U. Biobased rapeseed oil polyols and their use in polyurethane coatings. In*: 3rd Workshop Green Chemistry and Nanotechnologies in Polymer Chemistry*, Poland, Cracow, September 24–26, 2012, pp. 33-34 (*oral presentation*)

1. ESSENCE OF LITERATURE REVIEW

1.1. Sustainable Development and Its Challenges

The concept of sustainable development was first introduced to the public in the report "Our Common Future (1987)" (known as the Brundtland Report) by the World Commission on Environment and Development [7], where the sustainable development was defined as follows: "Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs". The goal of sustainable development is to achieve balance/harmony between environmental sustainability, economic sustainability and socio-political sustainability [8].

Over the decades, there have been several global initiatives to improve different aspects of sustainability issues. At the UN Sustainable Development Summit in 2015, world leaders adopted the latest landmark initiative – "Transforming our World: the 2030 Agenda for Sustainable Development", which includes a set of 17 Sustainable Development Goals aimed at ending poverty, fighting inequality and injustice, and tackling climate change by 2030. 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" [4].

Without doubt, greenhouse gas emissions and global climate change are one of the most central aspects of sustainability challenges the humankind is facing today. Today humankind is also completely dependent on petroleum products for materials – plastics. The plastics life cycle also contribute to the global environmental challenges, as fossil resources are used [9]. 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) [10].

1.2. Bio-Based Europe

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. The EU is fully committed to being a frontrunner and leader in implementing the global Agenda 2030 [11]. Latvia is one of the EU member states that have a dedicated bioeconomy strategy at a national level. LIBRA 2030 was published in 2017. 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 [1].

One of the sectors that bioeconomy covers is the conversion of produced, renewable biological resources into chemical products, it is an essential part of a sustainably sound transition [3] and is perceived as a means of "going green" [12]. The use of vegetable oils in the production of polymers and other chemicals is well integrated within the framework of the bioeconomy concept. 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 while in the 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 [13].

According to the published Sustainability Report by the European Chemical Industry Council in 2017, renewables comprise 10 % (7.8 million t) of total organic raw materials – material (feedstock) use only; vegetable oils comprise 18 % (1.42 million t) of total renewables [14].

Rapeseed is a widely cultivated crop around the world mainly due to its oil-rich seeds (>40 %). The EU-28, Canada and China are amongst the largest rapeseed producers in the world. Rapeseed is also a widely cultivated oil crop in Latvia. Since 2000, the amount of land devoted to rapeseed cultivation has increased vastly [15].

1.3. Polyurethane and Sustainability

The polymer industry continues to be under pressure to be more sustainable towards finding innovative solutions from an environmental and sustainability perspective [16].

The urethane group is the major repeating unit in PU (Fig. 1.1). It is synthesized in a reaction between isocyanate moiety containing isocyanate groups (-N=C=O) and polyhydroxylated (-OH) containing co-reactant (polyol) [17].

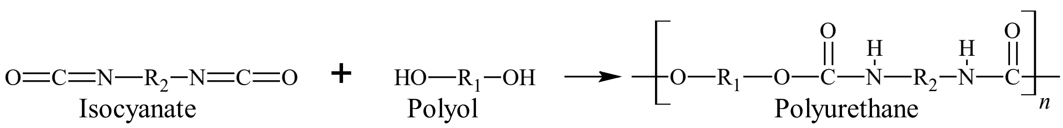

Fig. 1.1. Generic urethane linkage reaction [18].

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 to meet the needs for various applications (automotive industry, construction, appliances, furnishing, marine, medicine, and others, the breadth of PU applications is remarkable [18].

Millions of t of PUs are produced annually for use in widespread applications, it is the sixth most used polymer on a global scale [19]. In 2016, PU comprised 7.5 % of used plastics in Europe [20]. In 2018, it was estimated that the production of PU formulated with bio-polyols comprises around half of the total bio-based polymer production [21].

Natural oils have to be chemically modified to introduce -OH groups in their structure for them to be used in PU material production to fully or partially replace the petrochemical polyol. Different natural oils, such as castor [22], soybean oil [23], palm [24], jatropha [25], sunflower [26], rapeseed [27], and others (linseed, coconut [19]) 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 [19], [28]–[31]. There are several processes to convert vegetable oils into polyols, which include epoxidation and ring-opening, transesterification, amidization, hydroformylation, ozonolysis, and others [29].

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 regions depending on the geographical location and agricultural production in this area (soy dominant is the USA, rapeseed – Europe, palm oil – Asia) [32], with all being the most attractive for large-scale industrial products [28].

NOPs are drop-in replacements for their petrochemical counterpart, thus there is no need to adjust or develop new processing conditions, which are an important advantage to ensure faster uptake by the industry [33]. 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 equivalent or better performance than existing commercial petrochemical counterparts and 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 polymer production capacity in 2018, there still is fairly little information on their environmental performance.

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. However, 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 [34], [35] and palm oil [36]. LCA is necessary to fully understand the advantages and trade-offs of bio-based materials [37]. As there are several available feedstocks for NOPs development, along with different chemical routes, it is important to assess each case on its own. Using 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.

2. METHODOLOGY

The Thesis followed the ISO 14040 and ISO 14044 guidelines [6], [38]. The Life Cycle Impact Assessment (LCIA) methods used in this Thesis are briefly described further.

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 [39]. CED takes into account primary energy use, both renewable and non-renewable, and energy flows intended for both energy and material purposes [40]. A CED V1.11 was used for this Thesis.

ReCiPe method is the most recent and harmonized indicator approach [41]. 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.

Software and databases. The LCA software SimaPro 9.0 by Pré Consultants and ecoinvent v3.5 (Cut-off system model) were used to perform LCA calculations.

3. RESULTS AND DISCUSSION

The visual representation of research design and phases is depicted in Figure 3.1.

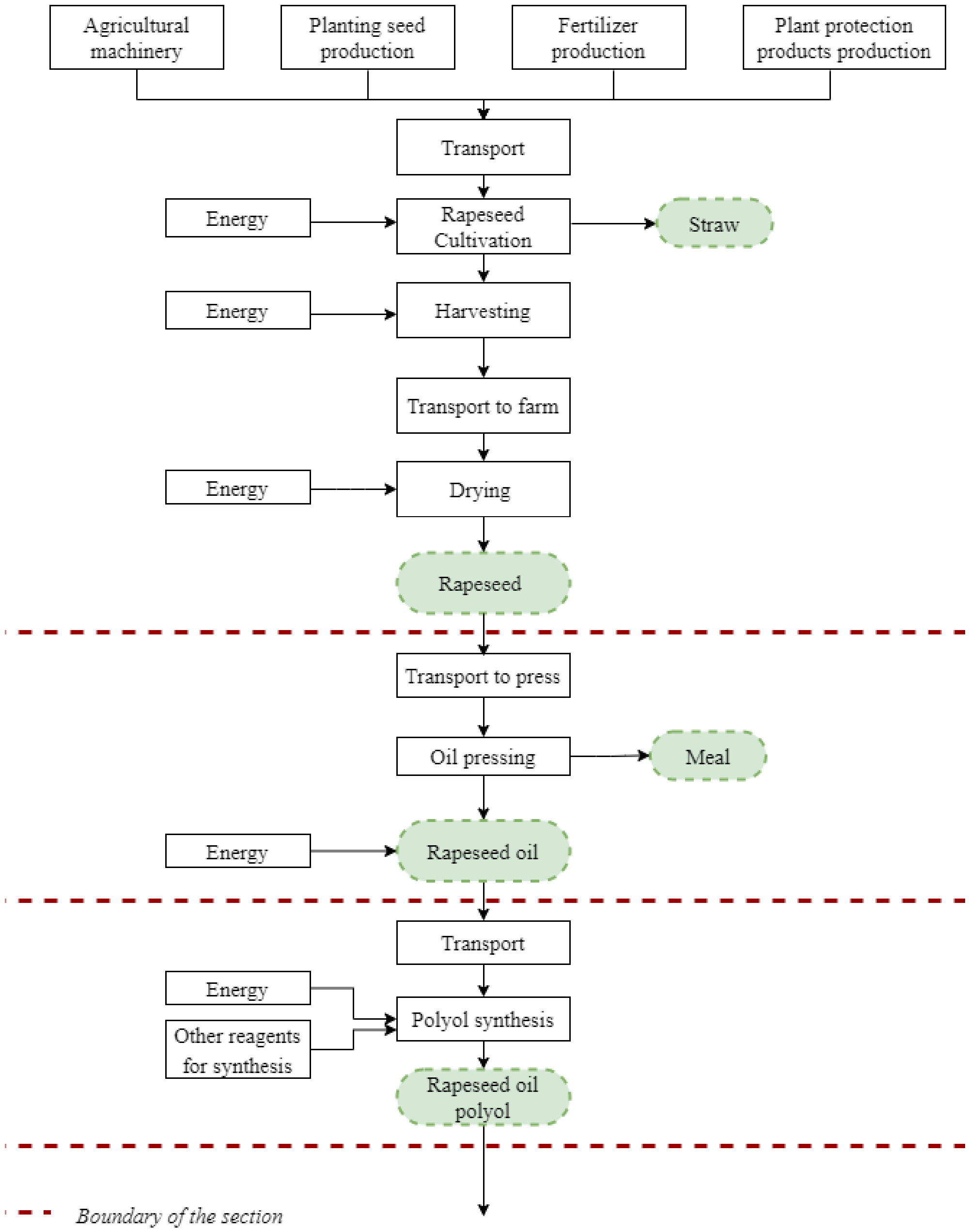

Fig. 3.1. Research design and system boundaries for renewable polyol production steps.

3.1. LCA of Rapeseed Agricultural Stage

3.1.1. Goal and Scope Definition, Functional Unit, System Boundaries

The goal was to carry out a cradle-to-farm gate LCI of rapeseed (both spring and winter) production in the Northern European country of Latvia. The functional unit (FU) was set as 1 t of rapeseed. Oilseed rape is grown by a cereal and oilseeds production company in the central part of the Zemgale plain in Zemgale region, which has a high proportion of arable land [77].

3.1.2. General Description of Rapeseed Production and Data Provider

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 % of which was used for winter rapeseed cultivation. The interviewed Latvian company practices intensive farming. No artificial irrigation is applied to rapeseed fields [42]. It was assumed that direct land use did not occur as there had not been any cropland management activities for more than 20 years [43]. The assessment of indirect land use change (ILUC) was beyond the scope of this study. 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. The company implements the type of an agricultural management practice where the remaining biomass generated is left on the field and incorporated back into the soil. Consequently, 100 % of the environmental impact was allocated to the oilseed [42].

3.1.3. LCI of Rapeseed Agricultural Stage, Summary

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 agricultural company. Data about fertilizers, plant protection products, and the seed supply chain – from factory/warehouse to farming company – were collected from distributors in Latvia. The LCI summary is presented in Table 3.1.

Table 3.1

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

Flows	Unit	Winter	Spring	Comments
Yield	t/ha	3.5	2.5	
Input				
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 an input of 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	–	NPKS fertilizer modelled 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 UAN 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 UAN

Flows	Unit	Winter	Spring	Comments
Plant protection product application				Input aggregated according to their chemical class in ecoinvent v3.5 [44].
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
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	Leaching 2.9 % of the surplus phosphorus [45]
Nitrate	kg NO_3/t	83.97	99.38	Calculated according to IPCC 2006 Tier 1 [46]
Plant protection products				0.50 % of the applied amount
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	GNOC*** [47]
Direct N_2O emissions from fertilizer application	kg N_2O/t	0.97	1.07	

Flows	Unit	Winter	Spring	Comments
Indirect N_2O emissions produced from leaching and runoff from fertilizer application	kg N_2O/t	0.22	0.26	
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				10 % of the applied amount
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	N_2O multiplied by 0.21 [48]
Ammonia	kg NH_3/t	2.69	3.35	Emission factor as in ecoinvent [48]
(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	Evaporated water in seed drying calculated as in [44]
To soil				
Plant protection products				50 % of the applied amount
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	
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

Flows	Unit	Winter	Spring	Comments

* Modelled as urea ammonium nitrate with N content 32 %. The amount was recalculated to correspond to nitrogen content in fertilizer KAS N25+S3.
** No emission in Ecoinvent v3.5. Proxy-Epoxicanozole [49].
*** GNOC - Global Nitrous Oxide Calculator.

Fertilizers used for rapeseed cultivation include nitrogen, potassium, sulphur and phosphorus. 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. 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. The in-depth LCI data about fertilizers also have to be harmonized with processes and materials available in the ecoinvent v3.5 database. To model fertilizers, the data from the State Plant Protection Service about the volume of produced and imported fertilizers in Latvia was used [50]. Drying of rapeseed is requested by industry players to avoid spoilage by fungi and mites during storage [51]. Depending on the year and amount of precipitation, rapeseed contains a different amount of moisture and the amount of gas needed for drying varies significantly. Rapeseed is dried till moisture content of 8 %, moisture content after harvest on average is 12 % [42].

No LCI have been identified for few fertilizers (such as sulphur and micronutrients) that are also used for rapeseed cultivation, thus they are not included in the final LCI (Table 3.1). Heavy metal emissions from fertilizers are not included as it was reported that heavy metals constitute only a minor share (0.065 %) of the total contribution to ecotoxicity [52]. Capital goods, overhead and human labour were not included in the inventory since it was not possible to obtain detailed data of these factors.

3.1.4. LCIA of Rapeseed Agricultural Stage

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). 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 [53]. Non-Renewable Cumulative Energy Demand (NRCED) represents the total of fossil energy and nuclear energy used, for winter and spring rapeseed NRCED is 94 % with the majority of that being fossil energy.

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 along with higher inputs in the agricultural stage. 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 %, agricultural field operations contributed 29.3 %.

In the ReCiPe method, there are 3 endpoint indicators – human health, ecosystem quality, and resources. The aggregated environmental impact is expressed as the ReCiPe score, written in normalized and weighted millipoints (mPt). For winter and spring rapeseed, the most impacted category at the endpoint level was human health with 67.2 % and 78.9 % of the impact, followed by ecosystems with 32.2 % and 20.4 %, respectively. Less than 1 % of contribution was to resources.

In the ReCiPe midpoint level, the environmental impact is translated into 18 environmental issues (midpoint indicators). The relative contribution of the agricultural inputs to environmental impacts of spring and winter rapeseed is presented in Figure 3.2.

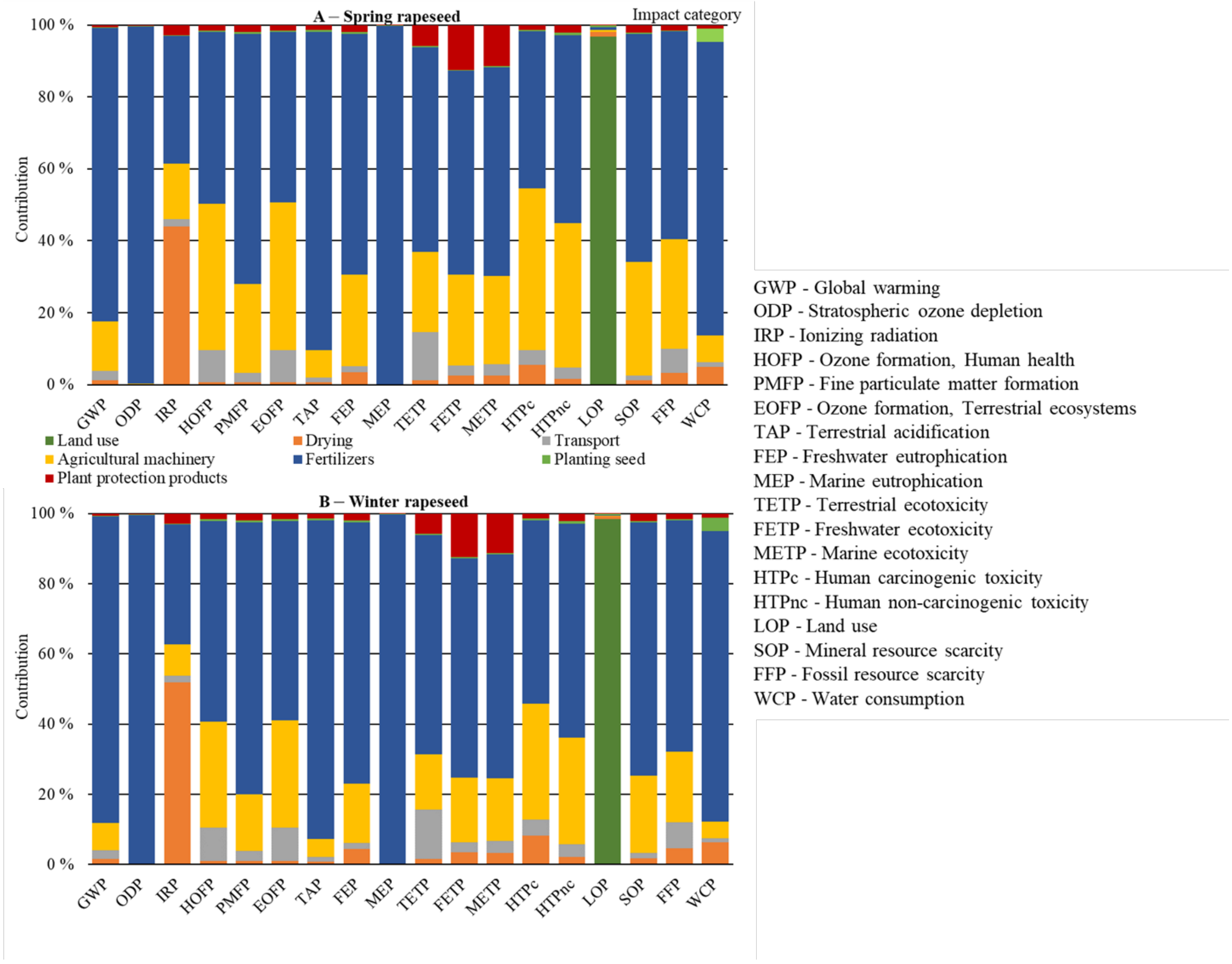

Fig. 3.2. Contribution of agricultural inputs to the environmental impacts of rapeseed production.

For both rapeseed types, mineral fertilizers are the agricultural input with the highest environmental emissions in all impact categories, except the land use and ionizing radiation. Agricultural machinery is also a large contributor. Drying of seeds contributes significantly to ionizing radiation midpoint impact category. The impact of planting seed material, plant protection products, and transport have minor influence with a contribution below 10 %.

Fertilizer use causes the largest GHG emissions with a contribution of 87.5 % for winter and 81.5 % for spring rapeseed, chiefly due to dinitrogen monoxide emissions during fertilizer application (Table 3.1). Spring rapeseed has higher GHG emissions mainly due to higher usage of N-containing fertilizers to produce 1 t of rapeseeds as 74.8 kg of N are applied (from

Table 3.1), in comparison 63.2 kg N/t for winter rape. Agricultural machinery is the second largest contributor with 7.8 % and 13.7 % for winter and spring rapeseed, respectively. The contribution of agricultural machinery is overall higher for spring rapeseed as the diesel consumption 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 total GHG emissions are 1267.9 kg CO_2eq/t for spring rapeseed and 1064.1 kgCO_2eq/t for winter rape. Forleo et al. reviewed different studies of rapeseed LCA and found that GHG emissions vary significantly [43]. GHG emissions vary in a wide range, it depends on multiple factors, starting from inputs in the LCI phase to the adopted LCIA method.

Sensitivity analysis for rapeseed production. 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 contribution to evaluating their effect on the impact categories (Table 3.2).

Table 3.2

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 global warming potential, stratospheric ozone depletion, and terrestrial acidification.

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. 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.

3.2. LCA of Rapeseed Oil Production

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

The FU selected was 1 t of edible rapeseed oil, produced using cold-press extraction at a factory gate (system boundaries and relevant unit processes presented in Fig. 3.1). A local oil producing company in Zemgale region, located 34 km from the rapeseed producing company, provided primary data about rapeseed oil pressing using cold extraction technique. Screw type press is used for rapeseed pressing. The company produces ~4000 t of rapeseed oil annually.

The LCI data for winter and spring rapeseed oil production systems per 1 t of rapeseed oil is as follows: to produce 1 t of rapeseed oil from winter rape 2778 kg of seeds are needed, 126 kWh of electricity, transportation with a tractor is 97.2 tkm, 1722 kg of by-product cake is produced; from spring rape – 3125 kg of seeds, 142 kWh, 109 tkm, 2063 kg of cake is formed [54].

Oil mill stage involves not only the product of interest (rapeseed oil) but also a co-product (cake/expeller) that is produced during oil crushing stage. Four different allocation methods were applied for the study: allocation with a system expansion (SE), mass allocation (MA); energy allocation (EA); market value allocation (MVA) (*allocation method abbreviations will be used only in Figures and Tables*). 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 (the replacement ratio – 1.4 kg of rape cake is needed to provide the same amount of protein as 1 kg of soybean meal [55]). The market value (economic) allocation is based on the data given by the oil-mill company for 2016, oil price 715 EUR/t, cake 235 EUR/t [54]. 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 to 2016 level. The price of rape cake has remained the same. For energy allocation, it was assumed that the lower heating value of oil is 36.0 MJ/kg, cake –18.4 MJ/kg [56].

3.2.2. LCIA of Rapeseed Oil Mill Stage

The company is predominantly producing cold-pressed rapeseed oil from winter rape due to higher outcome in comparison to spring rape [54]. For winter and spring rape, if system expansion was applied, meaning that the produced rape cake replaced soybean meal produced, the final CED value was negative –28 GJ/t of oil produced. In the ecoinvent v3.5, global soybean production dataset 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 needed to grow soybean.

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.

Results of ReCiPe's endpoint damage categories for rapeseed oil produced from winter and spring rapeseed using different allocation in oil mill stage show that overall the rapeseed oil produced from winter rape has slightly lower environmental footprint due to the higher yield of oil from seeds. For winter rapeseed, if system expansion scenario is set as a baseline with 45 mPt, 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 oil with system expansion scenario with a baseline score of 60 mPt the increase is as follows: 3.7 %, 56.4 %, and 89.5 % for mass, energy, and market value allocation, respectively.

Results of ReCiPe's midpoint damage category GWP followed the trend of ReCiPe's endpoint case, GHG emissions increased as follows: system expansion < mass allocation <

energy allocation < market value allocation. However, when oil is produced from winter rapeseed and system expansion is applied, the yielded result was a negative value (GHG saving of –100 kg CO_2eq), which means that by substituting soybean meal fed to ruminant and poultry by rape cake it would lead to lower GHG emissions. However, the midpoint value for GWP for spring rapeseed oil was 291.2 kg CO_2eq. 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. Analysis of the present case study confirms that the choice of allocation method has a significant impact on the results of the LCIA of oil mill products.

Sensitivity check on market value allocation was performed. The year 2016 data is chosen as a baseline scenario, but price relations are variating over time. Sensitivity was performed by changing the price of oil in the range of ±30 % with a step of 10 %. 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 [38], 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 [57]. 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 [58].

To further test the impact of a single unit process on the overall environmental performance, the potential impact of transport distance travelled from rapeseed storage to oil mill was evaluated. In the baseline scenario, the distance is only 34 km. It was modelled that rapeseeds are transported over a distance of 250 km. For scenarios where market value, mass and energy allocation were applied, the increase in ReCiPe final 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 this case, the increased impact is due to the larger distance travelled and more fossil fuels were burned, thus more fossil resources were depleted and emissions formed.

3.3. LCA of Rapeseed Oil-Based Bio-polyol Production

3.3.1. Goal and Scope Definition, Functional Unit and System Boundary

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. The allocation factors employed are discussed in Section 3.2.1. 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 Figure 3.1.

3.3.2. Bio-Polyol Production

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 a more detailed description of rapeseed oil-based polyol synthesis as given in previous work carried out by the author [27]. 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. The idealized synthesis scheme for rapeseed oil polyol synthesis is given in Figure 3.3, the characteristics of rapeseed oil polyols are described in Table 3.3.

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 [59].

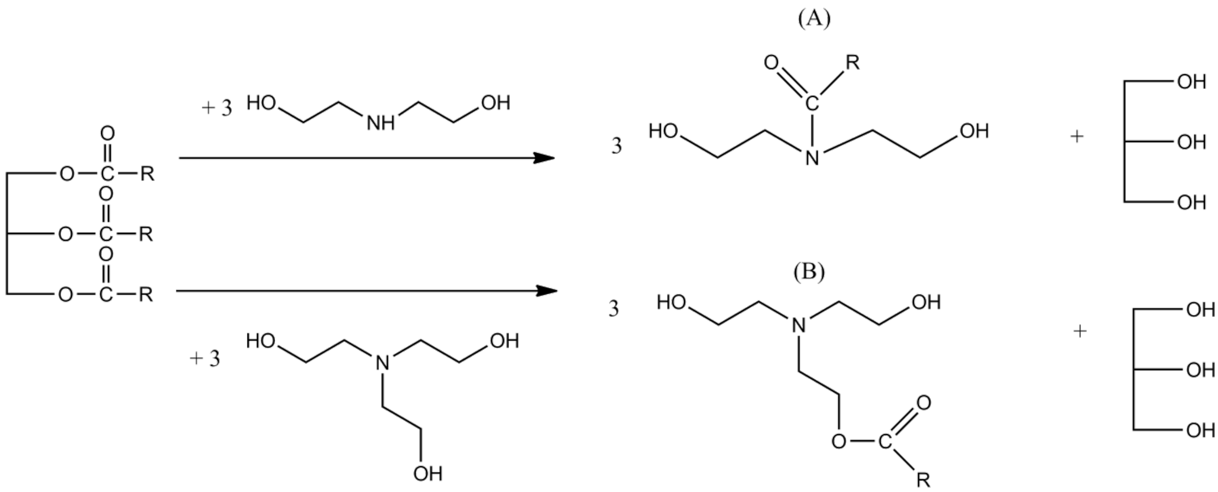

Fig. 3.3. Idealized synthesis scheme for rapeseed oil-based polyols: A – RO/DEA polyol; B – RO/TEA polyol; RO – rapeseed oil [27].

Table 3.3

Characterization of Rapeseed Oil-Based Polyols (Adapted From [27])

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

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 % [59]. Rigid PU thermal insulation foams were produced from these polyols by replacing 70 wt. % of a petrochemical polyol with bio-based rapeseed oil polyols, the bio-based content in rigid PU foams reached 16.1 % [60]−[61].

3.3.3. LCI Summary for the Rapeseed Oil-Based Polyols

The inventory summary for rapeseed oil-based polyol production is depicted in Table 3.4.

Table 3.4

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

Inputs	Unit	RO/DEA	RO/TEA	Comments/data source
Rapeseed oil	kg	0.74	0.67	Rapeseed LCI modelled by Fridrihsone et al. [62]
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 0.15wt %	kg	0.0015	0.0015	Approximated to 37 % zinc oxide and 55 % acetic acid, 8 % water by weight; ecoinvent v3.5
Inert gas	kg	0.021	0.18	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	
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 European average data provided by the European plastics industry (Plastics Europe) [63].

3.3.4. LCIA of Rapeseed Oil Bio-Polyols: ReCiPe Method

3.3.4.1. Endpoint Level

The LCIA results at the ReCiPe endpoint level for RO/DEA and RO/TEA polyol, when different allocation methods are applied for the oil mill stage and compared to the petrochemical alternative, show that both bio-based rapeseed oil polyols have lower ecological performance score than the petrochemical polyol. The slight difference between both polyols is due to slightly different inputs in each polyol (Table 3.4). 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. If 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.

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 78.7 % (mass allocation) to 75.8 % (market value allocation), with the lowest value for system expansion scenario with 72.8 %. In the ecosystems category, 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, oil has a significantly lower percentage of total impacts than cake, while in market value allocation it is the opposite. Regardless of the polyol type, bio-based or petrochemical-based, the lowest score was yielded by the endpoint resources category. For all the scenarios, it was in the range of 2−3 %. In the case of RO/TEA polyol, the overall trend remained the same as for the RO/DEA polyol across all Endpoint impact categories.

A more in-depth analysis of rapeseed oil polyols production system and individual production steps is depicted in Figure 3.4.

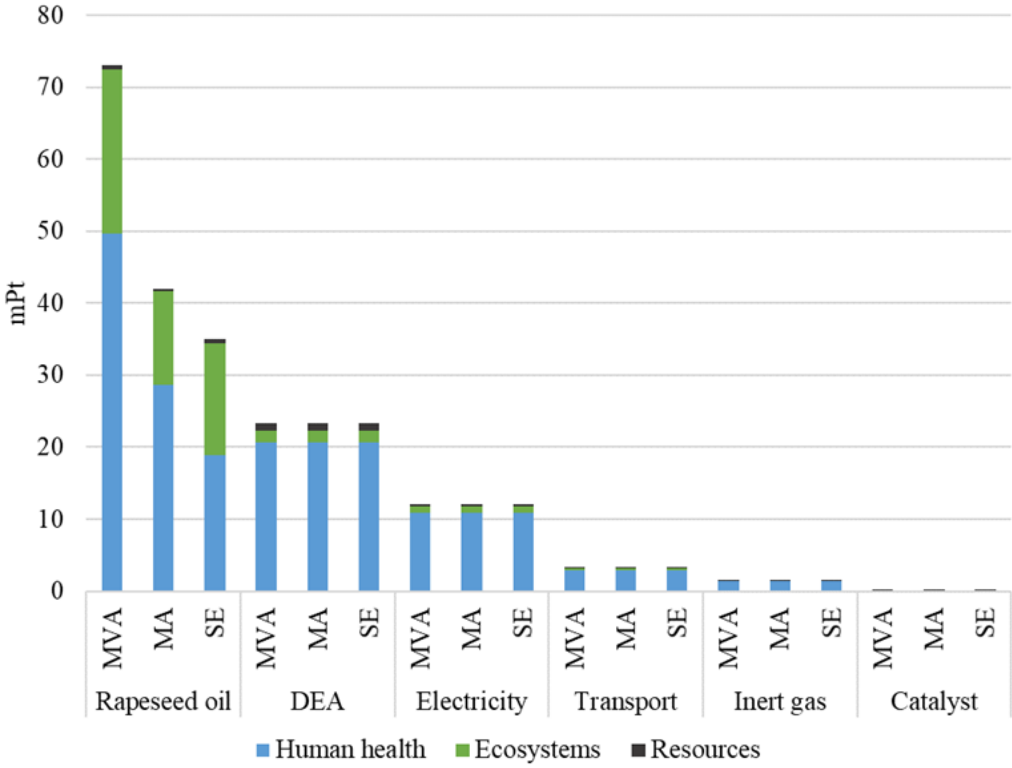

Fig. 3.4. ReCiPe's endpoint damage categories for bio-based rapeseed RO/DEA polyol from the perspective of their production inputs and depending on the allocation type.

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 [54]. The endpoint resources category 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 [64]. ReCiPe endpoint resources category is related to the CED as they both depict the use of fossil resources for the production of the given product. CED gives a more precise outlook and yields robust results on the depletion of non-renewable energy resources. The results of CED will be discussed in Section 3.3.5.

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. 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 contributors to the endpoint category human health are climate change, stratospheric ozone depletion, human toxicity, photochemical oxidant formation, particulate matter formation, and ionizing radiation [64]. Damage category human health is primarily affected by rapeseed oil production (44 %), alkanolamine production (32 %), and electricity (17 %). Rapeseed oil-based polyols yielded around half of the petrochemical polyol impact in human health category. For all endpoint categories, transport, inert gas and catalyst contributed insignificantly to the total value of endpoint category. 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 is 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 [64].

3.3.4.2. Midpoint Level

The characterization results were compared at the ReCiPe midpoint level (Fig. 3.5). 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 [58].

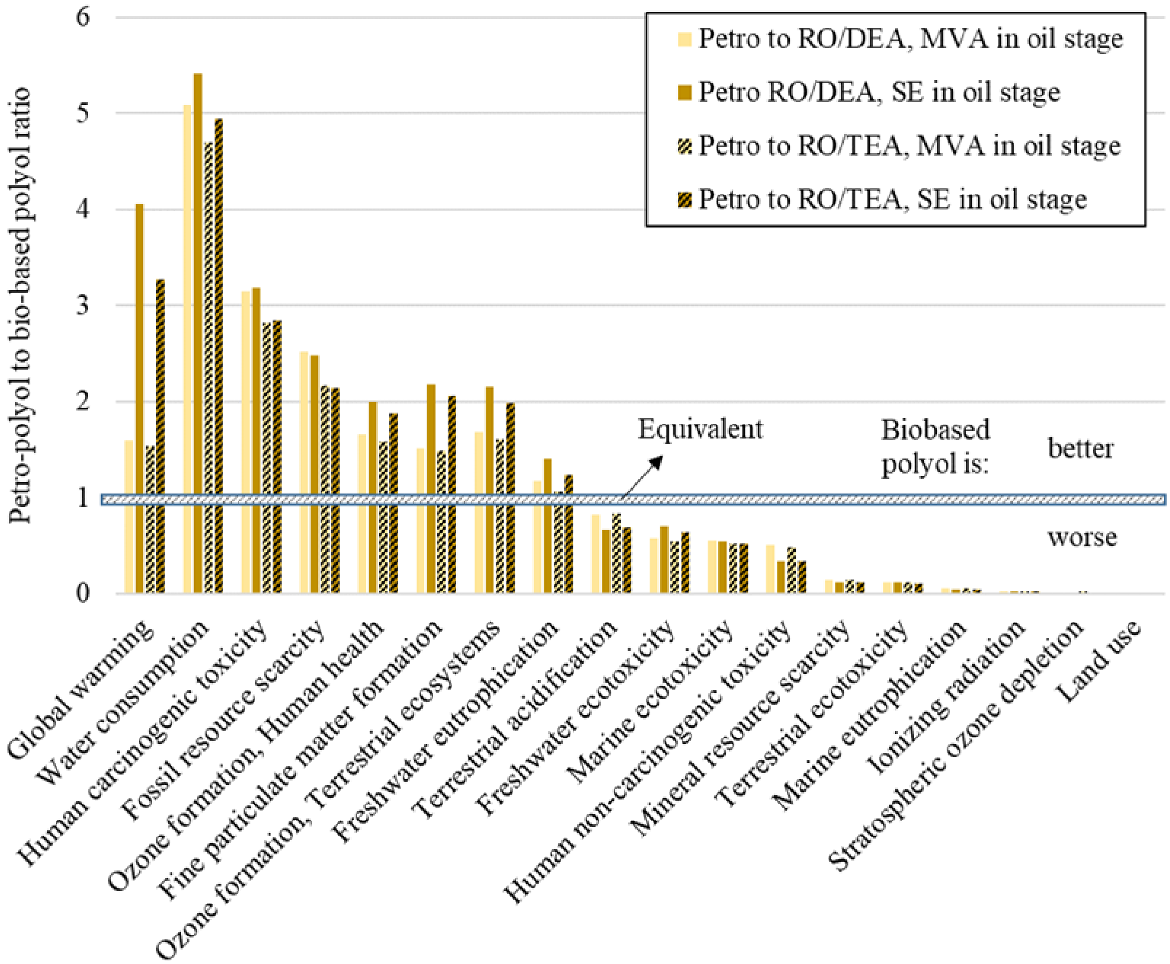

Fig. 3.5. Rapeseed oil-based polyols vs. petrochemical polyol (FU – 1 kg of polyol).

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 system [65]. 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 further.

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 use and other agricultural activity related impacts [66]. Patel et al. recommended that a *good practice target for bio-based polymers* is to reduce most other environmental impacts by at least 20 % [67], 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 petro polyol in Figure 3.6.

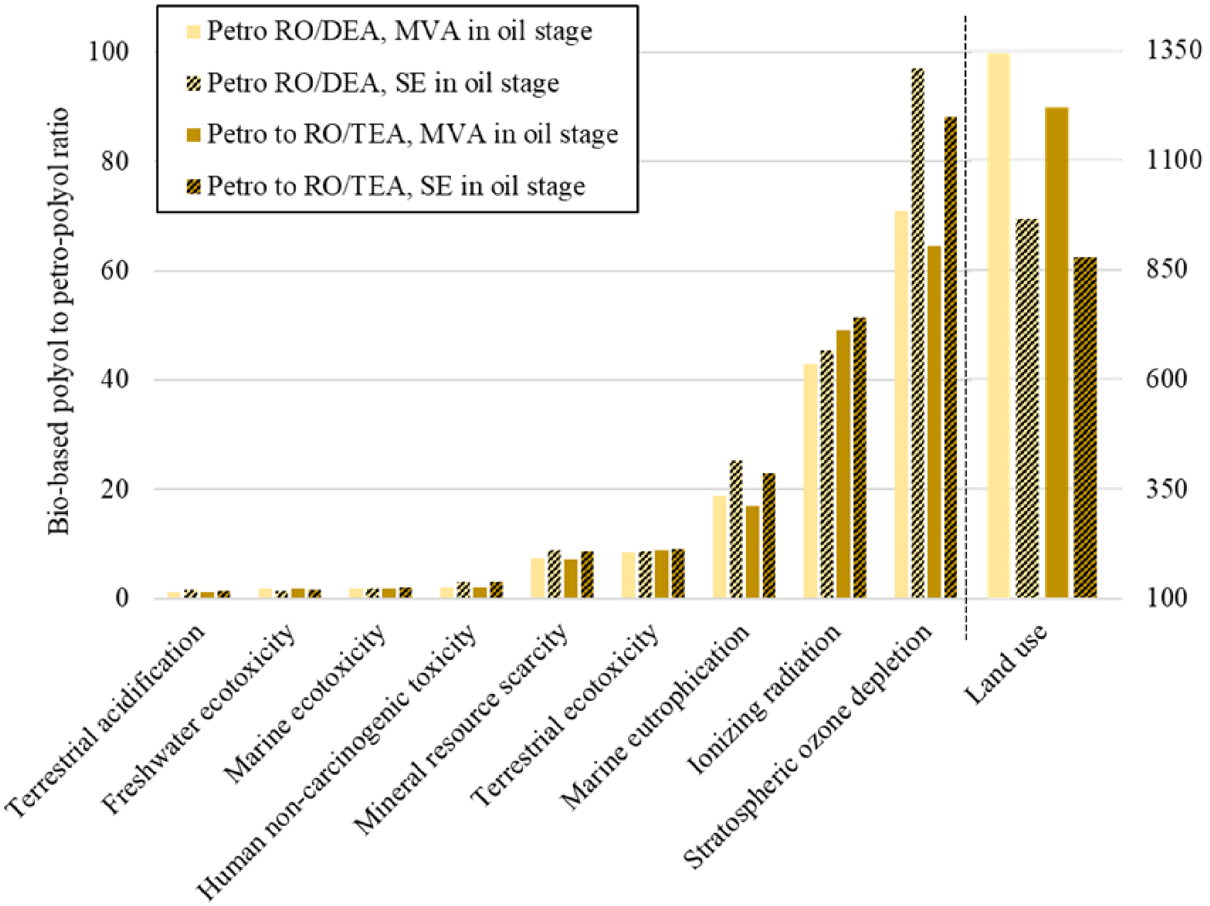

Fig. 3.6. ReCiPe Midpoint H impact categories, where rapeseed oil-based polyol performed worse in inverse ratio.

For category 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. 3.6). 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 from mineral fertilizer application, pesticide emissions, and use of agricultural machinery [68]. About one-third of the impact in marine and freshwater ecotoxicity category comes from the production of alkanolamine. Other midpoint impact categories, where rapeseed oil-based polyol performed significantly worse are stratospheric ozone depletion and ionizing radiation.

The midpoint characterization factor for climate change is GWP [64]. It is one of the key global life cycle indicators used in LCA. The GHG emission (kg CO_2eq) results are shown in Figure 3.7. In Figure 3.7 the results are presented as a contribution to different production steps in bio-based polyol production system when all three allocation methods are applied in oil mill stage along with the total GWP for rapeseed oil-based polyol production and the GWP for petrochemical polyol.

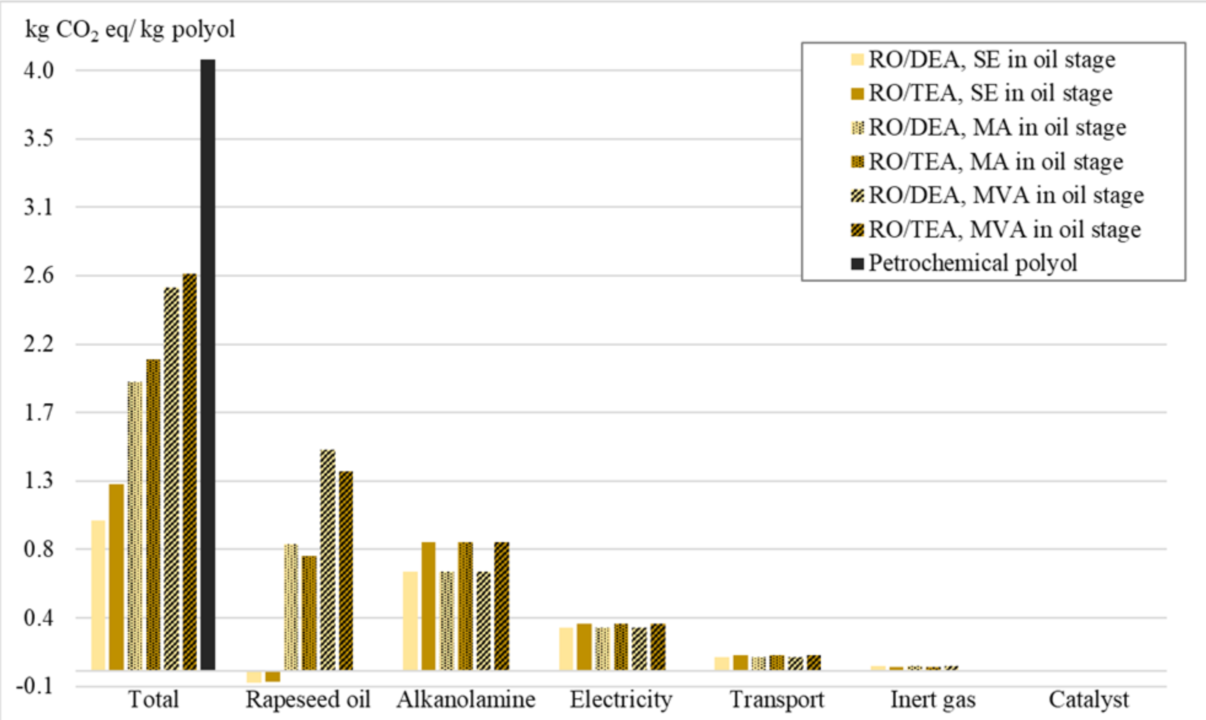

Fig. 3.7. Total GWP of rapeseed oil-based polyols and the GWP per individual production step compared to petrochemical polyol, depending on rapeseed oil allocation method.

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 (market value allocation) to 3.02 (system expansion) kg CO_2eq for RO/DEA, for RO/TEA polyol 1.40 (market value allocation) to 2.79 (system expansion) kg CO_2eq for 1 kg of produced polyol if compared to petrochemical polyol. Patel et al. recommended that *good practice targets for bio-based polymers* are to avoid at least 1 kg CO_2 per kg polymer [67].

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 system 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 3.3). Rapeseed oil is a large contributor to GWP and in general to GHG emissions related to (i) the use of fertilizers, (ii) 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.

3.3.5. LCIA Rapeseed Oil Bio-Polyols: CED Method

Concerns about non-renewable energy use along with GHG emissions have triggered and stimulated the growing interest in bio-based products, thus these are important parameters to characterize the environmental performance of a bio-based product [66]. Figure 3.8 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, and compared to the CED for the petrochemical polyol available in the ecoinvent v3.5 database.

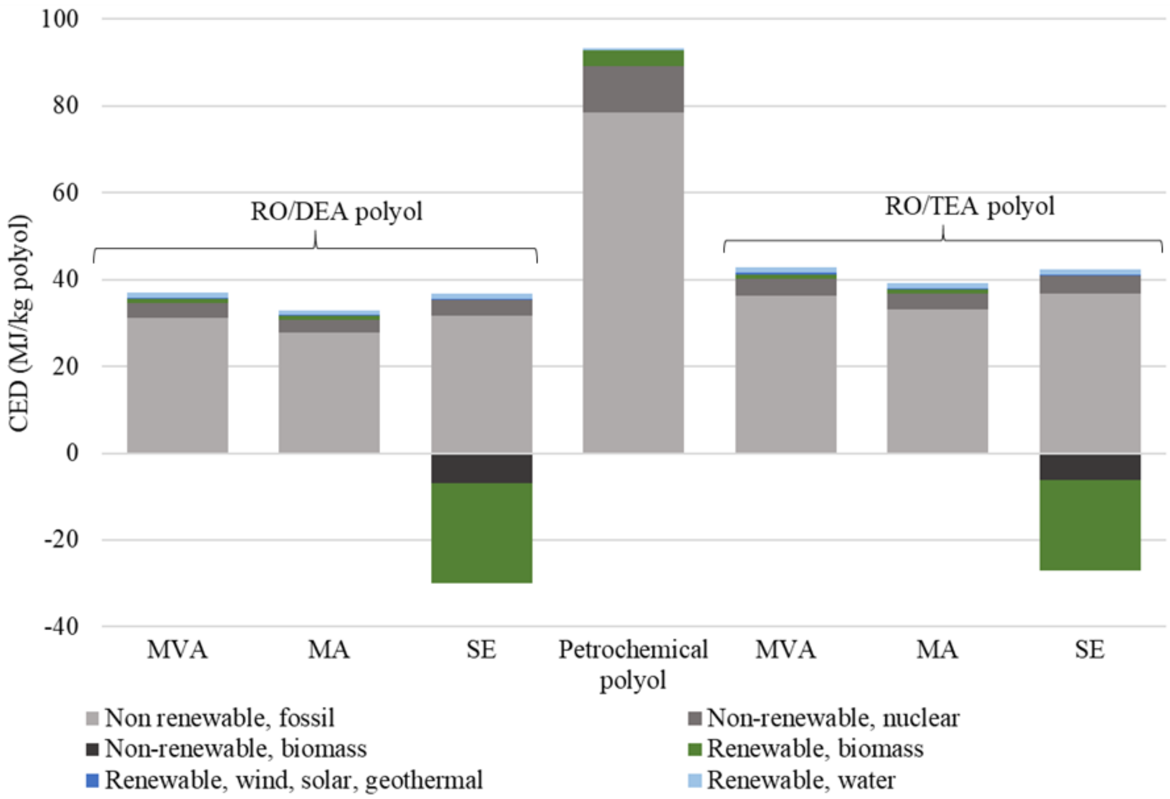

Fig. 3.8. CED for bio-based rapeseed oil polyols depending on rapeseed oil allocation method and their petrochemical counterpart.

The difference between both polyols is due to the different amount of oil and alkanolamine content in each polyol and energy consumption for synthesis (Table 3.4). 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 and 15.5 MJ/kg polyol for RO/DEA (83 % lower in comparison to petrochemical polyol) 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.

For bio-based polyols and petrochemical-based polyol, the NRCED 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, 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 %. Overall, the percentage of fossil resources savings is significant. Patel et al. 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.

A closer insight is given when CED results are analysed for a more in-depth analysis of rapeseed oil polyol production system (Fig. 3.9).

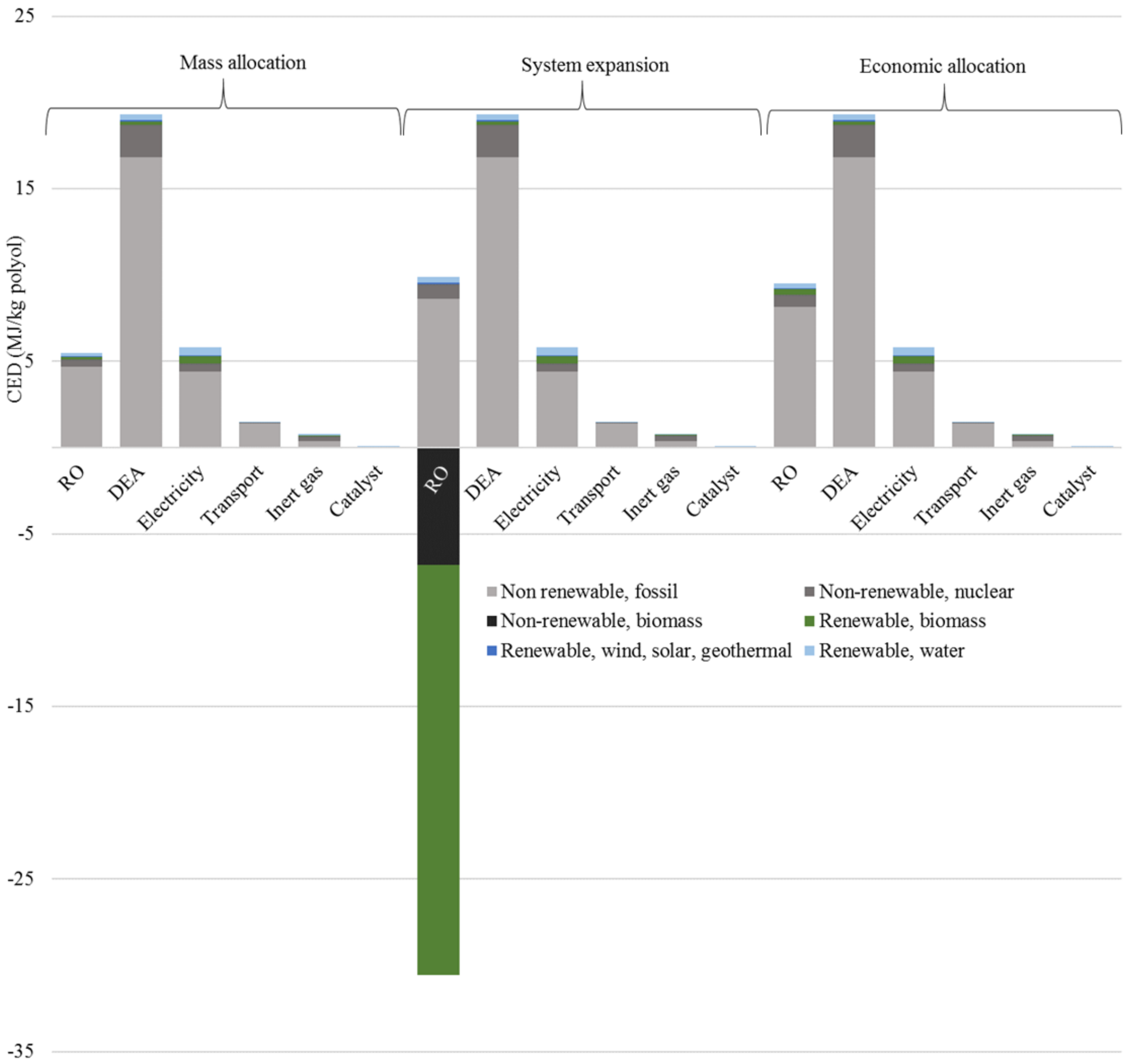

Fig. 3.9. CED results for bio-based RO/DEA polyol from the perspective of their production inputs and based on different allocation approaches.

The results clearly show that when system expansion is applied in oil mill stage, the total CED of both bio-based polyols is offset by the non-renewable biomass and renewable biomass impact categories, while for other polyol production inputs CED remains the same.

3.3.5.1. Sensitivity Analysis for Bio-Polyol Production

The purpose of this subsection is to analyse to what extent electricity mix, the higher or lower per cent point of renewables in the mix, is affecting the final environmental score. The change in quantitative material inputs for polyol synthesis is not desired because these polyols are already the optimal version of the chemical synthesis route [27]. Electricity is the third largest environmental hotspot, the sensitivity analysis was checked using electricity mixes of different countries present in the ecoinvent v3.5 database (Table 3.5). In the baseline scenario, rapeseed oil-based polyols were produced in Latvia. For comparison, several other EU countries were chosen.

Table 3.5

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

Polyol production country	Electricity mix description, according to Itten et al., 2014 [69]	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)	–	–		–	–	
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. Depending on the chosen country, there is a small improvement or decrease in environmental aspects. In the scenario with Swedish electricity mix, the total impact reduction would be 9 % to 14 % lower result than in baseline scenario, which is due to the high share of hydropower and a minor share (2 %) of fossil fuels in the electricity mix.

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.

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 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 (market value allocation) to 3.02 (system expansion) kg CO_2eq for RO/DEA, for RO/TEA polyol 1.40 (market value allocation) to 2.79 (system expansion) kg CO_2eq. 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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