Preliminary Life Cycle Inventory of Rapeseed Oil Polyols for Polyurethane Production

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ABSTRACT: This study assesses present preliminary Life Cycle Inventory for rapeseed oil polyols suitable for the production of polyurethane, which is one of the most widely used polymer materials. Due to growing environmental problems, the polyurethane industry is seeking bio-based raw materials. A study was carried out for rapeseed oil triethanolamine polyol developed at Latvian State Institute of Wood Chemistry. The cradle-to-gate study was carried out with functional unit of 1 kg rapeseed oil polyol synthesized in a scaled-up pilot reactor. The results show that at the midpoint level the production of rapeseed oil has the highest impact in the following environmental impact categories: agricultural land occupation with 59%, followed by climate change (human health) with 12%, fossil depletion with 8% and climate change (ecosystems) with 8%.

KEYWORDS: Bio-based, LCA, polyurethane, polyol, rapeseed

1 INTRODUCTION

In the 21st century, because of an increasing awareness of environmental problems and rapid depletion of fossil resources along with increasing pressure from society and legislators, the polymer industry has been forced to look for solutions to produce polymers from renewable raw materials to reduce petroleum consumption. Polyurethane (PU) is one of the most widely used polymers in various application areas—foams with different density, adhesives, sealants, elastomers, thermoplastics and coatings [1]. PU is synthesized in a reaction between isocyanate moiety containing isocyanate groups (-NCO) and polyol components containing hydroxyl groups (-OH) [2]. It is estimated that the world's PU demand will grow from 14.2 million tons in 2011 to 22.2 million tons by 2020 [3]. The PU industry has been mainly a petroleum-based industry, but in the 21st century growing attention is being paid to obtaining raw materials from bio-based feedstocks [4]. One of the most promising agricultural products for bio-renewable feedstock for the PU industry is vegetable oils [2]. Many investigations are devoted to the synthesis of polyols from different vegetable oils such as soybean oil [5], sunflower and rapeseed oil [6,7], palm kernel oil [8], linseed oil [9] and castor oil [10].

Rapeseed (*Brassica napus*) was chosen as a raw material for polyol production due to the fact that rapeseed is the only widely cultivated oil crop in Latvia. Also, Latvian State Institute of Wood Chemistry (LS IWC) has developed a polyol synthesis method using triethanolamine [11]. In previous works by our group we have already reported that rapeseed oil triethanolamine polyols can be characterized with catalytic activity in urethane-forming reactions due to the tertiary amine atom in their structure which acts as catalyst [11,12]. It is possible to develop PU coating formulations which do not contain volatile amine catalysts and organic tin catalysts [12]. The resulting PU coatings are more environmentally friendly and, for example, suitable for coating the surfaces of potable water tanks in an upright position [13].

Life cycle assessment (LCA) is a methodology to evaluate the environmental impact of products and processes, taking into account their entire life cycles. This study is carried out according to ISO standards ISO 14040:2006 and ISO 14044:2006, which describe the four phases that comprise LCA studies. These four

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phases are: 1) the goal and scope, 2) life cycle inventory (LCI), 3) life cycle impact assessment, 4) interpretation [14,15]. The end result depends on the goals and scope of the individual study. In the LCI stage, inputs and outputs within the system's boundaries are identified and quantified.

2 METHODS

2.1 Goal and Scope

This study was a preliminary cradle-to-gate LCI of the production of rapeseed oil polyol suitable for PU production. Rapeseed oil grown in Latvia is used as a raw material for polyol synthesis. The goal was to identify the main contributors to environmental impacts of rapeseed oil triethanolamine ester polyol production. Next our goal was to carry out full LCA using rapeseed cultivation data available in Latvia, paying special attention to the main contributors which are determined in this preliminary LCI study.

2.2 Functional Unit

The functional unit for rapeseed oil polyol production was one kilogram (1 kg) of rapeseed oil triethanolamine ester polyol. All input and output data, which are known from polyol synthesis in a pilot-scale reactor at LS IWC, were allocated to functional unit.

2.3 System Boundary

The overall process flow for rapeseed oil polyol is shown in Figure 1. The system has been divided into unit processes: rapeseed cultivation, rapeseed oil mill operation and rapeseed oil polyol production. Materials, energy and other inputs become part of each of these processes, which are detailed below in the inventory analysis.

The boundary of the system was considered rapeseed oil polyol production from rapeseed cultivation to the polyol synthesis. In this preliminary LCI the polyol use phase was not taken into account because the use phase of polyol includes reaction with isocyanate component and other chemicals to form PU. When PU is produced from bio-based polyols, part of the petrochemical polyol is replaced with bio-based polyol in PU composition, therefore the use phase of bio-based polyol would be the same as for petrochemical-based polyol.

2.4 Life Cycle Inventory Analysis

In the life cycle inventory phase of LCA, all relevant data is collected and organized. The unit processes for this study are: rapeseed cultivation, rapeseed oil mill operation and rapeseed oil polyol production. Data collection has been carried out to build LCI tables (Tables 1–5) for the main contributors of each unit process.

2.4.1 Rapeseed Cultivation

In this preliminary LCI study, data for rapeseed cultivation were taken from the ecoinvent 3.0 database, which is a widely recognized professional database and is incorporated in SimaPro 8.0 LCA software [16]. Data for rapeseed farming and land conversion represents data for 1 kg of rapeseeds grown in Denmark. The yield is 3500 kg/ha and inputs of seeds, mineral fertilizers and pesticides are considered. Dataset

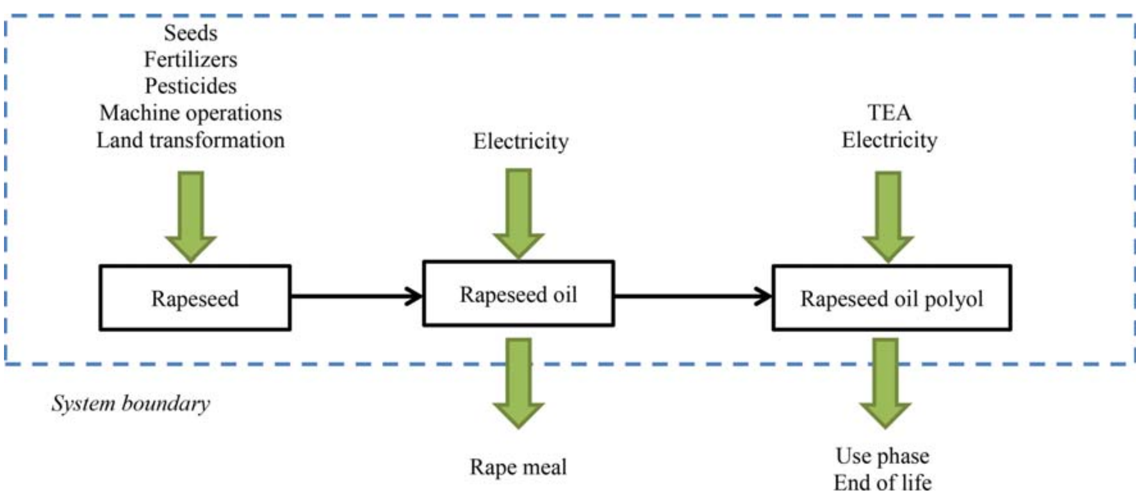

Figure 1 Schematic representation of system boundaries for rapeseed oil polyol.

Table 1 Inventory data for fertilizer and pesticide inputs in SimaPro model for cultivation 1 kg of rapeseed [16].

Fertilizer and pesticides inputs	Rapeseed farming DE, Inputs (g)
Ammonium nitrate, as N	17.6
Cyclic N-compound	0.10
Diphenylether-compound	0.023
Nitrogen fertilizer, as N	14.7
Pesticide, unspecified	0.24
Phosphate fertilizer, as P_2O_5	15.3
Potassium chloride, as K_2O	12.9
Pyrethroid-compound	0.005

Table 2 Machine operation inputs in SimaPro model for cultivation of 1 kg rapeseed [16].

Machine operation	Amount	Unit
Application of plant protection product, by field sprayer	0.0014	ha
Combine harvesting	0.00029	ha
Drying of bread grain, seed and legumes	0.010	l
Fertilizing, by broadcaster	0.00067	ha
Irrigation	0.20	m^3
Sowing	0.00029	ha
Tillage, harrowing, by rotary harrow	0.0014	ha
Tillage, ploughing	0.00029	ha
Transport, tractor and trailer, agricultural	0.004	metric ton*km

Table 3 Land transformations in SimaPro model for cultivation of 1 kg rapeseed [16].

Natural resource	Amount	Unit
Carbon dioxide, in air	1.91	kg
Occupation, annual crop, non-irrigated, intensive	2.86	m^2*year
Transformation, from annual crop, non-irrigated, intensive	2.86	m^2
Transformation, to annual crop, non-irrigated, intensive	2.86	m^2

from Denmark was chosen due to the fact that at the moment there has not been any LCA carried out for rapeseed grown in Latvia, and this data was most similar to Latvia`s conditions.

2.4.2 *Rapeseed Oil Mill Operation*

The largest rapeseed oil producer in Latvia, Iecavnieks, uses a cold-press technique to produce rapeseed oil due to the dataset for cold-press extraction technique (cold pressing of rape seeds in a standard oil press), which was chosen from the ecoinvent database [16]. This data includes the transport of rapeseeds to the mill, and the processing of the seeds to rapeseed oil and rape meal. Inventory refers to the multi-output process of rapeseed at the oil mill which delivers rapeseed oil and byproduct rape meal. In this case the allocation was done using economic allocation with allocation factor of 74.3% to rapeseed oil. Allocation is done according to carbon balance for CO_2 emissions. Electricity consumption for the rape oil mill operation was not changed; Latvian electricity grid was chosen (electricity consumers who use electricity directly from the grid).

2.4.3 *Rapeseed Oil Polyol Synthesis*

Latvian State Institute of Wood Chemistry has developed a new pathway for bio-based polyol synthesis using transesterification reaction with triethanolamine (TEA). The rapeseed oil polyol synthesis is described in detail in our previous work by Stirna *et al.* [11]. The rapeseed triethanolamine ester structure is presented in Figure 2. Rapeseed oil transesterification was carried out using TEA at 160°C using zinc acetate (0.15 wt%) as catalyst [11]. The bio-based rapeseed triethanolamine ester polyol contains 67% of bio-based raw material – rapeseed oil.

At the moment there are not any existing polyol production plants that use rapeseed oil transesterification with triethanolamine as the polyol synthesis method. In the life cycle inventory of this stage, the only available information is the input/output mass balance and approximated energy input. Data about possible overheads (operation of buildings, administration, etc.) were not included.

3 RESULTS AND DISSCUSION

For rapeseed cultivation the data related to the use of fertilizers and pesticides are listed in Table 1. No organic fertilizers were applied. Results show that nitrogen-containing fertilizers are important and heavily used for rapeseed cultivation.

Table 4 Input for rapeseed oil polyol synthesis carried out in 4 m^3 reactor and specific heat of materials and synthesis reactor.

Inputs for polyol synthesis	Molar mass, kg/mol	Molar ratio, M	Mass (input), kg	Specific heat c_p, kJ/K·kg
Rapeseed	880	1	1878	2.09 [18]
Triethanolamine	149	2.9	992	2.26 [19]
Steal reactor	-	-	3000	0.49 [20]

Table 5 Energy required for one rapeseed oil polyol synthesis in 4 m^3 reactor, which corresponds to 2800 kg of polyol.

Process	Required energy, MJ
Energy required to heat up the reactor	220.50
Energy required to heat up raw materials	925.7
Energy loss during heating of reactor and raw materials	114.6
Energy to maintain the temperature regime	420.2
Mechanical stirrer	75.6
Total	**1757 MJ**

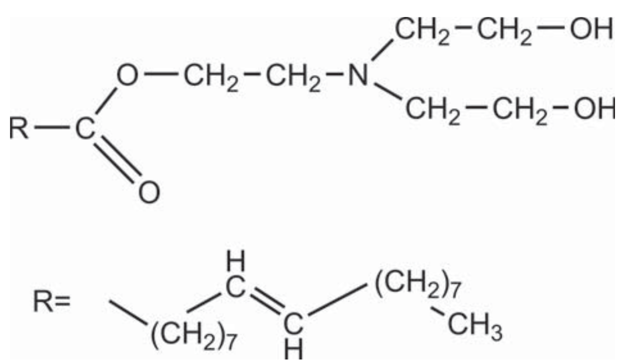

Figure 2 Structure of rapeseed triethanolamine ester.

Data related to machine use include all machine operations which are: soil cultivation, sowing, fertilization, weed control, pest and pathogen control, combine harvest and transport from field to farm (see Table 2).

The SimaPro model used for rapeseed farming includes factors for land transformation as shown in Table 3. Land transformation is a vital step in any crop farming. Carbon dioxide present in the air is considered to be a natural resource and is bounded from atmosphere. In SimaPro only harvested biomass is counted [17]. Also, in Denmark as well as in Latvia the land is not irrigated.

To model the dataset for polyol synthesis we used data from a pilot-scale synthesis reactor (4 m^3). There are no byproducts formed in this synthesis which need to be removed after the synthesis, the only output is polyol itself. Zinc acetate is a cheap catalyst commonly used for transesterification. The catalyst is left in the polyol due to the fact that separation would be too expensive and would decrease the hydroxyl value of the polyol.

Rapeseed oil triethanolamine polyol is synthesized at rapeseed molar ratio 1 M of rapeseed oil to 2.9 M of TEA. As mentioned before, the calculations were made for a reactor with volume 4 m^3. Maximal reactor fill factor was assumed to be 80% by volume, which corresponds to 2800 kg of polyol to be synthesized at a single synthesis. As a catalyst we used zinc acetate dihydrate 0.15 wt% from mass of total raw materials but in this preliminary LCI the amount of catalyst was excluded from inputs. This was done because negligible environmental impacts were expected.

To calculate energy requirements for rapeseed polyol synthesis the heating interval was assumed to be from 0 to 150°C. The fact that during synthesis not only is it necessary to heat up the chemical reagents, but also the reactor itself, was taken into account. The specific heat of materials is presented in Table 4. It is assumed that the heat energy loss during heating of the reactor and raw materials was 10%. During rapeseed oil polyol synthesis it is also necessary to maintain a temperature regime of 150°C. It is assumed that during this time energy loss was 20%. Energy required for rapeseed oil polyol synthesis broken down into processes is presented in Table 5.

Also, the reactor is equipped with a mechanical stirrer with power 3 kW and it runs for 7 h during one synthesis. The mechanical stirrer uses 21 kWh, which converts to 75.6 MJ (Table 5).

The total amount of energy required for polyol synthesis carried out in a 4 m^3 reactor was 1757 MJ. Accordingly, for 1 kg of rapeseed triethanolamine polyol the required energy is 0.63 MJ/kg. The obtained value is smaller than the value (3.74 MJ/kg) published in, "Life Cycle Impact of Soybean Production and Soy Industrial Products," where the authors looked

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at production of Agrol polyols (soy-based polyol) by BioBased Technologies, LLC [21]. According to the patent, “Method for vegetable oil derived polyols and polyurethanes made therefrom (US 20080262259 A1),” BioBased Technologies uses a two-stage process to obtain polyol [22], which results in higher energy demand respectively.

The environmental impact assessment was based on the internationally accepted ReCiPe method which transforms the LCI results to a limited number of indicator scores. In this LCI study to identify the most relevant midpoint categories, they were ranked by the total impact indicator in mPt. Midpoint categories with values higher than 10 mPt are shown. The environmental impact of the rapeseed oil polyol production system is shown in Figure 3.

As previously described, to synthesize rapeseed oil polyol energy, rapeseed and triethanolamine are needed, polyol is the output. SimaPro output for midpoint categories with total impact indicators is presented in Figure 3.

At the midpoint level the use of TEA contributes 20%, rapeseed oil 78.3% and use of electricity 1.7% of total environmental impact for rapeseed oil polyol production using the synthesis method developed at LS IWC.

Also, at the midpoint level the production of rapeseed oil has the highest impact in the following environmental impact categories: agricultural land occupation with 59%, followed by climate change (human health) with 12%, fossil depletion with 8% and climate change

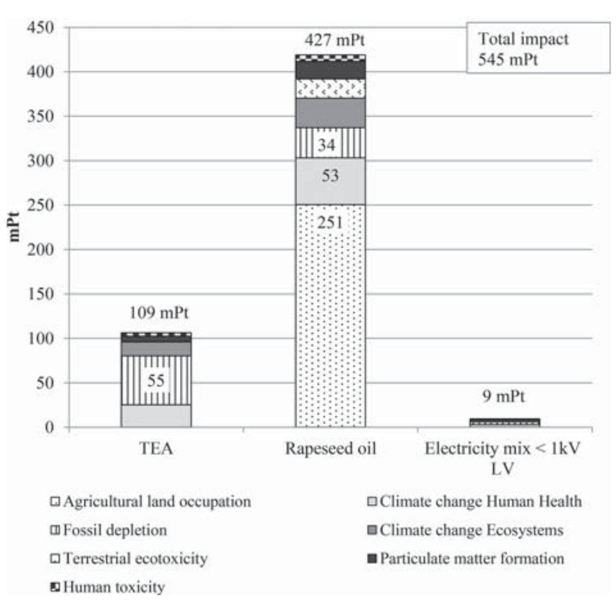

Figure 3 SimaPro output for midpoint categories for the production of rapeseed oil triethanolamine polyol per functional unit.

(ecosystems) with 8%. Agricultural land occupation is the amount of either agricultural land or urban land occupied for a certain time. To grow rapeseed a significant amount of land is necessary; because of this the negative impact of agricultural land occupation is the loss of biodiversity due to the fact that land is intensively managed using agricultural machinery and fertilizers and pesticides.

Triethanolamine (TEA) is a product of industrial petrochemistry which is produced from the reaction of ethylene oxide with aqueous ammonia. Ethylene oxide is a product of oxidation of ethylene, which is produced in the petrochemical industry by steam cracking of hydrocarbons. Respectively, TEA gives the highest impact in fossil depletion category, 51% of TEA’s total contribution.

4 CONCLUSIONS

This LCI study presents a representative and up-to-date preliminary cradle-to-gate life cycle inventory based on the ecoinvent 3.0 database and input/output data available at LS IWC about polyol synthesis in a scaled-up pilot reactor, and evaluates the environmental performance of rapeseed oil triethanolamine polyol production.

The preliminary cradle-to-gate LCI of rapeseed oil polyol synthesized by transesterification with TEA reveals that at midpoint level the use of TEA contributes 20%, rapeseed oil 78.3% and use of electricity 1.7% of total environmental impact.

As stated in Section 2.1, this was only a preliminary LCI of rapeseed oil triethanolamine polyol to identify the main environmental impact contributors. Further detailed LCA study of rapeseed oil polyols is needed. Possible future work would extend to provide specific data for rapeseed farming under Latvian climatic conditions and for a rapeseed oil mill stage using data from oil mills located in Latvia.

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