

Life cycle assessment of polyols for polyurethane production using CO₂ as feedstock: insights from an industrial case study†

Niklas von der Assen and André Bardow*

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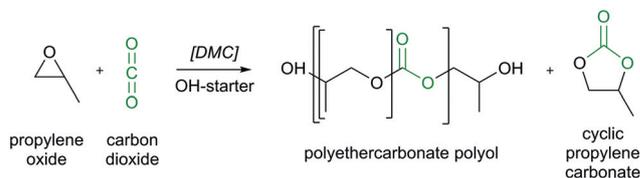
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Polyethercarbonate polyols from carbon dioxide (CO₂) are starting to be synthesized on industrial scale. These polyols can be further processed into polyurethanes enabling CO₂ to be utilized in large amounts. Utilization of CO₂ as alternative carbon feedstock for polyols is motivated from the potential to reduce greenhouse gas (GHG) emissions and fossil resource depletion. This article presents a life cycle assessment for production of CO₂-based polyethercarbonate polyols in a real industrial pilot plant. The considered cradle-to-gate system boundaries include polyol production and all upstream processes such as provision of energy and feedstocks. In particular, provision of CO₂ from a lignite power plant equipped with a pilot plant for CO₂ capture is considered. Production of polyols with 20 wt% CO₂ in the polymer chains causes GHG emissions of 2.65–2.86 kg CO₂-eq kg⁻¹ and thus, does not act as GHG sink. However, compared to production of conventional polyether polyols, production of polyols with 20 wt% CO₂ allows for GHG reductions of 11–19%. Relating GHG emission reductions to the amount of CO₂ incorporated, up to three kg CO₂-eq emissions can be avoided per kg CO₂ utilized. The use of fossil resources can be reduced by 13–16%. The impacts reductions increase with further increasing the CO₂ content in the polyols. All other investigated environmental impacts such as eutrophication, ionizing radiation, ozone depletion, particulate matter formation, photochemical oxidant formation, and terrestrial acidification are also lowered. Therefore, synthesis of polyethercarbonate polyols from CO₂ is clearly favorable compared to conventional polyether polyols from an environmental point of view.

1. Introduction

An environmentally promising measure to reduce greenhouse gas (GHG) emissions and fossil resource depletion is carbon dioxide capture and utilization (CCU). Carbon dioxide (CO₂) can be utilized as carbon feedstock in a variety of applications.^{1–4} An already technologically viable option is the utilization of CO₂ for polymers.^{5,6} The synthesis of alternating polypropylene carbonates (PPC) from propylene oxide (PO) and CO₂ has already been commercialized.⁷ However, the glass transition temperature of PPC is about 37 °C which limits its application to specialty polymers.^{7,8} Recently, the successful synthesis of polyethercarbonate polyols by copolymerization of CO₂ and epoxides has been reported (Scheme 1).⁸ Due to



Scheme 1 Polymerization of propylene oxide (PO) and carbon dioxide (CO₂) to polyethercarbonate polyols using a DMC catalyst and a multi-functional alcohol (e.g. glycerol) as starter. Adapted from ref. 7 and 8.

a favorable glass transition temperature and low viscosity, the polyethercarbonate polyols can readily be processed to polyurethane (PU) foams.⁸ Thus, polyethercarbonate polyols can substitute conventional polyether polyols of which the global production was 8 Mt a⁻¹ in 2012.⁹ Theoretically, production of polyethercarbonate polyols could therefore utilize up to 1.6 Mt a⁻¹ CO₂ as feedstock (assuming an average CO₂ content of 20 wt%).

CO₂ is a particularly promising feedstock since “CO₂ is an abundant, inexpensive and non-toxic renewable C₁ resource.”⁵ For polyethercarbonate polyols, in particular, CO₂ can be inserted

Lehrstuhl für Technische Thermodynamik, RWTH Aachen University, 52062 Aachen, Germany. E-mail: andre.bardow@ltt.rwth-aachen.de; Fax: +49 241 8092255;

Tel: +49 241 8095380

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'as such', *i.e.*, as monomeric C₁ building block, and the energy-intensive cleavage of C=O bonds can be avoided.¹⁰ Furthermore, CO₂ partially substitutes energy- and emission-intensive epoxides. Still, energy requirements and GHG emissions are caused by provision of epoxides required as co-reactants as well as by provision of CO₂ itself.¹¹

Therefore, the environmental impacts of CO₂-based polyol production should be determined in a detailed environmental assessment.^{11,12} As suitable tool for environmental assessment of CCU technologies, life cycle assessment (LCA) is often recommended.^{10,13,14} LCA is a methodology to evaluate environmental impacts of products and processes along their entire life cycles. However, LCA of CCU is not yet standard practice.^{11,12} In a recent book on CCU, Centi *et al.* explicitly state: "For the production of CO₂-based polymers, correct LCA assessments also do not exist [...]."¹⁵

In this work, we present an LCA study for production of polyethercarbonate polyols from PO and CO₂. For this purpose, we employ a cradle-to-gate LCA scope: the analyzed product system comprises production and purification of CO₂-based polyethercarbonate polyols as well as all processes for provision of energy and feedstocks. In particular, provision of the feedstock CO₂ is included: CO₂ is captured from a lignite power plant, compressed and transported to the polyol production plant. The major considered environmental impacts are global warming (CO₂-equivalents) and fossil resource depletion (oil-equivalents). Regarding these impacts, the product system for CO₂-based polyethercarbonate polyols is compared to an equivalent product system consisting of conventional polyols production and a lignite power plant without CO₂ capture. Sensitivity analyses for PO production technologies and CO₂ allocation options show that CO₂-based polyols have reduced impacts with respect to global warming and fossil resource depletion of 11–19% and 13–16%, respectively.

In section 2, the LCA methodology and underlying process data are described. Section 3 contains LCA results and sensitivity analyses as well as the discussion thereof. In section 4, we draw conclusions for the environmental benefits of CO₂-based polyols, and for the environmental assessment of CCU technologies in general.

2. Data and methodology

2.1 System boundaries and goal of LCA

Life cycle assessment (LCA) is a methodology to evaluate environmental impacts of products and processes taking into account their entire life cycles. A life cycle covers all activities from *cradle to grave*, *i.e.*, from extraction of raw materials, transport, production and product use to recycling and final disposal of wastes. However, a cradle-to-gate approach is often sufficient if products with identical downstream processes (gate-to-grave) are compared.¹²

The primary goal of this LCA is to determine whether it is environmentally favorable to utilize CO₂ as feedstock for polyols. For this purpose, we take into account the system-wide

effects of CO₂ utilization compared to conventional polyol production (Fig. 1). The product system for CO₂-based polyethercarbonate polyols is compared to an equivalent product system for conventional polyether polyols. It is sufficient to consider only production of polyols (cradle to gate) since product properties are similar for CO₂-based and conventional polyols, as well as for their subsequent polyurethanes.⁸ The downstream processes of polyurethane foaming, foam use and foam disposal are similar for CO₂-based and conventional polyols and therefore neglected. Potential differences in downstream processes are discussed in the ESI.† Sections 2.2 and 2.3 contain a description for the cradle-to-gate product systems for CO₂-based and conventional polyols.

Since the main environmental motivations for CCU are reducing CO₂ emissions and establishing an alternative carbon source, this study compares the product systems for CO₂-based and conventional polyols with respect to global warming and fossil resource depletion.¹² The global warming impacts (GW) are calculated as cumulated GHG emissions in CO₂-equivalents using 100-year global warming potentials (GWP_{100a}). Fossil resource depletion (FD) is calculated as the energy content of used fossil resources in oil-equivalents. Results are computed using GaBi LCA software and ReCiPe 1.08 Midpoint (Hierarchist) impact categories.^{16,17} Results for the midpoint impact categories eutrophication, ionizing radiation, ozone depletion, particulate matter formation, photochemical oxidant formation, and terrestrial acidification as well as corresponding normalized values have also been analyzed and are given in the ESI.†

2.2 Product system for CO₂-based polyols

The product system for CO₂-based polyols includes the production of polyethercarbonate polyols as well as provision of required energy and feedstocks. In our earlier work on LCA of CCU,¹² we highlighted the importance of including all upstream processes for feedstock production in LCA. In particular, the provision of feedstock CO₂ should be included in the product system.¹¹ The present LCA case study is conducted within the publicly funded research project "Dream Production". In this project, CO₂ is obtained from a lignite power plant with a pilot plant for CO₂ capture. Due to a significant energy penalty from CO₂ capture, the nominal net electricity output of the lignite power plant is reduced and must be compensated.¹⁸ Therefore, the product system for CO₂-based polyols consists of the following three stages: CO₂ source including CO₂ capture, electricity compensation, and CO₂ utilization for polyols production (Fig. 1a). We refer to this entire product system as *CCU system*. LCA data for the CCU system are taken from GaBi LCA database if not stated otherwise.¹⁷ A complete list of LCA data sources is given in the ESI.†

The CO₂ source in the project "Dream Production" is a lignite power plant in Niederaussem, Germany, operated by electricity supplier RWE.¹⁹ The plant unit provides a net power of 950 MW with an efficiency of 43%. The unit is equipped with a pilot plant for post-combustion CO₂ capture, which separates 300 kg h⁻¹ of CO₂ from a flue gas bypass with a capture



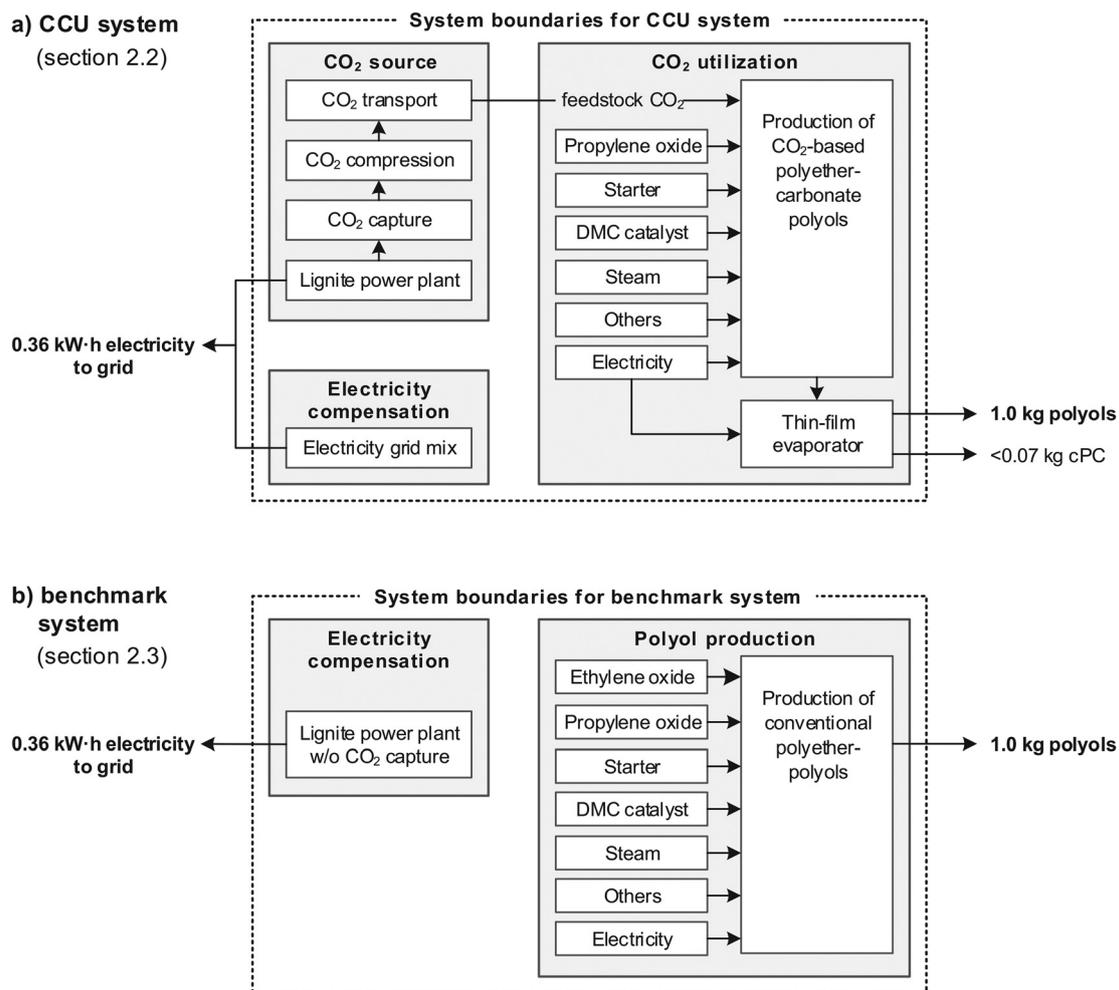


Fig. 1 (a) Product systems for CO₂-based polyethercarbonate polyols, CO₂ utilization (right box) comprises production of polyethercarbonate polyols and separation of the by-product cyclic propylene carbonate (cPC) as well as provision of all feedstocks and energy. Feedstock CO₂ is provided by a lignite power plant with CO₂ capture (CO₂ source, top left box). Additional electricity from the grid mix compensates for the energy penalty of CO₂ capture (electricity compensation, bottom left box). (b) Product system for conventional polyether polyols from fossil-based feedstocks. Polyol production (right box) comprises the production process itself as well as provision of all feedstocks and energy. Electricity generation (left box) from a lignite power plant without CO₂ capture is added to the product system to enable a sound comparison to the CCU system (a) with identical product outputs (functional unit).

rate of 90%.²⁰ We consider an amine-based solvent with a regeneration heat demand of 2760 MJ_{th} per ton CO₂ captured which corresponds to an equivalent work loss of 123 (kW h)_{el} per ton CO₂ captured.^{20–22} After CO₂ capture, the CO₂ stream is fed into a pilot plant for CO₂ cleaning, compression and filling in cylinders. Cleaning, compression to 17.5 bar and filling requires 142 kW h of electricity per ton CO₂. Cleaned CO₂ achieves EIGA standard (European Industrial Gases Association), complies with food grade quality²³ and proved suitable for polyols synthesis. CO₂ cylinder rags are transported to the 40 km distant polyol production plant by truck. Construction of the lignite power plant and facilities for CO₂ capture and filling was shown to have a minor contribution to total life cycle impacts²⁴ and is therefore not considered in this LCA.

Due to the electricity demand for CO₂ cleaning, compression and filling, and the work loss from solvent regener-

ation, the power plant's electricity output to the grid is reduced by 265 kW h per ton CO₂ captured. The power plant is limited by its boiler and cannot compensate for the reduced electricity. Consequently, the remaining electricity producers at the grid have to compensate for the reduced electricity with an increased electricity supply. Sathre *et al.* recommend accounting for electricity compensation in LCA.¹⁸ Following a simplified approach used by NETL,²⁵ we model the compensated electricity based on average grid characteristics in Germany in 2010 (0.60 kg CO₂-eq and 0.16 kg oil-eq per kW h).†

The main process of the CO₂ utilization stage is the production of polyethercarbonate polyols from PO and CO₂ using a multi-functional alcohol starter and a double metal cyanide (DMC) catalyst (*cf.* Scheme 1). For production of polyethercarbonate polyols within “Dream Production”, the chemical manufacturer Bayer set up a kg-scale pilot plant in Leverkusen,



Germany. From this pilot plant, primary input data for feedstocks, catalyst and energy demand such as steam or electricity as well as output data for (by-) products were collected. By using a DMC catalyst, the formation of the by-product cyclic propylene carbonate (cPC) can be limited to 0.02–0.07 kg cPC per kg polyol, depending on the CO₂ content in the final polyethercarbonate polyols. Suitable product properties are obtained for CO₂ contents of up to 30 wt% in the polymer chains.⁸ In this study, three different CO₂ contents in the polymer chains are evaluated: 10, 20 and 30 wt%. In the following, 'wt% CO₂' always refers to the CO₂ content in the polymer chains. Absolute mass fractions of CO₂ in the entire polyol are between 10 and 29%. The by-product cPC is separated from the polyols by passing the reactor output through a thin-film evaporator.

A cradle-to-gate LCA considers all upstream processes such as provision of feedstocks, catalyst and energy. The major feedstock PO can be obtained by alternative production technologies. The goal of this LCA is not to assess a particular PO technology for feedstock supply, but rather to assess CO₂-based polyol production in general. Therefore, a PO production mix with the following composition is used in the default scenario:²⁶ 43% chlorohydrin process (CHPO), 33% PO/SM process with styrene monomer as co-product, 16% PO/TBA with *t*-butyl alcohol as co-product (also called PO/MTBE), 5% hydrogen peroxide process (HPPO), and 4% Sumitomo process with cumene hydroperoxide as oxidant. The impact of replacing this mix by the individual PO technologies is assessed in a scenario analysis (section 3.2). LCA data for CHPO and PO/TBA are taken from GaBi LCA database.¹⁷ LCA data for PO/SM and HPPO processes were modeled according to material and energy flows from HIS Chemical PEP Yearbook.²⁷ The Sumitomo process is not considered due to missing LCA data and the other PO processes are rescaled accordingly. Glycerol is used as starter. A detailed sub-LCA for the production of DMC catalyst²⁸ was performed using data on material and energy flows provided by Bayer. Construction of the pilot plant or of any other components is not included for two reasons: first, production plants for CO₂-based and conventional polyols are similar and largely cancel each other out in a comparison; second, the share of environmental impacts from plant construction is typically found to be small in the chemical industry.²⁹

2.3 Product system for conventional polyols

The product system for conventional polyols serves as benchmark and is divided into electricity generation and conventional polyol production (Fig. 1b). For production of conventional polyether polyols, only fossil-based feedstocks PO and ethylene oxide (EO) are consumed. The same PO, starter, and DMC catalyst as in the CCU system are used in the LCA inventory. Since no by-products are formed, purification of polyols is not required. Conventional polyol production does not utilize CO₂ and is therefore not linked to a CO₂ source. However, electricity generation is added to the product system to account for the electricity generated in the CCU system (*cf.* Fig. 1 and

section 2.4). Electricity in the benchmark system is generated in an equivalent lignite power plant without CO₂ capture and a net efficiency of 43% (0.96 kg CO₂-eq and 0.26 kg oil-eq per kW h).

LCA data sources for the benchmark system are identical to the CCU system for all energy sources and feedstocks except EO.† EO is mainly produced by direct oxidation of ethylene with oxygen.³⁰ For this process, LCA data are taken from GaBi.†

2.4 Functional unit for system-wide assessment

The functional unit in LCA quantifies the functions of the investigated product systems and serves as basis for comparison.¹² The main functions of the CCU system (Fig. 1a) and the benchmark system (Fig. 1b) are production of polyols for polyurethane production, *and* supply of electricity to the German electricity grid. Production of cPC is not considered as main function (see below).

To quantify the main functions, we choose 1.0 kg of polyol as reference for the function 'polyol production'. The second function 'electricity supply' can be quantified through the amount of CO₂ that is captured to produce 1.0 kg of polyol. However, the CO₂ content and thus the amount of captured CO₂ are varied in our study. Since the amount of CO₂ captured determines the energy need for CO₂ capture, the second function 'electricity supply' would be different for each case. In order to still use one functional unit for all cases studied, we define the electricity supply as follows:

We consider the maximum amount of CO₂ used for production of polyethercarbonate polyol, *i.e.*, the case with 30 wt% CO₂. For 1.0 kg of polyol with 30 wt% CO₂ content, 0.31 kg CO₂ is captured from the flue gas. The difference of 0.01 kg between captured CO₂ and CO₂ incorporated into the polyol is due to unused CO₂ deposits in the CO₂ cylinders. While capturing 0.31 kg CO₂, the lignite power plant with CO₂ capture generates net electricity of 0.28 kW h. Using the same lignite input, net electricity of 0.36 kW h would be produced by an equivalent conventional lignite power plant without CO₂ capture since it does not suffer from the energy penalty from CO₂ capture. The lower electricity supply of 0.08 kW h of the power plant with CO₂ capture, *i.e.*, the energy demand of CO₂ capture, is assumed to be compensated by the grid mix (bottom left box in Fig. 1a). This approach to account for the so-called make-up power is commonly applied for LCA of CCS systems.^{18,25}

Thus, for each 1.0 kg polyols with 30 wt% CO₂, a total generation of 0.36 kW h of electricity (0.28 kW h from the lignite power plant and 0.08 kW h make-up power) is supplied to the grid. For production of 1.0 kg of conventional polyether polyols (0 wt% CO₂), no CO₂ is captured from the flue gas and the conventional lignite power plant directly supplies 0.36 kW h electricity to the grid. For production of 1.0 kg polyols with CO₂ contents between 0 and 30 wt%, the make-up power is between 0 and 0.08 kW h; the electricity by the lignite power plant is between 0.28 and 0.36 kW h, whereby both always total to 0.36 kW h.



Thus, we define the functional unit as production of 1.0 kg polyols for polyurethane production, and supply of 0.36 kW h electricity to the electricity grid (short: 1.0 kg polyols and 0.36 kW h grid electricity).

The formation of by-product cPC should be considered in LCA since cPC is a valuable chemical. CPC is used as aprotic polar solvent, electrolyte for batteries, cleaning solvent, plasticizer, precursor for linear (poly-) carbonates and additive for cosmetics and adhesives.^{5,31,32} Since only small amounts of less than 7 wt% cPC are formed, environmental impacts from CO₂ utilization processes (*cf.* Fig. 1a) are allocated to polyols and cPC. Feedstocks (PO, CO₂ and glycerin) are allocated according to the feedstock masses incorporated in polyols and cPC, respectively. The catalyst is fully assigned to the polyols. Other inputs are allocated according to polyol and cPC masses. The minor influence of alternative allocation options for cPC is illustrated in the ESI.†

2.5 Functional unit for product-specific assessment

A second functional unit is defined as solely 1.0 kg polyols to obtain product-specific LCA results for polyols. However, this approach requires ambiguous choices for allocation of impacts to polyol production and grid electricity supply as discussed in detail by von der Assen *et al.*¹¹ To illustrate the effect of alternative allocation options, two options are considered.

The first allocation option assigns all impacts of the entire CCU system fully to polyols whereas grid electricity is not assigned with any impacts at all. This option represents a *worst-case allocation* scenario for polyols. In the second allocation option, polyethercarbonate polyols in the CCU system are assigned with a credit for the supply of grid electricity. Grid electricity supplied in the CCU system is assumed to substitute electricity from the conventional power plant without CO₂ capture. This option assigns environmental benefits fully to CO₂-based polyol production and represents a *best-case allocation* scenario for CO₂ supply from lignite power plants.

In addition to these extreme allocation options, we assess an alternative ideal CO₂ source. The ideal, though hypothetical CO₂ source requires no energy for CO₂ capture and does not cause any indirect GHG emissions. Therefore, the ideal CO₂ source has a global warming impact of $GW(\text{CO}_{2,\text{feed,ideal}}) = -1 \text{ kg CO}_2\text{-eq per kg feed stock CO}_2$.¹²

3. LCA results and discussion

3.1 System-wide LCA results for polyols and grid electricity

The cradle-to-gate impacts on global warming and fossil resource depletion are assessed for the functional unit of 1.0 kg polyols and 0.36 kW h of grid electricity. Fig. 2 shows the global warming impacts for the benchmark system with conventional polyether polyols, and for the CCU system with polyethercarbonate polyols containing 20 wt% CO₂. In both systems, the largest contributor to total GHG emissions is the production of epoxides (81 and 80%). By utilizing CO₂ as feedstock for polyols, the system-wide GHG emissions can be

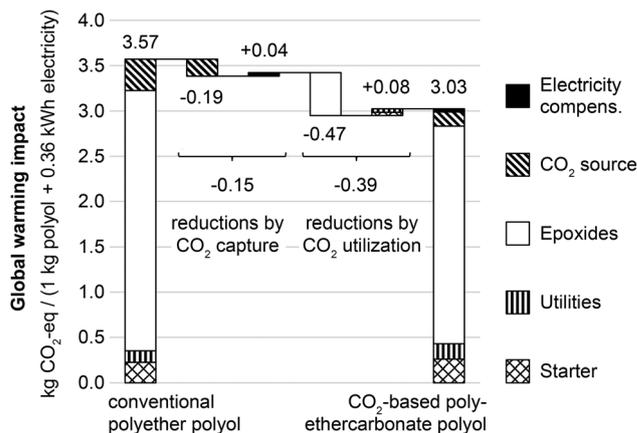


Fig. 2 Global warming impacts in kg CO₂-equivalents for product system of conventional polyether polyols (left) and CO₂-based polyethercarbonate polyols (right, 20 wt% CO₂ content). The CO₂ source includes the lignite power plant, CO₂ capture, CO₂ compression and CO₂ transport, if applicable. Utilities include DMC catalyst, steam, electricity, thin-film evaporator and others; *cf.* Fig. 1. Major reductions of GHG emissions originate from CO₂ capture (−0.15 kg CO₂-eq) and substitution of epoxides with CO₂ (−0.47 kg CO₂-eq). Changes in the polyol process do not add significantly to overall GHG emissions (+0.08 kg CO₂-eq).

reduced by 15% (−0.54 kg CO₂-eq per functional unit). About 28% of the total GHG emission reductions originate from CO₂ capture effects (−0.15 kg CO₂-eq per functional unit) as result from emission reductions at the CO₂ source and additional emissions for electricity compensation. Major GHG emission reductions of about 72% originate from CO₂ utilization in the polyol production (−0.39 kg CO₂-eq per functional unit) which can be explained by substitution of emission-intensive epoxides with CO₂. The contributions in Fig. 2 only show in which processes emissions (reductions) occur. These emissions

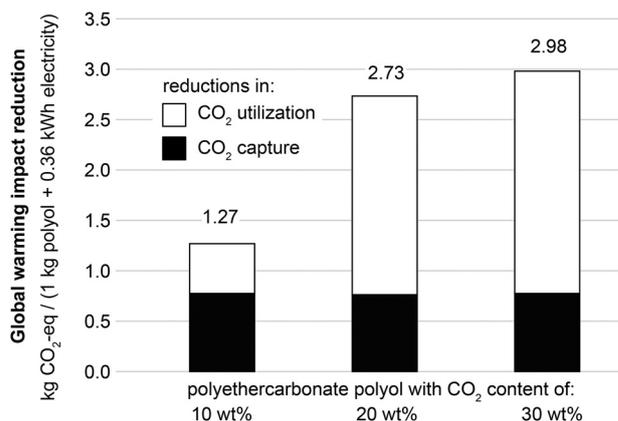


Fig. 3 Global warming impact reductions in kg CO₂-equivalents per kg feedstock CO₂ incorporated into polyols. Due to substitution of GHG emission intensive epoxides, the amount of avoided GHG emissions is higher than the amount of CO₂ used as feedstock. For 30 wt% CO₂, about three times as many CO₂-eq emissions are avoided as CO₂ is utilized as feedstock.



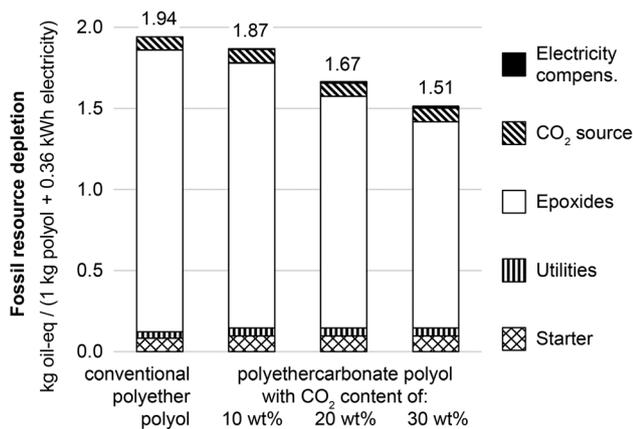


Fig. 4 Fossil resource depletion in kg oil-equivalents for product system of conventional polyether polyols (left) and CO₂-based polyethercarbonate polyols with 10, 20 and 30 wt% CO₂ content (second left to right). The CO₂ source includes the lignite power plant, CO₂ capture, CO₂ compression and CO₂ transport, if applicable. Utilities include DMC catalyst, steam, electricity, thin-film evaporator and others; *cf.* Fig. 1. Major reductions of fossil resource depletion originate from substitution of epoxides with CO₂ (−0.10, −0.31, and −0.47 kg oil-eq for 10, 20, and 30 wt% CO₂ content, respectively). Additional impacts from the CO₂ source, electricity compensation, and changes in the polyol process are small (between 0.03 and 0.04 kg oil-eq).

cannot directly be assigned to the processes' functions and products. For example, emissions from electricity compensation (0.04 kg CO₂-eq for the CCU system) cannot be assigned to either 0.36 kWh grid electricity or 1.0 kg polyols. Instead, product-specific impacts require a more detailed allocation approach (*cf.* section 3.3).

Recent CCU literature clearly distinguishes the amount of CO₂ used from the avoided CO₂-eq emissions.¹ Fig. 3 illustrates the amount of avoided CO₂-eq emissions per amount of

CO₂ incorporated into polyethercarbonate polyols for CO₂ contents of 10, 20 and 30 wt%. For all CO₂ contents, the amount of avoided CO₂-eq emissions is greater than the amount of CO₂ incorporated into polyols. The main reason for this effect is the much larger global warming impact of PO (1.74–4.5 kg CO₂-eq kg^{−1}) and EO (1.6 kg CO₂-eq kg^{−1}) compared to CO₂ (below 0.2 kg CO₂-eq kg^{−1}, *cf.* section 3.3). For 10 wt% CO₂ content, mainly EO is replaced. For higher CO₂ contents, the additional CO₂ incorporated substitutes PO allowing for larger reductions than EO substitution.

Fig. 4 shows the fossil resource depletion caused by the benchmark system with polyether polyols, and by the CCU system with polyethercarbonate polyols containing 10, 20 and 30 wt% CO₂. For fossil resource depletion, the utilization of CO₂ for polyols shows a similar behavior as for global warming impacts. The main impact source is epoxide production and a substitution of these fossil-based epoxides reduces overall fossil resource depletion. It is well known from LCA for CCS that the fossil resource demand of power plants increases due to the energy required for CO₂ capture.²⁴ However, the increased fossil resource demand from CO₂ capture is much smaller than the fossil resource reduction due to epoxide substitution. Therefore, the CCU system reduces overall fossil resource depletion by up to 22% for a 30 wt% CO₂ content compared to the benchmark system.

In addition to impact reductions for global warming and fossil resource depletion, the CCU system also lowers impacts for eutrophication, ionizing radiation, ozone depletion, particulate matter formation, photochemical oxidant formation, and terrestrial acidification as shown in the ESI.† For all impact categories, normalized values have also been calculated:† normalized values for fossil resource depletion are much larger than other environmental impacts indicating the importance of fossil resource depletion for polyol production.

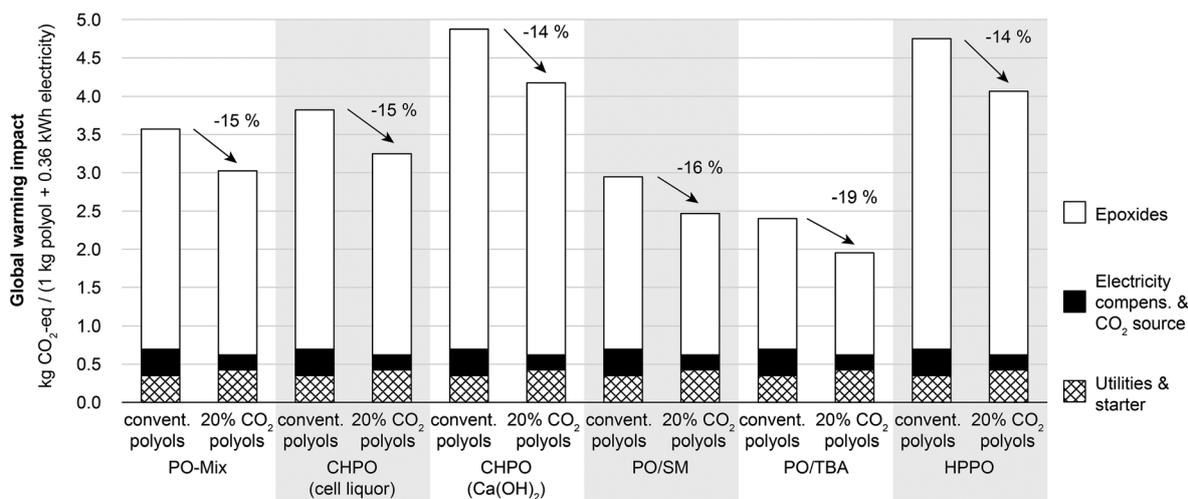


Fig. 5 Global warming impact considering alternative PO production technologies for product system of conventional polyether polyols (left bar for each PO technology) and CO₂-based polyethercarbonate polyols with 20 wt% CO₂ (right bar for each PO technology). Despite large variations between alternative PO production technologies, the global warming impact reduction for the CCU system varies only between 14 and 19%.



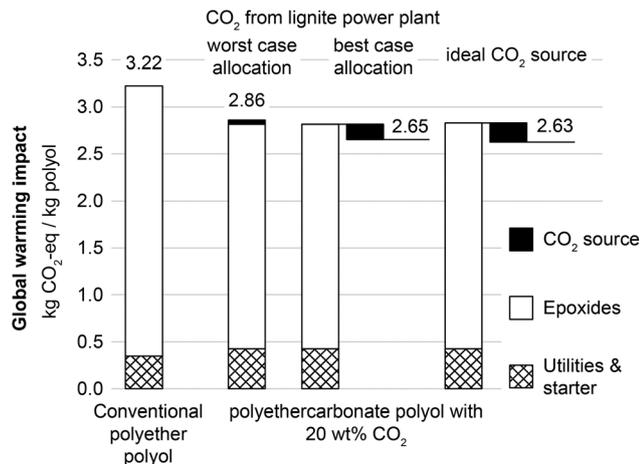


Fig. 6 Product-specific global warming impacts in kg CO₂-equivalents per kg of polyols. For polyethercarbonate polyols, impacts were obtained by 100% allocation to polyols (*worst case allocation*, second from left, $\text{GW}(\text{CO}_{2,\text{feed}}) = 0.2 \text{ kg CO}_2\text{-eq kg}^{-1}$) and by crediting an avoided burden for supply of grid electricity in the CCU system (*best case allocation*, third from left, $\text{GW}(\text{CO}_{2,\text{feed}}) = -0.8 \text{ kg CO}_2\text{-eq kg}^{-1}$). An *ideal CO₂ source* is added to illustrate the theoretically minimal global warming impact for CO₂ supply ($\text{GW}(\text{CO}_{2,\text{feed}}) = -1.0 \text{ kg CO}_2\text{-eq kg}^{-1}$).

3.2 Variation of propylene oxide production technologies

The results for the system-wide LCA illustrated in Fig. 2 and 4 show that the main source of impacts on global warming and fossil resource depletion is production of PO. This also holds for other environmental impact categories as shown in the ESI.† Thus, alternative production technologies for PO can significantly affect LCA results. Fig. 5 therefore shows the global

warming impact for the benchmark and the CCU system using alternative PO production technologies. The global warming impact varies substantially between PO production technologies, from 2.40 to 4.88 kg CO₂-eq per functional unit for the benchmark system, and from 1.95 to 4.18 kg CO₂-eq per functional unit for the CCU system. However, when comparing the CCU system to the benchmark based on the same PO production technology, the CCU system always leads to reduced GHG emissions regardless of the considered PO production technology. These GHG emission reductions vary only between 14 and 19%.

3.3 Product-specific global warming impact for polyols

The previous sections show global warming impacts of the entire CCU system including supply of grid electricity. In Fig. 6, product-specific global warming impacts are shown solely for 1.0 kg of polyols. Conventional polyether polyols cause GHG emissions of 3.22 kg CO₂-eq kg⁻¹. For polyethercarbonate polyols with 20 wt% CO₂ content, the global warming impact is between 2.65 and 2.86 kg CO₂-eq kg⁻¹ depending on the allocation approach. Thus, the global warming impact of CO₂-based polyols is between 11 and 18% lower than for conventional polyols. For an ideal CO₂ source with no energy demand for CO₂ capture (right bar in Fig. 6), the maximum global warming impact reduction is 18% compared to conventional polyols. This implies that switching to environmentally favorable CO₂ sources does not lead to major additional reductions in the total global warming impact for CO₂-based polyols.

For the different functional units and product systems, the results for the global warming impact and fossil resource depletion are summarized in Table 1.

Table 1 Summary of LCA results for the product systems of conventional and CO₂-based polyols with respect to impact on global warming (GW; in kg CO₂-equivalents) and fossil resource depletion (FD; in kg oil-equivalents). For the polyols with 20 wt% CO₂, the percentages in italics show the highest and lowest impact reductions for each impact category which are used in the conclusions

		Conventional polyether polyol	CO ₂ -based polyethercarbonate polyol		
			10 wt% CO ₂	20 wt% CO ₂	30 wt% CO ₂
Functional unit: 1 kg polyols and 0.36 kW h grid electricity					
GW	PO-Mix	3.57	3.45 (-3%)	3.03 (-15%)	2.68 (-25%)
GW	Lowest PO ^a	2.40	2.22 (-6%)	1.95 (-19%)	1.72 (-27%)
GW	Highest PO ^b	4.88	4.76 (-2%)	4.18 (-14%)	3.70 (-24%)
FD	PO-Mix	1.94	1.87 (-4%)	1.67 (-14%)	1.51 (-22%)
FD	Lowest PO ^a	1.43	1.35 (-6%)	1.22 (-15%)	1.11 (-22%)
FD	Highest PO ^c	2.53	2.46 (-2%)	2.19 (-13%)	1.98 (-22%)
Functional unit: 1 kg polyols					
GW	Lower bound ^d	3.22	3.07 (-5%)	2.63 (-18%)	2.26 (-30%)
GW	Upper bound ^e	3.22	3.20 (-1%)	2.86 (-11%)	2.63 (-18%)
FD	Lower bound ^d	1.87	1.78 (-5%)	1.58 (-16%)	1.42 (-24%)
FD	Upper bound ^e	1.87	1.81 (-3%)	1.63 (-13%)	1.50 (-20%)

^a Lowest PO for GW and FD is PO/TBA. ^b Highest PO for GW is CHPO (Ca(OH)₂). ^c Highest PO for FD is HPPO. ^d Lower bound obtained with ideal CO₂ source. ^e Upper bound obtained with 100% allocation to polyols (worst case allocation).



4. Conclusions

To the best of our knowledge, this work can be considered the first published LCA for CO₂-based polymers. LCA results show that the environmental impacts caused by polyol production mainly originate from PO production. Therefore, an environmentally favorable PO source should be chosen for PO supply. For further reductions of the environmental impacts of polyols, PO should be substituted by CO₂ as carbon feedstock. The resulting CO₂-based polyols cannot be considered as net GHG sink, *i.e.*, it is still better for climate protection not to produce polyols in the first place. However, if polyol production is desirable, the utilization of CO₂ allows for significant impact reductions: compared to conventional polyether polyols, polyethercarbonate polyols with 20 wt% CO₂ reduce GHG emissions by 11–19%, and save fossil resources by 13–16%. CO₂-based polyols can also lower impacts on eutrophication, ionizing radiation, ozone depletion, particulate matter formation, photochemical oxidant formation, and terrestrial acidification. Overall, CO₂-based polyols are an excellent option for CO₂ utilization: up to three kg CO₂-eq GHG emissions can be reduced per kg CO₂ incorporated. Furthermore, CO₂-based polyols can be readily processed to polyurethanes enabling utilization of large amounts of CO₂ and significant reductions of environmental impacts.

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References

- M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.*, 2014, **114**, 1709–1742.
- W. Leitner, *Coord. Chem. Rev.*, 1996, **153**, 257–284.
- P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber and T. E. Müller, *Energy Environ. Sci.*, 2012, **5**, 7281–7305.
- M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz and T. E. Müller, *ChemSusChem*, 2011, **4**, 1216–1240.
- X.-B. Lu and D. J. Darensbourg, *Chem. Soc. Rev.*, 2012, **41**, 1462–1484.
- J. Langanke, A. Wolf and M. Peters, *Polymers from CO₂ – An Industrial Perspective*, in *Carbon Dioxide Utilization – Closing the Carbon Cycle*, ed. P. Styring and A. Quadrelli, Elsevier, 2014, in print.
- D. J. Darensbourg and S. J. Wilson, *Green Chem.*, 2012, **14**, 2665–2671.
- J. Langanke, A. Wolf, J. Hofmann, K. Böhm, M. A. Subhani, T. E. Müller, W. Leitner and C. Gürtler, *Green Chem.*, 2014, **16**, 1865–1870.
- Bayer Material Science, *Personal communication*, 2014.
- E. A. Quadrelli, G. Centi, J.-L. Duplan and S. Perathoner, *ChemSusChem*, 2011, **4**, 1194–1215.
- N. von der Assen, J. Jung and A. Bardow, *Energy Environ. Sci.*, 2013, **6**, 2721–2734.
- N. von der Assen, P. Voll, M. Peters and A. Bardow, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/C3CS60373C.
- M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975–2992.
- G. Centi and S. Perathoner, *Greenhouse Gases: Sci. Technol.*, 2011, **1**, 21–35.
- G. Centi and S. Perathoner, *Perspectives and State of the Art in Producing Solar Fuels and Chemicals from CO₂*, in *Green Carbon Dioxide: Advances in CO₂ Utilization*, ed. G. Centi and S. Perathoner, WILEY-VCH, Hoboken, NJ, USA, 2014, p. 4.
- M. Goedkoop, R. Heijungs, M. Huijbregts, A. D. Schryver, J. Struijs and R. V. Zelm, *ReCiPe 2008, A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level; First edition (version 1.08) Report I: Characterisation*, 2013, <http://www.lcia-recipe.net>.
- PE International, *GaBi LCA Software and LCA Databases*, 2012, <http://www.gabi-software.com/databases/gabi-databases/>.
- R. Sathre, M. Chester, J. Cain and E. Masanet, *Energy*, 2012, **37**, 540–548.
- RWE Power AG, *Niederaussem Power Plant*, 2014, <http://www.rwe.com/web/cms/en/60132/rwe-power-ag/locations/lignite/niederaussem-power-plant/>.
- P. Moser, S. Schmidt, G. Sieder, H. Garcia, I. Ciattaglia and H. Klein, *Energy Procedia*, 2009, **1**, 807–814.
- M. E. Boot-Handford, J. C. Abanades, E. J. Anthony, M. J. Blunt, S. Brandani, N. Mac Dowell, J. R. Fernandez, M.-C. Ferrari, R. Gross, J. P. Hallett, R. S. Haszeldine, P. Heptonstall, A. Lyngfelt, Z. Makuch, E. Mangano, R. T. J. Porter, M. Pourkashanian, G. T. Rochelle, N. Shah, J. G. Yao and P. S. Fennell, *Energy Environ. Sci.*, 2014, **7**, 130–189.
- P. Moser, S. Schmidt, G. Sieder, H. Garcia, T. Stoffregen and V. Stamatov, *Energy Procedia*, 2011, **4**, 1310–1316.
- European Industrial Gases Association (EIGA), *Carbon Dioxide Source Qualification Quality Standards And Verification, IGC Doc 70/08/E, Appendix A, Table 1*, 2008.
- A. Schreiber, P. Zapp and J. Marx, *J. Ind. Ecol.*, 2012, **16**, S155–S168.
- National Energy Technology Laboratory, *Life Cycle Analysis: Existing Pulverized Coal (EXPC) Power Plant*, DOE/NETL-403-110809, 2010, http://www.netl.doe.gov/energy-analyses/pubs/EXPC_LCA_Report_093010.pdf.



- 26 ChemSystems, PERP Report Abstract PERP07/08-6, Propylene Oxide, 2009.
- 27 IHS Chemical, *Process Economics Program (PEP) Yearbook*, pp. 1089 (PO/SM Lyondell process), 1091 (PO/SM Shell process) and 1094 (HPPO BASF process), 2010, <http://www.ihs.com/products/chemical/technology/pep/>.
- 28 J. Hofmann, S. Ehlers, B. Klinksiek, T. Fechtel, M. Ruhland, J. Scholz, F. Föhles and U. Esser, *PCT Int. Appl*, WO-A-01/80994, 2001.
- 29 R. Frischknecht, *Int. J. Life Cycle Assess.*, 2007, **Special (1)**, 7–17.
- 30 S. Rebsdatt and D. Mayer, Ethylene Oxide, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2001, vol. 13, pp. 547–572.
- 31 A.-A. G. Shaikh and S. Sivaram, *Chem. Rev.*, 1996, **96**, 951–976.
- 32 J. Sun, S. Fujita and M. Arai, *J. Organomet. Chem.*, 2005, **690**, 3490–3497.

