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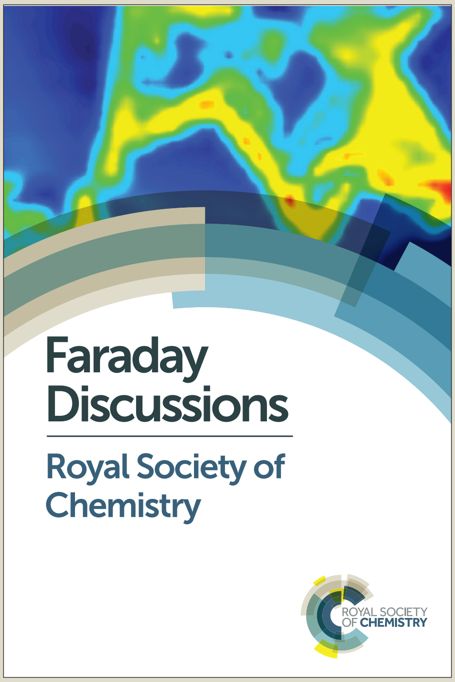

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Environmental potential of carbon dioxide utilization in the polyurethane supply chain[†]

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[†] Supplementary information (SI) is available: SI contains process data for polyurethane supply chain and additional figures for flexible and rigid polyurethane foams.

Abstract

Potential environmental benefits have been identified for the utilization of carbon dioxide (CO_2) as feedstock for polyurethanes (PUR). CO_2 can be utilized in the PUR supply chain in a wide variety of ways ranging from direct CO_2 utilization for polyols as PUR precursor to indirect CO_2 utilization for basic chemicals in the PUR supply chain. In this paper, we present a systematic exploration and environmental evaluation of all direct and indirect CO_2 utilization options for flexible and rigid PUR foams. The analysis is based on an LCA-based PUR supply chain optimization model using linear programming to identify PUR production with minimal environmental impacts. The direct utilization of CO_2 for polyols allows for large specific impact reductions of up to 4 kg CO_2-eq and 2 kg oil-eq per kg CO_2 utilized, but the amounts of CO_2 that can be utilized are limited to 0.30 kg CO_2 per kg PUR. The amount of CO_2 utilized can be increased to up to 1.7 kg CO_2 per kg PUR by indirect CO_2 utilization in the PUR supply chain. Indirect CO_2 utilization requires hydrogen (H_2). The environmental impacts of H_2 production strongly affect the impact of indirect CO_2 utilization in PUR. For current H_2 production, environmentally optimal PUR production utilizes much less CO_2 than theoretically possible. Thus, utilizing as much CO_2 in the PUR supply chain as possible is always not environmentally optimal. Clean H_2 production is required to exploit the full CO_2 utilization potential for environmental impact reduction in PUR production.

1. Introduction

The use of fossil fuels inherently leads to carbon dioxide (CO_2) emissions. Aiming at reducing both CO_2 emissions and fossil fuel use, CO_2 can be captured and utilized as feedstock for fuels, materials and chemicals.[1-3] In particular, CO_2 has recently been successfully utilized in the production of polyurethanes (PUR) resulting in both lower CO_2 emissions and lower use of fossil fuels than conventional PUR.[4-6]

PUR production is particularly well suited for incorporation of CO_2 as PUR allows for both direct and indirect CO_2 utilization as follows: Polyurethanes consist of polyols and isocyanates. In polyol synthesis, the CO_2 molecule can be directly inserted 'as such' in (poly) carbonate units, i.e., without energy-intensive full cleavage of the C=O bonds.[5,6] In addition to the direct CO_2 utilization in polycarbonate units of the polyols, CO_2 can also be utilized indirectly in upstream processes of the polyol supply chain. For example, CO_2 can be converted to methanol[7] and subsequently to formaldehyde, which constitutes a potential monomer for polyols.[8]

Next to direct and indirect CO_2 utilization for polyols, CO_2 can also be used in the production of isocyanates. While the direct utilization of CO_2 for isocyanates still remains a dream in industry today,[9] conventional isocyanate production requires the feedstock carbon monoxide (CO),[10] which can be obtained by reduction of CO_2.[11]

Thus, a wide variety of options exists for direct and indirect utilization of CO_2 in the supply chain of PUR. However, a systematic exploration and environmental evaluation of all direct and indirect CO_2 utilization options for PUR is missing. Therefore, the first goal of this article is to identify the total CO_2 utilization potential in the entire PUR supply chain. In other words, we identify the maximum amount of mass CO_2 utilized per mass PUR.

Intuitively, utilizing as much CO_2 as possible might seem environmentally most favorable. However, the energy requirements for both CO_2 capture and utilization (CCU) can lead to additional CO_2 emissions, fossil fuel use and other environmental impacts.[12] Thus, it is not always environmentally most reasonable to utilize as much CO_2 as possible. Instead, only those CO_2-based processes should be employed that allow for reductions of environmental impacts. Environmental impacts of processes can be determined by life cycle assessment (LCA). LCA is a methodology to quantify the environmental impacts of products and processes along the entire life cycle from cradle to grave. Applications of LCA to CCU process are still very limited as recently reviewed.[13] For the application of LCA to CO_2 utilization, specific guidelines have recently been developed.[12,14] Based on these guidelines, the second goal of this article is to analyze which CO_2-based processes in the PUR supply chain allow for the largest reduction of CO_2 emissions and fossil fuel use. From this analysis, we also determine the minimum CO_2 emissions and minimum fossil fuel use for the PUR supply chain.

Indirect CO_2 utilization processes usually require cleavage of C=O bonds, often via hydrogenation.[15-18] Whether CO_2 hydrogenation is environmentally favorable compared to a fossil-based benchmark depends strongly on the provision of hydrogen (H_2).[19,20] Conventional production of H_2 via steam methane reforming is typically energy- and emission-intensive.[21] The impacts of H_2 production can be significantly reduced by the combination of water electrolysis with renewable electricity sources.[19] Therefore, the third goal of this article is to analyze the minimum environmental impacts of CO_2 utilization in the PUR supply chain as function of the environmental impacts of H_2 production. Based on this analysis, we determine threshold values for the environmental impacts of H_2 production that are tipping points for utilization of major amounts of CO_2 for PUR production.

The article is structured as follows. In section 2, we review specific guidelines for the application of LCA for CO_2 utilization in polymers and state the goal and scope for the present LCA study of CO_2-based PUR. In section 3, we present the considered PUR supply chain including conventional and CO_2-based processes. Furthermore, we introduce the optimization model using linear programming for the analysis of maximum amounts of CO_2 utilization and minimal environmental impacts. In section 4, we present our findings, i.e., the maximum amounts of utilized CO_2 per kg PUR, the CO_2-based processes with largest environmental benefits, and the minimum environmental impacts of the PUR supply chain for H_2 production alternatives. Finally, in section 5, conclusions are drawn for the utilization of CO_2 in the PUR supply chain.

2. LCA for CO_2 utilization in PUR production

Both capture and utilization of CO_2 typically require energy whose provision is often based on fossil fuels and thus causes indirect CO_2 emissions. For example, post-combustion CO_2 capture from flue gases of power plants demands the equivalent of about 20-25 % of the total electricity output of the power plant.[22,23] Utilization, or more precisely, conversion of the inert CO_2 molecule usually requires direct energy input or high-energetic co-reactants such as epoxides or hydrogen (H_2).[24] Thus, the intuitively expected environmental impacts of CO_2 capture and utilization are not given by default and a detailed environmental assessment is required. Life cycle assessment (LCA) is frequently acknowledged as suitable methodology for the environmental assessment of CCU.[1,2,25-27] Recently developed guidelines[12,14] for the application of LCA to CCU have already been applied to CO_2-based polyol synthesis.[28] Relevant aspects of these guidelines are reviewed and specified for the present context of CO_2 utilization in PUR production in the following.

2.1. Functional unit and comparability

The basis for any LCA is the definition of the so-called functional unit. The functional unit is a quantitative measure for the function of the system under study.[29,30] In the case of polymer production, the functional unit could be defined as “1 kg of polymer produced”. However, since polymers have very different properties and a broad range of applications, the mass-based definition may fall short of a fair comparison of different polymers.[14]

In this work, we consider the theoretical production of polyurethanes from alternative fossil- and CO_2-based monomers. In reality, the product properties of the polyurethanes will differ for alternative monomers. An integrated approach to identify environmentally optimal polyols with specified properties has recently been proposed by our group.[8] However, accurate models for prediction of PUR properties are missing. As a first step, we therefore define the functional unit of this work as “production of 1 kg of polyurethane foam” regardless of its chemical structure and resulting properties. Nevertheless, chemicals limitations for the incorporation of CO_2 are taken into account (cf. section 3.1). Still, our study neglects many practical constraints on PUR production to explore the full design space and to provide inspiration to chemists facing the practical challenges. The obtained LCA results thus serve as lower bound estimates for the environmental impacts of PUR production and can guide chemists towards more sustainable PUR synthesis.

2.2. Co-product allocation

Polyurethanes are typically produced together with many co-products along the PUR supply chain. For example, most technologies for production of propylene oxide generate co-products such as tert-butyl alcohol or styrol.[28] In the context of CO_2-based PUR, the 'production' of CO_2 via CO_2 capture from point-sources is also coupled to production of the point-sources' primary product: for example, power plants with CO_2 capture provide electricity as primary product.[12] To account for co-products, three methods exist in LCA: *system expansion*, *allocation* and *avoided burden*.[31,32]

In *system expansion*, the scope of the study is extended to include the co-products as functions. In other words, the functional unit is defined as a basket of products: the original product, here PUR, and all co-products. Since system expansion can lead to very large baskets of products, interpretation and communication can be difficult. Therefore, it is often desirable to compute product-specific impacts for PUR.

Product-specific impacts can be obtained by the methods *allocation* and *avoided burden*. For *allocation*, environmental impacts are allocated to the individual products based on criteria such as mass content, energy content or price share. However, the choice of an allocation criterion is ambiguous.[33] For *avoided burden*, the co-products are assigned with an environmental credited since co-production avoids an alternative production of the co-product and the related environmental burdens. Thus, avoided burden implies a comparison to an alternative production. Avoided burden is therefore useful for a comparison with today's production technologies.

In this work, we are interested in the reduction of impacts compared to today's situation rather than in the exact value of absolute environmental impacts. For such a comparison, a change-oriented viewpoint is recommended[34] and thus, we employ the avoided burden method to obtain environmental impact reductions compared to the conventional PUR production today. Precisely, avoided burdens are credited for production of excess hydrogen (H_2) and heat. For some of the feedstocks, we use data from LCA databases where allocation has already been applied.[35,36]

2.3. Environmental impact categories

LCA intends to cover a broad range of environmental impacts to avoid problem shifting between impact categories. The most prominent impact category ‘global warming’ (also named ‘climate change’ or carbon footprint) aggregates CO_2 and other greenhouse gas emissions according to their global warming potential in CO_2-equivalents.[37] The impact category ‘fossil fuel depletion’ quantifies the use of the limited fossil resources based on their energy content in kg oil-equivalents.[38] CO_2 Capture and Utilization (CCU) aims at reducing CO_2 emissions and establishing an alternative carbon source, thus also reducing the use of fossil fuels. However, from Carbon Capture and Storage (CCS), a tradeoff is known between CO_2 emission reduction and fossil fuel use.[39-41] Therefore, CCU processes should be evaluated at least regarding impacts on global warming and fossil fuel use.[14] Of course, it is desirable to perform a more complete LCA study with a broad range of environmental impacts.[42,43]

In this work, we assess the environmental potential of CO_2 utilization in PUR production with respect to CO_2 emissions and fossil fuel use.

2.4. CO_2 sources and CO_2 capture

CO_2 capture from diluted CO_2 sources requires energy for separation of CO_2 from other gases. Moreover, CO_2 capture requires operating materials such as capture solvents, and process technologies such as absorption and desorption columns. All of these efforts for CO_2 capture are typically associated with fossil fuel use and thus CO_2 emissions. Therefore, the CO_2 emission reduction of CO_2 capture is lower than 1 kg CO_2-eq per kg $CO_{2,feed}$. Here, CO_2-eq refers to CO_2 emissions and other greenhouse gas emissions, and $CO_{2,feed}$ refers to the captured and subsequently utilized CO_2.

In this work, we consider a coal-fired power plant as standard CO_2 source. For the considered coal-fired power plant, CO_2 capture can reduce CO_2 emissions by 0.84 kg CO_2-eq and increases fossil fuels use by 0.05 kg oil-eq per kg $CO_{2,feed}$ compared to a power plant without CO_2 capture.[44] As worst-case scenario, we also consider CO_2 capture from ambient air with CO_2 emission reductions of 0.51 kg CO_2-eq and fossil fuel use of 0.18 kg oil-eq per kg $CO_{2,feed}$.[44] As best-case scenario, we consider a hypothetical, ideal CO_2 source with CO_2 emission reductions of 1 kg CO_2-eq per kg CO_2 captured and no increase in fossil fuel use. The best-case scenario corresponds to a CO_2 source which can be readily used in the CO_2 conversion but is vented to the atmosphere today.

2.5. Temporary carbon storage in PUR

Polyurethanes have a lifetime of several decades. Incorporating CO_2 into PUR can thus be considered as temporary carbon storage during the PUR lifetime. Temporary carbon storage generally has a positive effect on climate mitigation.[45,46] The absolute effect of temporary carbon storage is, however, argued to be small for the following reasons:[12]

If conventional and CO_2-based PUR syntheses yield PURs with identical properties, then use, lifetime and end-of-life (EOL) treatment of both PURs will also be identical. Differences only occur during PUR syntheses and thus, it is sufficient to limit an LCA-based comparison of conventional and CO_2-based PUR syntheses to a so-called cradle-to-gate scope. In this case, a climate benefit can only be achieved if CO_2-based PUR synthesis causes fewer emissions than conventional synthesis. A climate benefit from temporary carbon storage cannot be expected for CO_2-based PUR synthesis compared to conventional PUR synthesis.

If, however, CO_2 utilization for PUR synthesis alters PUR properties, changes in use, lifetime and EOL treatment can occur. An increased PUR lifetime and a reduction of EOL CO_2 emissions constitute relevant changes for assessing the effect of temporary carbon storage in LCA: A longer lifetime can shift EOL CO_2 emissions into the future. As rule of thumb, this shift of CO_2 emissions can reduce the global warming impact of EOL emissions by about 1 % for each year of lifetime extension.[†] Total EOL CO_2 emissions account for about one third of total CO_2-eq emissions in the

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[†] The rule of thumb of 1 % global warming impact reductions is only valid for considering the absorbed radiation over a fixed time horizon of 100 years.[12] In this context, it should be mentioned that the choice of an adequate time horizon plays a key role for the assessment of temporary carbon storage.[57]

life cycle of conventional PUR without credits for thermal energy recovery.[35] Thus, even for a 10 year longer lifetime, the temporary carbon storage effect reduces overall PUR global warming impact by only 3 %. However, this simple analysis does not consider the general environmental benefit of longer product use.[47]

For PUR, a tradeoff is expected regarding the effect of CO_2 incorporation on EOL emissions: On the one hand, CO_2 utilization in PUR typically lowers the C content in PUR and thus lowers EOL CO_2 emissions. On the other hand, the lower C content also reduces the heating value leading to reduced thermal energy recovery in EOL. The reduced thermal energy recovery usually has to be compensated by fossil-based heating leading to additional CO_2 emissions.

For the above mentioned reasons, the climate mitigation effect of temporary carbon storage of CO_2 utilization for PUR is expected to be small. Nevertheless, we suggest quantifying the exact climate mitigation effect of temporary carbon storage on a case-by-case basis.

Due to difficulties in predicting the PUR lifetime from the chemical structure and due to the expectedly small climate effect of a PUR lifetime extension, temporary carbon storage is not considered in this work.

3. The PUR supply chain optimization model

3.1 Overview of the PUR supply chain

The considered PUR supply chain is illustrated in Figure 1. In the main article, we focus on the production of flexible PUR foams. Results for rigid PUR foams are presented in the supplementary information. In the following, the considered production steps are briefly described.

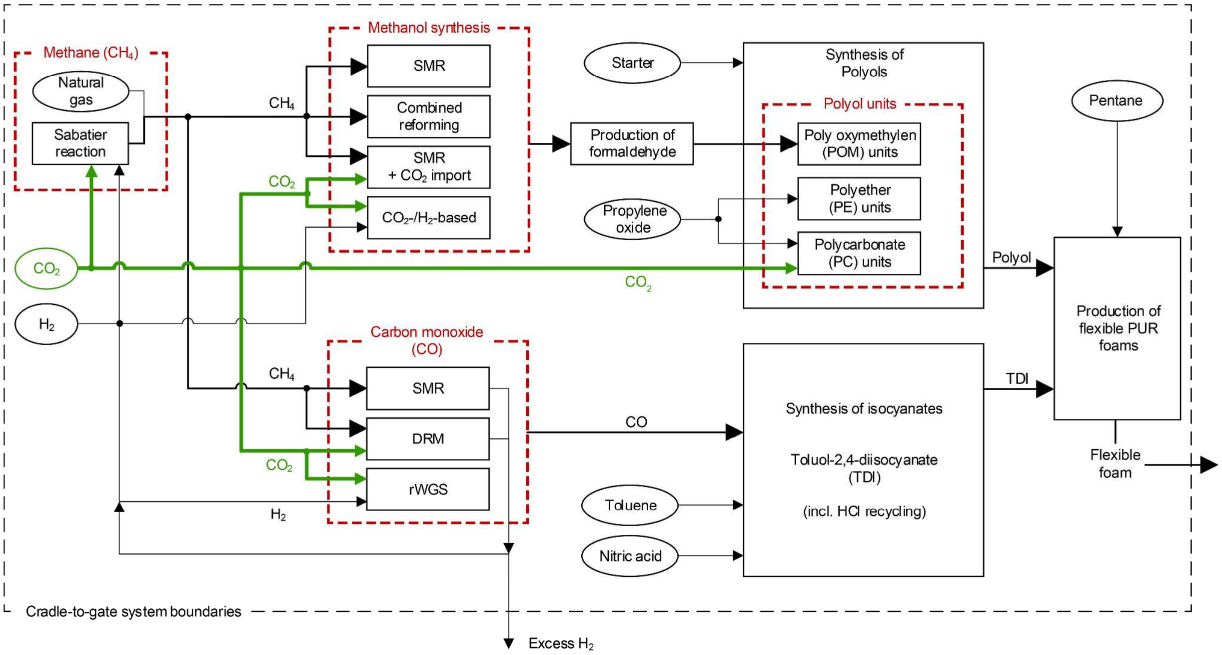

Figure 1 The PUR supply chain for flexible foams. For simplicity, only material flows are shown; heat and electricity are also considered in the supply chain optimization model. (Green) very thick arrows indicate CO_2 feedstock flows. Large arrowheads indicate feedstock flows with carbon that potentially stems from carbon dioxide. Smaller arrow heads indicate feedstock flows from non-CO_2 sources. The (red) dashed boxes indicate choices between i) methane sources, ii) methanol synthesis, iii) CO sources, and iv) polyol units. Color online.

3.1.1. Flexible PUR foam production

Flexible PUR foams are produced from the feedstocks polyol and toluol-2,4-diisocyanat (TDI).[36] We assume water as indirect foam blowing agent that reacts with TDI to CO_2 as the actual blowing agent. This CO_2 is directly released to the atmosphere. We consider a fixed mass ratio of TDI and polyol of $m_{TDI}/m_{polyol}=0.4$.[36]

3.1.2. Rigid PUR foam production

Rigid PUR foams are produced from the feedstocks polyol and methylene diphenyl diisocyanate (MDI).[36] We assume pentane as foam blowing agent although CO_2 can be used as alternative or co-blowing agent.[48] We consider a fixed mass ratio of MDI and polyol of $m_{MDI}/m_{polyol}=1.6$.[36]

3.1.3. Polyol production

Polyols are synthesized from a starter (here assumed as glycerol) and from the alternative monomer building blocks polyether, polycarbonate and poly oxymethylene. Conventional polyether polyols are made mainly from propylene oxide (PO).[10] For production of PO, environmental impacts are considered according to the technology mix.[28] PO can be partly substituted by CO_2 which co-polymerizes with PO to polycarbonate units.[5] Furthermore, poly oxymethylen (POM) diols have been tested for polyurethane production.[49] POM is polymerized from formaldehyde, which is exclusively produced from methanol.[50]

3.1.4. Methanol production

Conventionally, methanol is synthesized from syngas produced by steam methane reforming (SMR).[51] Since syngas from SMR usually does not have the optimal composition for methanol synthesis, CO_2 can be added (SMR + CO_2 import) to obtain the desired syngas composition. A fossil-based alternative for methanol production is the combined reforming using SMR and partial oxidation of methane.[52] This process requires O_2 as input. An exclusively CO_2-based alternative for methanol production is the direct reforming of CO_2 and H_2 to methanol.[7]

3.1.5. Methylene diphenyl diisocyanate (MDI) production

MDI is produced from phosgene and methylenedianiline (MDA). MDA is produced by the reaction of formaldehyde and aniline. Aniline results from the hydrogenation of nitrobenzene. Nitrobenzene is produced by the nitration of benzene with nitric acid. Phosgene is produced by the reaction of carbon monoxide (CO) and chlorine gas. A by-product of the MDI production is hydrochloric acid (HCl). HCl is separated by HCl electrolysis to provide chlorine as feedstock for the phosgenation. HCl electrolysis also provides H_2 which is assumed to be used internally in MDI production.[10]

For our analysis, the production of MDI described above is modeled as a single process based on stoichiometric inputs (formaldehyde, benzene, nitric acid, H_2 and CO) and outputs (MDI). Furthermore, electricity demand for HCl electrolysis is included.

3.1.6. Toluol-2,4-diisocyanate (TDI) production

TDI is produced from phosgene and diaminotoluene (TDA). TDA results from the hydrogenation of dinitrotoluene (DNT). DNT is produced by the nitration of toluene with nitric acid.[10] Phosgene production and HCl recycling via electrolysis are equivalent to the processes in MDI production (see section 3.1.5.).

For our analysis, the production of TDI described above is modeled as a single process based on stoichiometric inputs (toluene, nitric acid and CO) and outputs (TDI and waste). Furthermore, electricity demand for HCl electrolysis is included.

3.1.7. CO and hydrogen (H_2) supply

CO and hydrogen (H_2) are feedstocks for MDI and TDI production. If H_2 from internal HCl electrolysis is used (assumed here, see sections 3.1.5. and 3.1.6.), MDI production requires another 2 mol H_2 per mol CO, whereas TDI does not require additional H_2.[10] We consider the following processes for CO and H_2 supply for MDI and TDI production:

Conventionally, both CO and H_2 are supplied by SMR.[53] Part of the methane can be substituted by CO_2 through the dry reforming of methane (DRM).[11] However, for the same amount of CO, DRM produces less hydrogen compared to SMR. The complete substitution of methane is enabled by the reverse water gas shift (rWGS) reaction. For rWGS, hydrogen and CO_2 are required as feedstock. The rWGS reaction produces only CO (and water as by-product).[54]

3.1.8. Methane supply

Conventionally, the feedstock methane (CH_4) is supplied by natural gas. Methane can also be produced from H_2 and CO_2 through the Sabatier reaction.[55]

An overview of the employed LCA datasets for all processes is given in the supplementary information.

3.2 Optimization model

To rigorously study the environmental potential of utilizing CO_2 in the PUR supply chain, a superstructure-based optimization model is used. The superstructure comprises all processes of the PUR supply chain (cf. section 3.1). The optimization model is used to identify the maximum CO_2 utilization potential (section 3.2.1) and the minimal environmental impacts (section 3.2.2) for the PUR supply chain.

3.2.1. Maximum CO_2 amount in the PUR supply chain

As first step, optimization is carried out maximizing the total amount of CO_2 utilized ($\mathrm{m}_{\mathrm{CO2,feed}}$) to identify the maximum CO_2 utilization potential in the entire PUR supply chain. The amount of PUR produced is set to m_{PUR}=1 kg (functional unit, cf. section 2.2). While the total CO_2 feed ($m_{\mathrm{CO2,feed}}$) is to be maximized for 1 kg PUR, mass and energy balances must be fulfilled across the entire PUR supply chain. This optimization problem can be formulated as so-called linear program (LP):

$$\begin{aligned} &\max_{x} \; m_{\mathrm{CO2,feed}} = d^{T}\,x\,, \\ &\text{s.t.} \quad m_{\mathrm{PUR}} = 1\ \mathrm{kg} \qquad \text{(functional unit)}, \qquad\qquad (1) \\ &\qquad\;\; A\,x = 0 \qquad\qquad \text{(mass and energy balances in supply chain).} \end{aligned}$$

The so-called scaling vector *x* describes which processes are employed and to what extent. The vector *d* describes how much CO_2 is directly utilized in each process. Thus, the overall amount of CO_2 utilized is obtained by $m_{CO2,feed} = d^{T} x$, to be maximized here. The matrix *A* contains all inputs and outputs of the individual processes in the PUR supply chain. Matrix *A* and vector *d* are given explicitly in the supplementary information.

3.2.2. Minimal environmental impact for PUR supply chain: effect of CO2 utilized

To identify minimal environmental impacts for the PUR supply chain, optimization is carried out minimizing the total environmental impacts of all processes required for PUR production. In this paper, we consider the environmental impact categories ‘global warming’ and ‘fossil fuel use’ (cf. section 2.3.). The amount of PUR produced is again set to m_{PUR}=1 kg, and mass and energy balances must be fulfilled across the PUR supply chain. The corresponding optimization problem can be formulated as follows:

$$\begin{aligned} &\max_{x} \quad z = B\,x\,, \\ &\text{s.t.} \quad m_{\text{PUR}} = 1\text{ kg} \qquad \text{(functional unit)}, \qquad\qquad (2)\\ &\qquad\;\; A\,x = 0 \qquad\qquad \text{(mass and energy balances in supply chain).} \end{aligned}$$

The matrix *B* contains the direct environmental impacts of the individual processes in the PUR supply chain. The cradle-to-gate environmental impacts *z* for production of 1 kg PUR are obtained by $z = B\,x$. Matrix *B* is given in the supplementary information.

For the environmental impacts of CO_2 supply, the three cases presented in section 2.4 are analyzed: CO_2 capture from a coal-fired power plant (standard case), CO_2 capture from ambient air (worst case) and an ideal CO_2 source (best case).

Effect of CO_2 utilized. To determine the effect of the amount of CO_2 utilized, the minimization of environmental impacts is repeated for fixed amounts of CO_2 utilized. For this purpose, the amount of CO_2 utilized is varied between zero and $m_{\text{CO2,feed,max}}$. For this analysis, we consider three cases of hydrogen production: (i) conventional steam methane reforming (SMR), (ii) water electrolysis, and (iii) ideal hydrogen production with no environmental impacts at all. The corresponding environmental impacts are given in Table 1.

Table 1 Considered environmental impacts for hydrogen production alternatives.

	Global warming impact ($kg\ CO_2$-eq / $kg\ H_2$)	Fossil depletion impact (kg oil-eq / $kg\ H_2$)
Steam methane reforming	10	5
Water electrolysis*	5	2.5
Ideal H_2 production	0	0

*The environmental impacts for H_2 from water electrolysis depend largely on the electricity source for electrolysis. For production of 1 kg H_2, the electricity demand of electrolysis is about 50 kWh.[54] With this electricity demand, the presented environmental impacts of water electrolysis correspond to environmental impacts of electricity generation of 100 kg CO_2-eq and 50 kg oil-eq per MWh (similar to the grid mix characteristics of Sweden).[35]

Effect of H_2 production alternatives. To analyze the effect of hydrogen production alternatives more rigorously, the environmental impact of hydrogen supply is also varied continuously. For this purpose, the optimization is repeated for the full range of environmental impacts of the considered hydrogen production alternatives, i.e., for global warming impacts from zero to 10 kg CO_2-eq per kg H_2, and for fossil depletion impacts from zero to 5 kg oil-eq per kg H_2.

4. Results

In this section, we present the maximum CO_2 utilization potential and minimal environmental impacts for PUR production. In the first scenario, we consider only direct utilization of CO_2 for polycarbonate (PC) units in polyol production and indirect CO_2 utilization in the isocyanate supply chain. The utilization of poly oxymethylen (POM) units as polyol building block is not permitted, regardless whether POM is produced from fossil or CO_2-based feedstocks. This first scenario ('without POM') includes technically feasible CO_2 utilization options. The utilization of POM for polyols and PUR is a promising approach; however, utilization of POM in polyols is still in the research phase.[49] As second scenario, as future outlook, we consider all CO_2 utilization options in the PUR supply chain including fossil- and CO_2-based POM units for polyols (scenario 'with POM').

4.1 Maximum CO_2 utilization amount in the PUR supply chain

The maximum CO_2 utilization potential refers to the maximum amount of CO_2 utilized in the entire PUR supply chain. The amount of CO_2 utilized can be greater than 1 kg CO_2 for production of 1 kg PUR since it is simply the total amount of CO_2 utilized in the PUR supply chain; it does not refer to the amount of CO_2 incorporated or the CO_2 content in the final PUR. The maximum CO_2 amount in the PUR supply chain is presented in Figure 2 for both flexible and rigid PUR foams.

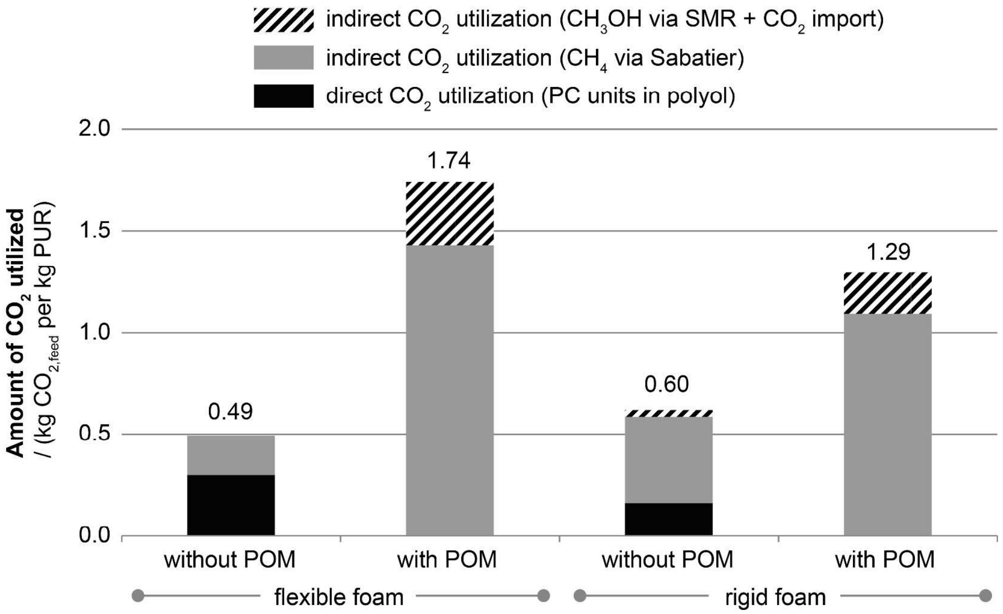

Figure 2 CO_2 utilization potential in PUR supply chain as amount of CO_2 utilized per kg PUR. Scenario 'without POM' does not permit utilization of poly oxymethylen (POM) units as polyol building block; all other CO_2 utilization options in the PUR supply chain are possible. Scenario 'with POM' alllows all CO_2 utilization options in the PUR supply chain including fossil- and CO_2-based POM units for polyols.

The maximum potential for direct CO_2 utilization in PC units in polyols is about twice as large in flexible PUR foam compared to rigid PUR foam: in flexible foam, up to 0.30 kg CO_2 per kg PUR can be utilized directly in polyols, while 0.16 kg CO_2 per kg PUR can be utilized for rigid foam. The larger potential for flexible foam is due to the typically higher mass content of polyols in flexible foams compared to rigid foams (cf. section 3.1.1 and 3.1.2).

If POM units are not allowed for polyol production, the maximum CO_2 utilization potential can still be increased by indirect CO_2 utilization in the isocyanate supply chain: the indirect CO_2 utilization potential is 0.20 kg CO_2 and 0.46 kg CO_2 per kg PUR for flexible and rigid foams, respectively. For flexible foams, the indirectly utilized CO_2 is completely converted to methane via the Sabatier reaction; methane is then converted via steam methane reforming (SMR) to CO and H_2 for isocyanate production. For rigid foams, 93 % of the indirectly utilized CO_2 are converted to methane, of which 69 % are converted via SMR to CO and H_2 and 31 % are converted via SMR (with CO_2 import) to methanol for subsequent formaldehyde and MDI production. Methanol production via SMR (with CO_2 import) utilizes the remaining 7 % of the indirectly utilized CO_2.

The global maximum CO_2 utilization potential can be achieved if POM units are allowed in polyol synthesis. For flexible foams, up to 1.74 kg CO_2 can be utilized, exclusively through indirect CO_2 utilization. 82 % of the indirectly utilized CO_2 are converted via the Sabatier reaction to methane, of which 14 % are converted via SMR to CO and H_2 and 86 % are converted via SMR (with CO_2 import) to methanol for subsequent formaldehyde and POM production. Methanol production via SMR (with CO_2 import) utilizes the remaining 18 % of the indirectly utilized CO_2. For rigid foams, up to 1.29 kg CO_2 can be utilized, again exclusively through indirect CO_2 utilization. 84 % of the indirectly utilized CO_2 are converted via the Sabatier reaction to methane, of which 27 % are converted via SMR to CO and H_2 and 73 % are converted via SMR (with CO_2 import) to methanol. Methanol production via SMR (with CO_2 import) also utilizes the remaining 16 % of the indirectly utilized CO_2. The produced methanol is converted to formaldehyde for subsequent POM (84 %) and MDI production (16 %).

In the following part of this paper, we focus on CO_2 utilization for flexible PUR foams. Corresponding results for rigid PUR foams are presented in the supplementary information.

4.2 Minimal environmental impact for PUR supply chain: effect of CO_2 utilization amount

In the previous section, maximum CO_2 utilization amounts have been identified. Since it might not be environmentally favorable to utilize as much CO_2 as possible, we now identify the minimal environmental impacts for PUR production for variable amounts of CO_2 utilized as described in section 3.2.2.

Figure 3 shows minimal global warming impacts for flexible PUR foams with and without POM units. For foams without POM units, increasing the amount of CO_2 utilized generally leads to a reduction of CO_2 emissions compared to conventional foams from fossil-based polyether (PE) polyols and TDI. In particular, the direct utilization of CO_2 in polycarbonate (PC) units of polyols allows for a reduction of 3.7 - 4.1 kg CO_2-eq per kg CO_2 utilized. The CO_2 reductions stem from

CO_2 capture (0 - 0.84 kg CO_2-eq per kg CO_2 utilized, cf. section 2.4) and from substitution of emission-intensive epoxides (3.1 kg CO_2-eq / kg CO_2 utilized; cf. von der Assen *et al.*, 2014[14]. The potential to further reduce CO_2 emissions through indirect CO_2 utilization depends on the emissions from hydrogen production. Nevertheless, for all hydrogen production alternatives, the CO_2 reduction potential for indirect CO_2 utilization is very small in flexible PUR foams without POM units.

If POM units can be incorporated into polyols for flexible PUR foams, the potential to reduce CO_2 emissions is much larger for two reasons: first, even fossil-based production of POM units causes much lower CO_2 emissions than production of conventional PE units (cf. Figure 3 for $m_{CO2,feed}=0$). Second, the CO_2 utilization potential is much higher for polyols with POM units (cf. section 4.1). More CO_2 utilization reduces CO_2 emissions at the CO_2 source by CO_2 capture. However, for indirect CO_2 utilization, POM units require provision of hydrogen as feedstock for methanol synthesis. Whether indirect CO_2 utilization for PUR with POM actually reduces CO_2 emissions depends therefore largely on the emissions from hydrogen production: for ideal hydrogen production with no CO_2 emissions, the computed minimal CO_2 emissions for PUR production strictly decrease with increasing amount of CO_2 utilized. For hydrogen from water electrolysis, the computed minimal CO_2 emissions are almost constant for variable amounts of CO_2 utilized. For today's conventional hydrogen production via SMR, the computed minimal CO_2 emissions decrease up to a CO_2 utilization amount of 0.35 kg CO_2. Further increasing the CO_2 utilization amount increases CO_2 emissions of PUR production. Thus, increasing the amount of CO_2 utilized then leads to additional CO_2 emissions.

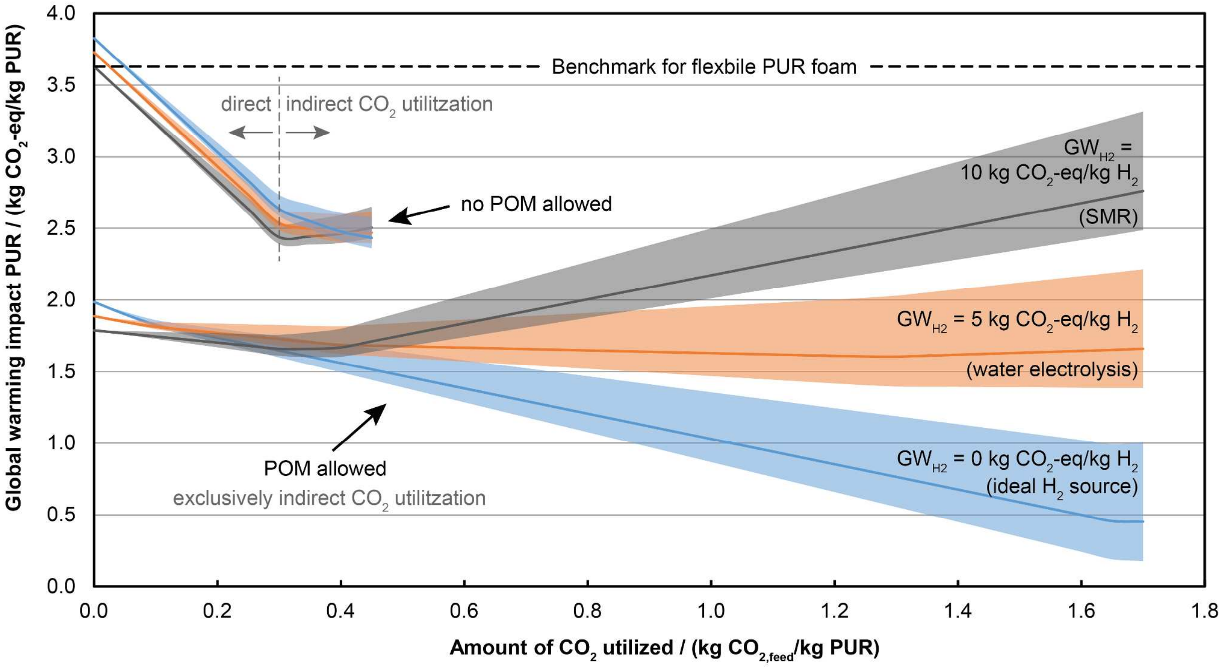

Figure 3 Minimum global warming impact for flexible PUR foams for variable amounts of CO_2 utilized. The transparent areas indicate the range for alternative CO_2 sources: lower bounds correspond to an ideal source, upper bounds correspond to CO_2 capture from ambient air, and the solid lines correspond to CO_2 capture from a coal-fired power plant.

Figure 3 also shows that utilization of 1 kg CO_2 does not lead to a reduction of 1 kg CO_2 emissions.[3,56] In some cases, utilization of CO_2 even increases CO_2 emissions. For this reason, the overall minimum CO_2 emissions do not necessarily occur for the maximum amount of CO_2 utilized. In most cases, CO_2 utilization reduces CO_2 emissions. Here, some processes reduce more CO_2 emissions per CO_2 utilized than others. For example, the direct utilization of CO_2 for PC units in polyols allows for the largest CO_2 reduction per amount of CO_2 utilized. However, since CO_2 is not a restricted resource, CO_2 should be utilized not only in process with largest CO_2 reductions but instead in such amounts that the overall minimum of CO_2 emissions is reached. The overall minimum for flexible PUR foams with POM units depends largely on the hydrogen production alternative.

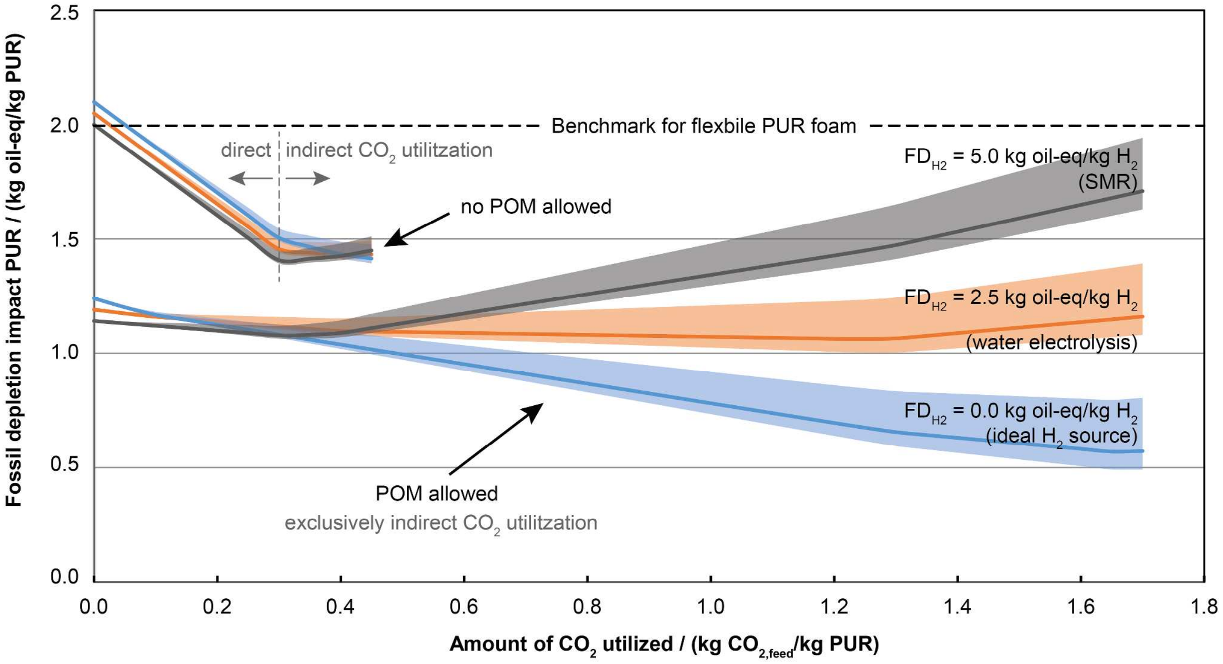

Figure 4 Minimum fossil depletion for flexible PUR foams for variable amounts of CO_2 utilized. The transparent areas indicate the range for alternative CO_2 sources: lower bounds correspond to an ideal source, upper bounds correspond to CO_2 capture from ambient air, and the solid lines correspond to CO_2 capture from a coal-fired power plant.

In addition to global warming impacts, we identified the minimal fossil fuel use in flexible PUR foam for variable CO_2 utilization amounts. The qualitative behavior is very similar for global warming impacts and fossil fuel use, c.f. Figure 3 and Figure 4. Thus, we focus on global warming impacts in the following. The corresponding results for fossil fuel use are given in the supplementary information.

4.3 Minimal environmental impact for PUR supply chain: effect of H_2 production alternatives

In the previous section, three discrete cases for hydrogen production have been analyzed in the context of minimal environmental impacts for CO_2 utilization in PUR production. Environmentally favorable hydrogen production has been identified as important factor to increase the amount of CO_2 utilized for environmentally favorable PUR production. In contrast to the three discrete cases, this section investigates the effects of the environmental impacts of hydrogen production in more detail. In the main article, impacts on global warming are shown; the fossil fuel use is presented in the supplementary information.

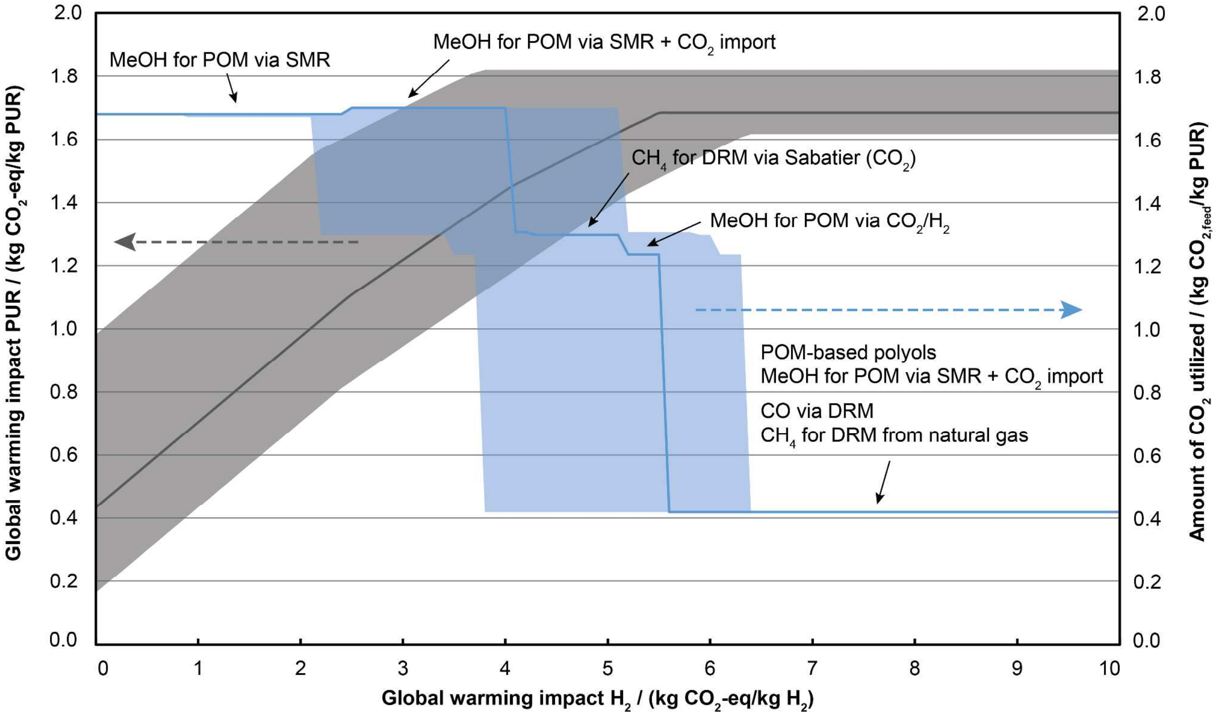

Figure 5 Minimum global warming impacts for flexible PUR foam for a variable global warming impact of hydrogen production. The solid lines refer to CO_2 captured from a coal-fired power plant. The lower bound of the global warming impact of PUR and the upper bound of the CO_2 utilization amount refer to an ideal CO_2 source (best case). The upper bound of the global warming impact of PUR and the lower bound of the CO_2 utilization amount refer to CO_2 capture from ambient air (worst case).

Figure 5 shows that the global warming impact of flexible PUR foam can be reduced from 1.68 to 0.43 kg CO_2-eq per kg PUR (for CO_2 captured from a coal-fired power plant, solid line) if the global warming impact of H_2 production decreases from 10 to 0 kg CO_2-eq per kg H_2. For this decrease of the global warming impact of H_2 production, the amount of CO_2 utilized increases from 0.42 to 1.68 kg CO_2 per kg PUR (right y-axis in Figure 5). In particular, the amount of CO_2 utilized increases sharply if the global warming impact of H_2 production drops below 5.6 kg CO_2-eq per kg H_2, and even further for a drop below 4.1 kg CO_2-eq per kg H_2. The first increase in CO_2 utilization is mainly due to a switch in methanol production from SMR + CO_2 import to entirely CO_2-based methanol production. Before the first increase (above 5.6 kg CO_2-eq per kg H_2), no hydrogen is utilized for PUR production and thus, the global warming impact of PUR is independent from the global warming impact of H_2 production. The second increase is mainly due to a switch from methane from natural gas to methane from CO_2 via the Sabatier reaction.

The analysis in this section highlights that hydrogen production with low environmental impacts is important for the indirect utilization of CO_2 in the PUR supply chain.

5. Conclusions

Many options exist for utilization of CO_2 in the polyurethane (PUR) supply chain. In this paper, we present a systematic exploration and environmental evaluation of all direct and indirect CO_2 utilization options for PUR production. Our analysis shows that direct CO_2 utilization for polycarbonate units in polyols is limited in the amount of CO_2 utilized; however, direct CO_2 utilization allows for large reductions of up to 4 kg CO_2-eq per kg CO_2 utilized. The CO_2 utilization amount can be increased by indirect CO_2 utilization for reduction to carbon monoxide in isocyanate production. However, the environmental potential of indirect CO_2 utilization in the isocyanate supply chain is rather small. Both the CO_2 utilization amount and the reduction of environmental impacts can be largely increased through indirect CO_2 utilization if poly oxymethylen (POM) units can be incorporated into polyols. In this case, large environmental impact reductions are already possible for fossil-based POM production. Additional environmental benefits from CO_2-based POM production depend largely on the required hydrogen (H_2) source. Current H_2 production via steam methane reforming (SMR) does not allow for additional reductions of environmental impacts. Even worse, for H_2 from SMR, increasing the amount of CO_2 utilized can even lead to additional CO_2 emissions. Thus, utilizing as much CO_2 in the PUR supply chain as possible is always not environmentally optimal. Instead, minimal environmental impacts are achieved for CO_2 utilization amounts below the maximum possible utilization amount. To still exploit the full CO_2 utilization potential for environmental impact reduction in PUR production with POM units, environmentally friendly H_2 production with CO_2 emissions below 4 kg CO_2-eq per kg H_2 is required. The present study has neglected many practical challenges for chemistry to be able to explore the full theoretical design space for environmentally optimal polyurethane production. Our work aims at inspiring future research on sustainable CO_2 utilization for polyurethanes.

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