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

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Received 8th May 2015, Accepted 8th June 2015

DOI: 10.1039/c5fd00067j

Potential environmental benefits have been identified for the utilization of carbon dioxide (CO₂) as a feedstock for polyurethanes (PUR). CO₂ can be utilized in the PUR supply chain in a wide variety of ways ranging from direct CO₂ utilization for polyols as a PUR precursor, to indirect CO₂ 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 CO₂ 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 CO₂ for polyols allows for large specific impact reductions of up to 4 kg CO₂-eq. and 2 kg oil-eq. per kg CO₂ utilized, but the amounts of CO₂ that can be utilized are limited to 0.30 kg CO₂ per kg PUR. The amount of CO₂ utilized can be increased to up to 1.7 kg CO₂ per kg PUR by indirect CO₂ utilization in the PUR supply chain. Indirect CO₂ utilization requires hydrogen (H₂). The environmental impacts of H₂ production strongly affect the impact of indirect CO₂ utilization in PUR. To achieve optimal environmental performance under the current fossil-based H₂ generation, PUR production can only utilize much less CO₂ than theoretically possible. Thus, utilizing as much CO₂ in the PUR supply chain as possible is not always environmentally optimal. Clean H₂ production is required to exploit the full CO₂ utilization potential for environmental impact reduction in PUR production.

1. Introduction

The use of fossil fuels inherently leads to carbon dioxide (CO₂) emissions. Aiming to reduce both CO₂ emissions and fossil fuel use, CO₂ can be captured and utilized as a feedstock for fuels, materials and chemicals.^{1–3} In particular, CO₂ has

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† Electronic supplementary information (ESI) available: ESI contains process data for polyurethane supply chain and additional figures for flexible and rigid polyurethane foams. See DOI: 10.1039/c5fd00067j

recently been successfully utilized in the production of polyurethanes (PUR), resulting in both lower CO₂ emissions and lower use of fossil fuels than conventional PUR.^{4–6}

PUR production is particularly well suited for incorporation of CO₂ as PUR allows for both direct and indirect CO₂ utilization as follows: polyurethanes consist of polyols and isocyanates. In polyol synthesis, the CO₂ 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 CO₂ utilization in polycarbonate units of the polyols, CO₂ can also be utilized indirectly in upstream processes of the polyol supply chain. For example, CO₂ can be converted to methanol⁷ and subsequently to formaldehyde, which constitutes a potential monomer for polyols.^{4,9}

As well as direct and indirect CO₂ utilization for polyols, CO₂ can also be used in the production of isocyanates. While the direct utilization of CO₂ 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 CO₂.¹¹

Thus, a wide variety of options exist for the direct and indirect utilization of CO₂ in the supply chain of PUR. However, a systematic exploration and environmental evaluation of all direct and indirect CO₂ utilization options for PUR is missing. Therefore, the first goal of this article is to identify the total CO₂ utilization potential in the entire PUR supply chain. In other words, we identify the maximum amount of mass CO₂ utilized per mass PUR.

Intuitively, utilizing as much CO₂ as possible might seem environmentally most favorable. However, the energy requirements for both CO₂ capture and utilization (CCU) can lead to additional CO₂ emissions, fossil fuel use and other environmental impacts.¹² Thus, it is not always environmentally most reasonable to utilize as much CO₂ as possible. Instead, only those CO₂-based processes should be employed that allow for reductions of environmental impacts. The environmental impacts of a process 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. Application of LCA to CCU processes is still very limited as recently reviewed.¹³ For the application of LCA to CO₂ utilization, specific guidelines have recently been developed.^{12,14} Based on these guidelines, the second goal of this article is to analyze which CO₂-based processes in the PUR supply chain allow for the largest reduction of CO₂ emissions and fossil fuel use. From this analysis, we determine the minimum CO₂ emissions and minimum fossil fuel use for the PUR supply chain.

Indirect CO₂ utilization processes usually require cleavage of C=O bonds, often *via* hydrogenation.^{15–18} Whether CO₂ hydrogenation is environmentally favorable compared to a fossil-based benchmark depends strongly on the provision of hydrogen (H₂).^{19,20} Conventional production of H₂ *via* steam methane reforming is typically energy- and emission-intensive.²¹ The impacts of H₂ 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 CO₂ utilization in the PUR supply chain as a function of the environmental impacts of H₂ production. Based on this analysis, we determine threshold values for the environmental impacts of

H₂ production that are tipping points for utilization of major amounts of CO₂ for PUR production.

The article is structured as follows. In Section 2, we review specific guidelines for the application of LCA for CO₂ utilization in polymers and state the goal and scope for the present LCA study of CO₂-based PUR. In Section 3, we present the considered PUR supply chain including conventional and CO₂-based processes. Furthermore, we introduce the optimization model using linear programming for the analysis of maximum amounts of CO₂ utilization and minimal environmental impacts. In Section 4, we present our findings, *i.e.*, the maximum amounts of utilized CO₂ per kg PUR, the CO₂-based processes with the largest environmental benefits, and the minimum environmental impacts of the PUR supply chain for H₂ production alternatives. Finally, in Section 5, conclusions are drawn for the utilization of CO₂ in the PUR supply chain.

2. LCA for CO₂ utilization in PUR production

Both capture and utilization of CO₂ typically require energy whose provision is often based on fossil fuels and thus causes indirect CO₂ emissions. For example, post-combustion CO₂ 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 CO₂ molecule usually requires direct energy input or high-energetic co-reactants such as epoxides or hydrogen (H₂).²⁴ Thus, the intuitively expected environmental benefits of CO₂ 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 CO₂-based polyol synthesis.²⁸ Relevant aspects of these guidelines are reviewed and specified for the present context of CO₂ 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, this 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 CO₂-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, chemical limitations for the incorporation of CO₂ are taken into account (*cf.* Section 3.1). Still, our study neglects many practical constraints on PUR production to be able to explore the

full design space and to provide inspiration to chemists facing the practical challenges involved. 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 the production of propylene oxide generate co-products such as *tert*-butyl alcohol or styrol.²⁸ In the context of CO₂-based PUR, the 'production' of CO₂ via CO₂ capture from point-sources is also coupled to production of the point-sources' primary product: for example, power plants with CO₂ capture provide electricity as a 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. As 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 methods of *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 credit 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 recommended³⁴ 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 the production of excess hydrogen (H₂), heat and electricity from the CO₂ supplying power plant. 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') aggregates CO₂ and other greenhouse gas emissions according to their global warming potential in CO₂-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 CO₂ Capture and Utilization (CCU) aims at reducing CO₂ 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 CO₂ 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 CO₂ utilization in PUR production with respect to global warming impacts and fossil fuel use.

2.4 CO₂ sources and CO₂ capture

CO₂ capture from diluted CO₂ sources requires energy for the separation of CO₂ from other gases. Moreover, CO₂ capture requires operating materials such as capture solvents, and process technologies such as absorption and desorption columns. All of these efforts for CO₂ capture are typically associated with fossil fuel use and thus CO₂ emissions. Therefore, the CO₂ emission reduction of CO₂ capture is lower than 1 kg CO₂-eq. per kg CO_{2,feed}. Here, CO₂-eq. refers to CO₂ emissions and other greenhouse gas emissions, and CO_{2,feed} refers to the captured and subsequently utilized CO₂.

In this work, we consider a coal-fired power plant as a standard CO₂ source. For the considered coal-fired power plant, CO₂ capture can reduce CO₂ emissions by 0.84 kg CO₂-eq. and increases fossil fuel use by 0.05 kg oil-eq. per kg CO_{2,feed} compared to a power plant without CO₂ capture.⁴⁴ As the worst-case scenario, we also consider CO₂ capture from ambient air with CO₂ emission reductions of 0.51 kg CO₂-eq. and fossil fuel use of 0.18 kg oil-eq. per kg CO_{2,feed}.⁴⁴ As the best-case scenario, we consider a hypothetical, ideal CO₂ source with CO₂ emission reductions of 1 kg CO₂-eq. per kg CO₂ captured and no increase in fossil fuel use. The best-case scenario corresponds to a CO₂ source which can be readily used in the CO₂ conversion but is vented to the atmosphere today.

2.5 Temporary carbon storage in PUR

Polyurethanes have a lifetime of several decades. Incorporating CO₂ 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 CO₂-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 CO₂-based PUR syntheses to a so-called cradle-to-gate scope. In this case, a climate benefit can only be achieved if CO₂-based PUR synthesis causes fewer emissions than conventional synthesis. A climate benefit from temporary carbon storage cannot be expected for CO₂-based PUR synthesis compared to conventional PUR synthesis.

If, however, CO₂ 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 CO₂ emissions constitute relevant changes for assessing the effect of temporary carbon storage in LCA: a longer lifetime can shift EOL CO₂ emissions into the future. As a rule of thumb, this shift of CO₂ emissions can

reduce the global warming impact of EOL emissions by about 1% for each year of lifetime extension.[‡] Total EOL CO₂ emissions account for about one third of the total CO₂-eq. emissions in the 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 CO₂ incorporation on EOL emissions: on the one hand, CO₂ utilization in PUR typically lowers the C content in PUR and thus lowers EOL CO₂ 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 CO₂ emissions.

For the above mentioned reasons, the climate mitigation effect of temporary carbon storage of CO₂ 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 using available time-dependent global warming metrics.¹²

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 Fig. 1. In the main article, we focus on the production of flexible PUR foams. Results for rigid PUR foams are presented in the ESI.[†] In the following, the considered production steps are briefly described.

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 an indirect foam blowing agent that reacts with TDI to CO₂ as the actual blowing agent. This CO₂ is directly released to the atmosphere. We consider a fixed mass ratio of TDI and polyol of $m_{\text{TDI}}/m_{\text{polyol}} = 0.4$.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 the foam blowing agent although CO₂ can be used as an alternative or co-blowing agent.⁴⁸ We consider a fixed mass ratio of MDI and polyol of $m_{\text{MDI}}/m_{\text{polyol}} = 1.6$.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

[‡] 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.³⁷

Fig. 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.

CO_2 which co-polymerizes with PO to polycarbonate units.⁵ Furthermore, poly oxymethylene (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 an 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 modelled as a single process based on stoichiometric inputs (formaldehyde, benzene, nitric acid, H_2 and CO) and outputs (MDI). Furthermore, the 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 modelled as a single process based on stoichiometric inputs (toluene, nitric acid and CO) and the main output (TDI). Furthermore, electricity demand for HCl electrolysis is included.

3.1.7 CO and hydrogen (H₂) supply. CO and hydrogen (H₂) are feedstocks for MDI and TDI production. If H₂ from internal HCl electrolysis is used (assumed here, see Sections 3.1.5 and 3.1.6), MDI production requires another 2 mol H₂ per mol CO, whereas TDI does not require additional H₂.¹⁰ We consider the following processes for CO and H₂ supply for MDI and TDI production.

Conventionally, both CO and H₂ are supplied by SMR.⁵³ Part of the methane can be substituted by CO₂ 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 CO₂ are required as feedstocks. The rWGS reaction produces only CO (and water as a by-product).⁵⁴

3.1.8 Methane supply. Conventionally, the feedstock methane (CH₄) is supplied by natural gas. Methane can also be produced from H₂ and CO₂ through the Sabatier reaction.⁵⁵

An overview of the employed LCA datasets for all processes is given in the ESI.†

3.2 Optimization model

To rigorously study the environmental potential of utilizing CO₂ 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 CO₂ utilization potential (Section 3.2.1) and the minimal environmental impacts (Section 3.2.2) for the PUR supply chain.

3.2.1 Maximum CO₂ amount in the PUR supply chain. As the first step, optimization is carried out maximizing the total amount of CO₂ utilized ($m_{\text{CO}_2, \text{feed}}$) to identify the maximum CO₂ utilization potential in the entire PUR supply chain. The amount of PUR produced is set to $m_{\text{PUR}} = 1$ kg in the functional unit vector f (*cf.* Section 2.1). While the total CO₂ feed ($m_{\text{CO}_2, \text{feed}}$) 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 a so-called linear program (LP):

$$\begin{aligned} \max_s \quad & m_{\text{CO}_2, \text{feed}} = d^T s, \\ \text{s.t.} \quad & A s = f \quad (\text{mass and energy balances in supply chain}). \end{aligned} \quad (1)$$

The so-called scaling vector s describes which processes are employed and to what extent. The vector d describes how much CO₂ is directly utilized in each process. Thus, the overall amount of CO₂ utilized is obtained by $m_{\text{CO}_2, \text{feed}} = d^T s$, to be maximized here. The matrix A contains all inputs and outputs of the individual

processes in the PUR supply chain. Matrix A and vectors d and f are given explicitly in the ESI.†

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 $m_{\text{PUR}} = 1$ kg, and mass and energy balances must be fulfilled across the PUR supply chain. The corresponding optimization problem can be formulated as follows:

$$\begin{aligned} \min_s \quad & g = B s, \\ \text{s.t.} \quad & A s = f \quad (\text{mass and energy balances in supply chain}). \end{aligned} \quad (2)$$

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 $z = Bx$. Matrix B is given in the ESI.†

For the environmental impacts of CO₂ supply, the three cases presented in Section 2.4 are analyzed: CO₂ capture from a coal-fired power plant (standard case), CO₂ capture from ambient air (worst case) and an ideal CO₂ source (best case).

Effect of CO₂ utilized. To determine the effect of the amount of CO₂ utilized, the minimization of environmental impacts is repeated for fixed amounts of CO₂ utilized. For this purpose, the amount of CO₂ utilized is varied between zero and $m_{\text{CO}_2, \text{feed}, \text{max}}$. 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 for H₂ are given in Table 1.

Effect of H₂ 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 CO₂-eq. per kg H₂, and for fossil depletion impacts from zero to 5 kg oil-eq. per kg H₂.

Table 1 Considered environmental impacts for hydrogen production alternatives

	Global warming impact (kg CO ₂ -eq. per kg H ₂)	Fossil depletion impact (kg oil-eq. per kg H ₂)
Steam methane reforming ³⁵	10	5
Water electrolysis ^a	5	2.5
Ideal H ₂ production	0	0

^a The environmental impacts for H₂ from water electrolysis depend largely on the electricity source for electrolysis. For production of 1 kg H₂, the electricity demand of electrolysis is about 50 kW h.⁵⁴ With this electricity demand, the presented environmental impacts of water electrolysis correspond to environmental impacts of electricity generation of 100 kg CO₂-eq. and 50 kg oil-eq. per MWh (similar to the grid mix characteristics of Sweden).³⁵

4. Results

In this section, we present the maximum CO₂ utilization potential and minimal environmental impacts for PUR production. In the first scenario, we consider only direct utilization of CO₂ for polycarbonate (PC) units in polyol production and indirect CO₂ utilization in the isocyanate supply chain. The utilization of poly oxymethylene (POM) units as polyol building blocks is not permitted, regardless of whether POM is produced from fossil or CO₂-based feedstocks. This first scenario ('without POM') includes technically feasible CO₂ 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 a second scenario, and for future outlook, we consider all CO₂ utilization options in the PUR supply chain including fossil- and CO₂-based POM units for polyols (scenario 'with POM').

4.1 Maximum CO₂ utilization amount in the PUR supply chain

The maximum CO₂ utilization potential refers to the maximum amount of CO₂ utilized in the entire PUR supply chain. The amount of CO₂ utilized can be greater than 1 kg CO₂ for production of 1 kg PUR since it is simply the total amount of CO₂ utilized in the PUR supply chain; it does not refer to the amount of CO₂ incorporated or the CO₂ content in the final PUR. The maximum CO₂ amount in the PUR supply chain is presented in Fig. 2 for both flexible and rigid PUR foams.

The maximum potential for direct CO₂ 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 CO₂ per kg PUR can be utilized directly in polyols, while 0.16 kg CO₂ 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).

Fig. 2 CO₂ utilization potential in the PUR supply chain as the amount of CO₂ utilized per kg PUR. Scenario 'without POM' does not permit utilization of poly oxymethylene (POM) units as polyol building blocks; all other CO₂ utilization options in the PUR supply chain are possible. Scenario 'with POM' allows all CO₂ utilization options in the PUR supply chain including fossil- and CO₂-based POM units for polyols.

If POM units are not allowed for polyol production, the maximum CO₂ utilization potential can still be increased by indirect CO₂ utilization in the isocyanate supply chain: the indirect CO₂ utilization potential is 0.20 kg CO₂ and 0.46 kg CO₂ per kg PUR for flexible and rigid foams, respectively. For flexible foams, the indirectly utilized CO₂ is completely converted to methane *via* the Sabatier reaction; methane is then converted *via* steam methane reforming (SMR) to CO and H₂ for isocyanate production. For rigid foams, 93% of the indirectly utilized CO₂ is converted to methane, of which 69% is converted *via* SMR to CO and H₂ and 31% is converted *via* SMR (with CO₂ import) to methanol for subsequent formaldehyde and MDI production. Methanol production *via* SMR (with CO₂ import) utilizes the remaining 7% of the indirectly utilized CO₂.

The global maximum CO₂ utilization potential can be achieved if POM units are allowed in polyol synthesis. For flexible foams, up to 1.74 kg CO₂ can be utilized, exclusively through indirect CO₂ utilization. 82% of the indirectly utilized CO₂ are converted *via* the Sabatier reaction to methane, of which 14% are converted *via* SMR to CO and H₂ and 86% are converted *via* SMR (with CO₂ import) to methanol for subsequent formaldehyde and POM production. Methanol production *via* SMR (with CO₂ import) utilizes the remaining 18% of the indirectly utilized CO₂. For rigid foams, up to 1.29 kg CO₂ can be utilized, again exclusively through indirect CO₂ utilization. 84% of the indirectly utilized CO₂ is converted *via* the Sabatier reaction to methane, of which 27% is converted *via* SMR to CO and H₂ and 73% is converted *via* SMR (with CO₂ import) to methanol. Methanol production *via* SMR (with CO₂ import) also utilizes the remaining 16% of the indirectly utilized CO₂. 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 CO₂ utilization for flexible PUR foams. The corresponding results for rigid PUR foams are presented in the ESI.†

4.2 Minimal environmental impact for PUR supply chain: effect of CO₂ utilization amount

In the previous section, maximum CO₂ utilization amounts have been identified. Since it might not be environmentally favorable to utilize as much CO₂ as possible, we now identify the minimal environmental impacts for PUR production for variable amounts of CO₂ utilized as described in Section 3.2.2.

Fig. 3 shows minimal global warming impacts for flexible PUR foams with and without POM units. For foams without POM units, increasing the amount of CO₂ utilized generally leads to a reduction of CO₂ emissions compared to conventional foams from fossil-based polyether (PE) polyols and TDI. In particular, the direct utilization of CO₂ in polycarbonate (PC) units of polyols allows for a reduction of 3.7–4.1 kg CO₂-eq. per kg CO₂ utilized. The CO₂ reductions stem from CO₂ capture (0–0.84 kg CO₂-eq. per kg CO₂ utilized, *cf.* Section 2.4) and from substitution of emission-intensive epoxides (3.1 kg CO₂-eq. per kg CO₂ utilized); *cf.* von der Assen *et al.*, 2014.¹⁴ The potential to further reduce CO₂ emissions through indirect CO₂ utilization depends on the emissions from hydrogen production. Nevertheless, for all hydrogen production alternatives, the CO₂ reduction potential for indirect CO₂ 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 CO₂ emissions is much larger for two reasons: first, even

Fig. 3 Minimum global warming impact for flexible PUR foams for variable amounts of CO₂ utilized. The transparent areas indicate the range for alternative CO₂ sources: lower bounds correspond to an ideal source, upper bounds correspond to CO₂ capture from ambient air, and the solid lines correspond to CO₂ capture from a coal-fired power plant.

fossil-based production of POM units causes much lower CO₂ emissions than production of conventional PE units (*cf.* Fig. 3 for $m_{\text{CO}_2, \text{feed}} = 0$). Second, the CO₂ utilization potential is much higher for polyols with POM units (*cf.* Section 4.1). More CO₂ utilization reduces CO₂ emissions at the CO₂ source by CO₂ capture. However, for indirect CO₂ utilization, POM units require provision of hydrogen as a feedstock for methanol synthesis. Whether indirect CO₂ utilization for PUR with POM actually reduces CO₂ emissions therefore depends largely on the emissions from hydrogen production: for ideal hydrogen production with no CO₂ emissions, the computed minimal CO₂ emissions for PUR production strictly decrease with increasing amounts of CO₂ utilized. For hydrogen from water electrolysis, the computed minimal CO₂ emissions are almost constant for variable amounts of CO₂ utilized. For today's conventional hydrogen production *via* SMR, the computed minimal CO₂ emissions decrease up to a CO₂ utilization amount of 0.35 kg CO₂. Further increasing the CO₂ utilization amount increases CO₂ emissions of PUR production. Thus, increasing the amount of CO₂ utilized then leads to additional CO₂ emissions.

Fig. 3 also shows that utilization of 1 kg CO₂ does not lead to a reduction of 1 kg CO₂ emissions.^{3,56} In some cases, utilization of CO₂ even increases CO₂ emissions. For this reason, the overall minimum CO₂ emissions do not necessarily occur for the maximum amount of CO₂ utilized. In most cases, CO₂ utilization reduces CO₂ emissions. Here, some processes reduce more CO₂ emissions per CO₂ utilized than others. For example, the direct utilization of CO₂ for PC units in polyols allows for the largest CO₂ reduction per amount of CO₂ utilized. However, since CO₂ is not a restricted resource, CO₂ should be utilized not only in processes with the largest CO₂ reductions but instead in such amounts that the overall minimum of CO₂ emissions is reached. The overall minimum for flexible PUR foams with POM units depends largely on the hydrogen production alternative.

In addition to global warming impacts, we identified the minimal fossil fuel use in flexible PUR foam for variable CO₂ utilization amounts. The qualitative behavior is very similar for global warming impacts and fossil fuel use, *cf.* Fig. 3 and 4. Thus, we focus on global warming impacts in the following. The corresponding results for fossil fuel use are given in the ESI.[†]

4.3 Minimal environmental impact for the PUR supply chain: effect of H₂ production alternatives

In the previous section, three distinct cases for hydrogen production have been analyzed in the context of minimal environmental impacts for CO₂ utilization in PUR production. Environmentally favorable hydrogen production has been identified as an important factor to increase the amount of CO₂ 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 ESI.[†]

Fig. 5 shows that the global warming impact of flexible PUR foam can be reduced from 1.68 to 0.43 kg CO₂-eq. per kg PUR (for CO₂ captured from a coal-fired power plant, solid line) if the global warming impact of H₂ production decreases from 10 to 0 kg CO₂-eq. per kg H₂. For this decrease in global warming impact of H₂ production, the amount of CO₂ utilized increases from 0.42 to 1.68 kg CO₂ per kg PUR (right y-axis in Fig. 5). In particular, the amount of CO₂ utilized increases sharply if the global warming impact of H₂ production drops below 5.6 kg CO₂-eq. per kg H₂, and even further for a drop below 4.1 kg CO₂-eq. per kg H₂. The first increase in CO₂ utilization is mainly due to a switch in methanol production from SMR + CO₂ import to entirely CO₂-based methanol production. Before the first increase (above 5.6 kg CO₂-eq. per kg H₂), no hydrogen

Fig. 4 Minimum fossil depletion for flexible PUR foams for variable amounts of CO₂ utilized. The transparent areas indicate the range for alternative CO₂ sources: lower bounds correspond to an ideal source, upper bounds correspond to CO₂ capture from ambient air, and the solid lines correspond to CO₂ capture from a coal-fired power plant.

Fig. 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).

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 the 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 oxymethylene (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 H₂ from SMR, increasing the amount of CO₂ utilized can even lead to additional CO₂ emissions. Thus, utilizing as much CO₂ in the PUR supply chain as possible is not always environmentally optimal. Instead, minimal environmental impacts are achieved for CO₂ utilization amounts below the maximum possible utilization amount. To still exploit the full CO₂ utilization potential for environmental impact reduction in PUR production with POM units, environmentally friendly H₂ production with CO₂ emissions below 4 kg CO₂-eq. per kg H₂ is required. The present study has neglected many practical challenges for researchers to be able to explore the full theoretical design space for environmentally optimal polyurethane production. Our work aims at inspiring future research on sustainable CO₂ utilization for polyurethanes.

Acknowledgements

Niklas von der Assen acknowledges financial support by the German Federal Ministry of Education and Research (BMBF) (Dream Polymers – Sustainable pathways to new polymers, Grant 033RC1104B). Niklas von der Assen, André Sternberg and Arne Kätelhön acknowledge financial support by the European Institute of Innovation & Technology, Climate Knowledge and Innovation Community (EIT Climate-KIC).

References

- 1 E. A. Quadrelli, G. Centi, J.-L. Duplan and S. Perathoner, *ChemSusChem*, 2011, **4**, 1194–1215.
- 2 M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz and T. E. Müller, *ChemSusChem*, 2011, **4**, 1216–1240.
- 3 M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.*, 2014, **114**, 1709–1742.
- 4 D. J. Darensbourg and S. J. Wilson, *Green Chem.*, 2012, **14**, 2665–2671.
- 5 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.
- 6 A. M. Chapman, C. Keyworth, M. R. Kember, A. J. J. Lennox and C. K. Williams, *ACS Catal.*, 2015, **5**, 1581–1588.
- 7 L. K. Rihko-Struckmann, A. Peschel, R. Hanke-Rauschenbach and K. Sundmacher, *Ind. Eng. Chem. Res.*, 2010, **49**, 11073–11078.
- 8 N. von der Assen, M. Lampe, L. Müller and A. Bardow, in *12th International Symposium on Process Systems Engineering and 25th European Symposium on Computer Aided Process Engineering*, ed. K. V. Gernaey, J. K. Huusom and R. Gani, Elsevier, 2015, vol. 37, pp. 1235–1240.
- 9 T. E. Waldman and W. D. McGhee, *J. Chem. Soc., Chem. Commun.*, 1994, 957–958.
- 10 PlasticsEurope, Eco-profiles, 2014, <http://www.plasticseurope.org/plasticssustainability/eco-profiles.aspx>, <http://www.plasticseurope.org/plasticssustainability/eco-profiles.aspx>, accessed 17 Dec 2014.
- 11 E. Schwab, A. Milanov, S. A. Schunk, A. Behrens and N. Schödel, *Chem. Ing. Tech.*, 2015, **87**, 347–353.
- 12 N. von der Assen, J. Jung and A. Bardow, *Energy Environ. Sci.*, 2013, **6**, 2721–2734.

- 13 R. M. Cuéllar-Franca and A. Azapagic, *J. CO₂ Util.*, 2015, **9**, 82–102.
- 14 N. von der Assen, P. Voll, M. Peters and A. Bardow, *Chem. Soc. Rev.*, 2014, **43**, 7982–7994.
- 15 P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1995, **95**, 259–272.
- 16 W. Wang, S. Wang, X. Ma and J. Gong, *Chem. Soc. Rev.*, 2011, **40**, 3703–3727.
- 17 S. Wesselbaum, U. Hintermair and W. Leitner, *Angew. Chem., Int. Ed.*, 2012, **51**, 8585–8588.
- 18 S. Wesselbaum, T. vom Stein, J. Klankermayer and W. Leitner, *Angew. Chem.*, 2012, **124**, 7617–7620.
- 19 G. Reiter and J. Lindorfer, *Int. J. Life Cycle Assess.*, 2015, **20**, 477–489.
- 20 C. van der Giesen, R. Kleijn and G. J. Kramer, *Environ. Sci. Technol.*, 2014, **48**, 7111–7121.
- 21 E. Cetinkaya, I. Dincer and G. Naterer, *Int. J. Hydrogen Energy*, 2012, **37**, 2071–2080.
- 22 International Energy Agency, *Cost and Performance of Carbon Dioxide Capture From Power Generation*, 2011, https://www.iea.org/publications/freepublications/publication/costperf_ccs_powergen.pdf, accessed 20 April 2015.
- 23 D. Y. Leung, G. Caramanna and M. M. Maroto-Valer, *Renewable Sustainable Energy Rev.*, 2014, **39**, 426–443.
- 24 T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
- 25 M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, **28**, 2975–2992.
- 26 G. Centi and S. Perathoner, *Greenhouse Gases: Sci. Technol.*, 2011, **1**, 21–35.
- 27 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.
- 28 N. von der Assen and A. Bardow, *Green Chem.*, 2014, **16**, 3272–3280.
- 29 ISO 14040:2009, *Environmental management – Life cycle assessment – Principles and framework*, European Committee for Standardisation, Brussels, 2009.
- 30 ISO 14044:2006, *Environmental management – Life cycle assessment – Requirements and guidelines*, European Committee for Standardisation, Brussels, 2006.
- 31 *Life Cycle Assessment Handbook: A Guide for Environmentally Sustainable Products*, ed. M. A. Curran, WILEY-VCH, Weinheim, 2012.
- 32 R. Heijungs and R. Frischknecht, *Int. J. Life Cycle Assess.*, 1998, **3**, 321–332.
- 33 J. Jung, N. von der Assen and A. Bardow, *Int. J. Life Cycle Assess.*, 2014, **19**, 661–676.
- 34 N. Pelletier, F. Ardente, M. Brandão, C. De Camillis and D. Pennington, *Int. J. Life Cycle Assess.*, 2015, **20**, 74–86.
- 35 PE International, *GaBi LCA Software and LCA Databases*, 2012, <http://www.gabi-software.com/databases/gabi-databases>, accessed nov 13, 2014.
- 36 Swiss Centre for Life Cycle Inventories, *Ecoinvent Data V2.2*, 2010, <http://www.ecoinvent.org/>, accessed Nov 13, 2014.
- 37 P. Forster, V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D. Fahey, J. Haywood, J. Lean, D. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz and R. V. Dorland, Climate Change, in *The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, ed. S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. Averyt, M. Tignor and H. Miller,

- Cambridge University Press, Cambridge, United Kingdom and New York, 2007, ch. 2, pp. 129–234.
- 38 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*, 1st edn, (version 1.08) Report I: Characterisation, 2013, <http://www.lcia-recipe.net>, accessed 17 Dec 2014.
- 39 R. Sathre, M. Chester, J. Cain and E. Masanet, *Energy*, 2012, **37**, 540–548.
- 40 J. Marx, A. Schreiber, P. Zapp, M. Haines, J.-F. Hake and J. Gale, *Energy Procedia*, 2011, **4**, 2448–2456.
- 41 A. Schreiber, P. Zapp and J. Marx, *J. Ind. Ecol.*, 2012, **16**, S155–S168.
- 42 M. Z. Hauschild, M. Goedkoop, J. Guinée, R. Heijungs, M. Huijbregts, O. Jolliet, M. Margni, A. De Schryver, S. Humbert, A. Laurent, S. Sala and R. Pant, *Int. J. Life Cycle Assess.*, 2013, **18**, 683–697.
- 43 ICCA, International Council of Chemical Associations, *How to Know If and When it's Time to Commission a Life Cycle Assessment*, 2013.
- 44 N. von der Assen, L. Müller, A. Steingrube, P. Voll and A. Bardow, *Selecting CO₂ sources for CO₂ utilization by environmental-merit-order curves*, 2015, submitted.
- 45 S. V. Jørgensen, M. Z. Hauschild and P. H. Nielsen, *Int. J. Life Cycle Assess.*, 2015, **20**, 451–462.
- 46 M. Brandão, A. Levasseur, M. Kirschbaum, B. Weidema, A. Cowie, S. Jørgensen, M. Hauschild, D. Pennington and K. Chomkamsri, *Int. J. Life Cycle Assess.*, 2012, **18**, 230–240.
- 47 M. Mequignon, L. Adolphe, F. Thellier and H. A. Haddou, *Build. Environ.*, 2013, **59**, 654–661.
- 48 U.S. Environmental Protection Agency, Transitioning to low-GWP foam blowing agents, 2011, http://www.epa.gov/ozone/downloads/EPA_HFC_ConstFoam.pdf, accessed 6 May 2015.
- 49 J. Langanke, J. Hofmann, C. Gürtler and A. Wolf, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 2071–2074.
- 50 G. Reuss, W. Disteldorf, A. O. Gamer and A. Hilt, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2012, vol. 15, ch. Formaldehyde, pp. 735–768.
- 51 S. G. Jadhav, P. D. Vaidya, B. M. Bhanage and J. B. Joshi, *Chem. Eng. Res. Des.*, 2014, **92**, 2557–2567.
- 52 N. Dave and G. A. Foulds, *Ind. Eng. Chem. Res.*, 1995, **34**, 1037–1043.
- 53 L. Chen, Y. Lu, Q. Hong, J. Lin and F. Dautzenberg, *Appl. Catal., A*, 2005, **292**, 295–304.
- 54 A. Sternberg and A. Bardow, *Energy Environ. Sci.*, 2015, **8**, 389–400.
- 55 E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazabal and J. Perez-Ramirez, *Energy Environ. Sci.*, 2013, **6**, 3112–3135.
- 56 M. Aresta and M. Galatola, *J. Cleaner Prod.*, 1999, **7**, 181–193.
- 57 S. V. Jørgensen and M. Z. Hauschild, *Int. J. Life Cycle Assess.*, 2013, **18**, 747–754.