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Comparative well-to-wheel life cycle assessment of OME₃₋₅ synfuel production via the power-to-liquid pathway†

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Oxymethylene Dimethyl Ethers (OMEs) are promising diesel fuel alternatives and interesting solvents for various industrial applications. In this report, a well-to-wheel life cycle assessment of short OME oligomers as produced via a Power-to-Liquid (PtL) pathway has been conducted. Variations in electricity and carbon dioxide supply as well as the hardware demand for the PtL plant components (e.g. PEM water electrolysis, carbon capturing, and 36 kta OME plant capacity) have been considered. Conventional diesel fuel is used as the comparative benchmark. In scenarios with a high share of renewable electricity well-to-wheel greenhouse gas emission for OME₃₋₅ fuel is advantageous compared to fossil diesel. For the best case, well-to-wheel greenhouse gas emissions can be reduced by 86%, corresponding to 29 g(CO_{2eq}) km⁻¹ (OME₃₋₅-fuel) compared to 209 g(CO_{2eq}) km⁻¹ (diesel fuel). However, these results are highly sensitive to the applied method with regard to system multifunctionality. A sensitivity analysis indicates that input electricity at ~50 g(CO_{2eq}) kWh_{el}⁻¹ enables well-to-wheel greenhouse gas emissions of <100 g(CO_{2eq}) km⁻¹. For other environmental impact categories, acidification, eutrophication, respiratory effects, photochemical ozone creation and resource depletion exceed significantly the fossil fuel reference. A high share of these impacts can be assigned to electricity production, either through direct electricity consumption in the PtL system or during upstream production of hardware components. The presented results and discussion demonstrate the necessity for global defossilisation including material efficient manufacturing of renewable energy plants which remains mandatory for synfuel production addressing a wide range of environmental impact categories. Furthermore, PtL production concerning well-to-wheel greenhouse gas emissions could be beneficial even in Germany if dedicated renewable energy capacities are considered. However, operation of large-scale PtL plants will predominantly be conducted in countries with high renewable energy potential, resulting in low leveled cost of electricity and high full load hours.

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Introduction

There is tremendous pressure to limit the global temperature increase to 1.5 °C, which requires intensive defossilisation

efforts by the international community.¹ In Germany especially the mobility sector stays way behind the sector specific targets which were set up in order to achieve the self-imposed national greenhouse gas (GHG) reduction targets.^{2,3} Additionally, we face controversial discussions about the impact and handling of high road traffic related local emissions, especially particulate matter (PM) and nitrogen oxides (NO_x). Based on renewable energy (RE), carbon dioxide (CO₂) capture and its downstream catalytic conversion with renewable hydrogen (H₂), the Power-to-Liquid (PtL) approach to chemical and fuel production can support defossilisation and enable integration of the energy, chemical and mobility sectors. PtL, as part of the Power-to-X (PtX) process schemes, is an important element of sector-coupling, enabling the infusion of RE into the primary energy demands of our global economies. The electrification of central end uses such as heating and road transport will lead to a significant rise of electricity in the final energy consumption from 19% today to 29% by 2050.⁴ In particular the electrification

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of mobility applications is expected to increase from <1% in 2016 to 27% in 2050. With regard to urban transport the European Union targets a 50% reduction in 2030 and a complete phase out of conventionally (fossil) fuelled cars.⁵ While battery electric vehicles are favourable for shorter driving distances (*i.e.* <300 km) long hauls or heavy road transports can in terms of life cycle GHG emissions be more sustainable when fuelled by hydrogen fuel cells or synthetic fuels.⁶ The Deutsche Energieagentur (DENA) assessed the potential of electricity-based fuels for low-emission transport in the EU. Even for 2050-scenarios favouring electric powertrains, more than 49% of the total fuel demand of all mobility applications will be met by electricity based liquid fuels.⁷ Studies with a focus on the future German energy system aiming at a 95% GHG reduction quantify a total necessary electricity provision of 129 TW h_{el} for PtL for its application in sector-coupling and future mobility⁸ (gross electricity generation in Germany in 2018: 649 TW h_{el}).⁹

In addition to reduction of life cycle GHG emissions, local emissions of PM and NO_x shift into the focus of political debate and legislation. In the context of new mobility fuels, short chain oligomeric Oxymethylene Dimethyl Ethers (denoted as OMEs; molecular formula H₃CO-(CH₂O)_n-CH₃; where *n* = 1–5) can be produced from CO₂ and H₂ typically *via* methanol (CH₃OH).¹⁰ OME_{3–5} are of interest as diesel additives or substitutes as they are non-hazardous, weakly corrosive, miscible with conventional diesel^{11,12} and their combustion is almost free of PM.^{13–17} Due to a high oxygen content (48 wt%)¹⁸ and cetane number, OME_{3–5} mixtures have been blended with conventional diesel without modification of the internal combustion engine.^{13,19,20} OMEs offer a high tolerance towards exhaust gas recirculation and hence can eliminate the PM–NO_x trade-off which inevitably occurs in the case of conventional long-chain diesel fuel.^{13,21,22} Another perspective and a promising market for OMEs is their application as solvents, with OME₁ already established as an industrially applied solvent.

Currently, industrial OME_n production provides capacities of *ca.* 30–40 kta but is characterized by low overall process efficiency.²³ The production is based on CH₃OH traditionally synthesised *via* syn-gas obtained from steam-reforming of fossil energy carriers (*e.g.* methane). For the production of OME_{3–5} from a PtL basis, whilst economically feasible (as we have reported previously),²⁴ life cycle assessment (LCA) and associated ecological impacts have yet to be examined in detail, especially with regard to the utilisation phase (*e.g.* combustion). A holistic Well-to-Wheel (WtW) LCA is thus important to determine whether this energy carrier offers environmental advantages compared to fossil-based equivalents. In this regard and within the framework of our current research^{24–27} this article addresses the following questions (*i.e.* the goal of the performed LCA):

→ Environmental efficiency of OME_{3–5}: what are the environmental impacts resulting from the production and utilisation of OME_{3–5} as a fuel? How does the synfuel perform in comparison to the production and utilisation of conventional fossil diesel fuel?

→ What are the systems most impacting life cycle phases and components in terms of environmental impact minimization?

Necessity for the environmental evaluation of OME_{3–5}

Thus far, reports in the literature regarding the LCA of OMEs have focused on either pure OME_{1–8} derived from forestry biomass with Canada as the geographical reference²⁸ or on the production of shorter chain OME₁ based on electrolytic H₂ applied in the form of OME₁–diesel-blend (35 vol% OME₁).²¹ OME₁, commercially known as “Methylal”, has a high vapor pressure, relatively lower specific volumetric energy and low flash point. These are drawbacks when blended with diesel fuel and when long-term storage in the current infrastructure is considered. Both previously reported LCAs indicated that at low blending rates (<35 vol% OME₁) soot emissions can be significantly reduced. The WtW GHG emissions can be reduced considerably when either forestry biomass or low-carbon electricity acts as the energy source for synthetic fuel production. A more detailed description of the addressed assessments is provided in the ESI (S1).†

Regarding testing of OME fuel in real internal combustion engines Avolio *et al.* conducted tests with different OME–diesel blends in different diesel engines.²⁹ Regarding life-cycle emissions it was stated that a 30% OME-content leads to an 18.5%-reduction in WtW CO₂-emissions ‘under the premise of a sustainable production from renewable sources’. Further explanation of the assessment background for the WtW emissions was not included in the report.

Therefore and to the best of our knowledge there is currently no publicly available LCA of OME_{3–5} which is required to support further R&D, process optimisation and indeed policy decision making.

As it is a critical consideration, when conducting the ecological evaluation of sustainable fuels and chemicals, terminologies such as “CO₂- or environmentally-neutral” or even “carbon-negative” have to be handled carefully.^{17,30–33} It is to be emphasised that none of the proposed future mobility options, if powered directly by electricity or by chemical energy carriers, will lead to CO₂-neutrality. As such in a WtW approach (*i.e.* including upstream impacts of fuel production), there will always be net-positive CO₂(equivalent) emissions (denoted as CO_{2eq}). Instead of discussing mobility concepts on the basis of Tank-to-Wheel system boundaries, it appears that WtW assessments should be handled as a fundamental prerequisite for environmental evaluation. It is also important to note that carbon emission reduction pathways only serve as temporal CO₂-storage mechanisms and aim when sourced from biogenic or atmospheric CO₂ at creating a highly integrated carbon cycle.

Thus, the Methodology section below describes the assessed product system and scenarios, the investigated OME synthesis route as well as the environmental indicators and the aspects of multifunctionality of the assessed PtL system.

Methodology for the life cycle assessment

The performed LCA was predominantly structured and conducted in compliance with ISO 14040:2009, ISO 14044:2006,^{25,34,35} and recommendations of the European

Commission.^{36–38} Synthesis process data are described in the “Theoretical background for the assessed OME_{3–5} synthesis” section. Umberto® NXT Universal LCA software was used for modelling and impact calculations. Background LCA data were sourced from the ecoinvent database (v.3.3), manufacturer specifications, published literature and in-house experience. For the applied ecoinvent background processes cut-off system models which build on economic allocation as the default methodology have been used.

Assessed product system, functional units and scenarios

The scale of the assessed PtL product system is based on the electricity production of a 100 MW_p RE park and it is designed for an annual production capacity of 36 kta of OME_{3–5}. In general it comprises nine main process steps (Fig. 1A): electrolytic H₂ production by proton exchange membrane water electrolysis (denoted as “PEM”), CO₂ capture from one of the three assessed CO₂ sources (*i.e.* biomethane, ammonia, and direct air capture), methanol synthesis with subsequent flash and distillation units, anhydrous dehydrogenation of methanol to formaldehyde followed by OME_n synthesis and the necessary distillation towards the target product OME_{3–5} (please see the

section “Theoretical background for the assessed OME_{3–5} synthesis” for further details). Necessary (by-)product separation, recirculation, cooling and compression are part of the related processes of methanol- or OME_{3–5}-synthesis. To reduce the thermal energy demand heat integration has been performed. The OME_{3–5} product is then assumed to be distributed and utilised in a mid-size diesel-car (WtW system boundaries). All of the described life cycle phases require process energies (electricity and steam), process and cooling water, parts and materials for plants and machinery construction, as well as maintenance and fuel transportation. The life cycle inventory provides further description of the single process steps.²⁵

To meet the goal of a comparative LCA study the investigated PtL OME production and the reference system need to fulfill the same primary function. Therefore a driving distance of 1 km is chosen as the functional unit (FU) for the WtW system boundaries.

Three main scenarios allow for variation of technology parameters and the applied electricity (Fig. 1B). They are characterized by a high to low GHG intensity of the applied electricity, a variation of the PEM efficiency and stack lifetime and the supply of thermal energy for the synthesis steps.

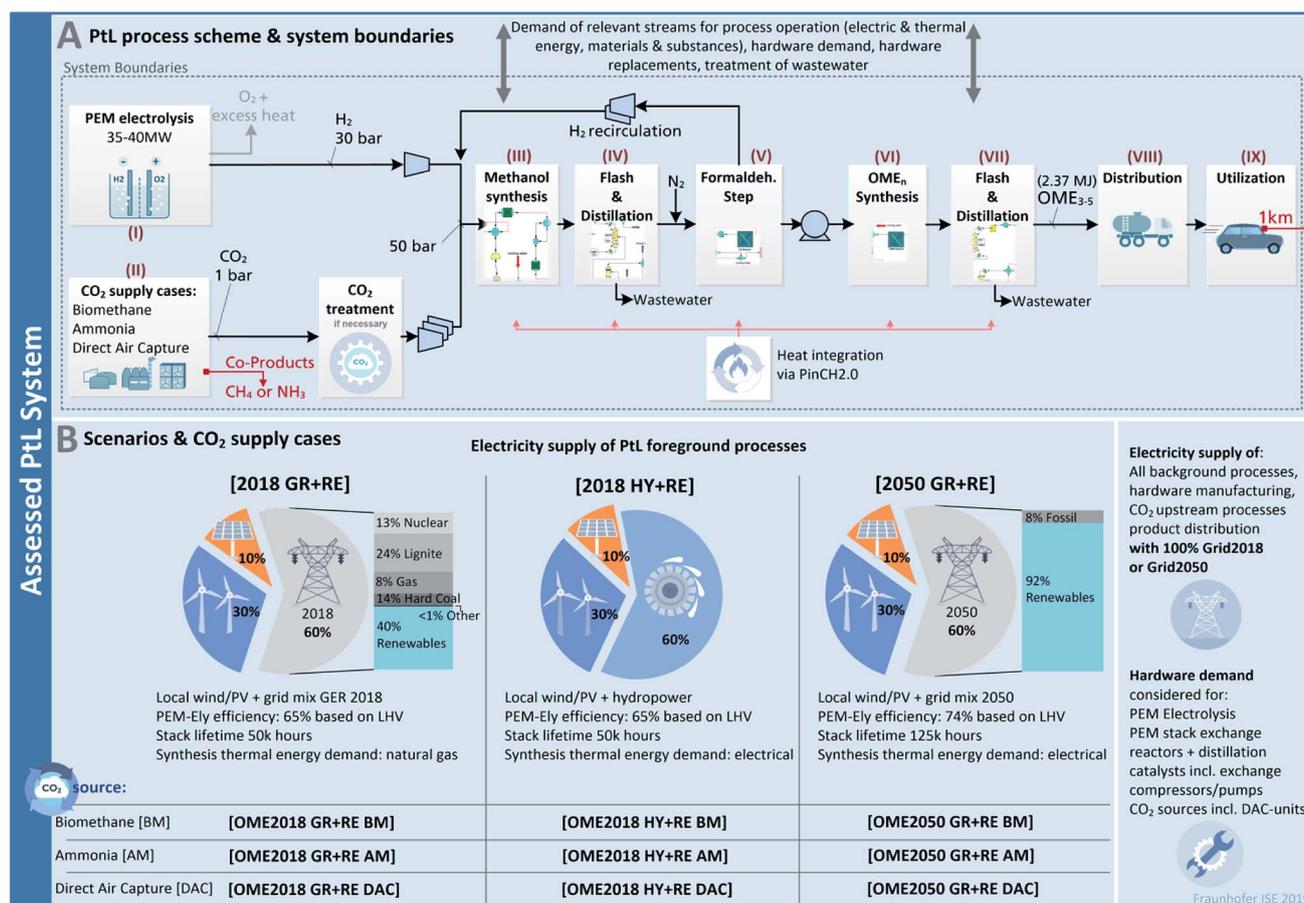


Fig. 1 A) Assessed PtL product system grouped into the relevant process steps. (B) The three technology scenarios varying in electricity supply, PEM efficiency, PEM stack lifetime and thermal energy supply. CO₂ is supplied from three sources: biomethane, ammonia and direct air capture. The resulting designation of the scenarios is indicated in square brackets.

The CO₂ supply cases consider a biogas upgrading plant separating mainly CO₂ from biomethane [BM], an ammonia production facility [AM] and a direct air capturing technology [DAC]. The designation of the resulting nine assessed combinations is indicated in square brackets.

Indicators for the environmental impacts

PtL (and CCU) systems are designed for the integration of the carbon cycle and hence the mitigation of fossil CO₂ emissions. This is why most discussions on PtL focus on the specific systems' Global warming potential. However, a holistic LCA shall aspire to cover as well further impact categories to disclose fully the potential environmental benefits/disadvantages. The selected impact categories in this study are climate change, GWP 100a [kg CO_{2eq}]; resources (minerals, fossils and renewables) [kg Sb_{eq}]; freshwater and terrestrial acidification [mol H_{eq}⁺]; freshwater eutrophication [kg P_{eq}]; marine eutrophication [kg N_{eq}]; terrestrial eutrophication [mol N_{eq}]; ozone layer depletion [kg CFC-11_{eq}]; respiratory effects, inorganics [kg PM2.5_{eq}]; photochemical ozone creation [kg ethylene_{eq}]; cumulative energy demand, total [MJ_{eq}]; and cumulative energy demand, non-renewable [MJ_{eq}]. The ILCD Handbook "Framework and requirements for LCIA models and indicators" provides general information on these categories.³⁹

Solving of multifunctionality

A comprehensive definition of multifunctionality in the context of CCU can be found in the ESI (S2)[†] together with references to relevant literature. A description of the avoided burden methodology applied in this study is also provided.

In this study system boundaries have been expanded to include the source of CO₂ (Fig. 2A). Besides the primary FU of 1

km driving distance, this leads to the inclusion of an additional functionality – *i.e.* the production of either biomethane or ammonia. Since the focus is on the production of OME₃₋₅ or fossil diesel fuel and driving over 1 km, these additional functions are designated as “co-products”. For multifunctional CO₂ supply cases, biomethane and ammonia life cycle impact results are presented on the basis of the avoided burden approach, sometimes referred to as substitution. This represents one solution for multifunctionality when the alternative approaches of subdivision and system expansion are either not applicable or considered as insufficient for the presentation of results.⁴⁰

Avoided burden presumes that co-product generation in the coupled product system enables the substitution of a conventionally produced co-product. The respective impact of the avoided conventional production is credited (subtracted) to the coupled product system. However, impact crediting can for some cases even lead to negative overall results. Negative results can be mistaken as a reversal of impacts; *i.e.* if operated the respective product system is assumed to lead to an improvement of environmental conditions. A correct interpretation for negative results is that the total impact of the coupled product system is smaller than the total impact of the avoided conventional production of the single co-product. This leads to a net benefit even though the coupled product system still has an environmental impact. The net benefit is valid as long as the market for the co-product is not saturated.^{36,40}

It is important to note that avoided burden is valid as long as the substitution of conventional production can be assured. The latter for example can be the case for carbon capture from already existing CO₂ sources or if the co-production enables a reduced production elsewhere. However, an ever increasing

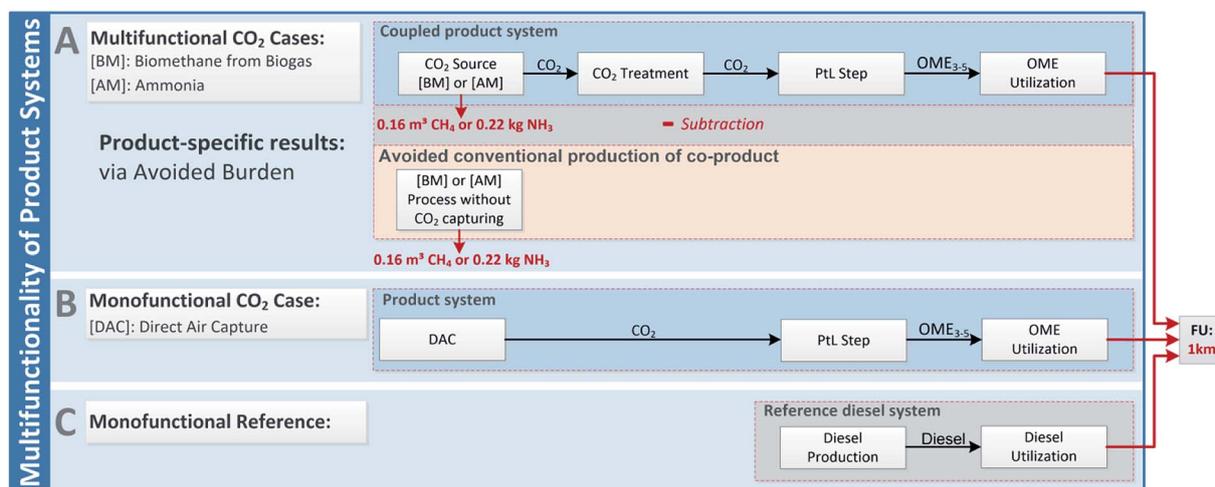


Fig. 2 A) The assessed product systems with a CO₂-supply based on biomethane [BM] or ammonia [AM] are multifunctional since they are providing an additional function (biomethane or ammonia) besides the main function (1 km driving distance). The avoided burden methodology subtracts a respective amount of avoided conventional production from the expanded system. By this, the obtained product specific results (FU: impact per km) can be compared to the other CO₂ cases and the reference diesel system. (B) In the case of a CO₂-supply from a Direct-Air-Capture [DAC] plant the sole function of the product system is a driving distance of 1 km. (C) This as well applies to the monofunctional reference diesel system. (B and C) The hereby obtained product specific results (FU: impact per km) can be compared to both the CO₂ case [DAC] and the reference diesel system.

production of the co-product can lead to saturation of the respective market. For this case, results based on the avoided burden approach might be misleading since the substitution cannot be assured. As recommended by the ISO 14044 the results for the expanded systems are included in the ESI (S7).†

For the monofunctional CO₂ case [DAC] (Fig. 2B) and the diesel reference process (Fig. 2C) no avoided burden needs to be credited since these product systems are already product-specific with a FU of 1 km.

Theoretical background for the assessed OME₃₋₅ synthesis

The LCA of OME₃₋₅ synthesis conducted in this paper is based on a synthesis process using methanol and anhydrous formaldehyde as described and economically assessed by Ouda *et al.*^{10,24} In this work the described process chain, formerly based on fossil methanol, was extended to include the preceding synthesis of CO₂-based methanol, the capturing of CO₂ and the electrolytic H₂ production. The OME₃₋₅ product mixture consists of 39 wt% OME₃, 34 wt% OME₄ and 27 wt% OME₅ resulting in a heating value (19.031 MJ_{LHV} per kg(OME₃₋₅)) of 44% compared to that of conventional diesel fuel (42.791 MJ_{LHV} per kg(diesel)). The process was simulated using the simulation software CHEMCAD® coupled with Matlab® *via* a VBA script to describe the process reactors.²⁴ A heat integration process has been performed using the software PinCH2.0.⁴¹ Here a heat exchanger network has been developed to maximize the process heat recovery while considering occurring investment costs. Afterwards the heat exchanger network was implemented in CHEMCAD®. Combining the methanol synthesis sub-plant with the formaldehyde and the OME sub-plants has been beneficial for the overall internal energy recovery. A detailed description of the synthesis steps and a simplified process flow diagram are provided in the ESI (S3).†

Inventory for the assessed OME₃₋₅ system

The order of the inventory is organised in analogy to the process scheme. A detailed tabular summary of the life cycle inventory (LCI) and complementing descriptions are included in the ESI (S5).† Since the hardware demand of the PtL components is included it was important to assume a technical lifetime for the overall system as well as exchange rates for the PEM stacks and catalysts. If not mentioned otherwise in the following description of the LCI a lifetime of 20 years has been assumed for H₂ production, CO₂ sourcing and the synthesis steps, including compression and distillation.

Electricity

Three different scenarios have been selected (compare with Fig. 1B) which combine steady-state electricity provision from grid mixes or hydropower with fluctuating RE. A complementing detailed description of the derivation of the applied electricity mixes is given in the ESI (S4).† The electricity provision scenarios are described as:

- [2018 GR + RE]. Consisting of 60% grid mix in Germany, 2018, plus 40% local RE. The 40% share of RE is based on load profiles of local wind and photovoltaic (PV) plants in the south of Germany. The grid data for 2018 are based on published data of the publicly accessible ISE energy charts.⁴²

- [2050 GR + RE]. Consisting of 60% grid electricity for a predicted 2050 mix in Germany plus 40% local RE (as described above). For an estimation of the 2050 grid electricity mix and its resulting footprint the REMod-D model developed at Fraunhofer ISE has been used.⁴³⁻⁴⁵

- [2018 HY + RE]. Consisting of 60% hydropower (run-of-river) and 40% local RE (as described above). The ecoinvent process “hydro, run-of-river [DE]” is used as the background process. When it comes to using limited forms of electricity generation such as the case for hydropower in Germany the argument for the PtL plants' additional electricity demand is justified. It can be argued that in the case of a large-scale PtL plant in Germany an electricity supply from dedicated hydroelectric power plants remains unlikely. However, the [2018 HY + RE] scenario is included to provide the estimation for PtL scenarios where low-carbon electricity is supplied as is already the case for anticipated pilot-projects in Scandinavia.⁴⁶⁻⁴⁸ By now, hydroelectricity provides the largest share of electricity from all RE sources within the EU member-states.

The electricity demand of the background processes such as distribution or production processes of hardware materials is fulfilled by the grid electricity mix defined by the scenarios (year 2018 or 2050). This is justified by the assumption that these external process steps cannot be influenced by the PtL process operator and any decisions promoting RE.

It is indeed important for Power-to-X systems powered by a high share of PV and wind electricity (*i.e.* without direct CO₂ emissions) to account as well for the indirect emissions during their production processes. The upstream emissions of RE plants can on the one hand be influenced by the RE plant's capacity utilization or, on the other, heavily influenced by the applied source of electricity for the RE plant production processes. For example a PV module processed in a factory which in turn is powered by an electricity mix featuring high shares of fossil based energy generation will as well show higher (indirect) GHG emissions per kWh_{eI}-produced. In contrast, a PV module from 100% RE-powered factory potentially enables lower GHG emissions per kWh_{eI}-produced. Therefore in the section discussing results we will analyse the source for specific life cycle impacts and trace them to their initial “causer”.

CO₂ sourcing

The three selected CO₂ sources mirror the capture of atmospheric or fossil CO₂ and cover a PtL feed demand of 227.6 t(CO₂) d⁻¹. For captured atmospheric CO₂, the feedstock has already been part of the atmosphere before its re-emission to the atmosphere during product utilisation. Hence for a WtW assessment it can be assumed that the same amount of CO₂ removed from the atmosphere will be released to the atmosphere at any point of the life cycle. Indeed that does not mean that ‘feedstock’ atmospheric CO₂ can be accounted with zero

burden since its upstream technology-based provision causes indirect impacts. Regarding the CO₂ feed demand of a PtL fuel production it should be noted that it will always be higher than the stoichiometric CO₂ formation during PtL fuel utilization. Part of the feed CO₂ is lost in the form of C-containing purge gases and waste streams and not bound in the synfuel. Thus for environmental evaluation of synfuel production it is important to consider the full CO₂ demand for correct impact assessment of CO₂ capturing, purification and compression.

For the supply case 'Biomethane', CO₂ is assumed to be supplied from a biogas upgrading plant used for the feed-in of biomethane to the natural gas grid. For the initial production of biogas from biomass and necessary materials and hardware demand theecoinvent dataset "biogas production from grass [CH]" was modified and adjusted to average substrate feeds for the German market.^{25,49} A CO₂ content of ~44 vol%, resp. 0.87 kg(CO₂) Nm⁻³ (biogas), was assumed.⁵⁰ Biogas upgrading includes desulphurisation to reduce H₂S content to >500 ppm. In order to protect and improve the lifetime of the methanol synthesis catalyst an additional fine-desulphurisation step has been considered with a final H₂S content below 5 ppm. A detailed description including the process parameters applied for the impact assessment is provided in the ESI (S5 – CO₂ sourcing).†

With the supply of biogenic CO₂, the biogas upgrading plant delivers two products: biomethane and feedstock CO₂, thus exhibiting multifunctionality. To obtain a product-specific result (FU = 1 km of driving) the respective amount of produced biomethane is credited (avoided burden approach): a driving distance of 1 km necessitates an upstream provision of 0.27 kg CO₂ which in turn can be captured from 0.16 Nm³ CH₄. Hence the avoided burden is defined by a conventional biomethane pathway producing an equivalent amount of CH₄.

For the supply case 'Ammonia', data are based on theecoinvent dataset "ammonia production, steam reforming, liquid [RER]".⁵¹ The process has been edited as the originalecoinvent process assumes 1.23 kg of CO₂ for the downstream production of urea which is not listed as emission in the original dataset.^{52,53} Thus this amount is assumed to be available for synfuel production at ambient pressure. Due to the high purity of the CO₂ desulphurisation is considered unnecessary. For the avoided burden approach the FU of 1 km driving results in 0.22 kg NH₃ as the co-product. A conventional ammonia production producing an equivalent amount without CO₂ capturing is credited. More information on ammonia as the CO₂ source is included in the ESI (S5 – CO₂ sourcing).†

For the monofunctional supply case 'Direct Air Capture', CO₂ is sourced directly from the atmosphere. Here thermal and electrical energy demands are considered as well as the hardware demand for DAC units. For the impact assessment either the available exhaust (burden free) heat or the burning of natural gas is assumed. Details on considered energy demands as well as hardware specification are included in the ESI.†

All three CO₂ sources including their upstream processing are assumed to be supplied by either the 2018 electricity grid mix ([2018 GR + RE]; [2018 HY + RE]) or the 2050 electricity grid mix ([2050 GR + RE]). Transportation and related losses for the

CO₂-feedstock provision are neglected following the assumption that the CO₂ sources are located nearby the OME plant.

H₂ production

PEM water electrolysis is selected for electrolytic H₂ production. PEM technology has not reached the state of year-long operational experience as is the case for alkaline electrolysis (AEL). However PEM systems offer specific advantages when placed in the context of fluctuating RE production and PtX-concepts: they offer faster start-up (cold-start) and response times than AEL, higher current densities, allow for a higher operational pressure and therefore potentially reduce H₂ compression demand for downstream synthesis steps.^{54,55} Today the investment cost for PEM electrolysis systems still exceeds that of AEL systems. However, a strong investment cost reduction and an increase of stack lifetime are expected in the next two decades enabling an alignment with the values for AEL systems.^{54–57}

Details regarding the PEM system's parameters are listed in Table 1. The PEM system for our LCA is based on the data for a 5 MW_{el} PEM water electrolyser system comprising 5 × 1 MW_{el} stacks. Since the H₂ production capacity is pre-set by the PtL plants' H₂ demand the total number of 5 MW_{el} PEM systems is dependent on the assumed PEM system efficiency defined in the scenarios. For the 2050 scenario a forward projection of the technological development can be assumed leading to a considerably reduced specific electricity demand. The values are based on a recent sector survey including manufacturer estimations for future electrolysis system performances depending on the system size.⁵⁵ The assumed PEM system efficiencies have been validated by further comparing to published measured or simulated efficiencies.^{58–61} Electricity is provided at high voltage, transformed to medium voltage and converted into direct voltage. Deionised water input and oxygen output were considered using stoichiometric calculation and in compliance with literature data. Oxygen is vented and not considered as a valuable product for this study. Cooling water demand is also included.⁶²

Hardware data for the 5 MW_{el} PEM systems are based mainly on the primary data of Fraunhofer ISE.^{25,63} To account for stack longevity the 2018 scenario assumes a stack lifetime of 50k h after which a complete replacement is necessary. For reasons of simplicity any partial recycling of stack components at the end of their lifetime is neglected. The stack hardware data comprise the complete membrane electrode assembly (MEA) consisting of Pt-loaded cathodes, IrO₂-loaded anodes, Cu current collectors, Ti-bipolar plates, Nafion® membranes, Ti-current collectors and device frames and sealing. The stack endplates are excluded from replacement. For the two 2050 scenarios a significant increase of stack lifetime to 125k h is assumed representing the median value obtained from statements in sector surveys.⁵⁵ Secondary data for power electronics are derived from theecoinvent "fuel cell production, polymer electrolyte membrane, 2 kW electrical, future", which is a source of uncertainties due to the high difference in installed capacities. Additionally an 800 m² building hall and three 40-foot intermodal shipping containers have been considered

based on presentations and publications from industry.^{59,64,65} Due to insufficient data availability a water–gas separator and a further H₂ purification (De-Oxo) have been excluded from the hardware demand.

Methanol & OME₃₋₅ synthesis steps

Process data of the two synthesis steps as well as related compression, pumps and distillation units are based on process simulation with CHEMCAD® and heat integration *via* PinCH2.0. The synthesis plant capacity is 36 kt per a(OME₃₋₅). Process data include the electricity for compressors and pumps, heat for the dehydrogenation of methanol to formaldehyde and steam for the necessary 5 distillation columns. Thermal energy supply is provided by either natural gas (GRID2018 + RE) or by the respective electricity mix (GRID2050 + RE, HYDRO2018). Material data consider catalysts, reactors, compressors and pumps. The utilities, ancillaries, and offsite infrastructure demand are estimated by means of a standard ecoinvent process. The ESI (S5 – Methanol synthesis and distillation)† provides detailed information on specific energy and material demands as well as additional information on the catalysts assumed for the assessment.

Distribution and utilisation of OME₃₋₅

The final OME₃₋₅ product is assumed to be distributed to the point of utilisation. Since the form of distribution is very dependent on geographical and case specific assumptions, a distribution mix including comparable shares of lorry, train and ship transportation is assumed. The necessary transportation distance is assumed to be 400 km. The differing energy densities of diesel and OME₃₋₅ result in a higher OME₃₋₅ distribution demand.

Utilisation in a medium size passenger car fuelled by OME₃₋₅ was assumed in the utilisation phase. Due to different heating values of diesel and OME₃₋₅, the engine has a higher mass flow in the case of OME fuel. Empirical data show that the injection demand of diesel is *ca.* 46% of that of OME₃₋₅ which corresponds to the ratio of heating values. However, OME fuel can show 1–3% efficiency improvement.^{20,66} Hence the OME₃₋₅ fuel consumption equals:²⁵

$$m_{\text{OME}} = m_{\text{diesel}} \frac{\text{LHV}_{\text{diesel}}}{\text{LHV}_{\text{OME}_{3-5}}} (1 - \Delta\eta)$$

m_{diesel} – mass of diesel fuel [kg]. $\text{LHV}_{\text{diesel}}$ – lower heating value of diesel = 42.791 MJ kg⁻¹.⁶⁷ $\text{LHV}_{\text{OME}_{3-5}}$ – lower heating value of OME₃₋₅ = 19.031 MJ kg⁻¹.^{68,69} $\Delta\eta$ – efficiency increase for OME vs. diesel = 2%.^{20,66}

The specific energy demand of the passenger car of 237 MJ or 12.5 kg OME₃₋₅ per 100 km is based on the EU-wide transport model TREMOVE of the European Union.⁷⁰ This specific energy demand equals a real-world fuel consumption of 11.7 and 6.6 litres of OME₃₋₅ and diesel fuel, respectively, for a mid- to upper-size passenger car. Wietschel *et al.* 2019 assessed a diesel fuel consumption of 5.7 and 8.2 litres for a mid- and upper size car, respectively.⁷¹ The German federal environmental agency (UBA) quantifies the average fuel consumption of cars in Germany to 7.4 litres.⁷² The assumption we make regarding the specific energy demand affects both fuel concepts equally. The ecoinvent process “transport, passenger car, medium size, diesel EURO 5” has been chosen. The environmental impacts resulting from car manufacturing are excluded since the fuel production and utilisation related emissions are of major interest in this assessment. Tire, brake and road wear emissions are also excluded since they are assumed to be independent of the used fuel. The detailed compilation for the emissions resulting from the utilisation of OME₃₋₅ in an internal combustion engine is provided in the ESI (S5 – OME₃₋₅ utilization).†

Diesel reference process

The diesel reference process has been selected based on secondary data obtained from the ecoinvent database; *i.e.* the “transport, passenger car, medium size, diesel, EURO 5” dataset has been selected for the impact assessment. Ecoinvent classifies vehicles with a gross weight of 1.6 t and an engine displacement of 1.4–2.0 L as “medium size” passenger cars. The diesel fuel consumption adds up to 0.055 kg diesel per km. Upstream processes of low-sulphur diesel production, petroleum refinery operation and petroleum extraction are included in the reference system boundaries. Electricity consumptions of the diesel production and the petroleum refinery operation have been adapted to the respective electricity mix of either 2018 ([2018 GR + RE], [2018 HY + RE]) or 2050 ([2050 GR + RE]). However, the results for the diesel product system showed that a variation of the electricity mix only has a negligible impact on

Table 1 PEM electrolysis operating parameters

	2018 GR + RE	2018 HY + RE	2050 GR + RE
Production capacity (t(H ₂) d ⁻¹)	18.7	18.7	18.7
Electricity demand system (kWh _{el} /Nm ³ (H ₂))	4.6	4.6	4.1
Efficiency system (% _{LHV, H₂})	65	65	74
Efficiency rectifier (%)	98	98	98
Installed capacity (MW _{el})	40	40	35
Deionised water demand (t(H ₂ O _{DI}) per t(H ₂))	8.92	8.92	8.92
Cooling water demand (t(H ₂ O _{cooling}) per t(H ₂))	1.62	1.62	1.62
Oxygen output, vented (t(O ₂) per t(H ₂))	7.90	7.90	7.90
Lifetime PEM stacks (1000 hours)	50	50	125

the total GHG emissions (<0.1%). For reasons of a clear presentation the results of the OME₃₋₅ product systems are solely compared to the results of the diesel product system based on the 2050 grid electricity mix. Technological improvements for 2050 in the case of fossil diesel production have not been considered. It can be assumed that these conventional processes are established and mature. As for OME₃₋₅ production, emissions from the manufacturing of the car as well as tire, brake and road wear emissions have been excluded from the assessment.

Environmental impacts of OME₃₋₅ as synfuel – via the avoided burden approach

To answer the main research questions (environmental impacts of OME₃₋₅ production and utilisation compared to conventional fossil diesel fuel) the life cycle impact assessment results are first discussed for the global warming potential (GWP₁₀₀). Subsequently, additional assessed impact categories will be addressed to disclose a more complete picture of the environmental implications. A sensitivity analysis regarding the footprint of supplied electricity as well as the PEM system efficiency concludes the section on results. The whole section on results is based on and valid for the avoided burden approach (compare with the section “Solving of multifunctionality”). The life cycle impact assessment results for the expanded system are included in the ESI (S7 – Life cycle impact assessment results for system expansion).†

Global warming potential

Fig. 3 presents the product specific GWP results (expressed as GHG emissions g(CO_{2eq}) km⁻¹; overall impact as green bars). The product specific FU of 1 km allows the comparison of all CO₂ cases and the diesel reference. For the CO₂ cases Biomethane and Ammonia, the avoided burden approach has been applied and a conventional production of the co-product is credited to the OME product system (*i.e.* a negative value in light blue). For the CO₂ cases Biomethane and Direct Air Capture (*i.e.* atmospheric CO₂ sources), the final exhaust pipe CO₂ emissions are considered without GWP (compare with the section CO₂ sourcing). By contrast, the fossil CO₂ case Ammonia and the reference diesel process show GWP during the utilisation phases (grey bar). In the following all three CO₂ sources based on the 2018 grid and RE mix [OME2018 GR + RE] will be discussed. Subsequently the results for the additional two electricity cases are analysed.

Case [OME2018 GR + RE]. The electricity mix consisting of 60% grid 2018 + 40% RE carries a GWP burden of 350 g(CO_{2eq}) kWh_{el}⁻¹, with the highest contribution from lignite and hard coal based electricity production. The 40% share of local wind and PV production accounts for only 6% of the electricity's GWP. Regarding the WtW driving emissions, results clearly show that for all three CO₂ sources the assessed OME₃₋₅ production pathway is not favourable in comparison to driving with conventional diesel fuel. The corresponding GHG

emissions per km of driving distance with OME₃₋₅ exceed those of driving with conventional diesel fuel by up to 263% for the worst case [OME2018 GR + RE DAC, natural gas as heat supply]. The calculated WtW emissions of 209 g(CO_{2eq}) km⁻¹ for the diesel reference align with the values published by Mahbub *et al.* of 199 g(CO_{2eq}) km⁻¹.²⁸ The diesel exhaust pipe emissions (Tank-to-Wheel) for the present LCA account for 177 g(CO_{2eq}) km⁻¹. The 2020 European fleet target value aims at 95 g(CO_{2eq}) km⁻¹ and takes manufacturer specifications as a calculation basis. For the present study the specific energy demand of the passenger car orientates on a current mid-class vehicle under real driving conditions (2.37 MJ km⁻¹; 6.6 L of diesel fuel).

With regard to H₂ production it should be recalled that in the case of PtX all of the final fuel energy content is provided by H₂ or rather the upstream electricity. Due to a chain of involved conversion efficiencies even minor shares of a carbon intensive electricity supplier (coal-fired or natural gas power plants) are mirrored in the PtX products' GWP footprint. The same accounts for the thermal heat supply for synthesis and distillation steps. The WtW results for the Direct-Air-Capture cases increase by 114 g(CO_{2eq}) km⁻¹ in the case of a natural gas based provision of necessary low-temperature heat for CO₂ desorption.

The steps of methanol- and OME-synthesis account for 31–42% of the total OME₃₋₅ life-cycle GHG emissions. Here the synthesis steps in the case of ammonia result in a slightly higher GHG emission since CO₂ containing purge streams are of fossil origin.

Case [OME2050 GR + RE]. The GHG footprint of the REMod based 2050 electricity grid mix results in 100 g(CO_{2eq}) kWh_{el}⁻¹. Accompanied by a 40% share of local wind and PV electricity the applied electricity's total footprint results in 81 g(CO_{2eq}) kWh_{el}⁻¹. With a less carbon-intensive electricity provision the GHG emissions per km of driving distance can be lowered significantly by up to –40% and fall below the ones of the diesel reference system. The scenarios' total specific GHG emissions of the OME₃₋₅ product system result in 124–151 g(CO_{2eq}) km⁻¹.

Case [OME2018 HY + RE]. The [OME2018 HY + RE] scenarios profit from a very low GWP for an electricity of 20 g(CO_{2eq}) kWh_{el}⁻¹ (*i.e.* hydropower). However, when assessing life cycle impacts of hydropower it is important to consider that further environmental impact categories are heavily dependent on the type, capacity and location of the facility.^{73,74} For this low-carbon electricity provision the GHG emissions for OME₃₋₅ fuel clearly fall below the emissions of driving with conventional diesel fuel by –59% to –86%. The DAC supplied with thermal energy from natural gas is in the range of fossil diesel fuel.

GWP of the electrolytic H₂ production. When based on the 2018 grid + RE electricity mix the life cycle phase of H₂ production accounts for 53–68% of the PtL systems' total overall GWP. GHG emissions arising from PEM electrolyzers sum up to 18.3 kg(CO_{2eq}) per kg(H₂), which is significantly higher than that of conventional H₂ production such as steam-reforming of natural gas (9.0–13.0 kg(CO_{2eq}) per kg(H₂))^{75–77} or coal gasification (11.0–12.5 kg(CO_{2eq}) per kg(H₂)).⁷⁷ In the case of [OME2050

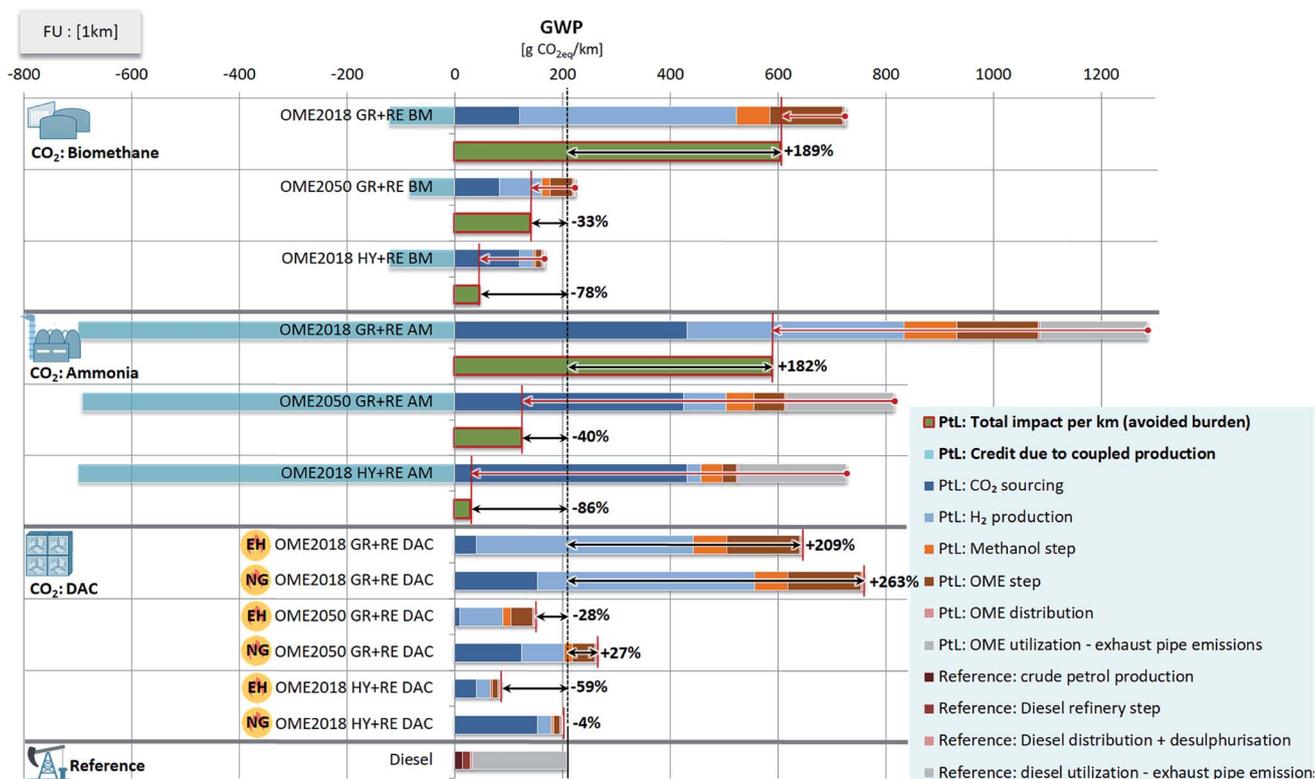


Fig. 3 Product specific well-to-wheel life cycle impact assessment results (GWP_{100a} [$g\ CO_{2eq}\ km^{-1}$]) for the assessed product systems. In the case of subtraction of an avoided burden the respective negative value is indicated in light blue. The resulting total impact is plotted as a green bar. The difference compared to the conventional diesel is specified with black arrows. For the CO_2 case Direct-Air-Capture, the thermal demand of the DAC plant is met either by exhaust heat (EH, burden-free) or natural gas (NG).

GR + RE] the life cycle phase of H_2 production results in a reduced GWP impact of $3.5\ kg(CO_{2eq})$ per $kg(H_2)$. Other published GWP footprints for low-carbon H_2 production also clearly depend on the electricity source and vary between $0.6\ kg(CO_{2eq})$ per $kg(H_2)$,^{75,78} $1.9\ kg(CO_{2eq})$ per $kg(H_2)$ ⁷⁸ and $3.0\ kg(CO_{2eq})$ per $kg(H_2)$.⁷⁹ Electrolysis hardware is, if part of the respective LCA, identified to have a minor impact. In the present assessment the share of GWP impact resulting from the PEM hardware varies between 0.6% (2018: 40 MW_{el} PEM, lifetime 50k h) and 1.8% (2018: 35 MW_{el} PEM, lifetime 125k h) of the H_2 production phase.

Thermal demand of synthesis and distillation. The synthesis and distillation steps are characterised by a high thermal energy demand ($4.84\ MWh_{th}$ per $t(OME_{3-5})$ produced). In case low-carbon-electricity is available these steps can benefit from thermal energy provided *via* electric energy. If natural gas is used for steam and heat production its proportional GWP sums up to $144\ g(CO_{2eq})\ km^{-1}$. A switch to an electricity based thermal supply in the 2050 grid mix decreases the total GWP of the two synthesis steps by 72%. At the same time the electricity demand of the PtL foreground system (PEM electrolyser + synthesis and distillation) is increased from $1.27\ kWh_{el}\ km^{-1}$ to $1.79\ kWh_{el}\ km^{-1}$. The temperature level of the necessary heat supply for methanol dehydrogenation to formaldehyde is at ca. $700\ ^\circ C$, equal to a thermal demand of $6.93\ MWh_{th}$. Thus a thermal supply *via* excess heat at such high temperatures

seems highly case-dependent. However, industrial processes requiring high temperature process heat ($>500\ ^\circ C$) such as pig iron and steel mills, stone and brick production or the glass and ceramics industry are available and at the same time due to high direct CO_2 emissions, a potential CCU case.⁸⁰ If not utilised otherwise the available high temperature excess heat can thus be available as a “burden free” heat source to meet the thermal demand of the PtL process. For a hypothetical scenario in 2050 where the assessed OME_{3-5} production is supplied with high temperature excess heat the overall GWP can be lowered to $94\ g(CO_{2eq})\ km^{-1}$, -55% in comparison to the reference diesel process' GWP. The impact related to the provision of PtL plant hardware and infrastructure lies between 0.8% [OME2018 GR + RE] and 17% [OME2018 HY + RE] of the overall WtW GHG emissions.

Further environmental impacts

Fig. 4 shows the further assessed environmental impact categories for the CO_2 case Biomethane. The results are normalised to the diesel reference. All results are again based on the avoided burden methodology.

For the [OME2018 GR + RE] scenarios synthetic fuel production and utilisation performs worse than the diesel reference for all impact categories. The largest contributor for most categories is the fossil share of the electricity used. With

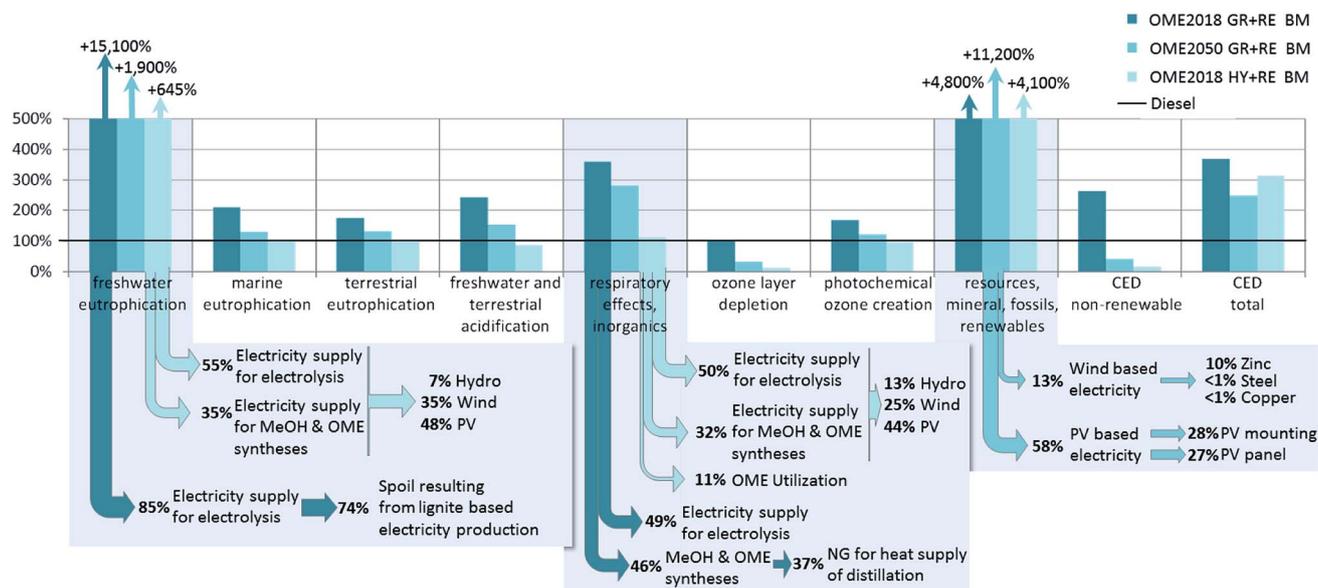


Fig. 4 Further evaluated impact categories by means of the CO₂ case [BM]. Relative shares relate to the diesel reference (100%). The flows presented exemplify the cause of specific impact categories. The percentage value for the specific initial causer relates to the absolute value of the impact category (e.g. spoil from lignite mining causes 74% of the overall freshwater eutrophication in the scenario [OME2018 GR + RE BM]).

a reduction of fossil energy shares for the [OME2050 GR + RE] and the [OME2018 HY + RE] scenarios the impacts can be reduced significantly for most cases. However, the categories addressing impacts on ecosystems remain high even with a low carbon electricity provision. The following subsections focus on the worse performing categories and analyze the respective cause in this context.

Freshwater eutrophication. The impact category freshwater eutrophication (kg P_{eq}) is outstanding by exceeding the diesel reference by 15 100% for the [OME2018 + RE] scenario. Here the largest share (74%) can be attributed to lignite based electricity provision, more precisely to the spoil and tailing wastes resulting from opencast mining.⁸¹ However, even without any direct fossil-based electricity in the [OME2018 HY + RE] scenario, the contribution to freshwater eutrophication remains high (+645%). One main reason for eutrophication even for RE-based electricity is the provision of minerals and metals for the manufacturing of RE plants. Additionally the electricity for the upstream manufacturing processes of wind energy generators and solar modules is supplied by the manufacturing country's electricity mix and hence include fossil energies. Forthcoming LCA studies for future scenarios should therefore account for changes in the electricity supply of RE manufacturing processes. The assessed environmental footprints of RE technologies will otherwise appear high and not reflect any progress in future defossilisation.

Respiratory effects, inorganics. The category respiratory effects is represented by particulate matter (PM) formation (kg PM_{2.5eq}). In the case of the [OME2018 GR + RE] scenario PM formation is dominated by the combustion of fossil resources for the supply of electricity (49%) and syntheses' thermal energy (46%). For the low carbon scenario [OME2018 HY + RE] 82% of PM-formation can be attributed to the electricity supply. Up to

11% of the respiratory effects can be accounted to the OME utilisation phase although direct PM formation has been considered as non-existent in the case of 100% OME₃₋₅ fuel. This is due to the formation of secondary PM equivalents such as NO_x which are part of this impact category.

Resource depletion. The depletion of resources (minerals, fossils, renewables, kg Sb_{eq}) clearly exceeds the fossil reference for all PtL scenarios. The major share is attributed to the demand for minerals and metals during the manufacturing of RE plants, more precisely to the need for molybdenum (alloy), zinc (galvanizing), copper (generators and cables), cobalt (magnets), and iron (steel constructions). These minerals and metals represent an integral part of RE technologies and thus increase even more for the RE dominated scenario [OME2050 GR + RE]. However, future RE plants will feature increased efficiencies and installed capacities. This in turn will lead to specifically lower amounts of incorporated minerals and metals per energy harvested.⁸² Nonetheless, the very high increase up to 11 200% resource depletion represents a rising future environmental issue which has to be addressed by material efficiency including improved recycling ratios and as well less extensive mining processes.

Cumulative energy demand. The total cumulative energy demand (CED total; MJ_{eq}) for the production of OME₃₋₅ is increased when compared to fossil-based production. This relates to the concept of the "free-lunch" for fossil-based energy carrier production. Fossil fuels and energy carriers source their energy content from high-carbon containing fossil resources. The amount of primary energy to be considered is the amount of heating value extracted from these fossil resources. For PtL products all of the final energy content is to be provided electrically and hence linked to multiple conversion steps and efficiencies. Hence, on the one hand, it is essential to decrease

the total energy demand by further technology development/efficiency improvements whilst fulfilling the energy demand using a very high share of RE. This allows for a low share of fossil-based energy content, mirrored in the CED non-renewable. Here the [OME2050 GR + RE BM] and the [OME2018 HY + RE BM] scenarios are clearly less fossil-intensive than the fossil diesel reference. All statements made in terms of the qualitative results are transferable to the other two evaluated CO₂ sources.

Sensitivity of life cycle impact assessment results

Variations in supplied electricity and water electrolysis efficiency. The life cycle impact assessment results demonstrated that the process energies both electric as well as thermal energies significantly influence the overall GHG emission intensity. Similar to the case of previous power-to-hydrogen and -methanol studies our results show that the energy intensity of the electrolytic H₂ supply proves to be a main driver of the overall GHG intensity.^{79,83–85} The specific energy demand for H₂ generation strongly impacts on the PtL plants' total energy demand, whilst GHG emission intensity of the electricity supply also heavily impacts on the synfuels' GHG emissions.

Therefore it is clear that high efficiency water splitting processes are even more necessary in the cases of a carbon-intensive electricity supply. Fig. 5 shows the dependency of the WtW GHG emissions [g(CO_{2eq}) km⁻¹] on the water electrolysis system efficiency and the GWP intensity of the input electricity [g(CO_{2eq}) kWh_{el}⁻¹]. The CO₂ case Biomethane serves as a basis for this sensitivity evaluation. Thermal energy is assumed to be supplied electrically. The sensitivity results reveal that, depending on the water electrolysis system efficiency, an electricity supply with a GWP > 95–115 g(CO_{2eq}) kWh_{el}⁻¹ will result in

emissions exceeding the WtW emissions of driving with conventional diesel fuel. Input electricity with a GWP < 50 g(CO_{2eq}) kWh_{el}⁻¹ such as hydro, wind and solar offers WtW GHG emissions considerably below 100 g(CO_{2eq}) km⁻¹. In the case of a supply from national electricity grids only a few European countries (*i.e.* Sweden, Norway or Iceland) currently offer low GHG intensive grid electricity. Furthermore, the sensitivity analysis shows that for low GHG intensive electricity, water electrolysis efficiency plays a minor role in GWP impact reduction. From an economic perspective, a high water electrolysis efficiency remains, besides the utilisation rate, a key driver for low levelized cost of H₂.^{55,86}

Further discussion regarding the dependency of the results based on an expanded system with or without crediting an avoided burden is provided in the ESI (S6).[†] It should be noted that the way of solving multifunctionality can influence life cycle impact results heavily as is the case for the present LCA: based on a preliminary study¹⁷ two common allocation procedures have been applied to the multifunctional system: economical and cut-off allocation (CO₂ sourcing without impact). The effect can be high: economical and cut-off allocation show the potential to shift the above-mentioned results with a maximum increase of 300%.

Conclusions

The presented LCA of OME_{3–5} production based on a PtL approach and different scenarios (*e.g.* CO₂ source and electricity source) was performed on WtW emission basis using an avoided burden approach. Both 2018 and 2050 scenarios have been included to allow for technology developments and an increasing share of RE in the future grid electricity mix for Germany (Fig. 1). The results are very sensitive to the allocation procedure used in the LCA. Solving multifunctionality by an economical or cut-off allocation approach shows high sensitivity and can even reverse the results.

The GWP results (Fig. 3), representing the WtW GHG emissions, show that for a high share of RE the OME_{3–5} fuel is advantageous compared to fossil diesel. For the best assessed cases the WtW GHG emissions can be reduced by 86% to 59%, equating to 29–86 g(CO_{2eq}) km⁻¹. However, this significant reduction can only be assured with a very high RE electricity contribution. This is due to the fact that all of the synfuels' energy content has to be provided by electricity, chemically stored in the form of H₂. Hence, even low shares of fossil-based electricity, as will be the case for the current and near-future European grid mixes, will lead to a noticeable increase in related environmental impacts.

For conventional fossil fuels the bulk of WtW emissions (CO₂, CO, NO_x, PM, SO₂, and HC) arise during the utilisation phase. This results in high local exhaust pipe emissions. For fossil fuels the production phase is of comparatively minor environmental significance – *i.e.* nature has already done the work. Conversely for synthetic fuels such as OME_{3–5}, exhaust pipe emissions, in particular NO_x, PM and SO₂, can be reduced significantly due to their purity and combustion chemistry.^{29,66} Thus, the cause of WtW emissions is rather shifted to the life

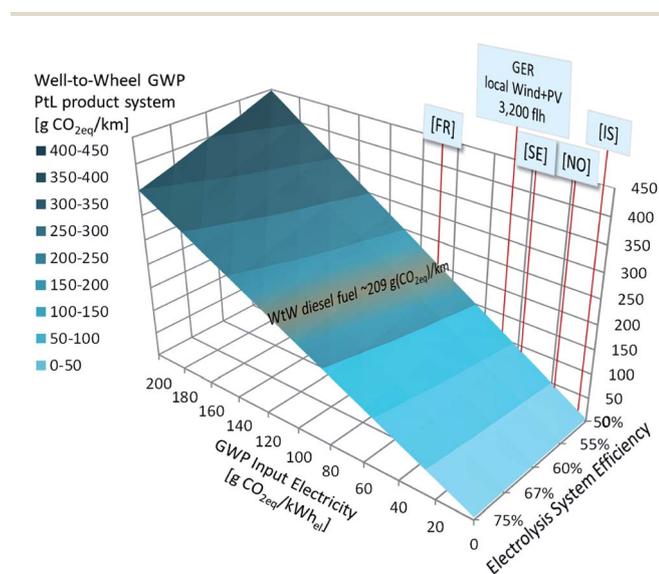


Fig. 5 Dependency of the PtL WtW GWP [g(CO_{2eq}) km⁻¹] on the GWP intensity of the input electricity [g(CO_{2eq}) kWh_{el}⁻¹] and the electrolysis system efficiency. Exemplary GWP intensities of national grid electricity mixes are indicated with red markers (FR: France, GER: Germany, SE: Sweden, NO: Norway, and IS: Iceland).

cycle phase of synfuel production, more precisely the phase of electricity production.

Varying of CO₂ sources showed existing but small impacts on the total WtW GHG emissions depending on the required capturing effort. Hence, higher CO₂ concentrations and less contained impurities are beneficial. As a consequence this emphasises the utilisation of concentrated industrial waste gases.⁸⁷ However, to close the carbon cycle in the long-term the utilisation of atmospheric CO₂ either based on biomass or DAC is inevitable. DAC demands further technology development in terms of thermal energy demand but benefits from an integration of low-temperature excess heat.

Through the discussed sensitivity analysis, it was demonstrated that future defossilisation of grid electricity will lead to a significant reduction in synfuel GWP. In order to enable significantly reduced WtW GHG emissions of <100 g(CO_{2eq}) km⁻¹ an electricity footprint of <50 g(CO_{2eq}) kWh_{el}⁻¹ is identified for the assessed process configuration. Currently, only a few countries offer an electricity grid mix below this footprint. If powered by local RE it is important to emphasise that large-scale PtL plants of the future (*i.e.* going beyond pilot-phase) must be powered by dedicated installed RE capacities. A grid-connection should remain in any case enabling PtL plants to provide important energy balancing and limit expansion of the grid. The legal interpretation in Germany of electrolysis and PtL plants acting as “end consumers” is, in turn, inhibiting faster progress in this respect. However, in the case of a 100% supply from local RE the annual full load hours can be significantly reduced accompanied by a fluctuating H₂ production. This in turn necessitates intermediate H₂ storage for the decoupling of H₂ production and steady-state synthesis. Techno-economic studies assessing such PtL scenarios exhibit increased depreciation and production cost.^{27,88} For these cases system optimization towards high full load hours, reasonable H₂ storage demand and leveled cost of H₂ are the main target. Such aspects are expected to be addressed by further, more expansive LCA studies. Future large-scale PtL plants (and PtX in general) are even more likely to be realised in countries with higher solar irradiance and wind occurrence resulting in (besides potentially low GWP) optimised leveled cost of electricity and increased full load hours (*e.g.* Australia or Chile).

In addition it should be emphasised that an environmentally beneficial PtL production depends not only on GWP but also on a multitude of other impact categories. The further assessed impact categories show that even for an electricity supply completely based on the present RE technologies their upstream manufacturing processes can still cause significant increases in acidification, eutrophication, particulate matter, photochemical ozone creation and resource depletion (Fig. 5). This holistic consideration thus sheds light on the necessity of an ongoing radical, complete “system” defossilisation, material efficient manufacturing of RE plants, increased recycling ratios and improved mining processes. Only this holistic approach can enable a PtL and synfuel production which ensures, besides CO₂ mitigation, environmental advances over the present fossil fuelled liquid energy carriers.

Finally, as addressed in the Introduction, our findings indicate that future private transport is more likely to be fuelled by batteries (short- to mid-range distances), fuel cells (mid- to long-range) or, as a near-term solution for bringing down local PM- and NO_x-emissions, by blends of synthetic fuels such as OME_n. Synthetic fuels based on PtL processes will in turn be indispensable for use in heavy-duty applications, in the rail and maritime sector and in aviation.

Conflicts of interest

There are no conflicts to declare.

Nomenclature

a	Year
AEL	Alkaline water electrolysis
AM	Scenario with CO ₂ from ammonia plant
BM	Scenario with CO ₂ from biomethane upgrading plant
CED	Cumulative energy demand
CH ₄	Methane
CO ₂	Carbon dioxide
CO _{2eq}	Carbon dioxide equivalents
DAC	Direct air capture of CO ₂ /scenario with CO ₂ from DAC
FU	Functional unit
GHG	Greenhouse gas
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
MEA	Membrane electrode assembly
NH ₃	Ammonia
NO _x	Nitrogen oxides
OME	Oxymethylene dimethyl ethers
PEM	Proton exchange membrane water electrolysis
PM	Particulate matter
PtL	Power-to-liquid
PtX	Power-to-X
RE	Renewable energy
REMod	Fh ISE renewable energy model
TtW	Tank-to-wheel
vol%	Volume percent
wt%	Weight percent
WtT	Well-to-tank
WtW	Well-to-wheel

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References

- 1 J. Rogelj, D. Shindell, K. Jiang, S. Fifita, P. Forster, V. Ginzburg, C. Handa, H. Khesghi, S. Kobayashi, E. Kriegler and L. Mundaca, *Mitigation Pathways Compatible with 1.5 °C in the Context of Sustainable Development: Global Warming of 1.5 °C. An IPCC Special Report on the impacts of global warming of 1.5 °C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty*, Geneva, 2018.
- 2 M. Deutsch, M. Buck, P. Graichen and F. Vorholz, *Die Kosten von unterlassenen Klimaschutz für den Bundeshaushalt: Die Klimaschutzverpflichtungen Deutschlands bei Verkehr, Gebäuden und Landwirtschaft nach der EU-Effort-Sharing-Entscheidung und der EUClimate-Action-Verordnung*, Studie, Berlin, 2018.
- 3 Umweltbundesamt, *Berichterstattung unter der Klimarahmenkonvention der Vereinten Nationen und dem Kyoto-Protokoll 2018: Nationaler Inventarbericht zum Deutschen Treibhausgasinventar 1990–2016*, Umweltbundesamt – UNFCCC-Submission, Berlin, 2018.
- 4 C. Tyggestad, N. Scharma, O. Rolser and B. Smeets, *Global Energy Perspective 2019: Reference Case: Energy Insights, Summary*, New York, USA, 2019.
- 5 European Commission, *Electrification of the Transport System: Studies and Reports*, Brussels, 2017.
- 6 A. Sternberg, C. Hank and C. Hebling, *Greenhouse Gas Emissions for Battery Electric and Fuel Cell Electric Vehicles with Ranges over 300 kilometers: Study Commissioned by H₂ Mobility*, Freiburg, 2019.
- 7 S. Siegemund, M. Trommler, O. Kolb and V. Zinnecker, *The Potential of Electricity-Based Fuels for Low-Emission Transport in the EU: E-Fuels Study, An Expertise by LBST and Dena*, Berlin, 2017.
- 8 Öko-Institut and Fraunhofer-Institut für System- und Innovationsforschung ISI, *Klimaschutzszenario 2050: 2. Endbericht, Studie im Auftrag des Bundesministeriums für*, Berlin, Karlsruhe, 2015.
- 9 <https://www.destatis.de/DE/Themen/Branchen-Unternehmen/Energie/Erzeugung/Tabellen/bruttostromerzeugung.html>, last accessed September 2019.
- 10 M. Ouda, F. K. Mantei, M. Elmehlawy, R. J. White, H. Klein and S.-E. K. Fateen, *React. Chem. Eng.*, 2018, 3(3), 277.
- 11 W. Ying, L. Genbao, Z. Wei and Z. Longbao, *Fuel Process. Technol.*, 2008, 89(12), 1272.
- 12 B. Lumpp, D. Rothe, C. Pastoetter, R. Laemmermann and E. Jacob, *Motortech. Z.*, 2011, 2011(72–3), 198.
- 13 M. Härtl, K. Gaukel, D. Pélerin and G. Wachtmeister, *Motortech. Z.*, 2017, 78(02), 52.
- 14 M. Münz, A. Mokros, D. Töpfer and C. Beidl, *Motortech. Z.*, 2018, (03), 16.
- 15 E. Jacob and M. Härtl, *Tagungsband des 37. Internationalen Wiener Motorenymposiums*, 2016.
- 16 M. Härtl, P. Seidenspinner, E. Jacob and G. Wachtmeister, *Fuel*, 2015, 153, 328.
- 17 W. Maus and E. Jacob, *Synthetic Fuels – OME1: A Potentially Sustainable Diesel Fuel*, 2014.
- 18 *The Power to Liquid Concept: Hydrogenation of CO₂ to Methanol and the Production of Oxymethylene Ethers, Catalysis – Novel Aspects in Petrochemistry and Refining*, ed. M. Ouda, G. Yarce, K. Hesterwerth, M. Hadrich, R. J. White, A. Schaadt and H. Klein, 2016.
- 19 L. Pellegrini, M. Marchionna, R. Patrini and S. Florio, *SAE Int.*, 2013, 2013.
- 20 G. Richter and H. Zellbeck, *Motortech. Z.*, 2017, 78(12), 66.
- 21 S. Deutz, D. Bongartz, B. Heuser, A. Kätelhön, L. Schulze Langenhorst, A. Omari, M. Walters, J. Klankermayer, W. Leitner, A. Mitsos, S. Pischinger and A. Bardow, *Energy Environ. Sci.*, 2017, 55(Part B), 7296.
- 22 L. Lautenschütz, D. Oestreich, P. Seidenspinner, U. Arnold, E. Dinjus and J. Sauer, *Fuel*, 2016, 173, 129.
- 23 E. Jacob and W. Maus, *Motortech. Z.*, 2017, 78(3), 54.
- 24 M. Ouda, F. Mantei, K. Hesterwerth, E. Bargiacchi, H. Klein and R. J. White, *React. Chem. Eng.*, 2018, 3(5), 676.
- 25 L. Lazar, Environmental performance of liquid energy carriers and fuels based on renewable hydrogen and recycled carbon dioxide (Power-to-Liquid), Master thesis, Pforzheim University, Pforzheim, 2018.
- 26 N. Köppel, Life Cycle Assessment of Synthetic Fuel: Environmental Performance of Oxymethylene Ethers (OME) Based on Recycled Carbon Dioxide and Renewable Hydrogen, Master thesis, Technical University of Munich, München, 2019.
- 27 C. Hank, S. Gelpke, A. Schnabl, R. J. White, J. Full, N. Wiebe, T. Smolinka, A. Schaadt, H.-M. Henning and C. Hebling, *Sustainable Energy Fuels*, 2018, 2(6), 1244.
- 28 N. Mahbub, A. O. Oyedun, A. Kumar, D. Oestreich, U. Arnold and J. Sauer, *J. Cleaner Prod.*, 2017, 165, 1249.
- 29 G. Avolio, O. Kastner, G. Rösel and R. Brück, *Motortech. Z.*, 2018, 79(07), 16.
- 30 G. A. Olah, A. Goepfert and G. K. S. Prakash, *J. Org. Chem. USSR*, 2009, 74(2), 487.
- 31 A. Feiling, M. Münz and C. Beidl, *Motortech. Z.*, 2016, 2016(02/2016), 16.
- 32 Umweltbundesamt, *Postfossile Energieversorgungsoptionen für einen treibhausgasneutralen Verkehr im Jahr 2050: Eine verkehrsträger-übergreifende Bewertung, Dessau-Roßlau*, 2015.
- 33 Continental AG, *Climate-Neutral Driving: Continental Successfully Tests the Synthetic Diesel Fuel OME*, Regensburg, 2017.
- 34 DIN Deutsches Institut für Normung e.V., DIN EN ISO 14040, 2006th edn. 13.020.10, 2009.
- 35 DIN Deutsches Institut für Normung e.V., DIN EN ISO 14044, 2006th edn. 13.020.10, 2006.

- 36 European Commission Joint Research Centre, *ILCD-Handbook – General Guide for Life Cycle Assessment: Detailed Guidance*, Luxembourg, 2010.
- 37 European Commission Joint Research Centre, *ILCD-Handbook – Recommendations for Life Cycle Impact Assessment in the European Context: Based on Existing Environmental Impact Assessment Models and Factors*, Luxembourg, 2011.
- 38 European Commission Joint Research Centre, *ILCD-Handbook – Characterisation Factors of the ILCD Recommended Life Cycle Impact Assessment Methods: Database and Supporting Information*, Luxembourg, 2012.
- 39 European Commission Joint Research Centre, *ILCD-Handbook – Framework and Requirements for Life Cycle Impact Assessments Models and Indicators*, Luxembourg, 2010.
- 40 A. Zimmerman, J. Wunderlich, G. Buchner, L. Müller, K. Armstrong, S. Michailos, A. Marxen, H. Naims, F. Mason, G. Stokes and E. Williams, *Techno-Economic Assessment & Life-Cycle Assessment Guidelines for CO₂ Utilization, Global CO₂ Initiative*, University of Michigan, Berlin, 2018.
- 41 <https://pinch-analyse.ch/index.php/de/last> accessed January 2019.
- 42 https://www.energy-charts.de/index_de.html last accessed September 2018.
- 43 A. Palzer, Sektorübergreifende Modellierung und Optimierung eines zukünftigen deutschen Energiesystems unter Berücksichtigung von Energieeffizienzmaßnahmen im Gebäudesektor, PhD Dissertation, Karlsruhe Institute of Technology KIT, Karlsruhe, 2016.
- 44 A. Palzer and H.-M. Henning, *Renewable Sustainable Energy Rev.*, 2014, **30**, 1019.
- 45 A. Palzer and H.-M. Henning, *Energy Technol.*, 2014, **2**(1), 13.
- 46 Sunfire GmbH, *First commercial Plant for the production of Blue Crude planned in Norway*, Dresden, 2017.
- 47 A. Varone, *Sustainable Fuels in the Nordic Countries*, Potsdam, 2015.
- 48 J. Perner and D. Bothe, *International Aspects of a Power-to-X Roadmap: A Report Prepared for the World Energy Council Germany*, 2018.
- 49 P. Adler, E. Billig and A. Brosowski, *Leitfaden Biogasaufbereitung und -einspeisung*, Gülzow-Prüzen, 2014.
- 50 W. Urban, K. Girod and H. Lohmann, *Technologien und Kosten der Biogasaufbereitung und Einspeisung in das Erdgasnetz: Ergebnisse der Markterhebung 2007–2008*, Oberhausen, 2009.
- 51 <https://v31.ecoquery.ecoinvent.org/Details/UPR/044d2021-1c7b-4975-b283-6744737d0f28/8b738ea0-f89e-4627-8679-433616064e82>.
- 52 H.-J. Althaus, R. Hischer, M. Osses, A. Primas, S. Hellweg, N. Jungbluth and C. Mike, *Life Cycle Inventory of Chemicals: Data v2.0*, ecoinvent report no. 8, Düsseldorf, 2007.
- 53 T. Nemecek and T. Kägi, *Life Cycle Inventory of Agricultural Production Systems: Ecoinvent Report No. 15*, Zürich, Switzerland, Dübendorf, 2007.
- 54 A. Buttler and H. Spliethoff, *Renewable Sustainable Energy Rev.*, 2018, **82**, 2440.
- 55 T. Smolinka, N. Wiebe, S. Philip, A. Palzer, F. Lehner, M. Jansen, S. Kiemel, M. Robert, S. Wahren and F. Zimmermann, *Studie IndWEde: Industrialisierung der Wasserelektrolyse in Deutschland: Chancen und Herausforderungen für nachhaltigen Wasserstoff für Verkehr, Strom und Wärme*, Berlin, 2018.
- 56 Fuel Cell and Hydrogen Joint Undertaking – FCH JU, *Study on Early Business Cases for H₂ in Energy and More Broadly Power to H₂ Applications: Final Report*, Brüssel, 2017.
- 57 O. Schmidt, A. Gambhir, I. Staffell, A. Hawkes, J. Nelson and S. Few, *Int. J. Hydrogen Energy*, 2017, **42**(52), 30470.
- 58 *Energiespeicher - Bedarf, Technologien, Integration*, ed. M. Sterner and I. Stadler, Springer, Berlin Heidelberg, Berlin, Heidelberg, 2014.
- 59 T. Smolinka, T. Raksha, T. Pregger, A. Friedrich and G.-S. Schneider, *Studie über die Planung einer Demonstrationsanlage zur Wasserstoff-Kraftstoffgewinnung durch Elektrolyse mit Zwischenspeicherung in Salzkavernen unter Druck: Plan Delykad*, Plan Delykad, Stuttgart, 2014.
- 60 T. Smolinka, M. Günther and J. Garcke, *Stand und Entwicklungspotenzial der Wasserelektrolyse zur Herstellung von Wasserstoff aus regenerativen Energien: Kurzfassung des Abschlussberichts*, NOW-Studie, Freiburg, 2011.
- 61 A. Ursua, L. M. Gandia and P. Sanchis, *Proc. IEEE*, 2012, **100**(2), 410.
- 62 S. Estelmann, Efficiency optimization and simulation of Power-to-Liquid-(PtL)-Process using the example of methanol synthesis in consideration of heat integration models, Master thesis, Technical University of Braunschweig, Braunschweig, 2016.
- 63 T. Smolinka, *Material data for Proton Exchange Membrane stacks and related BoP-Hardware demand*, EMail, personal conversation, Freiburg, 2018.
- 64 B. Pitschak, *Power-to-X progress and developments at Hydrogenics*, Düsseldorf, 2016.
- 65 H.-J. Fell, *Hydrogen from large scale alkaline electrolysis for methanol production*, Copenhagen, 2017.
- 66 A. Omari, B. Heuser and S. Pischinger, *Fuel*, 2017, **209**, 232.
- 67 U. Albrecht, S. Patrick, W. Weindorf, R. Wurster and W. Zittel, *FVV*, 2013, (1031/2013).
- 68 U. Albrecht, P. Schmidt, W. Weindorf, R. Wurster and W. Zittel, *Eine Expertise für die Forschungsvereinigung Verbrennungskraftmaschinen e. V. Abschlussbericht*, 2013, 30, Heft 1031-2013.
- 69 F. K. Mantei, Combined Theoretical and Experimental Approaches to Oxymethylene Ethers Synthesis, Master thesis, Technical University of Berlin, Berlin, 2017.
- 70 <https://ec.europa.eu/environment/archives/air/models/tremove.htm>.
- 71 M. Wietschel, M. Kühnbaach and R. David, *Die aktuelle Treibhausgas-emissionsbilanz von Elektrofahrzeugen in Deutschland: Working Paper Sustainability and Innovation No. 5 02/2019*, Karlsruhe, 2019.
- 72 <https://www.umweltbundesamt.de/daten/verkehr/kraftstoffe>, last accessed September 2019.

- 73 O. Edenhofer, R. P. Madruga and Y. Sokona, *Renewable Energy Sources and Climate Change Mitigation: Special Report of the Intergovernmental Panel on Climate Change*, 2012.
- 74 M. M. Hand, S. Baldwin, E. DeMeo, J. M. Reilly, T. Mai, D. Arent, G. Porro, M. Meshek and D. Sandor, *Renewable Electricity Futures Study (Entire Report)*, Golden, 2012.
- 75 G. Reiter and J. Lindorfer, *Int. J. Life Cycle Assess.*, 2015, **20**(4), 477.
- 76 Shell Deutschland Oil GmbH, *Shell Hydrogen Study*, 2017.
- 77 R. Bhandari, C. A. Trudewind and P. Zapp, *J. Cleaner Prod.*, 2014, **85**, 151.
- 78 J. Burkhardt, A. Patyk, P. Tanguy and C. Retzke, *Appl. Energy*, 2016, **181**, 54.
- 79 K. Bareiß, C. de La Rua, M. Möckl and T. Hamacher, *Appl. Energy*, 2019, **237**, 862.
- 80 Deutsche Energie-Agentur GmbH (dena), *Process heat in industry and commerce: Technology solutions for waste heat utilisation and renewable provision*, Hannover, 2016.
- 81 G. Doka, *Life Cycle Inventory of the Disposal of Lignite Spoil, Coal Spoil and Coal Tailings*, Zürich, Switzerland, 2009.
- 82 J. Lieberei and S. H. Gheewala, *Int. J. Life Cycle Assess.*, 2017, **22**(2), 185.
- 83 X. Zhang, C. Bauer, C. L. Mutel and K. Volkart, *Appl. Energy*, 2017, **190**, 326.
- 84 V. Uusitalo, S. Väisänen, E. Inkeri and R. Soukka, *Energy Convers. Manage.*, 2017, **134**, 125.
- 85 W. Hoppe, N. Thonemann and S. Bringezu, *J. Ind. Ecol.*, 2017, **7**(3), 181.
- 86 T. Smolinka, N. Wiebe and M. Thomassen, *Cost Break Down and Cost Reduction Strategies for PEM Water Electrolysis Systems: Session B05: H₂ from Electrolysers: Concepts & Costs*, Luzern, Schweiz, 2017.
- 87 N. v. d. Assen, L. J. Müller, A. Steingrube, P. Voll and A. Bardow, *Environ. Sci. Technol.*, 2016, **50**(3), 1093.
- 88 M. Decker, F. Schorn, R. C. Samsun, R. Peters and D. Stolten, *Appl. Energy*, 2019, **250**, 1099.
- 89 <https://dribbble.com/vectorsmarket>, last accessed March 2019.