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Energy efficiency and economic assessment of imported energy carriers based on renewable electricity†

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The production of energy carriers based on renewable electricity *via* the Power-to-X (PtX) approach holds the key for a holistic transformation of our global industries from fossil fuels towards renewable energy sources. To compete with cheap fossils, PtX products demand energy-efficient processes and low-cost renewable electricity. Therefore, the import of PtX products from countries with high renewable energy potentials to countries with high energy demand presents a promising pathway. However, the question which set of PtX products qualifies as suitable for long-distance transport has not yet been answered. In this context, this paper assesses the energy and cost efficiency of five PtX energy carriers (methane, methanol, ammonia, liquefied hydrogen and hydrogen bound in LOHC). Furthermore, we evaluate the influence of fluctuating renewables, availability of water and transport distance in a case study for large-scale PtX production in Morocco. Our results show that the evaluated PtX pathway efficiencies vary between 40–52% (base cases) and 44–58% (optimistic cases). None of the pathways assessed is significantly affected in its overall efficiency by a ship transport over an exemplary distance of 4000 km. However, for longer transport distances the cost difference between the assessed pathways increases. The production cost of the PtX energy carriers (124–156 € per MWh) depends on the availability of excess heat, energy density of the product and, if required, liquefaction efforts. In summary, the paper reveals that the long-distance transport and import of PtX products present an interesting option for the ongoing integration of renewable electricity into our energy system and industries. The petrochemical and steel industries in particular, as well as heavy goods transport, shipping and aviation, will be highly dependent on these imported synthetic energy sources.

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Introduction

The global carbon cycle is out of balance due to drastically increased fossil greenhouse gas (GHG) emissions to the atmosphere and thus exceeding the capacity of our biogeochemical cycles.[1] The result is an anthropogenic greenhouse effect with its associated environmental problems[2] and extreme weather events – the latter having tripled since 1980.[3] In order to reach the goal of keeping the global temperature rise below 1.5 °C, a radical defossilisation of the global economies is necessary.[4,5] The good news is that even the scenarios with highest energy demands for 2050 are well surpassed by the latest estimations on the total renewable energy (RE) potential that could be harvested by utilisation of present technologies.[6] Characterised by an intense growth within the last two decades modern RE (*i.e.* excluding nuclear and traditional bioenergy) accounted for 10.6% of total final energy consumption in 2017 (+4.4% compared to 2016),[7] but only 2% is yet covered by *electricity* generated with modern renewable technologies. Up to 80% of the total final energy consumption is still covered by fossil fuels.

The integration of RE beyond direct electrification into the energy, mobility, industry and private sectors *via* hydrogen (H_2) based renewable energy carriers is referred to as "Power-to-X" (PtX). When powered with renewable electricity PtX can enable highly defossilised primary energy provision. It represents a cornerstone for integrated energy systems and thus, a closing of the carbon cycle.[8] However, shifting our sectors from fossil to RE based primary energy resources requires magnitudes of already installed RE capacities.[9,10] For example, replacing fossil based precursors in the chemical sector with PtX based chemicals would lead to a significant increase in the electricity demand. In this context, Kätelhön *et al.* 2019 substituted the fossil based precursors for the production of 20 large-volume

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chemicals (accounting for more than 75% of the GHG emitted in the chemical industry) with RE-based PtX pathways.[10] The result has been a demand for low-carbon electricity between 18.1 and 32.0 PWh_{el} per year – which surpasses the current global electricity demand (23.0 PWh_{el} per year in 2018).[11] For another sector, global transports, the total energy demand currently sums up to ~35 PWh per year.[12] Enormous efforts are underway to electrify it, either in a direct form *via* electric vehicles or indirectly *via* H_2 based power trains (fuel cells and internal combustion engines with synthetic fuels). Although, the electrification of global transport has a certain efficiency potential, it can be assumed that the global demand for renewable electricity will also increase significantly for this sector.

In countries with high energy demands, the production of sufficient renewable electricity is not always possible. Thus, energy carriers based on renewable electricity are required. For example, the European Union targets at a decrease of the future primary energy demand from 18.2 PWh_{el} in 2017 to 17.3 PWh_{el} in 2020 and 15.9 PWh_{el} in 2030.[13,14] However, the total technical renewable electricity potential in the European Union sums up to 9–14 PWh_{el} per year (depending on installation density and yield parameters).[15] It remains questionable if this potential will be fully tapped within the next decades under the light of a slow expansion of national power grids and storage technologies, hesitant political frameworks and a "not-in-my-backyard" mentality in case of renewable energy projects.[16–21]

The future need for an import of renewable energy carriers

In their "Clean Energy for All Europeans" package[22] the European Commission recognises H_2 and PtX processes as key technologies on the pathway towards a defossilised system but at the same time underlines that "(PtX) technologies become attractive in the context of abundant electricity generated from carbon-free sources […]". It is very likely that regions characterised by a restricted RE potential and a present net-import of fossil energy carriers will as well in the future be dependent on an import of low-carbon energy carriers (*e.g. via* PtX). Considering that the generation cost of PtX products highly depend on the price of the input electricity[15,23,24] it becomes clear that any large-scale PtX production becomes relevant in countries with high RE potential and full-load-hours. In the context of a global PtX market the World Energy Council describes three criterions for potential large-scale PtX producers: (1) low-cost RE power, (2) large available areas exhibiting high solar and/or wind potentials, (3) political stability and an energy political framework.[25] In this context Fasihi *et al.* 2018 analysed the full load hours and levelised cost of electricity generation from photovoltaic and wind power plants on a global scale.[26] Levelised cost of renewable electricity as low as 17–20 € per MWh_{el} are described for the top sites in the world. Considering a proximity to the coast (desalinised seawater, access to ports) LCo(E) in the range of 25–30 € per MWh_{el} seem realistic. The here identified regions such as Spain, Morocco, Chile or Australia are as well listed by the World Energy Council as potential *PtX exporters*.

However, for a future export of PtX products from these identified countries, the aspects of social compatibility and sufficient RE availability have to be taken into account.[27] Scenarios based on the stated global energy policies show that the global demand for fossil fuels will significantly increase within the next decades mainly driven by an increasing population (with a better standard of living).[28] Additionally, many of these identified PtX exporters and their energy production are still characterised by a high share of fossil energies, a privatised energy sector and partially depend on energy imports from other countries. Therefore, the existing RE potential and a build-up of a sustainable energy infrastructure beyond export should also be used for macroeconomic and green development in the PtX exporting countries themselves.

Scope of the study

On the basis of the aspects discussed above it can be stated that: (1) a transformation of the global economies from fossil to RE based requires large amounts of installed RE capacities, (2) H_2 based energy carriers will be an important part of this transformation and (3) a global trade of RE *via* H_2 and other gaseous and liquid PtX products from regions with high RE availability to economic centers with high energy demand emerges unavoidable. In addition, the development of a global RE trade should only take place in combination with the introduction of socially acceptable and sustainable energy production in the RE-exporting countries themselves. This paper builds on these considerations and questions:

- What is the energy efficiency of different PtX pathways for long-distance distribution of RE *via* H_2 based energy carriers?
- How does the energy efficiency of these PtX pathways relate to their respective economic efficiency for a specific case study?

Under the background of the defined research questions this paper assesses five PtX production pathways from the perspective of energy and cost efficiency. The included PtX products are potential options for future renewable energy storage and transport at large scales and are a frequent part in recent scientific and politic debates: H_2 distributed in liquid state (LH_2), H_2 distributed with liquid organic hydrogen carriers (LOHC) as transportation medium (LOHC–H_2), liquid methane (LCH_4), methanol (CH_3OH) and ammonia (NH_3). A detailed combined assessment of these energy carriers is currently missing in the scientific literature.

During its first part, the paper is intended to offer estimations on PtX efficiencies when operated on a base-load and without any intermediate storage demands. We do not aspire to provide a pure efficiency ranking of these PtX pathways but rather highlight potential hotspots for efficiency optimisation. The efficiency analysis differentiates between a base and an optimistic case. The base case applies conversion efficiencies, electricity and heat demands at present technology levels. In turn, the optimistic case considers published near-future (~2030) target values for some of the process steps. By this we aim at giving a perspective on how overall pathway efficiencies can change if central process steps undergo technological advances. The selection of process parameters is outlined in the section "parameter inventory".

The second part of this work assesses the detailed cost distributions of the PtX pathways for an exemplary case study (Morocco) considering large-scale production and downstream long-distance ship transport to North-western Europe. The case study includes more detailed systemic and site-dependent parameters such as local availability of RE, their fluctuation, availability of water and necessary storage demands.

Part I – energy efficiency analysis

Fig. 1 shows the basic scheme for the five assessed PtX pathways. For the basic efficiency analysis we assume renewable electricity (1) to be available without fluctuation (fluctuating RE rendering storage technologies necessary will be considered for the case study in the second part of the paper). Renewable electricity covers both electrical and thermal energy demand of all process steps. The water supply for the electrolysis step is realised *via* a seawater desalination plant (2). This enables technical availability of water for all arid regions with high RE availability next to the sea. Hydrogen is produced *via* polymer exchange membrane (PEM) electrolysis (3) and in case of LCH_4, CH_3OH and NH_3 conditioned to synthesis pressure and temperature and fed to the reactor for catalytic conversion (4). In case of LCH_4 and LH_2 the product is brought to liquid state by cryogenic liquefaction (5). For this study, direct air capture technology (DAC) ((6) pathways LCH_4 and CH_3OH) is assumed as carbon source. Carbon capturing from industrial and biomass point-sources represents another less energy intensive CO_2 option. However, the availability of large-scale industrial CO_2 sources depends on the PtX location and CO_2 transportation to the point of further conversion could be necessary. The energetic effort for CO_2 liquefaction and transport *via* ship from quite remote areas to the PtX plant is limited and technically feasible.[29] From an energy point of view, atmospheric CO_2 capturing can be seen as a conservative assumption for PtX scenarios but enables location-independent CO_2 sourcing. DAC necessitates besides electricity, a heat source. On the one hand, the use of fossil natural gas for heat supply is not in the scope of this paper which focuses on fully defossilised pathways. On the other hand, utilisation of the final product (synthetic CH_4 or CH_3OH) would mean an efficiency loss compared to utilising direct electricity. Instead, the necessary heat demand is assumed to be covered by available excess heat from the exothermal synthesis step and an electric heating module. Finally, the respective PtX product is transported by ship (7) to the importing country (8). The functional unit of our assessment is 1 MJ of renewable energy carrier arrived at the final location. The assumed long-distance transportation covers 4000 km, representative for marine transport from Northwest Africa to North-western European ports (*e.g.* Hamburg or Rotterdam). The distance will be varied in a sensitivity analysis to cover as well longer routes. The International Maritime Organisation's (IMO) objective to lower the GHG emissions by at least 50% by 2050 (compared to 2008) and eliminate other harmful emissions necessitates intense defossilisation of the shipping sector.[30] Therefore, we assume that the ships use their transported energy carrier as fuel. The use of fossil based heavy oil contradicts an envisioned defossilised system and is therefore not in our scope.

Parameter inventory for the analysed PtX pathways

This chapter provides more information on the five PtX pathways, explains respective parameters and energy demands. In general the scale of the components orientates on an annual H_2 production of 42 500 t. The specifications of the seawater desalination and deionisation as well as the H_2 production apply to all assessed PtX pathways and will be described at the beginning of this section. A summarising parameter table is part of the ESI (ESI-S1†).

Sea water desalination and deionisation. Water provision *via* desalination of marine sea water is assumed to be based on seawater reverse osmosis (SWRO). Voutchkov *et al.* 2018 analysed the actual state and technological trend regarding SWRO with a focus on energy use.[31] Depending on salinity and temperature of the seawater, the applied membrane and plant capacity the energy demand for SWRO can vary between 2.5–3.1 $kWh_{el}\ m^{-3}$. Considering that the actual SWRO energy demand accounts for 65–80% of a desalination plants' total energy demand a range of 3.1–4.8 $kWh_{el}\ m^{-3}$ is possible for state-of-the-art medium to large size desalination plants. The surface salinity of marine regions varies depending on temperature, freshwater inflow from coastal regions and ocean currents.

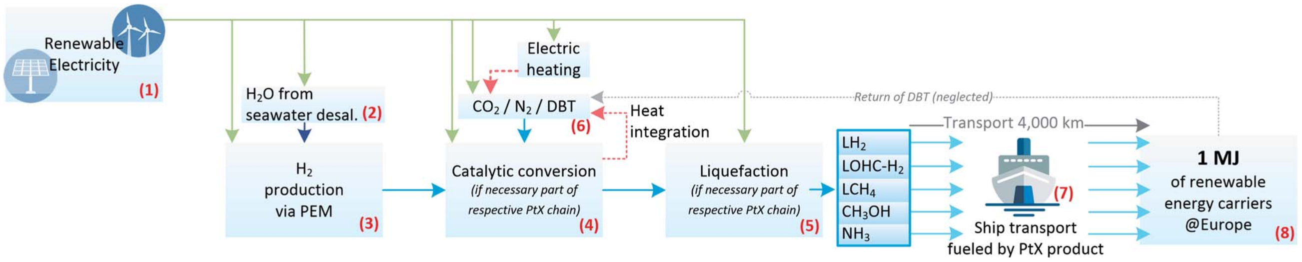

Fig. 1 System layout Part I – energy efficiency analysis: renewable electricity is the sole energy source for all process steps enabling a fully defossilised PtX product: H_2 distributed in liquid state (LH_2), H_2 distributed with liquid organic hydrogen carriers (LOHC) as transportation medium (LOHC–H_2), liquid methane (LCH_4), methanol (CH_3OH) and ammonia (NH_3). For the efficiency analysis (part I) fluctuations in renewable electricity production are neglected in order to be able to analyse the pure electricity-to-product efficiency. Part II of the paper will address the aspect of renewable electricity availability including the effects on storage requirements and economic efficiency.

Based on satellite measurements[32] a surface salinity of 35 000–37 000 mg L^{-1} can be seen as the higher range of salinity at global coastal regions in the subtropics (*e.g.* coast of Brazil, Argentina, parts of Australia) or the eastern Atlantic ocean (*e.g.* coast of Morocco).

For the hypothetical near-future small to medium scale plant of our study (~1200 m^3 per day), we assumed a conservative total energy demand of 3.75 kWh_{el} m^{-3}. Following the desalination it is assumed that the water will be deionised to fit the demands of the downstream water electrolysis. The process for deionisation is based on a process from the ecoinvent v3.3 database and considers an energy demand of 0.45 kWh_{el} m^{-3}.[33]

Hydrogen production *via* PEM water electrolysis. For the large-scale water electrolysis system (~200–300 MW_{el}), the emerging technology of proton exchange membrane (PEM) electrolysis has been considered. PEM systems offer specific advantages when placed in the context of fluctuating RE production and PtX-concepts: they enable a shorter start-up time (cold-start) and response time than other water electrolysis concepts (*e.g.* alkaline or high temperature sold-oxide electrolysis), low energy consumption in standby mode, elevated operational pressures (*e.g.* 30 bar) and higher current densities (potentially reducing stack size). The inputs of the assessed PEM system are water and electricity. The assumptions for the PEM systems' energy demand are based on a recent sector survey on manufacturer estimations for state-of-the-art and future electrolysis systems.[34] The base case assumes 4.81 kWh_{el} per $Nm^3(H_2)$ and considers the range in manufacturer estimations (4.40–5.20 kWh_{el} per $Nm^3(H_2)$) for existing to near-future PEM systems with capacities from 1–100 MW_{el}. The optimistic case calculates with 4.46 kWh_{el} per $Nm^3(H_2)$ and is based on the range in estimations (4.10–4.80 kWh_{el} per $Nm^3(H_2)$) for advanced PEM systems after 2030. The stoichiometric water demand of water electrolysis amounts to 8.94 $kg(H_2O)$ per $kg(H_2)$. Based on manufacturer specifications for a commercial PEM system we assume a water consumption of 10 $kg(H_2O)$ per $kg(H_2)$.[35]

$$H_2O(l) \rightarrow H_2(g) + 0.5O_2(g),\ \Delta H^0_R = +285.8\ \mathrm{kJ}$$

PtX pathway for renewable liquid hydrogen – LH_2. The pathway liquid hydrogen (LH_2) comprises the smallest number of conversion steps and is therefore promising in terms of overall system efficiency.

Hydrogen liquefaction. Liquefaction of H_2 is based on a liquefaction plant design as described in the IDEALHY project.[36] LH_2 is provided at an absolute pressure of 2 bar, 23 K and a purity of 100%. Losses of hydrogen are assumed to be 1.6%, mainly caused at the feed gas compression step. Concerning the energy requirements of liquefaction, several investigations indicate that large-scale liquefiers will most probably be able to reach electricity consumption rates as low as 6.0 kWh_{el} per $kg(LH_2)$.[37] Today's hydrogen liquefiers with capacities up to 15 $t(H_2)$ per day show values of 10.0–12.0 kWh_{el} per $kg(LH_2)$.[38] Considering even larger conceptualised and as well existing liquefaction plants with capacities of several hundred tons per day, lower energy demands of 5.30–8.50 kWh_{el} per $kg(LH_2)$ are in a realistic range of technological feasibility. Accordingly, the H_2 liquefaction in our study differentiates between a base (8.0 kWh_{el} per $kg(LH_2)$) and an optimistic case (6.0 kWh_{el} per $kg(LH_2)$).

Transport of LH_2 via ship. The shipping of the liquefied H_2 to the final destination over a distance of 4000 km is assumed to be realised with a novel LH_2 carrier as conceptualised by Kamiya *et al.* 2015.[39] The proposed concept describes a large-scale carrier consisting of four vacuum panel type spherical tanks. The boil-off rate is described as 0.2% per day (or less). Since the study of Kamiya *et al.* 2015 does not include information on the ships propulsion energy demand we orientate on values based on propulsion datasheets for large conventional LNG carriers with a total capacity of 140 000 m^3 from MAN Diesel & Turbo.[40] The suitable engine results in a necessary SMCR power (specified maximum continuous rating) of 28 000 kW (at 20 knots/36 km per hour) for the selected ship size. Assuming that the propulsion system of the LH_2 carrier concept will be based on a H_2 gas motor with a rated efficiency of $\eta = 0.43$ the resulting specific LH_2 consumption sums up to 0.181 kWh per tkm ("per ton-kilometres") or 54 $kg(H_2)$ per km:

$$\dot{W}_{LH_2\ \mathrm{carrier}} = \frac{P_{SMCR}}{\mathrm{cap}_{ship} \times \rho_{LH_2} \times v_{ship} \times \eta_{H_2M}}$$

with

$\dot{W}_{LH_2\ \mathrm{carrier}}$ = energy demand of the LH_2 carrier in [kWh per tkm]

P_{SMCR} = specified maximum continuous rating of selected ship class (28 000 kW)

cap_{ship} = ship capacity (140 000 m^3)

ρ_{LH_2} = volumetric density of LH_2 (0.071 t per m^3)

v_{ship} = ship speed (36 km per hour)

η_{H_2M} = efficiency of H_2 gas motor.

The boil-off rate of 0.2% per day results in a maximum evaporation of 28 $kg(LH_2)$ per km. This enables the use of the evaporating H_2 as fuel without any losses due to venting. Any losses during port times are neglected.

PtX pathway for renewable H_2 *via* LOHC – LOHC–H_2. The concept of LOHC comprises a reversible chemical reaction where a specific chemical molecule (the "LOHC") is loaded with gaseous H_2 which can be stored in liquid form showing elevated volumetric energy densities. Subsequent long-distance transportation of the hydrogenated LOHC is thus possible without any boil-off losses and is manageable in an easy way. To enable utilisation of the stored H_2 at the point of destination an endothermal dehydrogenation step has to be performed necessitating elevated temperatures at ambient pressure. A direct combustion of the loaded LOHCs is due to their high market prices and the fossil origin (*i.e.* release of fossil carbon) not in the scope of the concept. The most appropriate LOHC medium depends on a multitude of parameters such as the respective market price, the availability of waste heat at the place of dehydrogenation or the technological maturity of the conversion and release units.[41] Chemicals such as 1,2-dihydro-1,2-azaborine or *N*-ethylcarbazole either require additional solvents (reducing the storage capacity) and thus additional H_2

purification[42] or show lower conversion efficiencies during dehydrogenation.[43] Within our study, we focus on dibenzyltoluene (DBT), a chemical applicable as LOHC without further solvents and already applied for the LOHC concept at commercial but still comparably small scale (~4000 t(H_2) per year).[43,44]

Hydrogenation of LOHC. After its production *via* PEM electrolysis the pressurised H_2 is fed to the hydrogenation unit. The hydrogenation of DBT has to be performed at elevated pressures and temperatures. For this study, a pressure of 25 bar is applied fitting the pressure output level of the PEM electrolysis of 30 bar. Apart from start-up times, the exothermal hydrogenation reaction provides sufficient heat to realise a necessary temperature level of ~200–250 °C.[45] The LOHC loading density (wt% of H_2 in LOHC) is among other things relevant for the initial amount of LOHC medium to be purchased to realise a certain H_2 supply chain. For this study a LOHC loading density of 6.23 wt% H_2 is assumed.[45]

Transport of LOHC via ship. The handling of loaded LOHC (perhydro-DBT) is assumed to be comparable to the handling of conventional thermal oil and is assumed to be shipped in a tanker. Due to high purchase cost for DBT the assumed shipping size is smaller (73 000 t perhydro-DBT) than for the other assessed PtX pathways (compare section "Inventory of the economic parameters"). The tanker type and necessary engine size is selected based on propulsion datasheets for tankers from MAN Diesel & Turbo and results in an engine size of 12 300 kW (SMCR, at 28 km per hour) representing the "Aframax" class.[46] As for every PtX pathway in this study, it is assumed that the ship uses the transported PtX product as fuel. Therefore, propulsion power is assumed to be realised by means of a H_2 gas motor ($\eta = 0.43$; 30.8 kg(H_2) per km). The heat demand for necessary on-board dehydrogenation of perhydro-DBT (0.495 t(DBT) per km) is covered by the excess heat of the gas turbine.

Dehydrogenation of LOHC at the port of destination. An endothermal dehydrogenation (310 °C, 1 bar) step is required to release the stored H_2 from the perhydro-DBT. The necessary heat demand can either be supplied *via* oxidation of a share of released H_2 or, if available, *via* excess heat. For the efficiency analysis we consider a base (30 wt% of H_2 is burned) and an optimistic case (25 wt% of H_2 is burned)[47] and will as well discuss the effect if excess heat can be applied. A loss of DBT during dehydrogenation and the DBT return transport is not part of the efficiency analysis but will be considered within the case study.

PtX pathway for renewable liquid methane – LCH_4. The pathway for liquid methane production is based on CH_4 synthesis *via* Sabatier reaction with electrolytic H_2 and atmospheric CO_2 as educts commonly referred to as power-to-gas.[48] After downstream CH_4 liquefaction the LCH_4 can be handled comparable to liquefied natural gas (LNG) and is shipped *via* a large-scale LNG carrier. According to the number of necessary process steps the pathway for LCH_4 presents the longest conversion chain from all assessed PtX pathways.

CO_2 via direct air capture. CO_2 is obtained *via* direct air capture (DAC), a technology enabling site-independent availability of carbon – relevant for regions characterised by high RE availability but low availability of CO_2 containing industrial waste gases (*e.g.* North Africa, Argentina, Chile, parts of Australia). Additionally, DAC represents, besides CO_2 from biomass, the only CO_2 source for a possible closing of the carbon-cycle. However, due to low atmospheric CO_2 concentrations DAC technology is characterised by a high total energy demand compared to other higher concentrated CO_2 sources.[49,50] For this study, we assume the low-temperature solid sorbent based DAC technology as developed by the Suisse company Climeworks.[51] The capturing process is based on adsorbing CO_2 molecules onto special amine supported cellulose fibre filters. After full adsorption the filter is regenerated at elevated temperatures (100 °C) releasing a concentrated CO_2 stream (>99.9 vol%). Running multiple units in parallel enables a constant supply with atmospheric CO_2. Besides thermal heat (1.5–2.0 kWh_{th} per kg(CO_2)) electrical energy (0.2–0.3 kWh_{el} per kg(CO_2)) is required for operation of blowers and control units.[50,52] A base case (1.75 kWh_{th}; 0.25 kWh_{el}) represents the technological status for the capturing of 1 kg of CO_2.[53,54] An optimistic case (1.5 kWh_{th}; 0.2 kWh_{el}) represents a target value for mid-term energy demands.[50] Thermal energy is partially covered by means of heat integration from downstream methanation reaction. The remaining thermal energy demand is covered by an electric heater ($\eta = 0.95$). A burning of the CH_4 product is not reasonable from an efficiency point of view.

Methanation. Sabatier reaction for methanation of pure CO_2 represents a combination of the reversed water gas shift reaction (endothermal) and methanation of carbon monoxide (exothermal). The highly exothermal reaction is currently under research and takes place under moderate pressures of 6–8 bar and 280 °C.[55] The process concept as assessed by Müller *et al.* 2002 serves as basis for conversion parameters and energy demands.[56] The methanation reactor is operated at 8 bar and 280 °C. The Sabatier reaction provides excess heat (−3.0 kWh_{th} per kg(CH_4)) which is assumed to partially cover the thermal energy demand of the DAC modules. This in turn significantly reduces the heat demand of the DAC modules by 58–68%. For the compression of the CO_2 from ambient to synthesis pressure, an electricity demand of 0.14 kWh_{el} per kg(CH_4) is considered. The H_2 as obtained from the pressurised PEM electrolysis is already on reactor pressure.

$$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(g), \Delta H_R^0 = -167.9 \text{ kJ}$$

Liquefaction of CH_4. Depending on its composition liquefied natural gas (LNG) demands 540–590 times less storage volume than gaseous natural gas and is therefore already used as energy carrier for long distances. For distances >2000 km (offshore) or >4000 km (onshore) transport of LNG *via* ship is more economical than distribution *via* pipelines in gaseous state.[57] LNG trade has increased fivefold to 250 Mt per year compared to 1990.[58] In case of CH_4 which represents the largest share of LNG (87–99%, depending on origin),[59] a liquefaction step is therefore obvious. Pospíšil *et al.* 2019 assessed the energy demand of NG liquefaction processes based on literature and own simulations. Besides the process type, the specific liquefaction electricity demand is influenced by the size of the liquefaction plant and ranges from <0.25 to 0.75 kWh_{el} per kg(NG). Conducting an energy optimisation by means of improved flow rates for the mixed refrigerants within a liquefaction process Ali *et al.* 2018 reduced the theoretical electricity demand from 0.46 kWh_{el} per kg(NG) to 0.27 kWh_{el} per kg(NG).[60] Based on these considerations we assume for liquefaction of pure CH_4 an electricity demand of 0.5 $kWh_{el}\ kg^{-1}$ for the base case and 0.25 $kWh_{el}\ kg^{-1}$ for the optimistic case.

Transport of LCH_4 via ship. A conventional LNG carrier with a capacity of 140 000 m^3 is considered for transport of the liquefied CH_4. The carrier class and the necessary engine size are selected based on propulsion datasheets for LNG carriers from MAN Diesel & Turbo and results in an engine size of 28 000 kW (SMCR, at 36 km per hour) representing the "small conventional" class.[61] In our study, to avoid the use of fossil based fuel, this propulsion power shall be delivered by burning of the transported LCH_4. Therefore, we assume a dual fuel engine possible to be operated with natural gas at a rated efficiency of $\eta = 0.5$.[62] The resulting fuel consumption sums up to 0.026 kWh per tkm or 112 kg(CH_4) per km. The boil-off during ship transport should be prevented due to the high global warming potential of CH_4. To minimise the slip on LNG carriers reliquefaction systems are installed.[63] Modern LNG carriers feature boil-off rates between 0.10–0.15% per day.[64] For this study, an improved tank insulation system with a boil-off rate of 0.10% per day as recently proposed by the Kawasaki Shipbuilding Corporation is assumed.[65] The boil-off results in an evaporation of 68 kg(LH_2) per km enabling use of evaporating CH_4 as fuel without any losses.

PtX pathway for renewable methanol – CH_3OH. The CO_2 based methanol production for seasonal storage of RE and the implicit reuse of CO_2 has been frequently discussed in literature and has already been realised in pilot plants like the George Olah Renewable methanol plant.[23,66,67]

CO_2 via direct air capture. As for synthetic CH_4 production, the methanol pathway necessitates a carbon source which is assumed to be based on DAC as well. Compared to the LCH_4 pathway the methanol step is less exothermal and covers only a minor share of the DAC's thermal demand *via* excess heat. The remaining thermal demand is assumed to be covered by electric heating.

Methanol step. The process concept for the methanol reaction and distillation step is based on publication of Bongartz *et al.* 2019.[68] A new kinetic model (for commercial $Cu/ZnO_2/Al_2O_3$ catalysts) developed at Fraunhofer ISE and implemented in an Aspen simulation (see ESI-S2†) leads to conversion parameters and energy demands. The reactor system is operated at a pressure of 70 bar and a temperature of 250 °C. Heat integration *via* pinch-analysis enables pre-heating of the educt streams CO_2 and H_2. The remaining excess heat (0.09 kWh_{th} per kg(CH_3OH)) released below the internal heat utilisation range (<65 °C) is assumed to be available for the DAC modules' thermal energy demand. This in turn only slightly reduces the heat demand of the DAC modules by ~4%. The compression energy demand (0.31 kWh_{el} per kg(CH_3OH)) considers single-stage H_2, four-stage CO_2 and the recycle compressors. A process flow diagram for the CH_3OH step is included in the ESI.†

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l),\ \Delta H^0_R = -49.2\ kJ$$

Transport of CH_3OH via ship. In contrast to the LCH_4 pathway, the methanol pathway does not necessitate a separate liquefaction step to enable ship transport of a liquefied product. The ship transport orientates on a conventional tanker with a cargo capacity of 140 000 m^3. Tanker class and the resultant engine size are again based on propulsion datasheets for tankers from MAN Diesel & Turbo resulting in a necessary engine size of 15 200 kW (SMCR, at 28 km per hour, "Suezmax" class).[46] The first marine engines running on methanol are already in operation. A growing number of tests demonstrate feasibility of retrofitting existing diesel two-stroke engines for use with methanol.[69,70] Besides reduced NOx emissions, engine efficiency is reported as equal or even increased (+1–2%) when running on methanol. Therefore, efficiency of a conventional marine diesel engine is as well assumed for the methanol engine ($\eta = 0.5$). The resulting fuel consumption sums up to 0.010 kWh per tkm or 198 kg(CH_3OH) per km.

PtX pathway for renewable ammonia – NH_3. Ammonia is the most important feedstock for global fertiliser production. The conventional fossil based NH_3 production is largely based (77%) on syngas obtained from catalytic steam reforming of natural gas.[71] With an annual production of ~150 Mt NH_3 (2017), the annual global NH_3 economy is expected to grow significantly to an annual demand of 230 Mt(NH_3) by the end of 2025.[72,73] Additionally, NH_3 is considered as one promising carrier for renewably produced H_2 since it is easier to store and transport than gaseous H_2 and offers a higher energy density.[71,74] Moreover, liquefaction effort is lower than in case of LH_2 or LCH_4. However, as for CH_4 and CH_3OH a carrier for the H_2 molecule has to be provided.

N_2 via cryogenic air separation. Nitrogen (N_2) can be provided *via* cryogenic air separation units (ASU). Cryogenic distillation, a technology well proven and established at large scale, presents the major technology for N_2 supply in case of high volume and purity requirements.[75] Electricity requirement of the ASU is based on Althaus *et al.* 2007 (ref. 76) and the corresponding ecoinvent process.[77] The total electricity demand of an ASU largely depends on plant size and the grade of refrigeration recovery and varies between 0.5–0.8 kWh_{el} per kg(N_2). This spread is considered for the base and the optimistic case, respectively.

Ammonia production step. The Haber–Bosch process presents the most common method for the production of NH_3.[78] The iron-based catalyst facilitates an exothermic reaction of N_2 and H_2 at temperatures between 400–600 °C and pressure levels around 200–400 bar. Conversion parameters and energy requirements are based on own Aspen simulation (see ESI-S2†). Corresponding feed demands per kg of NH_3 sum up to 0.18 kg(H_2) and 0.84 kg(N_2) respectively. N_2 obtained from the ASU at −196 °C is vaporised and subsequently compressed to 250 bar like H_2. The exothermic ammonia formation yields the necessary energy to preheat the reactor feed stream. The electricity demand for feed compression and the recycle loop results in 0.48 kWh_{el} per kg(NH_3). The consumption of electrical energy can mainly be attributed to the compression of the two feed gas streams. The NH_3 product stream is liquefied (−33 °C) *via* cooling from evaporation of the N_2 feed obtained from the ASU.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g),\ \Delta H^0_R = -91.8\ kJ$$

Transport of NH_3 via ship. Long-distance shipping of NH_3 *via* ocean-going vessels is realised at low but non-cryogenic temperature (−33 °C) enabling transport in liquid state. The carrier class and the resultant engine size are aligned to conventional LNG carriers with a cargo capacity of 140 000 m^3. Similar to the LCH_4 PtX pathway, the engine size representing the "small conventional" class results in a necessary SMCR propulsion power demand of 28 000 kW (at 36 km per hour). Due to its high energy density (5.18 kWh_{LHV} per kg(LNH_3)) and efficient production process renewable NH_3 as shipping fuel is assessed in a number of research and pilot projects aiming at demonstrational container cargo vessels.[79–81] MAN Energy Solutions announced operation of its first naval NH_3 engine by 2022.[82] In a recent study, the Environmental Defense Fund Europe identified green NH_3 as one of the most promising alternatives for future electricity based fuels.[83] Advantages discussed by the authors are practicability in existing combustion engines or future fuel cells, the comparably high energy density when stored as liquid, the utilisation of existing logistics infrastructure and a safety and environmental risk profile manageable by existing standards. We assume NH_3 to be utilised in a combustion engine ($\eta = 0.5$) due to the potentially higher technology readiness level (TRL) than in case of promising full cell technology.[84] The fuel consumption of 0.016 kWh per tkm exceeds the boil-off rate of 0.04% per day (0.002 kWh per tkm), which is therefore included in the fuel demand.

Energy flow chart and energy efficiency for the analysed PtX pathways

Fig. 2 shows the energy flow charts and the overall efficiencies for the assessed PtX pathways including transportation *via* ship over 4000 km. The overall PtX efficiencies vary between 40.2–52.4% for the base and 44.1–57.9% for the optimistic cases. For all pathways, the electrolytic H_2 production is the main energy-intensive process step heavily affecting overall efficiencies. Hence, any technical improvement increasing electrolysis efficiency (*e.g.* reduction of internal losses, reduced current densities) or the H_2 conversion to final products will clearly increase the overall pathway efficiencies.

The provision of carbon and nitrogen (CH_3OH, LCH_4, NH_3) also requires energy. The NH_3 production pathway clearly benefits from a less energy intensive provision of the hydrogen carrier N_2 (0.08–0.13 MJ_{el} per MJ of product). Cryogenic air separation presents an industrially mature process at high TRL. At the same time, the low energy demanding availability of atmospheric N_2 poses a chance for future large-scale PtX projects to be more location-independent and focus on the availability of low-cost RE. In turn, the provision with atmospheric carbon for the LCH_4 and CH_3OH pathways *via* DAC emerges as energy intensive process step (LCH_4: 0.15–0.21 MJ_{el} per MJ of product; CH_3OH: 0.52–0.44 MJ_{el} per MJ of product). One reason is the low concentration of carbon in the ambient air. The provision of thermal energy *via* electric heating adds up to the electricity demand for the fans of the DAC units. For the case LCH_4, the thermal demand of the DAC units can be significantly reduced due to the integration of excess heat from the methanation step. The availability of unused heat sources poses an important efficiency enhancement in case CO_2 has to be provided *via* DAC. With the exception of one, all companies currently involved in the development of DAC technologies are focused on regeneration temperatures ≤ 100 °C.[50] This can enable the integration of excess heat even from processes with moderate temperature levels (*e.g.* food/beverage or textile industry).[85] For this study, DAC technology has been assumed to enable location-independent sourcing of carbon. Assuming, for example, high-concentrated industrial CO_2 point-sources such as the conventional, fossil based NH_3 or ethylene oxide production enables capturing of CO_2 with significantly reduced energy efforts of ∼0.4 MJ_{el} per kg(CO_2).[49,86] Sourcing carbon from these kind of sources can lead to a significant efficiency increase in case of the LCH_4 (47.9–52.0%) and the CH_3OH (50.2–54.0%) pathway. In this case, the efficiencies are comparable to the NH_3 pathway.

The three synthesis steps are within a comparable range of efficiencies. Their performances depend besides the electricity demand for feed and recycle compression steps on their respective H_2 conversion efficiencies. Although the methanol synthesis inherently leads to a liquid synthesis product, it requires more energy for CO_2 sourcing and the compression of feed gases than the methane reaction *via* Sabatier. The Sabatier reactor operated at a moderate pressure shows a clear advantage over CH_3OH and NH_3 syntheses which need higher pressures. With regard to the CO_2 based methanol synthesis some other published process concepts show an improved H_2 conversion efficiency. However, for these cases the volume of the recycle stream and thus the recycle compressors' energy demand increased significantly.[87] We identified that a limitation of the recycle stream and the resulting reduced compression demand is beneficial for overall CH_3OH synthesis efficiency despite the slight increase in H_2 demand. A H_2 recovery concept (*e.g. via* pressure swing adsorption) for H_2 recirculation could further enhance synthesis efficiency.

The energy efficiency of the cryogenic liquefaction steps for the LH_2 and LCH_4 pathways clearly depends on the PtX plant scale and the possibilities for a thermal integration into the overall process chain. Within the range of the assumed process parameters the LH_2 pathway shows a higher specific energy demand (0.18–0.24 MJ_{el} per MJ(LH_2)) for the cryogenic liquefaction than the LCH_4 pathway (0.02–0.04 MJ_{el} per MJ(LCH_4)). The latter, in turn, necessitates a carbon source.

Long-distance shipping (4000 km) does not present a notable energy loss for the PtX pathways assessed and mostly depends on the energy-density of the product carried. Uncertainty

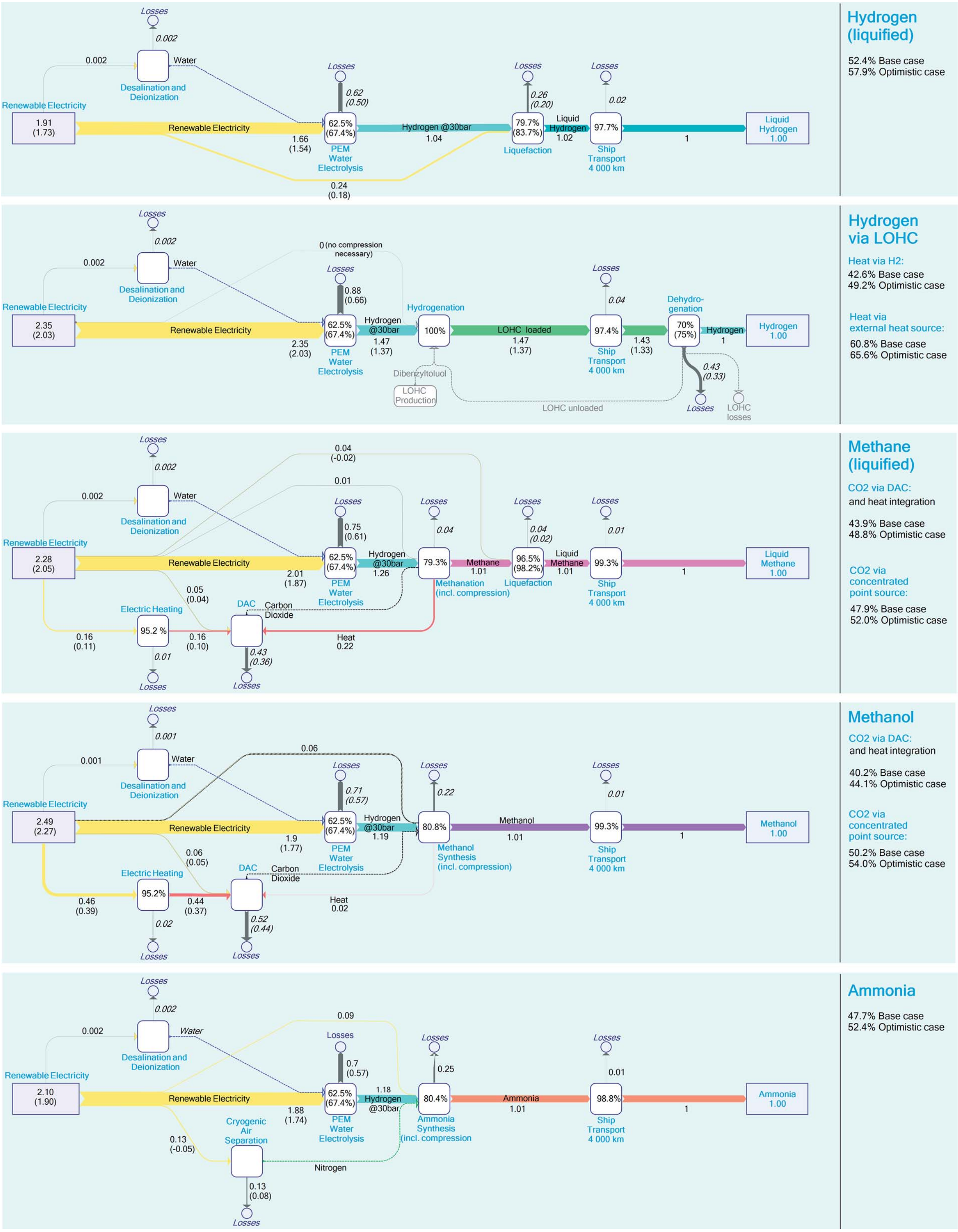

Fig. 2 Energy flows (in MJ) for the assessed PtX pathways based on a functional unit of 1 MJ (LHV) of renewable energy carrier. Values for the optimistic case are indicated in brackets for the respective process step.

remains with regard to the efficiency of the assumed H_2 and NH_3 engines which are so far not realised for dynamic applications and at this scale. Utilising fuel cells presents another option for on-board utilisation of the LH_2 which potentially can offer even elevated efficiencies > $50\%_{LHV}$. The considered LOHC, perhydro-DBT, with an H_2-content of 6.23 wt% has the lowest volumetric energy density of all assessed PtX shipping cargos and thus demands the most propulsion energy per unit of transported energy ($E_{\mathrm{ship,LOHC-H_2}}$: 6.8×10^{-6} kWh per kWh and km); +278% compared to CH_3OH. Note that for the case LOHC–H_2 a smaller ship has been assumed than for the other PtX products due to economic reasons. Considering a comparable vessel (140 000 m^3) and ignoring high DBT purchase cost leads to a clear decrease of $E_{\mathrm{ship,LOHC-H_2}}$ to 4.4×10^{-6} kWh per kWh and km. This results in a clear decrease, falling below the specific energy demand for the LH_2 carrier. The shipping processes of both, CH_3OH and cryogenic LCH_4, benefit from high volumetric energy densities and thus show the lowest propulsion energy demand per unit of transported energy (1.8×10^{-6} and 1.9×10^{-6} kWh per kWh and km respectively).

In summary, the pathway for LH_2 shows the highest overall efficiency (52.4–57.9%). The NH_3 pathway (47.7–52.4%) benefits from an energy-efficient provision of N_2, the absence of energy-intensive liquefaction and a PtX product with comparably high energy-density. The pathways for LOHC–H_2 (42.6–49.2%), LCH_4 (43.9–48.8%) and CH_3OH (40.2–44.1%) remain within a comparable range of efficiencies. Deviations here can occur for the amount of integrable excess heat (LCH_4, CH_3OH) and the necessary thermal demand for the dehydrogenation of the LOHC–H_2.

The final utilisation of the energy carriers is not included in the efficiency analysis due to the versatile field of potential applications. Hydrogen can be used with very high efficiencies (*e.g.* in fuel cell cars or fuel cells for stationary applications) where, in turn, CH_4 and CH_3OH will offer lower efficiencies at least in mobile applications. For the direct utilisation of NH_3, further investigation on direct utilisation is required. In case of cracking of NH_3 as H_2 supplier the losses could be limited by optimised catalysts enabling cracking at reduced temperatures (see "conclusions").

The presented efficiency analysis serves for the identification of energy loss hot-spots and potential levers for the energy optimisation of PtX pathways. The final criteria by which the suitability and realisation potential of PtX-processes is determined rather depends on their techno-economic competitiveness. Additionally, the environmental efficiency assessed by a holistic life-cycle-assessment should be included for any decision-making. The subsequent section presents a case study for the assessed PtX routes including long-distance shipping to provide an estimate of their economic efficiency.

Part II – case study for the economic assessment of the proposed PtX pathways

For a holistic assessment of PtX pathways, the total cost of the respective PtX product must also be included in the considerations. The following case study, located in the region Morocco/Western Sahara, adds economic conclusions to the preceding discussion on PtX pathway efficiencies. By this the influence of site and weather conditions on plant scales, storage demands, full load hours and finally the cost of production can be taken into account. It should be noted that the Western Sahara is on the one hand a top region for harvesting RE but on the other remains a region whose international legal status is still not finally determined.[88,89] For a future implementation of large RE and PtX capacities it is therefore important to involve local stakeholders and to respect socio-economic boundary conditions.[90]

Economics of imported synthetic fuels – existing studies

Fasihi *et al.* 2016 assessed the production and shipping cost of synthetic fuels (jet fuel and FT-diesel *via* Power-to-Liquid (PtL)) from large-scale Fischer–Tropsch (FT) synthesis fed with CO_2 captured from the atmosphere and renewable H_2 from an alkaline electrolyser.[91] The overall process efficiency (excluding the FT side product naphtha) resulted in 49.4%. The production cost for the FT-diesel was between 64–75 € per $\mathrm{MWh_{FT\text{-}Diesel,LHV}}$ equalling 0.59–0.69 € per liter, values comparably low for studies on PtL economics. This can be explained in part by the high full load hours for the assumed hybrid PV-wind power plant (6840 hours per year) resulting in low cost for the PtL systems' input electricity of 23 € per $\mathrm{MWh_{el}}$. Additionally, assumptions regarding low investment cost of 319 € per $\mathrm{kW_{el}}$ and high electrolysis efficiency ($73.1\%_{\mathrm{LHV}}$) lead to low FT-diesel production cost. For another study, Fasihi *et al.* 2015 analysed the production of synthetic CH_4 in Patagonia and shipping of the liquefied product to Japan.[92] The parameters used for the economic assessment are comparable to their study on PtL. The final product cost including the shipping over 17 500 km summed up to 62–73 € per $\mathrm{MWh_{CH_4,LHV}}$. Fasihi's assessments already show the importance of high RE full load hours which indicate the price of the renewable input electricity and PtX production cost. This, in turn, leads to the presumption that a large-scale PtL production site should rather be selected based on high RE potentials than based on a close proximity to the end consumer.

In another study, Heuser *et al.* 2019 avoid any downstream catalytic conversion of produced electrolytic H_2.[93] Their proposed system is designed to cover a prospected future Japanese annual hydrogen demand of 8.8 $\mathrm{Mt(H_2)}$ *via* marine LH_2 transport from Patagonia. Their GW-scale PtG system (115 $\mathrm{GW_{el}}$) for the cost assessment includes electrolytic H_2 production (115 $\mathrm{GW_{el}}$) based on wind electricity, gaseous H_2-pipeline transport, cryogenic H_2 storage and liquefaction and finally LH_2 transport *via* LH_2 carrier to Japan. The LH_2 product cost excluding long-distance transport sum up to 99 € per $\mathrm{MWh_{LH_2,LHV}}$. The assumed shipping to Japan increases the product cost to 133 € per $\mathrm{MWh_{LH_2,LHV}}$. As the authors conclude, at this price level and used in efficient fuel cells, H_2 can be considered competitive with combustion engines running on conventional gasoline.

Niermann *et al.* 2019 analysed various LOHCs for long-distance ship transport of renewable energy.[41] Among the substances analysed DBT and methanol (including methanol cracking to H_2 at the point of utilisation) performed best from an economic perspective. The authors concluded that the provision of necessary heat for dehydrogenation/cracking is one of the largest cost factors and that the transport by ships is significantly cheaper than H_2 transport *via* pipeline within the assessed distance of 5000 km.

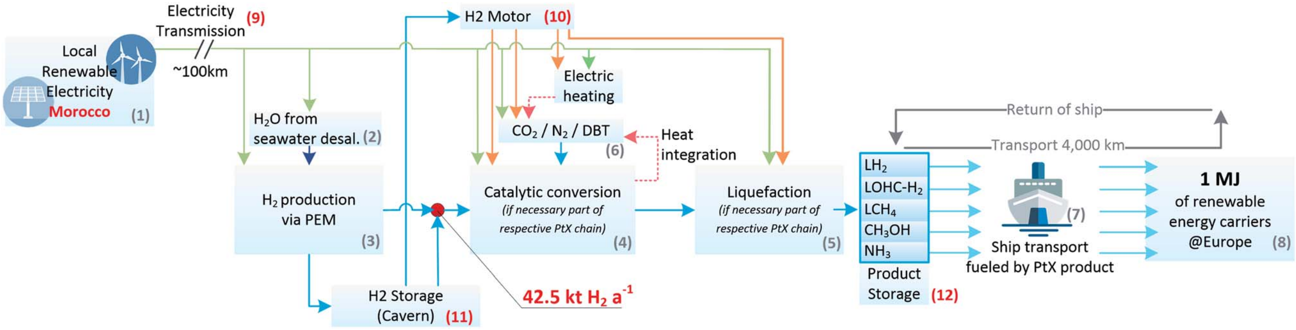

Fig. 3 System layout part II – case study: components (9–12) have been added to enable an operation with 100% fluctuating local renewables and a steady-state provision with 42 500 t(H_2) per year.

Scope and methodology of the case study

The general system layout is depicted in Fig. 3. Scale and layout of the assessed PtX systems orientate on a near future (~2030) medium- to large-scale PtX product system 100% based on local renewable electricity generation. Hence, applied conversion parameters and efficiencies are based on the optimistic values which have as well been used for the preceding efficiency analysis. The dynamic electricity and H_2 production is coupled downstream with steady-state synthesis and liquefaction steps converting 42 500 t(H_2) per year into valuable PtX products. During periods of insufficient renewable electricity production, the steady state processes are supplied with electricity generated in an H_2 motor (10) which in turn is operated with H_2 stored in a cavern (11). The existence of suitable salt deposits for the installation of cost-efficient H_2 caverns (<10 € per kg(H_2)) is a necessary prerequisite for this case study. South-western Morocco is characterised by the existence of large Mesozoic and Permian salt deposits which are potential geological structures for the installation of H_2 cavern storages.[94] The use of very large underground pipe storages (250–400 € per kg(H_2)) is not in the scope of the assessment since preceding PtX studies already showed their economic inefficiency.[23,95] The PtX plant is assumed close to the sea to allow for the use of seawater desalination. Therefore, a transmission (~100 km) of the renewable electricity (9) from the chosen region of the RE plants (26°15′03.6″N, 13°45′39.6″W) to the location of the PtX plant has been assumed. In order to decouple PtX production and shipping processes, product storage tanks are provided (12).

Weather data (solar irradiation and wind speeds) for the respective RE location (Fig. 4, top) using a ten-year dataset (2007–2016, typical meteorological years TMY) served as basis for the PtX process simulations.[96] The RE location has been chosen based on criteria considering a distance to the sea not larger than 150 km and an optimised combination of annual average wind speeds[97] and solar irradiation.[98] The weather data has been used for simulation of fluctuating electricity generation using the RE-simulation software "System Advisor Model" (SAM).[99] Siemens Gamesa G128 (4.5 $MW_{p,el}$) wind turbines and ground-mounted PV panels (multiple 4 $kW_{p,el}$, 1-axis tracking) have been selected as basis for the RE power curves (compare ESI-S3†). The fluctuating RE generation data has then been applied in the self-developed MATLAB® Simulink toolbox *H2ProSim* for simulation and optimisation of each assessed PtX process. The *H2ProSim* results have than been used for the calculation of the respective production cost (levelised cost of PtX product, LCo(X)):

$$\mathrm{LCo(X)} = \frac{\mathrm{ANF} \times \mathrm{CAPEX}_x + \mathrm{OPEX}_x}{\mathrm{PC}_x}$$

with

CAPEX_x = total investment cost of the respective PtX pathway

OPEX_x = annual operational cost of the respective PtX pathway

PC_x = production capacity of the respective PtX pathway.

ANF = annuity factor:

$$\mathrm{ANF} = \frac{(1+i)^n \times i}{(1+i)^n - 1}$$

i = assumed rate of interest: 5% per a

n = plant lifetime: 20 years.

The lifetime of the PtX components is assumed with 20 years. The replacement of electrolysis stacks becomes necessary after 10 years. If given for different scales, cost data from literature have been adjusted to the scale of the respective PtX components *via* the rule of the rule of six-tenths:

$$I_\mathrm{B} = I_\mathrm{A} \times \left(\frac{C_\mathrm{B}}{C_\mathrm{A}}\right)^x$$

with

I_B = investment cost for the component at capacity B

I_A = known investment cost for the component at capacity A

$C_\mathrm{B}/C_\mathrm{A}$ = capacity ratio of the two components

x = size exponent; 0.6 as "hands-on" value for process equipment.

Inventory of the economic parameters

This section discusses the installed capacities for each of the PtX pathways (Table 1). They serve as initial information for the economic assessment. The ESI (ESI-S4†) contains detailed information on the chosen cost parameters, corresponding literature and as well a description for the calculation of the shipping processes.

Prices for the generated wind and PV electricity have been chosen based on a comparison of the site dependent full load

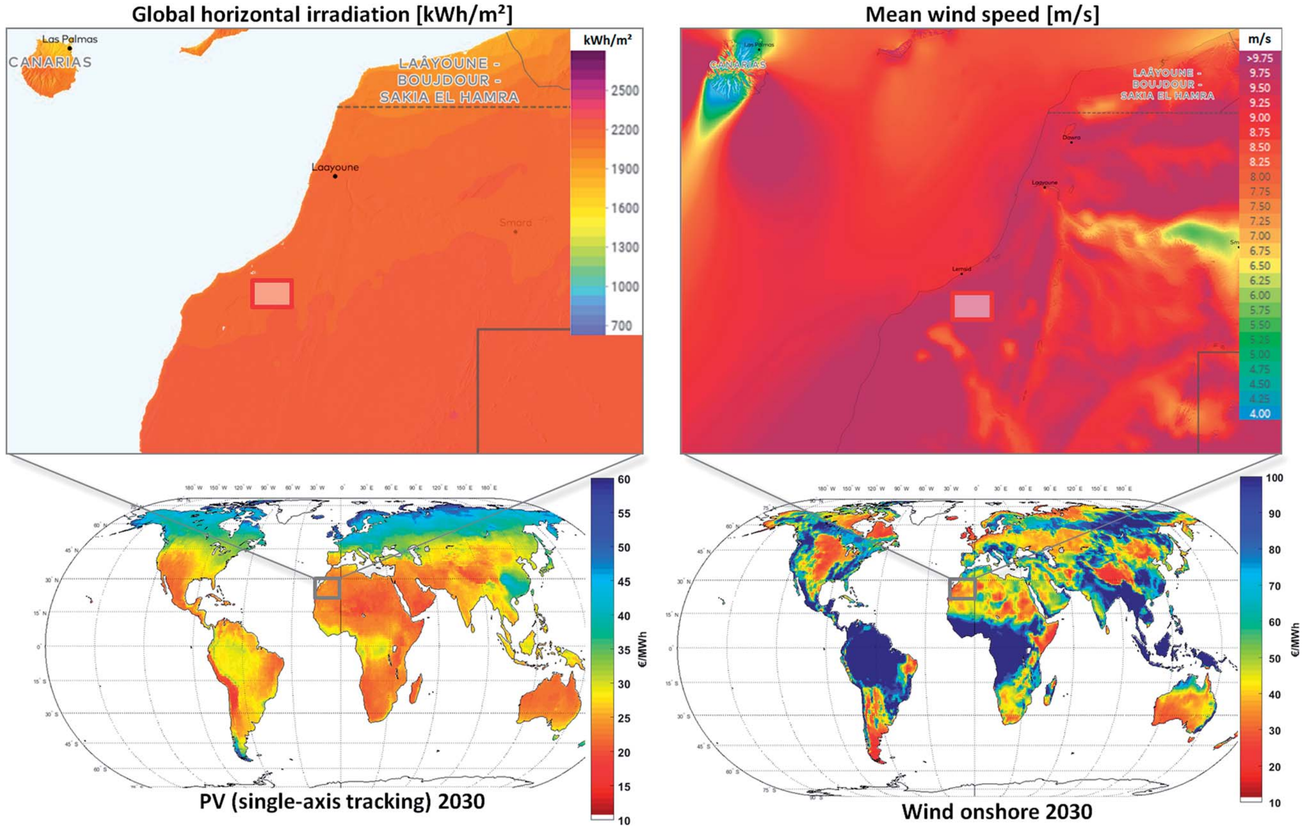

Fig. 4 Top: solar and wind potential map for south-west Morocco/Western Sahara (Global Solar and Wind Atlas 2.0 by Technical University of Denmark DTU[93,94]) bottom (based on Fasihi *et al.* 2020): 2030 global renewable electricity generation cost for PV 1-axis tracking and wind power (considering 2005 weather data and 7% weighted average capital cost).

hours (FLH) and global horizontal irradiation (GHI) with recent literature. For prospected wind energy generation cost in 2030 annual full load hours > 4000 h lead to cost varying between 20–40 € per MWh_{el}.[100] In case of PV in 2030 a global horizontal irradiation (GHI) of ~2000 kWh per (m^2 a) enables electricity production between 19–27 € per MWh_{el}. This cost range has been validated by a recent study of Fasihi *et al.* 2020, assessing the global levelised cost of electricity for wind and PV in 2030 (Fig. 4, bottom).[101] Therefore, for both, wind and PV electricity cost of 25 € per MWh_{el} have been considered for the economic calculations. The optimum installed capacities of RE, PEM electrolysis, H_2 motor and the cavern orientate on the determined production capacity of 42 500 t(H_2) per year and depend on the PtX pathway and its respective process parameters. The total installed capacities of wind and PV vary between 595 MW_p (LOHC–H_2) and 781 MW_p (CH_3OH). The share of installed PV *versus* wind capacities varies between 28–34%, highlighting the installation of wind turbines over PV modules. Shares within this range are representative for locations with high average annual wind speeds and have already been proposed by Fasihi *et al.* 2018 regarding an optimised electricity supply for remote PtX systems.[26] The use of solar-thermal electricity generation to increase full load hours could be taken into account in future studies.

The capacity of the PEM electrolysis varies between 453 MW_p (LOHC–H_2) and 584 MW_p (CH_3OH) since it depends on the pathways' electricity demand which is covered by H_2 during times of non-sufficient fluctuating RE. The LOHC–H_2 pathway is characterised by comparably low installed capacities for PEM electrolysis, H_2 motor and cavern because of few aggregates demanding electricity on a base-load. In turn, the CH_3OH pathway requires larger installed capacities due to a high thermal demand for the DAC units which has to be partially covered by electric heating. Due to production scale-up and advancing technological maturity, a significant reduction of electrolysis capital cost, especially in case of PEM electrolysis, can be assumed for the next decade placing this technology in the focus of future large-scale PtX applications.[34,102] For this case study, an investment of 600 € per kW_{el} has been assumed resulting from manufacturer estimations for state-of-the-art and future electrolysis systems.[34] The product storage capacities depend on the respective production rate, the ship's transport capacity and its two-way travel time. A safety margin of 20% for the storage capacity is assumed.

The shipping cost depend on ship type, transport capacity and the utilisation. The transport capacities are oriented to large conventional vessels with volumes of 140 000 m^3. The ascribed ship investment depends on the respective annual utilisation of the ships. For example, in case of the LOHC–H_2 pathway, the ship is utilised 44% of the year and assumed to be available for other transport tasks during the remaining time. For the LOHC–H_2 pathway a 50% reduced ship size (70 000 m^3;

Table 1 Installed capacities for the assessed PtX pathways. The capacities orientate on a constant conversion of 42 500 t H_2 per a into PtX products

Installed capacities	NH_3	LH_2	LOHC–H_2	LCH_4	CH_3OH
Renewables					
Wind installed capacity [MW_p]	506	506	453	509	578
Wind capacity factor	50%	50%	50%	50%	50%
PV installed capacity [MW_p]	144	172	142	153	220
PV capacity factor	27%	27%	27%	27%	27%
RE produced [GWh_{el} per a]	2573	2638	2331	2606	3067
RE utilisation factor PtX system					
RE cost [€ per MWh_{el}]	25	25	25	25	25
Seawater desalination					
Installed capacity [m^3 per a]	425 000	425 000	425 000	425 000	425 000
PEM electrolysis					
Installed capacity [MW_{el}]	440	450	419	446	481
Lifetime system [a]	20	20	20	20	20
Lifetime stack [a]	10	10	10	10	10
Replacement cost [% of CAPEX]	34%	34%	34%	34%	34%
H_2 motor					
Installed capacity [MW_{el}]	26.2	32.6	2	29	68
H_2 cavern					
Installed capacity [m^3]	608 410	631 980	516 430	630 240	756 230
ASU/DAC					
Installed capacity [t per day]	556	—	—	708	873
Synthesis (NH_3, CH_4, CH_3OH)					
Installed capacity [t per day]	667	—	—	241	612
Liquefaction (H_2, CH_4)					
Installed capacity [t per day]	—	120	—	241	—
(De-)hydrogenation set					
Installed capacity [t per day]	—	—	120	—	—
Product storage					
Installed capacity [t]	114 576	11 928	87 696	71 000	132 367
Shipping					
Assumed vessel type	LNG carrier	LH_2 carrier	Tanker	LNG carrier	Tanker
Transport volume [m^3]	140 000	140 000	70 000	140 000	140 000
Transport capacity [t product]	95 480	9940	73 080	59 167	110 306
Ship utilisation [% of year]	10%	17%	44%	6%	10%
Product amount at destination					
Total [GJ per a]	4 301 048	4 821 688	3 399 347	4 204 030	4 426 097

~73 100 t perhydro-DBT) has been assumed to limit the necessary amount of the LOHC-medium DBT. Reason is the high initial purchase cost of DBT ranging from 2–4 € per kg(DBT) (assumed: 2 € per kg(DBT)).[47]

Operating costs other than energy costs are calculated as a proportion of the respective investment costs and are described in detail in the ESI (ESI-S4†).

Economics for the analysed PtX pathways

Fig. 5 shows the production cost (in € per MWh_{LHV}) without and with shipping from Morocco to Germany for each PtX pathway. The components contain both the CAPEX depreciation and OPEX (excl. electricity). The price for the fossil reference product is indicated with a maximum and minimum spread based on available data (H_2: steam reforming of natural gas;[103,104] NH_3: conventional large-scale Haber–Bosch synthesis in Western Europe;[105] CH_3OH syngas based on natural gas;[106] natural gas: European Union natural gas import price[107]). The production cost including ship transport vary between 124 € per MWh_{LHV} (NH_3) and 156 € per MWh_{LHV} (LOHC–H_2) with LCH_4 showing the biggest cost difference to its fossil substitute (+705%). The PtX production cost are therefore clearly higher

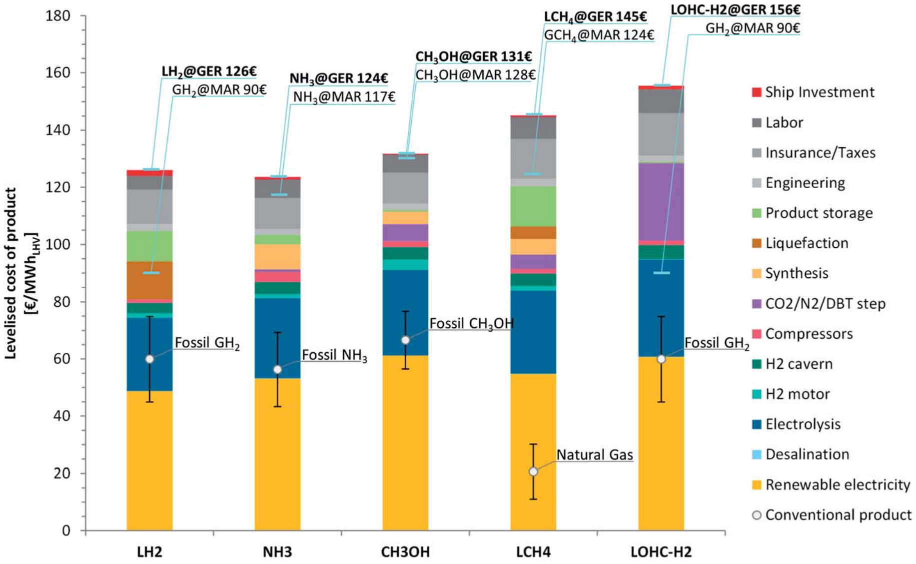

Fig. 5 Production cost of PtX-products ("@GER", incl. shipping Morocco – Germany) based on energy content (LHV). The product cost in Morocco ("@MAR") exclude the cost for shipping, product storage and liquefaction. Levelised cost for the conventional product indicated by including a respective maximum/minimum price spread based on available data.

than the fossil based reference product. That PtX products tend to be more expensive than their fossil counterparts is not a new finding of this study. The fact that, on the one hand, fossils are too cheap due to a missing inclusion of environmental and social costs and, on the other hand, general PtX production still being a technology and hence capital intensive undertaking has recently been discussed in preceding papers.[23,108–110] Assuming that the PtX products are already utilised at the PtX location, any cost for shipping, product storage and liquefaction can be excluded. In this case the cost for gaseous H_2 are significantly lower (90 € per MWh(H_2)) than the other PtX product costs.

It becomes obvious that for all PtX pathways, the electricity demand, mainly caused by electrolytic H_2 production, represents the major share of production cost (39–46%). Additionally, the capital and further operational cost of the PEM electrolysis contribute with a notable cost share (20–23%). For the LH_2 pathway the necessary liquefaction increases the production cost of LH_2 by 10%. The on-site product storages for LH_2, LCH_4 and NH_3, requiring a more complex construction due to high insulation efforts and boil-off reliquefaction, are characterised with higher specific investment than the tanks containing CH_3OH or LOHC. In case of the LOHC–H_2 pathway on-site storage cost are comparable to the CH_3OH pathway due to the practicable substance. However, the high initial purchase cost for the LOHC medium DBT (2 € per kg(DBT); 30% of CAPEX) drive the overall pathway cost. Further cost increase had been avoided due to the assumption of a smaller ship resulting in less DBT to be initially purchased. The consequent increase in ship utilisation and ascribed investment (a smaller ship has to travel more frequent for the same annual amount of delivered energy carrier) was however offset by the savings in reduced DBT purchase. A clear reduction of the DBT market price from currently ~4 € per kg(DBT) to the assumed 2 € per kg(DBT) poses a clear target for future application of DBT as long-distance H_2-carrier. Other discussed LOHC's such as *N*-ethylcarbazole or 1,2-dihydro-1,2-azaborine have even higher market prices.[41] This case study assumes an H_2 cavern as a temporary storage facility for H_2 acting as buffer between fluctuating RE generation and downstream steady-state process steps. In case that due to geological restrictions underground H_2 storage in a cavern is not possible CAPEX would be significantly increased due to the high necessary investment for pressurised pipe storage systems. In such a case, the dynamic operation of subsequent process steps can significantly reduce the H_2 storage demand and thus limit the respective investment. For the steady-state syntheses a dynamic operation is by now at low TRL and investigated at lab-scale within numerous research projects.[111–114]

For a better understanding how the production cost depend on key economic indicators, a variation of renewable electricity cost, electrolysis investment and the interest rate has been conducted. These three parameters have been identified as the major influencing among all economic and technological indicators. Fig. 6 shows the sensitivity for all PtX pathways. For a clear representation, the paths are represented in an averaged form. This enables a first discussion about the impact of the key economic indicators of all PtX pathways assessed. A more detailed sensitivity is included in the ESI (ESI-S5†). An increase of the renewable electricity price to 50 € per MWh_{LHV} (+200%) results in an increase of the averaged production cost to an average of 187 € per MWh_{LHV} (+39%). Levelised cost of renewable electricity around 50 € per MWh_{el} are already today representative for large parts of central Europe.[101,115] However, such PtX production cost are far from the market price due to the cheap fossil reference products. An increased PEM electrolysis investment of 1200 € per kW_{el} (+200%), a value which can be discussed as a realistic value for present PEM systems,[34,102] leads to averaged production cost of 172 € per MWh_{LHV} (+27%). Regarding a variation of interest to 10% production cost increase

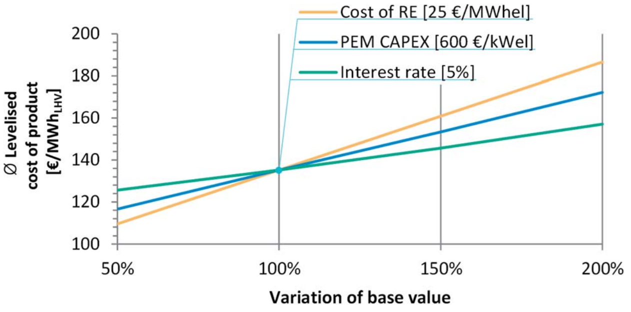

Fig. 6 Averaged levelised cost of PtX products depending on a variation of renewable electricity cost [base value = 25 € per MWh$_{el}$], PEM CAPEX [base value = 600 € per kW$_{el}$] and interest [base value = 5%].

to 157 € per MWh$_{LHV}$. The feasibility of RE projects and contract prices heavily depending on interest rates has recently been discussed in literature highlighting this factor as often underestimated.[116,117] Especially when assessing future or foreign RE projects the final estimation of project cost can be considerably undermined by diverging *real* interest conditions.

Additionally, to these key economic indicators, the ship transport distance has been varied. Fig. 7 shows the influence of the shipping distance on the production cost (top) and the cargo-specific shipping fuel demand (bottom). Since the ships use their own cargo as fuel, the cargo-specific ship energy demand describes the amount of energy carrier "consumed" to transport one MWh of energy carrier over the respective distance. To give an idea on global shipping distances exemplary routes from Morocco to the US American East Coast or to Japan are indicated. The graphs make clear that the LOHC–H_2 and LH_2 pathway are influenced the most by increasing transport distances. In case of the LH_2 pathway, reason for increased product cost is on the one hand an increase of on-site LH_2 storage demand for the times when the ship is on the move. On the other hand, the H_2 consumption caused by the ship itself drives the LCo(LH_2) since less product arrives at the final destination. In case of the LOHC–H_2 pathway, more DBT must be kept available as local storage medium for the times the ship is on the cruise. Even in the event that the LH_2 storage costs or the DBT market prices can be significantly reduced, the cargo-specific shipping fuel demand represents a cost factor whose influence should not be underestimated. CH_3OH and LCH_4 profit from higher volumetric energy densities and therefore require a smaller share of their stored cargo as fuel.

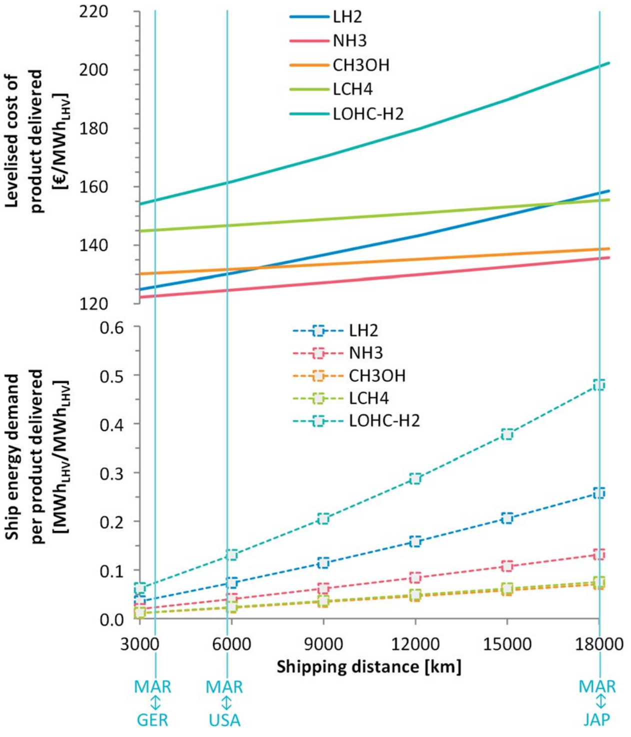

Fig. 7 Top: levelised cost of PtX-product depending shipping distance. Bottom: MWh of fuel demand per MWh of product delivered at final destination.

Conclusions

With this study we provide an overview on the energy and cost efficiency of five different PtX pathways. While the first part of the paper assessed the pathways respective overall efficiency differentiated by base and optimistic parameters, the second part devoted to production cost and a specific case study (Morocco/Western Sahara) considering more site and weather dependent factors.

In general, it can be concluded that the calculated differences in the pathways total efficiencies are not too significant. For all pathways, the H_2 providing water electrolysis acts as the main energy consumer. The reason for this is that the entire energy content of the final PtX product is provided by H_2, which is produced by water electrolysis. Hence, their electricity consumption shall not be seen as lost power but rather as a necessary transformation of renewable energy into a storable form of sustainable energy carrier. This aspect is an important reason why, to date, PtX pathways for energy carriers and fuels have tended to be less energy efficient than their fossil counterparts. The latter profit from a "free" sourcing of fossil stored hydrocarbons with high energy densities, in turn charge their indirect (environmental) cost in the form of massive greenhouse gas emissions. In order to improve PtX pathways' energy and cost efficiencies, a reduction of the electrolysis energy demand will be clearly beneficial in case high full load hours can be expected. However, R&D efforts by the electrolyser industry are more focused on a reduction of capital cost.[102] Reason is the higher share of capital cost for electrolysis systems operated with low-cost RE and at moderate full load hours.

The LH_2 pathway proved to be the most efficient of all evaluated process chains (52–58% overall efficiency). Although an energy intensive liquefaction is part of the process chain, the overall efficiency profits from not being dependent on CO_2- or N_2-sourcing. Large-scale ship transport of LH_2 is still in its pilot phase and has to be demonstrated within the coming years.[118] In terms of levelised cost of product, LH_2 (126 € per MWh@GER) is roughly on a par with the low production cost of NH_3 (124 € per MWh@GER) and

CH_3OH (131 € per MWh@GER). Furthermore, when focussing on potential end-user applications, using H_2 as a fuel offers high electrical conversion efficiencies (*e.g.* fuel cell based combined heat and power plants with $\eta_{el} \sim 60\%$ and $\eta_{el+th} \sim 85\%$).

The NH_3 pathway characterised by a comparable high pathway efficiency (48–52%) and low levelised cost of product, clearly benefits from a reduced energy demand for N_2 provision *via* ASU. However, final application of NH_3 as energy carrier or fuel is still at an early stage. Currently, energy-intensive NH_3 cracking for H_2 recovery at the point of use appears to be the most realistic route. With further technological advances either on the side of direct NH_3 application as fuel[82,83] or in terms of NH_3 cracking at lower temperatures and with alternative catalysts[119,120] this pathway can be very promising for large-scale and long-distance energy transport and utilisation.

The overall efficiency of the CH_3OH (40–44%) and LCH_4 pathway (44–49%) clearly increase in case CO_2 can be sourced from a concentrated stream (4–10% increase in total efficiency). If CO_2 shall be sourced from the atmosphere, the availability of additional excess or solar thermal heat to cover the necessary DAC desorption energy demand raises the pathway efficiencies. In terms of LCH_4 production cost (145 € per MWh@GER) the pathway has to deal with high capital costs for cryogenic storage and a cheap market price of the competing fossil natural gas. Furthermore, when considering the production, distribution and utilisation of synthetic CH_4 at large scales, the high global warming potential of this gas must be critically considered. Both, LNG and methanol are already globally traded on large scales (317 and 75 Mt per year, respectively[121,122]), with methanol profiting from a less complex infrastructure for transport and distribution.

The LOHC–H_2 pathway is characterised by high initial investment for the LOHC medium DBT (2 € per kg(DBT) assumed) and the high thermal demand for the dehydrogenation step at the final destination (25–30% of $H_{2,LHV}$ assumed). In case excess heat integration for dehydrogenation is possible, the LOHC pathway significantly increases its overall efficiency (16–18% increase in total efficiency). One idea could be the integration of excess heat from a downstream H_2 based combined heat and power plant. However, such integration is case-dependent and only possible if H_2 is utilised at the point of dehydrogenation.

Besides renewable electricity, the access to water presents a crucial aspect of large-scale PtX processes. The efficiency analysis (as well as the cost analysis) showed that for arid regions water provision *via* seawater reverse osmosis can be very promising. The specific energy demand and attributed costs are low. However, it should be noted that for large plants a disposal system for the resulting brine must be included without increasing the pressure on the marine environment.[123,124]

When comparing our assessment to the other PtX import studies assuming even better RE generation locations (*e.g.* Patagonia or South West Australia) it gets clear that PtX production costs can be even further reduced due to even higher full load hours. The integration of less fluctuating solar-thermal electricity generation and small-scale battery storage could present a way to reduce storage demands. This is an important aspect for PtX locations without the possibility for H_2 storage in caverns.

In summary, it can be concluded that the long-distance transport of renewable electricity in the form of PtX products is an important step towards defossilised global societies. However, before the great hope for a defossilisation of global societies is placed solely on cheap imported PtX energy sources, other strict measures should be continued in parallel. Aspects in this context are an increased eco-sufficiency, a significant reduction in transport, the use of regionally available RE potentials and, where reasonable, the direct electrification in combination with batteries. In any case, both the direct and indirect electrification of our currently fossil-fuelled societies will require large amounts of renewable energy, which for many countries cannot be fully covered by locally available RE plants. The ongoing market ramp-up of H_2 technologies and steadily increasing technological readiness levels lead to a constant reduction in costs at all PtX levels. Imported renewable energy in the form of PtX products is not a far-off future vision. They will enable the urgent step towards a defossilisation of sectors such as the heavy-duty, marine traffic, aviation and (petro-) chemicals industry at acceptable costs.

In any case, the export of large RE and PtX capacities from promising RE countries must also contribute to the defossilisation of the local energy system. The local population should benefit from the added value and environmental regulations should be strictly respected. This is the only way to avoid the significant deficits associated with the current global trade of fossil fuels.

Conflicts of interest

There are no conflicts to declare.

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