Process Engineering Analysis of Transport Options for Green Hydrogen and Green Hydrogen Derivatives

Christiane Staudt,* Clemens Hofsäß, Benedikt von Lewinski,* Friedemann Mörs, Praseeth Prabhakaran, Siegfried Bajohr, Frank Graf, and Thomas Kolb

The transition of the German economy and energy system toward CO₂ neutrality requires large quantities of climate-friendly chemical energy carriers, such as green hydrogen, to be imported. The decision on the most favorable import routes must consider its energy efficiency To respect the remaining CO₂ budget to achieve the 1.5° climate target, the implementation time and therefore additional evaluation criteria must be taken into account. In this article, as a first step, the energy utilization rate (η_{H_2,H_1}) for different hydrogen import options is evaluated. Starting off from hydrogen at 25 °C and 25 bar produced in the exporting country, liquid hydrogen, ammonia, liquid methane (Green LNG), methanol, and liquid organic hydrogen carrier are considered as chemical energy carries. Liquid hydrogen is in future the most efficient import option ($\eta_{H_2, H_1} = 7\%$) when gaseous hydrogen is supplied in the importing country. When direct utilization of the H₂ derivatives is considered, the ammonia import route has the highest energy utilization rate with 77%. If point sources for CO2 are considered, direct utilization of methanol $(\eta_{H_2,H_i} = 83\%)$ and Green LNG $(\eta_{H_2,H_i} = 76\%)$ are energetically favorable import options. Additional significant criteria for a technological assessment are maturity of technologies, available capacities, infrastructures, and production processes.

1. Introduction

Green hydrogen will play an important role in future climateneutral energy supply and for energy security in Germany.

C. Staudt, C. Hofsäß, F. Mörs, P. Prabhakaran, F. Graf, T. Kolb Gastechnology

DVGW-Research Center at Engler-Bunte-Institute of Karlsruhe Institute of Technology (KIT)

Engler-Bunte-Ring 1, Karlsruhe 76131, Germany E-mail: staudt@dvgw-ebi.de

B. von Lewinski, P. Prabhakaran, S. Bajohr, F. Graf, T. Kolb

Engler-Bunte-Institut – Fuel Technology

Karlsruhe Institute of Technology (KIT)

Engler-Bunte-Ring 1, 76131 Karlsruhe, Germany

E-mail: benedikt.lewinski@kit.edu

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/ente.202301526.

© 2024 The Authors. Energy Technology published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

DOI: 10.1002/ente.202301526

Hydrogen demand in Germany is expected to rise significantly over the next 20-30 years. Depending on the scenario, the projected energy demand for hydrogen in 2045 ranges from 50 to 430 TWh (lower heating value [LHV]).^[1-3] While some of the hydrogen demand can be met locally, hydrogen imports will be required. For greater transport distances, such as hydrogen imports from North or South America, pipelines are not a feasible option. Therefore, the transport of hydrogen by ship will be crucial in the future. In addition to the liquefaction of hydrogen, there are other options for shipborne hydrogen transport. For this purpose, hydrogen can be converted into other chemical energy carriers, known as H2 derivatives.

The following hydrogen transport options are discussed in the context of this study: liquid hydrogen (LH₂), liquid methane (Green LNG), ammonia (NH₃), liquid organic hydrogen carrier (LOHC), and methanol (MeOH).

Several criteria can be used to technically evaluate an import option, shown in **Figure 1**. The technical evaluation criteria mentioned are: technological readiness of the steps in the process chain of the import options, shipping infrastructure, volumetric energy density, and handling of the energy carrier. This list is by no means complete and can be further expanded.

In the first step, this study focuses on the energetic utilization rate, i.e., how much energy is required to transport hydrogen or its derivatives to the importing country.

Figure 2 provides an overview of the content which is covered in this study. While conversion back to hydrogen is possible and considered for each transport option, some H_2 derivatives can also be used directly in the importing country. For Green LNG, ammonia, and methanol, direct utilization was therefore considered in addition to conversion back to hydrogen. Most studies focus on single energy carriers or their associated costs of import.

International Renewable Energy Agency (IRENA) 2022 evaluates NH₃, LH₂, and LOHC for hydrogen import;^[4] Staiß et al. 2022 compares import options by ship for LH₂, NH₃, MeOH, and Fischer-Tropsch products.^[5] While Hank et al. 2020 also regard the same energy carriers as this article (LH₂, LOHC, CH₄, MeOH, and NH₃), for H₂ derivatives CH₄, MeOH, and NH₃, no reconversion (cracking or reforming) in the importing





Figure 1. Overview of different evaluation criteria for hydrogen imports to Germany.

www.entechnol.de

country was investigated.^[6] The Joint Research Center (JRC) Report by Ortiz et al. 2022 focuses on LH₂, NH₃, MeOH, and LOHC, missing hydrogen import trough CH_{4} .^[7] On the contrary to the Agora Industrie report by Carels et al. 2023 who considers primarily CH_{4} .^[8]

This publication discusses a greater number of import options (5 in total: LH_2 , Green LNG, NH_3 , MeOH, and LOHC) compared to the previous mentioned publications. To be able to compare the energy utilization rate of the import options LH_2 , Green LNG, NH_3 , MeOH, and LOHC, it is essential that the same assumptions are made in all calculations. This cannot be guaranteed by comparing different studies with therefore different assumptions. For this reason, in this study, energy calculations for each import option are carried out with the same assumptions to be able to evaluate and compare the import options in terms of energy utilization.

For the conversion in the exporting and importing countries, the processes and their respective reaction conditions are also discussed. For energy carriers that exist in gaseous form under standard conditions, the boil-off rates (BORs) are also taken into account. To compare the import options with each other, the energy utilization rate of the import options was estimated with the help of the energy requirements. While energy requirements



Figure 2. Overview of the hydrogen transport pathways investigated in this study: liquefied methane, liquefied hydrogen, liquid organic hydrogen carrier, and ammonia and methanol.

Energy Technology

www.entechnol.de

of each step of the process chain were examined, heat utilization between different steps of the process chain or the hydrogen production was not considered. This results in lower degrees of energy utilization than an optimally interconnected process chain.

This article provides a better and deeper understanding of the necessary steps of the process chain to import $\rm H_2$ via $\rm H_2$ derivatives.

2. Methodology

DVANCED

www.advancedsciencenews.com

Despite the fact that energy requirements for different steps of import options vary, there are common assumptions for all import options. This study investigates the conversion of hydrogen in countries of import and export, as well as its storage, loading, and transport. The production of green hydrogen is not a part of the calculations. While the transportation of hydrogen via pipeline is an option for import from relatively short distances, for crossing longer distances, transportation with ships is unavoidable. In this study, the transportation distance is assumed to be 6000 km, equaling the distance between North America and Germany. The duration of the transport results from the speed of the ship and the transport distance. It is assumed that the boil-off is in general reliquefied on board. An exception is the transport chain Green LNG, where the vessels operate with the ensuing boil-off. The storage period in the exporting country is assumed to be 7 days for all transport options. The assumption was made based on the travel time of the LNG carrier, which requires about 7 days at \approx 20 knots, for the distance of 6000 km. It is therefore possible to operate one terminal in the exporting country with two ships. The storage period in the importing country was assumed to be 4 days. It was assumed that the takeover of hydrogen in the exporting country from electrolysis and importing country is in gaseous form at 25 bar and 25 °C.

The overall energy utilization rates η_{H_2, H_i} of the import options in % are calculated using Equation (1).

$$\eta_{\rm H_2, \, H_i} = \frac{m_{\rm H_2, \, out} \cdot {\rm H}_{i, \rm H_2}}{m_{\rm H_2, \, in} \cdot {\rm H}_{i, \rm H_2} + \sum E_{\rm el} + \sum E_{\rm chem}} \cdot 100$$
(1)

kg $m_{\rm H_2,\,in}$ is the amount of hydrogen produced in the exporting country in kg $m_{\rm H_2,\,out}$ describes the amount of hydrogen required in the importing country in kg; $\eta_{\rm H_2,\,H_i}$ Hydrogen or H₂ derivatives can be used either as ship fuel or as a combustion medium for conversions in the importing country. Therefore, the amount of hydrogen that is produced in the exporting country can be higher than the amount of hydrogen that can be used in the importing country. H_{i,H_2} is the LHV of hydrogen in kWh kg⁻¹. All energy content in this article is based on LHV. The electrical energy required in the process chain, for example necessary for compression of hydrogen, is E_{el} in kWh. Chemical energy, such as fuel for vessels, is considered with E_{chem} in kWh. A detailed literature research was carried out for each and the results are presented in Section 3. All calculations in this publication are based on literature data. As only the individual process steps are considered in this study, there are no interconnections between the processes with electrolysis units. Therefore, no heat usage could be considered. Otherwise, exothermic losses could have been much lower.

3. Hydrogen Transport Chains

All hydrogen transport chains can be divided into the following steps: conversion of gaseous hydrogen to H_2 derivatives in the exporting country, storage and loading in the exporting country, shipping to the importing country, unloading, storage, and reconversion of H_2 derivatives in the importing country. For methanol, methane, and ammonia, the direct utilization in the importing country is also considered.

3.1. LH₂

liquefaction

Ship transport

 $E_{\rm el} + E_{\rm che}$

 LH_2 is neither toxic nor corrosive, yet handling is challenging due to the low temperatures required. Hydrogen is liquid at ambient prerssure and -253 °C.

In Figure 3, the complete process chain of importing hydrogen as LH_2 is shown.

3.1.1. Processing in Exporting Country

Re

liquefaction

Storage and

Loading

Although hydrogen liquefaction has been known since 1898, no large-scale hydrogen liquefaction plants exist at present. In 2019, global daily LH₂ production was 358 t d⁻¹.^[9] The largest plant in the U.S. has a capacity of 35 t d⁻¹ or 120 MWh d⁻¹.^[10] For comparison, the largest liquefied natural gas (LNG) liquefaction plant has a capacity of 10 million tons per year, equaling to 380 GWh d⁻¹.^[11]

Cooling hydrogen for liquefaction to -253 °C requires an energy-intensive process. Small plants available today have an

555

(a) p = 25 bar

 $T = 25 \ ^{\circ}\text{C}$

Regasification

(with sea

water)

Figure 3. Process chain for hydrogen import option liquid hydrogen (LH₂).

Liquefaction

(*a*) p = 25 bar,

 $T = 25 \ ^{\circ}\text{C}$

liquefaction

Storage and

Loading

approximate energy requirement of 10–15 kWh kg⁻¹ H₂, which corresponds to 30% of the energy contained in the hydrogen based on LHV. For comparison, liquefaction of LNG takes around 5% of the energy contained in LNG. Energy requirements of 4–10 kWh kg⁻¹ H₂ are predicted for large hydrogen liquefaction plants in the future.^[4,12]

3.1.2. Storage and Loading

www.advancedsciencenews.com

Presently, LH₂ tanks are available, but only on a limited scale. NASA is currently operating tanks with volumes of \approx 3800 m³, which corresponds to 9 GWh energy.^[13] Kawasaki is developing LH₂ tanks with 10 000 m³ capacity.^[14] Boil-off in state-of-the-art LH₂ tanks is about 0.05–0.1% d⁻¹. With increasing tank capacity, boil-off will become easier to reduce.^[7,15] When transferring LH₂ from tank to ship, about 1% of the pumped cargo evaporates.^[16] All boil-off gas is assumed to be reliquefied immediately. The energy required for pumping LH₂ at the import and export port is assumed to be 1 kWh kg⁻¹ H₂.^[16,17]

3.1.3. Shipping

Only one ship has been built so far to transport liquid hydrogen. In 2022, Kawasaki Heavy Industries constructed the LH₂-Carrier "Suiso Frontier".^[18] Currently, it is traveling between Australia and Japan and transporting hydrogen from Australia to Japan. The Suiso Frontier has a loading capacity of approximately 1300 m³ or 3 GWh of LH₂. Kawasaki declared its intention to construct a LH₂ carrier with a capacity of 160 000 m³ or 380 GWh LH₂.^[14] In this study, this vessel is assumed to have a similar energy consumption as a state-of-the-art LNG carrier.

W. Amos estimates the boil-off during the shipment of liquid hydrogen to be 0.1–0.6% d⁻¹.^[19] No actual data on boil-off in LH₂ in vessels is available. Smith et al. modeled the boil-off and sloshing in LH₂-Carriers and found the BOR to be around nine times higher than in LNG-Carriers.^[20] As more LH₂ ships are built, the real BOR will become more apparent. In this study, it has been assumed that in future ships, reliquefaction systems will be available on board to utilize the gas formed because of boil-off.

3.1.4. Processing in Importing Country

Liquid hydrogen, similar to LNG, must be regasified at the import site. This step is yet to be demonstrated at an industrial scale, as there are currently no LH₂ terminals. Analogies could be made with LNG regasification, so this step is expected to be feasible in the future.^[21] Usually, cryogenic fluids are vaporized using evaporators heated with sea water. Electric energy demand for this step was assumed to be similar with LNG regasification, which is about 1% of the transported energy. If consumers are available, the cold energy of LH₂ regasification could be utilized.^[22]

3.2. Green LNG

Methane is gaseous under standard conditions, but it can be converted into the liquid phase at ambient pressure and -161.5 °C. It can either be converted to hydrogen in the importing country or injected to the gas grid, and it can be utilized directly in the importing country. **Figure 4** shows the process chain of Green LNG. The direct utilization of methane is presented in the dashed line. The CO₂ pathway is also represented. Since not all CO₂ can be captured in the importing country, the missing 10% of CO₂ for synthesis in the exporting country can be extracted from the air using direct air capture (DAC).^[23]

3.2.1. Conversion in Exporting Country

Methane can be produced from CO_2 and H_2 via the Sabatier reaction (Equation (2)), usually using nickel catalysts.^[24,25]

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O; \quad \Delta_R H^0 = -165 \text{ kJ mol}^{-1}$$
(2)



Figure 4. Process chain for hydrogen import option liquefied methane (Green LNG). The dashed line shows the path for direct utilization of Green LNG.



www.entechnol.de

 $\Delta_R H^0$ is the reaction enthalpy in kJ mol⁻¹. Although there have been historical applications for methanation of hydrogen in coalto-gas processes, a green methanation plant (power-to-gas) has not yet been demonstrated on a commercial scale.^[26] The supply of CO₂ is energy intensive, as either DAC or some form of carbon capture and utilization (CCU) must be used. DAC provides more flexibility concerning the location of a plant. It would enable carbon-neutral use of methane without a CCU system but is currently not available at a commercial scale. DAC consumes between 1.7 and 2.8 kWh kg⁻¹ CO₂.^[27] In the case of CCU, 1 kWh kg⁻¹ CO₂ would likely be sufficient.^[28,29] Based on pilot methanation plants, an electric energy consumption of 0.3 kWh m⁻³ CH₄ could be assumed.^[30] Methanation of CO₂ provides 165 kJ mol⁻¹ heat, which can be used to optimize other steps of the process chain.^[24] The energy consumption for liquefaction of methane is 0.7 kWh kg⁻¹ CH₄.^[22,31]

3.2.2. Storage and Loading

DVANCED

www.advancedsciencenews.com

Due to the flourishing LNG trade, high storage capacities of LNG are currently available worldwide. The worldwide LNG storage capacity is around 70 million m³. Japan, China, and South Korea have the largest storage capacities. Their share is over 60% of the world capacity.^[11] Boil-off during storage lies between 0.012% and 0.12% d⁻¹ and is assumed to be liquefied immediately.^[22,32] The required energy to pump the Green LNG at the harbor is 5×10^{-4} kWh kg⁻¹ CH₄.^[33]

3.2.3. Shipping

Green LNG is comparable to fossil LNG and global shipping of LNG is already established. In 2021, around 370 million tons of LNG was supplied to customers all over the world.^[34,35] A large fleet of 641 LNG carriers is already available with average capacities ranging from 70 000 to 180 000 m³ or 410–1000 GWh.^[10] Vessel data sheets for LNG carriers with capacities of 174 000 m³ from capital gas indicate BORs of 0.085% d⁻¹ and fuel consumption of 77 t d⁻¹ LNG.^[36] Furthermore boil-off gas can be used to propel LNG carriers.^[37]

3.2.4. Reconversion in Importing Country

LNG regasification is a mature technology and requires little energy.^[22] In 2021, the worldwide regasification was 570 million tons of methane. Hydrogen can be extracted from the methane

via steam reforming (SR) (Equation (3)). Water and CO can be converted to CO_2 and H_2 in a subsequent water gas shift reaction to increase the H_2 yield (Equation (4)). The CO_2 released can be captured and either stored or transported back to the exporting country as a CO_2 source. SR is a commercially established process. However, it is energy intensive as methane and steam must be heated to 800–900 °C at 30 bar.^[38]

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2; \quad \Delta_R H^0 = 206 \text{ kJ mol}^{-1}$$
 (3)

$$H_2O + CO \rightleftharpoons H_2 + CO_2; \quad \Delta_R H^0 = -41 \text{ kJ mol}^{-1}$$
 (4)

Part of the methane is burned to provide the necessary heat for the endothermic reaction (Equation (3)). After SR, carbon monoxide must be shifted to maximize hydrogen output. According to the project Roadmap Gas 2050, 50 kWh of methane is needed to produce 1 kg of H₂ through SR.^[28] Additionally, the SR and carbon capture steps require 1 kWh kg⁻¹ of electric energy each.^[28] Considering these energy requirements, a steam reformer with carbon capture system works only at an efficiency of about 65%, which raises interest in the direct utilization of methane instead of SR in the importing country.^[38]

3.3. Ammonia

Ammonia is gaseous at room temperatures but can be liquefied at much higher temperatures than hydrogen or methane. At ambient pressure, -33 °C is sufficient for liquefaction and at ambient temperature, approximately 9 bar of pressure is required. If ammonia is converted to hydrogen, special attention must be paid to the purity, since ammonia is toxic to proton exchange membrane fuel cells even in ranges of a few parts per million, so cracking processes with high turnovers or effective treatment processes must be developed.^[39] The complete process chain for the import of hydrogen through NH₃ is represented in Figure 5. Since the direct utilization of ammonia is also an option, this pathway is shown with a dashed line. Ammonia is in general suitable to be used as a fuel for internal combustion engines. However, combustion of NH₃ causes NOx emissions. Reduction NOx emissions requires high pressure and an abundance of NH3 in the fuel air mixture. There is still need for research in this field to fully understand NH₃ combustion and NOx formation.^[40]



Figure 5. Process chain for hydrogen import option ammonia (NH₃). The dashed line shows the path for direct utilization of NH₃.

Energy Technology

www.advancedsciencenews.com

3.3.1. Conversion in Exporting Country

Ammonia is produced from nitrogen and hydrogen via the Haber–Bosch process (Equation (5)). While hydrogen production for ammonia plants today relies heavily on SR of natural gas, it is also possible to realize an ammonia plant which uses green hydrogen, e.g., from electrolysis.^[41] However, the electrified Haber–Bosch process is yet to be demonstrated at a commercial scale. The ammonia reactor is operated at 150–350 bar and around 300–550 °C.^[42,43]

$$N_2 + 3H_2 \rightleftharpoons 2NH_3; \quad \Delta_R H^0 = -92 \, kJ \, mol^{-1}$$
 (5)

The highly optimized ammonia synthesis from natural gas reaches efficiencies around 66%, which will be the benchmark for electrolysis-based processes. However, the efficiency is mainly affected by the energy requirements for electrolysis.^[44] High purity of N₂ from air separation unit (ASU) and H₂ from electrolysis allows the Haber–Bosch process to be carried out minimized purge stream.^[42] The required energy for the ASU varies between 0.1 and 0.17 kWh kg⁻¹ NH₃ in published literature and the Haber–Bosch Synloop consumes 0.33–0.75 kWh kg⁻¹ NH₃.^[43,45–47]

3.3.2. Storage and Loading

Ammonia storage is already established commercially and can be carried out in the liquid state, which can be achieved by applying low temperatures or elevated pressures. Smaller tanks with capacities of around 300 t store NH₃ pressurized at 18 bar, larger tanks are refrigerated and store ammonia at -33 °C and atmospheric pressure.^[48,49] Refrigerated ammonia tanks can reach storage capacities of up to 45 kt. While storing ammonia, around 0.04% d⁻¹ will evaporate (boil-off) and is usually reliquefied immediately.^[50] Loading of ammonia takes about 5×10^{-4} kWh kg⁻¹ NH₃.^[33]

3.3.3. Shipping

Ammonia is shipped at similar conditions as LPG. LPG vessels could be retrofitted to carry NH3.^[51] To this date, NH3 is mostly traded as a precursor to fertilizer production, leading to global trade in the order of 20 MT year⁻¹ equaling around 100 TWh year^{-1 [50,52]} Capacities of existing NH₃ carriers vary between 30 000 and 70 000 m³ or 100-250 GWh, although construction of larger carriers would be possible.^[53] To this day, NH₃ carriers have been propelled by heavy fuel oil (HFO). The development of marine combustion engines which use ammonia as an energy source is advanced and expected to be available within a few years. Based on a vessel data sheet of Hartmann Reederei, a carrier size of 35 000 m^3 and a fuel consumption of 37 t d^{-1} was assumed in this study.^[51] Large-scale ammonia shipping uses ammonia in liquid form at -33 °C and atmospheric pressure; therefore part of the cargo will evaporate.^[48] This boil-off is usually reliquefied in the vessel.^[53] According to Al-Breiki et al. boil-off is around 0.024% d^{-1} , resulting in additional energy consumption of 0.224 kWh kg⁻¹ NH₃ for liquefaction.^[33,54]

3.3.4. Reconversion in Importing Country

Currently, ammonia is barely applied in the energy sector, so direct applications such as fuel cells or gas turbines are limited at technology readiness level (TRLs) of 4–5.^[55] One option is to recover the hydrogen from ammonia, which could be realized using an ammonia cracker. At around 20 bar and 400–550 °C, ammonia can be converted to nitrogen and hydrogen (Equation (6)). However, this step is energy intensive and not demonstrated at a commercial scale vet.^[4,43]

$$2NH_3 \rightleftharpoons N_2 + 3 H_2; \quad \Delta_R H^0 = 92 \,\text{kJ} \,\text{mol}^{-1} \tag{6}$$

ThyssenKrupp Uhde GmbH has announced to build a commercial NH₃ cracker, but the timeline remains uncertain.^[56] In this article, an average energy consumption of 8 kWh kg⁻¹ H₂ for NH₃ cracking and 2 kWh kg⁻¹ H₂ for the subsequent product separation via pressure swing adsorption (PSA) was assumed.

Literature offers a wide range of $6-16 \text{ kWh kg}^{-1} \text{ H}_2$, for NH₃ cracking. Availability of real-plant data will most likely enable better assessment of the feasibility and energy demand of ammonia cracking.^[4,57,58]

3.4. LOHC

Another option to import hydrogen is to chemical bind the hydrogen to an LOHC. In this study, dibenzyl toluene (DBT) is considered, since it is one of the most widely studied LOHC.^[59,60]

The process chain for hydrogen import with LOHC is presented in **Figure 6**. It includes the conversion in the exporting country, the hydrogenation, the storage and loading in the exporting country, shipping of the carrier, and the unloading and storage in the importing country and also its dehydrogenation in the importing country. To complete the cycle, LOHC is shipped back to the export county to be reused.

3.4.1. Conversion in Exporting Country

The reaction to chemically bind the hydrogen to the energy carrier is called hydrogenation. The chemical equation is presented in Equation (7).

$$H0 - DBT + 9H_2 \rightleftharpoons H18 - DBT$$
, $\Delta_R H^0 = -65 \text{ kJ mol}^{-1}$ (7)

If 1 mol of DBT is hydrogenated with 9 mol H_2 , it can carry up to 6.2 wt% of hydrogen.^[61] This corresponds to 2 kWh kg⁻¹. The process conditions are 150 °C and 50 bar; therefore it is necessary to compress the hydrogen from 25 to 50 bar beforehand.^[4]

Due to the strong exothermic reaction, the reactor needs a cooling system to maintain a constant temperature of 150 °C. The electric energy required for the conversion in the exporting country consists of energy needed for compression of hydrogen to 50 bar and electric energy for the synthesis. The information on the energy requirement of hydrogenation in the literature ranges from 0.4 to 1.8 kWh kg⁻¹ H₂.^[62–64] Since the hydrogenation takes place at elevated pressure, part of the hydrogen is also physically stored in the DBT.^[65] Since LOHC is transported

ADVANCED SCIENCE NEWS _____ www.advancedsciencenews.com

www.entechnol.de



Figure 6. Process chain for hydrogen import option LOHC.

under atmospheric conditions, the pressure and temperature are then reduced to ambient pressure and temperature. The pressure and temperature reduction releases the dissolved hydrogen. This only accounts for 2% of the hydrogen. The amount was estimated with Henry coefficients, which were determined by Aslam et al.^[65] The additional energy required to compress the released hydrogen back at 50 bar is about 0.05 kWh kg⁻¹ and comparable small to the overall energy of hydrogenation and therefore in the following neglected.

3.4.2. Storage and Loading

The physical properties of DBT allow for storage at room temperature and pressure (25 °C and 1 bar). The viscosity and the density of DBT are similar to diesel.^[61] The vapor pressure is negligible; therefore boil-off is not expected. This simplifies the pumping and storage of DBT in refinery facilities, even over longer periods of time.^[7] The energy required to pump DBT into a vessel is 0.0023 kWh kg⁻¹ DBT.^[66]

3.4.3. Shipping

An advantage of the similar properties of DBT and diesel is that fuel transport chains are already established for diesel and can be used for DBT. For example, in 2021, the worldwide transported quantity of clean petroleum products was \approx 1225 Mio. t.^[34] The average capacity of oil carriers is 100 000 m³, with the possibility to use even larger vessels.^[67] A carrier with a capacity of 100 000 m³ can carry an equivalent of 190 MWh of hydrogen, related to the LHV.

3.4.4. Reconversion in Importing Country

To release hydrogen, DBT needs to be dehydrogenated. It is the reverse reaction of the hydrogenation and shown in Equation (8). The dehydrogenation is an endothermic reaction and needs about $11 \text{ kWh kg}^{-1} \text{ H}_2$ for the complete hydrogen release.^[68] Also, a catalyst is used for the dehydrogenation.^[60]

 $\mathrm{H18}-\mathrm{DBT} \rightleftharpoons \mathrm{H0}-\mathrm{DBT}+9\mathrm{H}_2, \quad \Delta_{\mathrm{R}}\mathrm{H}^0=65\,\mathrm{kJ\,mol^{-1}} \qquad (8)$

Since the dehydrogenation is an endothermic reaction, a high reaction temperature above 300 °C is necessary to archive reasonable reaction rates.^[68] After leaving the reactor, hydrogen and DBT are cooled down and separated in a heat exchanger. The dehydrogenated DBT is stored and shipped back to the exporting country. As the reaction is carried out at ambient pressure, hydrogen must be compressed to 25 bar to match the required boundary conditions (Section 3). This will however create an urgent need for large compressors in the importing country. There are currently no large dehydrogenation plants present. About 0.1 wt% of DBT degrades in a transport cycle, including hydrogenation, transport, and dehydrogenation. In every cycle, that amount of DBT needs to be replaced. For example, a ship with the capacity of 100 000 m³ can carry about 84 000 t of DBT. For comparison, the annual global DBT production capacity is about 9000 t a^{-1} . The production of the DBT has an energy requirement of 12.12 kWh kg⁻¹ DBT.^[4,69]

3.5. Methanol

Methanol (MeOH) is the simplest alcohol and is liquid under standard conditions.

The process chain for MeOH closely resembles the Green LNG process chain. The process steps (**Figure 7**) include MeOH synthesis, storage, and loading, shipping to the import country, unloading, storage, and reconversion to hydrogen through SR.

While the synthesis in the exporting country has a high CO₂ demand, the synthesis in the importing country releases CO₂. This CO₂ can be captured with the help of carbon capture techniques. The capture efficiency is \approx 90%. CO₂ can then be liquefied and transported back to the exporting country by ship. The missing 10% CO₂ for synthesis in the exporting country can be obtained from the air by DAC.^[23]

Since methanol can also be used directly both as a chemical energy carrier and as an important basic chemical, direct utilization was also considered in this study (shown as a dashed line in





Figure 7. Process chain for the hydrogen transport via methanol (MeOH), including CO₂ recovery and back shipping. The dashed line shows the path for direct utilization of MeOH.

Figure 7). In this case, no return transport of CO_2 was assumed. All CO_2 required for the methanol synthesis was obtained with DAC in the exporting country.

3.5.1. Conversion in Exporting Country

 H_2 and CO or CO₂ are required for the synthesis of MeOH. In an exothermic catalytic supported reaction, they are converted to MeOH (Equation (9)–(11)).

$$CO + 2H_2 \rightleftharpoons CH_3OH; \quad \Delta_R H^0 = -91 \, \text{kJ} \, \text{mol}^{-1}$$
 (9)

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O; \quad \Delta_R H^0 = -49.5 \, \text{kJ} \, \text{mol}^{-1}$$
(10)

$$H_2O + CO \rightleftharpoons H_2 + CO_2; \quad \Delta_R H^0 = -41 \, \text{kJ} \, \text{mol}^{-1}$$
 (11)

The reforming is conducted at 200–250 °C and 50–80 bar with a Cu/Zn/Al₂O₃ catalyst. Due to the exothermic reaction, cooling of the reactor is necessary. In a single reactor pass, only 50–80% of the reactants are converted to MeOH, this means that part of the reactants must be recycled.^[70] In addition to MeOH, water is also produced. In a further step, the water is separated from the MeOH. As an important basic chemical, annual methanol production exceeds 100 million tons. Today, methanol is largely produced from fossil synthesis gas (Equation (9)).

In the future, Green LNG will be produced directly from hydrogen and CO₂ (Equation (10)). In the process, large amounts of water will also be produced, which can have an influence on catalyst activity and service life. Catalyst research is therefore needed for Green LNG synthesis.^[70] Currently 24 facilities for Green LNG production worldwide exist or are planned with a capacity around 844 thousand tons. Making up less than 1% of the current global production.^[71,72]

3.5.2. Storage and Loading

The next step in the process chain is the storage and loading of the MeOH at the export port. Storage of MeOH is possible at ambient temperature and pressure.

Energy Technology

www.entechnol.de

The energy demand for pumping MeOH is 05×10^{-4} kWh kg⁻¹ MeOH.^[33]

3.5.3. Shipping

MeOH is liquid at ambient temperature and pressure. It can therefore be transported under these conditions. With low BOR of 0.005 wt% d⁻¹, the boil-off can be neglected.^[33,73] MeOH vessels have a capacity of up to 120 000 m³ or 520 GWh.^[74] Clean petroleum product vessels could also be used to transport MeOH. Presently, research is being conducted into the use of MeOH as a marine fuel. MAN Energy Solutions SE is currently working on dual-fuel engines that can use both diesel and MeOH for propulsion.^[75]

3.5.4. Reconversion in Importing Country

In the importing country, MeOH is converted back into hydrogen and CO₂ in an SR process. Steam and gaseous MeOH are mixed in an allotherm reformer, according to the stoichiometry in Equation (12). The conditions of SR are similar to the reforming process of methane. One difference is the lower reaction temperature of about 400 °C. The energy demand for the conversion of MeOH to H₂ and CO₂ is between 10.5 and 12.9 kWh kg⁻¹ H₂.^[76] The reforming process is conducted at 30 bar. Therefore, hydrogen can be used directly, without further compression.

$$CH_3OH + H_2O \Rightarrow CO_2 + 3H_2; \quad \Delta_R H^0 = 49.5 \text{ kJ mol}^{-1}$$
 (12)

While small methanol steam reformers exist for fuel cells, only a few concepts are found for larger plants.^[77]

A PSA is used to meet the required gas quality.^[78]

/ΔΝCFD

www.advancedsciencenews.com

The off-gas from the PSA contains a mixture of CO_2 , CO, H_2 , and MeOH and is fed back into the SR furnace. CO_2 from the SR furnace exhaust gas is removed and liquefied in the next step. About 90% of the CO_2 in the exhaust gas are captured.^[28] With a suitable ship, the liquefied CO_2 gets transported back to the importing country and can be reused in the MeOH synthesis. The Stella Maris CCS project plans CO_2 ships with a capacity up to 50 000 m³.^[79]

4. Comparison of Different Hydrogen Transport Chains

To compare the energy carriers for importing hydrogen, the different transport options were examined based on their energy utilization ratio and additional (technical) evaluation criteria, such as volumetric energy density, TRL, global production, and handling.

4.1. Energy Utilization

Based on the literature described in Section 3, energy requirements were determined for each process step of the various hydrogen import options. **Table 1** shows the assumptions which are made in this study. The respective literature sources are also listed. The BORs of the process steps storage and loading as well as shipping are presented in **Table 2**.

Based on the energy requirements and BORs of the individual process steps assumed in Table 1 and 2, the energy utilization rate of the individual import options was calculated using Equation (1) (see also Section 2, Methodology). The unit used is kWh kWh⁻¹, describing the energy requirement in kWh to obtain one kWh in the importing country. Where necessary, other units from the literature were converted using the stoichiometry and LHV of the respective reactions and derivatives. The fuel consumption of the ships in kWh per kWh was calculated using the transporting distance as well as the speed and capacity of the vessel. The resulting energy utilization rates of the import options are shown in Table S1, Supporting Information and Figure 8. In addition, the energy requirements of the import options were grouped in "conversion in the exporting country", "loading and unloading" "ship transportation", and "conversion in the importing country" and totaled. The energy requirements of the individual process steps are also shown in Table S1, Supporting Information.

Figure 8 depicts the energy of each process step which is required for one kWh (LHV) in the importing country for each importing option (LH₂ or H₂ derivatives: LOHC, MeOH, NH₃, and Green LNG). The process steps are conversion in the exporting country, loading and unloading, ship transportation, and conversion in the importing country.

In addition to the subdivision process steps, it is also distinguished between the type of energy: conversion losses due to the

Table 1. Energy requirements for each step of the process chain (conversion in export country, storage and loading, shipping, and reconversion in import country) for different import options of hydrogen: LH_2 , Green LNG, NH_3 , LOHC, and MeOH.

Energy requirement	LH ₂	Green LNG	NH ₃	LOHC	MeOH
Conversion export country	8 kWh kg ⁻¹ H ₂ (liquefaction) ^[4,12]	0.3 kWh m ⁻³ CH ₄ (methanation) ^[81] 2.2 kWh kg ⁻¹ CO ₂ (DAC) ^[29,81]	0.556 kWh kg ⁻¹ NH ₃ (Haber–Bosch) ^[43,45–47] 0.15 kWh kg ⁻¹ NH ₃ (ASU)	1.5 kWh kg ⁻¹ H ₂ (hydrogenation and compression) ^[62-64]	3 kWh kg ⁻¹ H ₂ (methanc synthesis) ^[82] 2.2 kWh kg ⁻¹ CO ₂ (DAC) ^[29,81]
Storage and loading	1 kWh kg ⁻¹ H ₂ (pumping) ^[16,17]	$\begin{array}{l} 0.7 \ \text{kWh} \ \text{kg}^{-1} \ \text{CH}_4 \ \left(\text{liquefaction}\right)^{[22,31]} \\ 5 \times 10^{-4} \ \text{kWh} \ \text{kg}^{-1} \ \text{LNG} \\ (\text{pumping})^{[33]} \end{array}$	$\begin{array}{l} 5\times 10^{-4} \text{kWh} \text{kg}^{-1} \text{NH}_3 \\ (\text{pumping})^{[33]} \\ 0.224 \text{kWh} \text{kg}^{-1} \text{NH}_3 \\ (\text{liquefaction})^{[54]} \end{array}$	$1.2 \times 10^{-3} \text{ kWh kg}^{-1} \text{ H}_2^{[66]}$ (pumping)	$5 imes 10^{-4} \text{kWh kg}^{-1}$ MeOH (pumping) ^[33]
Shipping	160 000 m ^{3[14,36]} 92 t (HFO) d ⁻¹ (similar to LNG carrier)	180 000 m ^{3[36]} 77 t (LNG) d ⁻¹	87 000 m ^{3[83]} 37 t (HFO) d ⁻¹	112 000 m ^{3[74]} 35 t (HFO) d ⁻¹	112 000 m ^{3[74]} 35 t (HFO) d ⁻¹
Reconversion in import country	0.33 kWh kg ⁻¹ H ₂ (regasification)	16.67 kWh kg ⁻¹ H ₂ (steam methane reforming) ^[28] 1 kWh kg ⁻¹ CO ₂ (carbon capture) ^[28]	8 kWh kg ⁻¹ H ₂ (cracking) ^[4,57,58] 2 kWh kg ⁻¹ H ₂ (PSA) ^[4]	11 kWh kg ⁻¹ H ₂ (dehydrogenation) ^[68] 1.5 kWh kg ⁻¹ H ₂ (compression of H ₂) ^[84]	12.9 kWh kg ⁻¹ H ₂ (stean reforming) ^[85] 1 kWh kg ⁻¹ CO ₂ (carbor capture) ^[28]

Table 2. Boil-off rates (BORs) for storage and loading as well as for transportation by ship for LH₂, green LNG, NH₃, LOHC, and MeOH.

BOR	LH ₂	Green LNG	NH ₃	LOHC	MeOH
Storage and loading	$0.075\% d^{-1[7,15]}$	0.07% d ^{1[22,32]}	$0.04\% d^{-1[50]}$	Neglectable	Neglectable
Shipping	0.45% d ^{-1[19]}	0.085% d ^{-1[36]}	$0.024\% d^{-1[33]}$	Neglectable	Neglectable



www.entechnol.de



Figure 8. Required energy in kWh for each step of the process chain to obtain one kWh hydrogen or H_2 derivative (direct utilization, D. U.) in the importing country (I. C.). Comparison of different import options. The electrical energy demand in the exporting (E. C.) and importing country (I. C.) is shown in black stripes. Exothermic losses in the E. C. as well as chemical energy needed in the I. C. are shown in gray stripes. Shipping in black, and storage and loading in gray. Diagram data in Table S1, Supporting Information.

exothermy of the reaction, electrical energy, or chemical energy needed for heating. The electrical energy demand in the exporting and importing country is shown in black stripes. Exothermic losses in the exporting country as well as chemical energy needed in the importing country are shown in gray stripes, shipping in black, storage and loading in gray. The lower the energy input in kilowatt-hour per kilowatt-hour, the higher the energy utilization rate. The one kWh available in the importing country is represented by the solid gray bar. Everything provided earlier represents the additional effort which is needed to import hydrogen.

If the direct utilization of the derivatives is considered for MeOH and Green LNG, the electrical energy requirement in the importing country increases to 0.51 and 0.62 kWh kWh⁻¹ for MeOH and Green LNG. The direct use of the derivatives in the importing country eliminates the need to capture and transport the CO₂ back. CO₂ must therefore be supplied to the exporting country in a different way. In the first step, a DAC, an energy-intensive process, was therefore assumed, but other ways of supplying CO₂ are also conceivable.

The influence of the source of CO_2 to the energy demand is later discussed in this article. The liquefaction of hydrogen consumes about 0.24 kWh kWh⁻¹. In comparison, that is only half of the electric energy required in the exporting country for direct utilization of Green LNG or MeOH. It is therefore the process step with the highest energy consumption in the LH₂ process chain.

Energy is released in the form of heat during all exothermic conversions in the exporting country these processes are Haber–Bosch synthesis for NH₃, methanation for Green LNG,

hydrogenation for LOHC, and methanol synthesis for MeOH. The import option MeOH direct utilization has the smallest exothermic losses with 0.13 kWh k h⁻¹. While during importing hydrogen through Green LNG with SR, 0.3 kWh kWh⁻¹ are lost due to the exothermic reaction.

The energy required for storage and loading is comparable small for NH₃, MeOH, and LOHC with $E_{\rm el} < 0.003 \,\rm kWh \, kWh^{-1}$. When energy carriers, that must be stored or loaded in extremely cold temperatures, remain liquid, this energy is much larger. Methane is liquid at $-161 \,^{\circ}$ C and LH₂ at $-253 \,^{\circ}$ C. So, boil-off is much larger and needs to be relique-fied. Boil-off occurs not only during storage but also during pumping the cold liquids. The liquefaction of hydrogen in particular requires a significant amount of energy. It consumes approximately six times as much energy as methane liquefaction (based on LHV).

The actual ship transport has the lowest energy consumption of all process steps. That is true for all importing options, even if CO_2 is shipped back to the exporting country in a separate vessel. It accounts for between 0.006 kWh kWh⁻¹ (MeOH direct utilization) and 0.05 kWh kWh⁻¹ (NH₃ direct utilization).

Because of its endothermic nature, the reconversion of H_2 derivatives to hydrogen in the importing country is energy intensive. Methane SR has the highest chemical energy demand with 0.5 kWh kWh⁻¹ in this context. Although information in literature about the energy demand for ammonia cracking, methanol reforming, and LOHC dehydrogenation is available, none of these processes are currently available commercially. Hence, exact information on energy consumption for existing large-scale plants is only available for methane reforming.

The import option via LH₂ is thus the most efficient and apart from liquefaction, no energy-consuming syntheses and thus no exothermic losses are present.

DVANCED

The import options with the highest energy utilization rate above 70% are LH_2 (73%) and direct utilization of NH_3 (77%).

For LH₂, this is due to the non-required syntheses. For this import option, the most energy-intensive step is the liquefaction of hydrogen. With the direct use of NH₃, only the synthesis in the exporting country is needed. The energy-intensive cracking in the importing country is not necessary for direct use, so the energy utilization rate increases from 63% (NH₃ + cracking) to 77% (NH₃ direct utilization).

The LOHC import option has a utilization rate of 68%. Exothermic hydrogenation in the exporting country and endothermic dehydrogenation in the importing country are the most energy-intensive process steps in this process chain. Heat utilization in the exporting or importing country was not considered. In comparison to the previously mentioned import options, Green LNG and MeOH with SR have significant lower energy utilization rates of 47% and 57%, respectively.

On the one hand, this is due to the endothermic synthesis for hydrogen production in the importing country, SR, and on the other hand, CO₂ must be provided for both import options. It can be managed as a cycle, as in the import options including SR and carbon capture in the importing country. Only the percentage that cannot be captured must then be produced with DAC in the exporting country, in this study 10%. Therefore, if the direct use of the energy sources is considered, CO₂ is not captured in the importing country. CO₂ must be provided elsewhere. If the CO₂ is provided in the exporting country with DAC, an energyintensive process, the energy utilization rate of the import

2.5

2.0

1.5

1.0

0.5

0.0

Green

Green

Energy input in kWh kWh⁻¹

options increases only marginally, even though the synthesis in the importing country is not necessary. For Green LNG, the energy utilization rate improves from 48% (Green LNG + SR) to 51% (Green LNG direct utilization + DAC). For MeOH, the energy utilization rate even decreases by 1%, from 57% (MeOH + SR) to 56% (MeOH direct utilization + DAC).

The way CO_2 is supplied has a major impact on the energy utilization rate of import options that require CO_2 . Therefore, the influence of the source of CO_2 was further investigated in this article.

Therefore, a sensitivity analysis (see **Figure 9**) was performed with respect to the CO_2 source and the effect of heat usage in the exporting country. Aside from the previously mentioned two considered cases of SR and direct utilization with DAC in the exporting country of Green LNG and MeOH, three additional cases were examined.

So, for both Green LNG and MeOH, five different cases were compared. They are: 1) Green LNG or MeOH with SR and carbon cycle, where only 10% of the CO_2 is provided with DAC in the exporting country. 2) Green LNG or MeOH with SR, where the CO_2 is provided from a point source in the exporting country. Possible point sources are biogas plants, biomass gasification, or industry. 3) Direct utilization of Green LNG or MeOH, where the CO_2 is provided with DAC in the exporting country. DAC ensures location independence for the synthesis, since point sources are not always available. 4) Direct utilization of Green LNG or MeOH, where the CO_2 is provided by DAC. The heat for the DAC is provided from the exothermic synthesis to produce Green LNG or MeOH. 5) Direct utilization of Green LNG or MeOH, where the CO_2 is provided from a point source in the exporting country.

100

80

60

40

20

0

MeOH

////

%

Energy Utilization in

Electric Energy I. C. Chemical Energy I. C. Shipping Storage and Loading Electric Energy E. C.

1 kWh in I. C.

Exothermic Losses E. C



Green

MeOH

MeOH

MeOH

MeOH

Green

Figure 9. Required energy in kWh for each step of the process chain to obtain one kWh in the import country. The influence of the CO_2 source is compared for the import options methanol (MeOH) and Green LNG. Steam reforming (SR) as well as direct utilization (D.U.) were compared.

Green

There are many different, well-known processes for capturing CO_2 from CO_2 -rich gases (point sources), which have a lower energy requirement compared to DAC. This publication therefore considers the extreme case where no additional energy requirement for CO_2 supply needs to be taken into account. The exact type of separation process was therefore not considered in this article. The assumed cases of CO_2 provision with DAC and point source represent the two extreme assumptions of the energy requirement for CO_2 provision. The provision by means of DAC represents the highest energy requirement, the point source the lowest. In addition to the options mentioned here, other options for CO_2 supply are also conceivable; the energy requirement for such an option will then be between the two scenarios considered (DAC, point source).

IDVANCED

The source of CO_2 has only a small influence on the utilization rates for reforming methane or methanol back to hydrogen (first two bars for Green LNG and MeOH, respectively). If a point source is considered, the utilization rate increases only by 3% for Green LNG and 5% for MeOH. The reason is that a CO_2 cycle is considered in which only 10% of the CO_2 must be made available in the exporting country (due to losses in carbon capture after SR).

If the direct utilization of Green LNG or MeOH is considered, the energy intensive synthesis back to hydrogen is not necessary for both import options. As a result, no carbon is captured capture at SR in the importing country. CO_2 must be made available elsewhere. If CO_2 is provided by DAC in the exporting country, the energy utilization rate increases by 10% for Green LNG from 47% to 57% for direct utilization. For MeOH, the energy utilization rate even decreases slightly by 1%. This is due to the high energy demand of DAC in the exporting country.

Most of the energy needed for DAC is heat. Both, methanation and methanol synthesis are exothermic reactions, releasing heat. A heat integration to DAC was therefore investigated. For both import options, it is not possible to operate the DAC only with heat from the synthesis. Additional energy is still required. Nevertheless, the energy utilization rate for direct utilization increases for Green LNG further by 8% from 57% (direct 65% (direct utilization + heat utilization + DAC) to integration + DAC). During the methanol synthesis, not as much heat is released as during methanation. It is also reflected in the utilization rate. It increases for this scenario only by 4% from 56% to 60%.

The last option studied is that CO_2 is provided by a point source in the exporting country. In this case no additional energy is required to obtain the CO_2 . Possible point sources are: biogas plants, biomass gasification, or exhaust fumes from industry. For Green LNG, the energy utilization rate increases to 76%, for MeOH even further to 83%.

In general, the differences in the increase of utilization rates between the two import options can be explained in the difference of the exothermic or endothermic of the reactions (synthesis and reforming). Methanation releases more energy and reforming of methane requires more energy, than methanol synthesis and reforming of methanol (see Equation (2), (3), (10), and (12)). Furthermore, the ratio of how many mol CO₂ is required per mol H₂ (CO₂/H₂) for methanol synthesis is 7.3 (Equation (10)), while the ratio for methanation is 5.5 (Equation (2)). So, more CO_2 per H_2 is needed for methanol. The source of the CO_2 therefore has a particularly large influence on this import option.

In summary, it can therefore be said that for import options that require CO₂, a favorable CO₂ source is particularly important. If a point source is available in the exporting country, the direct utilization of the H_2 derivatives is particularly advantageous in terms of energy.

Figure 10 investigates the influence of transportation distance on the energy utilization rate of the different import options. In addition, it compares the import of hydrogen and its derivatives by ship with the transport of gaseous hydrogen by pipeline. The energy required in kWh for one kWh in the importing country is shown for distances between 0 and 14 000 km. The compressors for transporting the hydrogen are operated electrically.^[28] The energy consumption for pipeline transport was calculated according to Leiblein et al.^[28]

Due to the relatively small share of ship transport in the total energy demand, the transport distance has a small influence on the required energy and therefore the energy utilization rate of the import options. Doubling the distance from 7000 to 14 000 km only leads to a reduction in the energy utilization rate of 1–2% for all import options. If gaseous hydrogen is the target product in the importing country, LH_2 is the most energy efficient transport option by ship for all distances. Only if the direct use of the energy carriers is also considered, NH_3 performs better. The required additional energy required from 0 to 14 000 km is highest for the transport of NH_3 with cracking which is approximately 0.1 kWh kWh⁻¹. For short distances, pipeline transport is the most energy efficient compared to all import options. This is true for distances up to 9000 km.

It brings the focus to H_2 which is exported from regions that can be reached by pipeline. H_2 imports from these regions via pipeline are the most energetically reasonable option.



Figure 10. Required energy in kWh for different import options for hydrogen to obtain one kWh in the importing country for transport distances from 0 to 14 000 km. Pipeline transport is calculated from ref. [28].



4.2. Additional Important Evaluation Criteria

The Intergovernmental Panel on Climate Change (IPCC) states that with a CO₂ budget of 420 Gt CO₂ there is a two-third chance that global warming will remain below 1.5°. With a budget of 580 Gt CO₂, the chances drop to 50%.^[80] A rapid reduction in greenhouse gas emissions is therefore essential to comply with the existing, diminishing budget and prevent global warming exceeding 1.5°. Therefore, not only the efficiency of climatefriendly hydrogen import options is crucial, but also their rapid implementation. So, replacing fossil hydrogen or other energy sources with renewable energy sources as quickly as possible is important to achieve the 1.5° target.

Therefore, in addition to the degree of energy utilization, other factors must be taken into account when evaluating import options. Further required evaluation criteria are the technological maturity of the process chain and the already existing infrastructure for transport by ship, volumetric energy density, as well as handling of the energy carrier.

4.2.1. Technology Readiness Level

One way of describing the technical maturity of a process chain is the TRL. The process step with the lowest TRL determines the TRL of the overall process chain. While large-scale plants already exist for some import options, there are process steps for other import options for which only labscale plants are available. The higher the TRL, the more technologically mature the process chain is and the faster it can be implemented.

4.2.2. Shipping Infrastructure and Global Trade by Sea

The number and capacity of vessels available for the respective derivatives is also an important parameter for assessing the speed of implementation. The current world trade volume of H_2 derivatives provides information on their availability and establishment on the world market. Both factors allow an estimate of the quantities of the derivative that can be transported by ship in the short term. If a large part of the energy source is already traded by ship, a rapid expansion of green imports is feasible.

4.2.3. Volumetric Energy Density

The volumetric energy density is the amount of energy stored per unit volume of the energy carrier. With a higher energy density, it is possible to transport more energy to the importing country in defined spaces, like the hold of a vessel. High energy densities are therefore favorable for efficient ship transport.

4.2.4. Handling and Safety Regulations

Other criteria worthy of note are the handling and safety regulations of the energy sources. While some energy sources can be stored and transported at ambient temperature and pressure, others must be kept liquid at cryogenic temperatures and/or pressure. Another important aspect is the toxicity of the energy carriers. The list of further criteria for technical evaluation is by no means complete. Other criteria include the currently available capacities of all process steps (e.g., ships), the domestic infrastructure for the energy sources in Germany and the future technological development and market ramp-up of the individual process steps of the import options. This further technical evaluation is the subject of current research. The results will be presented in a subsequent scientific publication. In addition to the technical evaluation, the economic and environmental evaluation and a related global hydrogen potential analysis for producing renewable hydrogen are also crucial in assessing the import options.

5. Conclusion

The goal of this article was to evaluate different hydrogen transport options to Germany from an energetic point of view. Starting off from hydrogen at 25 °C and 25 bar produced in the exporting country, liquid hydrogen, ammonia, Green LNG, methanol, and LOHC were considered as chemical energy carries for transport. The reconversion of H₂ derivatives to hydrogen at 25 °C and 25 bar as well as the direct use of ammonia, methane, and methanol was considered. The process chains were defined and technically analyzed using data from literature. The energy utilization rates of the process chains were determined based on the energy demand of the single elements of the process chains.

From the energetic evaluation, liquid hydrogen is the most efficient import option when gaseous hydrogen is supplied in the importing country, with an energy utilization rate of 73%. When direct utilization of the H₂ derivatives is considered, the ammonia import route has the highest energy efficiency with 77%. For import options that require carbon in the synthesis like Green LNG and methanol, the provision of CO₂ is an essential process step. If point sources for CO₂ are considered, direct utilization of methanol (energy utilization rate = 83%) and Green LNG (energy utilization rate = 76%) are the energetically favorable import options.

Furthermore, it was shown that the transport distance has only a minor influence on the energy utilization rate. Even doubling the distance only leads to a 1-2% reduction in the energy utilization rate. This is true for all import options.

This study focuses on quantifying the energy utilization rate of different hydrogen import routes to Germany. Bearing in mind that not the highest energy efficiency but the fastest realization and as a result the highest accumulated CO₂-saving potential must be the main evaluation criteria, more information must be considered for the selection of the best import route. In this context, the following aspects need to be evaluated: degree of maturity of the single elements of the process chains (e.g., TRL), global production, and volume of trade by ship. The volumetric energy density as well as the handling and safety regulations of each energy carrier are other important evaluation criteria. As this list of criteria is not exhaustive, a further scientific publication will discuss these and other criteria for the technical evaluation of import options.

4DVANCED

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work is part of the TransHyDE-Project "TransHyDE-Sys – Systemanalyse zu Transportlösungen für grünen Wasserstoff", which is sponsored by the German Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF) under funding code: 03HY201C. This work is also part of the study "H₂-Import – Kurzstudie zu Transportoptionen von Wasserstoff", which was sponsored by DVGW—German Technical and Scientific Association for Gas and Water (Deutscher Verein des Gas- und Wasserfachs e.V.) under funding code: G 202224.

Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

ammonia, energy, hydrogen, import, methane, methanol, renewable

Received: November 29, 2023 Revised: February 19, 2024 Published online:

- Prognos, W.-I. Öko-Institut, Klimaneutrales Deutschland 2045. Wie Deutschland seine Klimaziele schon vor 2050 erreichen kann 2021.
- [2] G. Luderer, C. Kost, Deutschland auf dem Weg zur Klimaneutralität 2045 - Szenarien und Pfade im Modellvergleich, Potsdam Institute for Climate Impact Research, Dominika 2021.
- [3] F. Sensfuß, B. Lux, C. Bernath, C. Kiefer, B. Pfluger, C. Kleinschmitt, K. Franke, J. Fragoso Garcia, G. Deac, W. Männer, H. Brugger, T. Fleiter, M. Rehfeldt, A. Herbst, P. Manz, M. Neuwirth, M. Wietschel, T. Gnann, D. Speth, M. Krail, P. Mellwig, S. Blömer, S. Köppen, B. Tersteegen, C. Maurer, A. Ladermann, T. Dröscher, S. Willemsen, J. Müller-Kirchenbauer, M. Evers, O. Akca, D. Jiang, J. Hollnagel, J. Giehl, T. Mielich, Langfristszenarien für doe Transformation des Energiesystems in Deutschland Treibhausgasneutralle Szenarien T45. Überblickswebinar, November 2022
- [4] IRENA, Global Hydrogen Trade to Meet the 1.5 °C Climate Goal: Part II-Technology Review of Hydrogen Carriers, International Renewable Energy Agency, Abu Dhabi 2022.
- [5] F. Staiß, J. Adolf, F. Ausfelder, C. Erdmann, C. Hebling, T. Jordan, G. Klepper, T. Müller, R. Palkovits, W.-R. Poganietz, W.-P. Schill, M. Schmidt, C. Stephanos, P. Stöcker, U. Wagner, K. Westphal, S. Wurbs, Optionen für den Import grünen Wasserstoffs nach Deutschland bis zum Jahr 2030, Acatech, acatech - Deutsche Akademie der Technikwissenschaften, München 2022.

- [6] C. Hank, A. Sternberg, N. Köppel, M. Holst, T. Smolinka, A. Schaadt, C. Hebling, H.-M. Henning, Sustainable Energy Fuels 2020, 4, 2256.
- [7] R. Ortiz Cebolla, F. Dolci, E. Weidner, Assessment of Hydrogen Delivery Options Feasibility of Transport of Green Hydrogen Within Europe, Publications Office of the European Union, Luxembourg 2022.
- [8] F. Carels, L. Sens, M. Kaltschmitt, L. Janke, M. Deutsch, Wasserstoff-Importoptionen für Deutschland. Analyse mit einer Vertiefung zu Synthetischem Erdgas (SNG) bei nahezu geschlossenem Kohlenstoffkreislauf, Agora Energiewende, Agora Industrie, Hamburg 2023.
- [9] L. Decker, https://www.sintef.no/globalassets/project/hyper/ presentations-day-1/day1_1430_decker_latest-global-trend-in-liquidhydrogen-production_linde.pdf (accessed: November 2023).
- [10] A. Alekseev, T. Arndt, C. Haberstroh, T. Jordan, D. Lindackers, S. Palacios, A. Pundt, P. Saß, C. Schulz, K.-P. Weiss, C. Wolf, M. J. Wolf, C. Wu, Wasserstoff-Verflüssigung, Speicherung, Transport Und Anwendung Von Flüssigem Wasserstoff 2023.
- [11] International Gas Union, World LNG Report 2022, International Gas Union, UK 2022
- [12] S. Krasae-in, J. H. Stang, P. Neksa, Int. J. Hydrogen Energy 2010, 35, 4524.
- [13] B. Breitschopf, L. Zheng, M. Plaisir, J. Bard, R. Schröer, D. Kawale, J. Koornneef, Y. Melese, M. Schaaphok, J. Gorenstein Dedecca, C. Bene, O. Cerny, F. Gerard, *The role of renewable H2 Import & storage* to scale up the EU deployment of renewable H2, Publications Office of the European Union **2022**.
- J. Kawasaki, https://global.kawasaki.com/en/corp/newsroom/news/ detail/?f=20220422_3378 (accessed: December 2022).
- [15] A. Krenn, D. Desenberg, Return to Service of a Liquid Hydrogen Storage Sphere, NASA 2019.
- [16] A. Petitpas, S. M. Aceves, *Int. J. Hydrogen Energy* 2018, 43, 18403.
 [17] Cryostar, https://cryostar-hydrogen-solutions.com/liquid-hydrogen-
- high-pressure-pumps/ (accessed: November 2023).
 [18] Bairdmaritime, https://www.bairdmaritime.com/ship-world/tanker-world/gas-tanker-world/vessel-review-suiso-frontier-japanese-lh2-
- carrier-sets-the-pace-in-hydrogen-transport/ (accessed: September 2023).[19] W. A. Amos, Costs of Storing and Transporting Hydrogen, National
- Renewable Energy Laboratory, Golden Colorado 1998.
- [20] J. R. Smith, S. Gkantonas, E. Mastorakos, Energies 2022, 15, 2046.
 [21] M. Riemer, F. Schreiner, J. Wachsmuth, Conversion of LNG Terminals for Liquid Hydrogen or Ammonia, Analysis of Technical Feasibility und
- Economic Considerations, Frauenhofer ISI, Karlsruhe 2022.
 [22] J. Pospíšil, P. Charvát, O. Arsenyeva, L. Klimeš, M. Špiláček, J. J. Klemeš, Renewable Sustainable Energy Rev. 2019, 99, 1.
- [23] A. O. Oni, K. Anaya, T. Giwa, G. Di Lullo, A. Kumar, Energy Convers. Manage. 2022, 254, 115245.
- [24] K. Müller, M. Städter, F. Rachow, D. Hoffmannbeck, D. Schmeißer, Environ. Earth Sci. 2013, 70, 3771.
- [25] K. Stangeland, D. Kalai, H. Li, Z. Yu, Energy Procedia 2017, 105, 2022.
- [26] World's Largest SNG Plant goes On-Stream with Topsoe Catalysts and Process Technology, https://www.digitalrefining.com/news/1002492/ worlds-largest-sng-plant-goes-on-stream-with-tops-e-catalysts-andprocess-technology (accessed: 2013).
- [27] M. Fasihi, O. Efimova, C. Breyer, J. Cleaner Prod. 2019, 224, 957.
- [28] J. Leiblein, K. Bär, F. Mörs, F. Graf, Roadmap Gas 2050 Deliverable D1.1. Bewertung Von Alternativen Verfahren Zur Bereitstellung Von Grünem Und Blauem H2, DVGW Deutscher Verein des Gas- und Wasserfaches e.V., Bonn 2022.
- [29] F. Sabatino, A. Grimm, F. Gallucci, M. van Sint Annaland, G. J. Kramer, M. Gazzani, *Joule* 2021, 5, 2047.
- [30] F. Mörs, R. Schlautmann, J. Gorre, R. Leonhard, Final Report on Evaluation of Technologies and Processes 2020.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [31] M. Łaciak, K. Sztekler, A. Szurlej, T. Włodek, IOP Conf. Ser.: Earth Environ. Sci. 2019, 214, 12138.
- [32] M. S. Khan, M. A. Qyyum, W. Ali, A. Wazwaz, K. B. Ansari, M. Lee, *Energies* **2020**, *13*, 5578.
- [33] M. Al-Breiki, Y. Bicer, Int. J. Hydrogen Energy 2020, 45, 34927.
- [34] BP, Statistical Review of World Energy 2022, BP, London UK 2022.
 [35] giignl.org, https://giignl.org/market-trends/global-lng-trade/ (accessed: February 2023).
- [36] Capital Gas, https://www.capitalgas.gr/our-fleet (accessed: November 2023)
- [37] I. A. Fernández, M. R. Gómez, J. R. Gómez, Á. B. Insua, Renewable Sustainable Energy Rev. 2017, 67, 1395.
- [38] J. R. Rostrup-Nielsen, in Advances in Comparative and Environmental Physiology (Eds: R. Gilles, D. F. Houlihan, D. R. Livingstone, R. F. Lee), Springer Berlin Heidelberg, Berlin, Heidelberg 1991, pp. 1–117.
- [39] H. Miyaoka, H. Miyaoka, T. Ichikawa, T. Ichikawa, Y. Kojima, Int. J. Hydrogen Energy 2018, 43, 14486.
- [40] J. Li, S. Lai, D. Chen, R. Wu, N. Kobayashi, L. Deng, H. Huang, Front. Energy Res. 2021, 9, 602.
- [41] R. Lan, J. T. Irvine, S. Tao, Int. J. Hydrogen Energy 2012, 37, 1482.
- [42] C. Smith, A. K. Hill, L. Torrente-Murciano, Energy Environ. Sci. 2020, 13, 331.
- [43] A. Klerke, C. H. Christensen, J. K. Nørskov, T. Vegge, J. Mater. Chem. 2008, 18, 2304.
- [44] I. Rafiqul, C. Weber, B. Lehmann, A. Voss, Energy 2005, 30, 2487.
- [45] R. Nayak-Luke, R. Bañares-Alcántara, I. Wilkinson, Ind. Eng. Chem. Res. 2018, 57, 14607.
- [46] Z. Cesaro, M. Ives, R. Nayak-Luke, M. Mason, R. Bañares-Alcántara, Appl. Energy 2021, 282, 116009.
- [47] O. Oner, K. Khalilpour, Renewable Sustainable Energy Rev. 2022, 168, 112764.
- [48] M. Appl, Ammonia. Principles and Industrial Practice, Wiley-VCH, Weinheim, NY 2007.
- [49] Ammonia. Catalysis and Manufacture (Ed: A. Nielsen), Springer Berlin Heidelberg, Berlin, Heidelberg 1995.
- [50] E. R. Morgan, Dissertation, University of Massachusetts Amherst 2013.
- [51] Gaschem, https://www.hartmann-reederei.de/shared_files/fleet/pdf/ ship-info/stade.pdf (accessed: November 2023).
- [52] Argus, https://www.argusmedia.com/en/news/2158915-global-ammoniatrade-to-recover-in-2021 (accessed: November 2023).
- [53] Our Business Gas Carriers, https://www.prime-marine.net/ourbusiness/gas-carriers/ (accessed: November 2023).
- [54] J. Lee, Y. Choi, J. Choi, JMSE 2022, 10, 1500.
- [55] O. Herbinet, P. Bartocci, A. Grinberg Dana, Fuel Commun. 2022, 11, 100064.
- [56] Chemietechnik, https://www.chemietechnik.de/anlagenbau/thyssenkrupp-uhde-plant-ammoniak-cracking-anlage-900.html (accessed: September 2023).
- [57] F. Jackson, Ammonia to Green Hydrogen Project. Feasibility Study 2020.
- [58] R. Nielsen, https://www.ammoniaenergy.org/wp-content/uploads/ 2021/11/Rasmus-Topsoe-NH3-cracking-AEA-2021.pdf (accessed: August 2021).
- [59] M. Niermann, S. Drünert, M. Kaltschmitt, K. Bonhoff, Energy Environ. Sci. 2019, 12, 290.

- [60] P. Preuster, C. Papp, P. Wasserscheid, Acc. Chem. Res. 2017, 50, 74.
- [61] N. Brückner, K. Obesser, A. Bösmann, D. Teichmann, W. Arlt, J. Dungs, P. Wasserscheid, *ChemSusChem* 2014, 7, 229.
- [62] M. Reuß, T. Grube, M. Robinius, P. Preuster, P. Wasserscheid, D. Stolten, Appl. Energy 2017, 200, 290.
- [63] M. Niermann, S. Timmerberg, S. Drünert, M. Kaltschmitt, Renewable Sustainable Energy Rev. 2021, 135, 110171.
- [64] F. Stöckl, W.-P. Schill, A. Zerrahn, Sci. Rep. 2021, 11, 1.
- [65] R. Aslam, K. Müller, M. Müller, M. Koch, P. Wasserscheid, W. Arlt, J. Chem. Eng. Data 2016, 61, 643.
- [66] F. Piehl, https://epb.bibl.th-koeln.de/frontdoor/deliver/index/docId/ 1374/file/MA_Piehl_LOHC_48_20190610.pdf (accessed: 2019).
- [67] EIA, https://www.eia.gov/todayinenergy/detail.php?id=17991 (accessed: November 2023).
- [68] Hydrogenious, https://hydrogenious.net/what/#release-plants (accessed: November 2023).
- [69] HyStoc Hydrogen Supply and Transportation Using Liquid Organic Hydrogen Carriers, D 8.4 LOHC Production Cost Estimation Study 2019.
- [70] M. Bowker, ChemCatChem 2019, 11, 4238.
- [71] Methanol Institute, MARINE METHANOL. Future-Proof Shipping Fuel, Methanol Institute **2023**.
- [72] IRENA, Innovation Outlook: Renewable Methanol, Methanol Institute, Abu Dhabi 2021
- [73] Q. Song, R. R. Tinoco, H. Yang, Q. Yang, H. Jiang, Y. Chen, H. Chen, Carbon Capture Sci. Technol. 2022, 4, 100056.
- [74] Wärtsilä Encyclopedia of Ship Technology (Ed: J. Babicz), Wärtsilä Corporation, Helsinki 2015.
- [75] Methanol for the Maritime Energy Transition, https://www.man-es. com/marine/strategic-expertise/future-fuels/methanol (accessed: November 2023).
- [76] C. Stemmer, J. Thesen, M. Bartusevičiūtė, HySupply. A Meta-Analysis towards a German-Australian Supply- Chain for Renewable Hydrogen 2021.
- [77] Hydrogen Generation by Methanol Reforming | Mahler AGS, https:// www.mahler-ags.com/en/plants/hydrogen-plant-hydroform-m/ (accessed: November 2023).
- [78] M. Yavary, H. Ale-Ebrahim, C. Falamaki, Chem. Eng. Sci. 2011, 66, 2587.
- [79] Altera Infrastructure, The Stella Maris CCS Project.
- [80] J. Rogelj, et al., in *Global Warming of 1.5* °C (Ed: IPCC), Cambridge University Press, Cambridge, UK and New York, NY 2022, pp. 93–174.
- [81] F. Mörs, R. Schlautmann, J. Gorre, R. Leonhard, D 5.9 Final Report on Evaluation of Technologies and Processes 2020.
- [82] S. Schemme, Dissertation, RWTH Aachen 2020.
- [83] MI News Network, https://www.marineinsight.com/shipping-news/ worlds-largest-ammonia-loadable-lpg-vessels-ordered-by-molsphoenix-tankers/ (accessed: November 2023).
- [84] Dubbel Taschenbuch für den Maschinenbau (Eds: B. Bender, D. Göhlich), Springer Vieweg, Berlin 2020.
- [85] R. Terwel, J. Kerkhoven, Hydrohub HyChain 2. Cost Implications of Importing Renewable Electricity, Hydrogen and Hydrogen Carriers into the Netherlands from a 2050 Perspective Model User Guide, Technical Documentation, First Results and Country Profiles 2019.

www.entechnol.de