

REVIEW

Renewable hydrogen for the chemical industry

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ABSTRACT

Hydrogen is often touted as the fuel of the future, but hydrogen is already an important feedstock for the chemical industry. This review highlights current means for hydrogen production and use, and the importance of progressing R&D along key technologies and policies to drive a cost reduction in renewable hydrogen production and enable the transition of chemical manufacturing toward green hydrogen as a feedstock and fuel.

The chemical industry is at the core of what is considered a modern economy. It provides commodities and important materials, e.g., fertilizers, synthetic textiles, and drug precursors, supporting economies and more broadly our needs. The chemical sector is to become the major driver for oil production by 2030 as it entirely relies on sufficient oil supply. In this respect, renewable hydrogen has an important role to play beyond its use in the transport sector. Hydrogen not only has three times the energy density of natural gas and using hydrogen as a fuel could help decarbonize the entire chemical manufacturing, but also the use of green hydrogen as an essential reactant at the basis of many chemical products could facilitate the convergence toward virtuous circles. Enabling the production of green hydrogen at cost could not only enable new opportunities but also strengthen economies through a localized production and use of hydrogen. Herein, existing technologies for the production of renewable hydrogen including biomass and water electrolysis, and methods for the effective storage of hydrogen are reviewed with an emphasis on the need for mitigation strategies to enable such a transition.

Key words: chemical synthesis; circular economy; energy generation; energy storage; environment; environmentally protective; sustainability

Introduction

Hydrogen in the chemical industry

Hydrogen (H₂) is an important component of the universe with an enormous extent of applications. However, it does not

exist in free form in nature, but rather is bonded inside ubiquitous compounds such as water and hydrocarbons. As a key building block in chemical processes, a huge fraction of current hydrogen production is used in industrial processes such as the synthesis of ammonia and petrochemicals. The global demand for hydrogen, which has tripled since 1975, is growing every year with no signs of slowing down (Fig. 1). As of 2018, the worldwide annual hydrogen production is estimated to be ~74 Mt, with up to ~96% used in the chemical industry, ~42% alone for ammonia production, and ~52% in different refineries.¹ The remaining hydrogen (~6%) is used in other sectors such as glass production and reduction of iron ores (Figs. 1 and 2).

In the chemical industry, ammonia is globally produced through the well-known Haber–Bosch process, in which hydrogen and atmospheric nitrogen are passed over a catalyst at elevated temperatures and pressures. Ammonia is used extensively in agriculture, explosives, and cleaning streams.

DISCUSSION POINTS

- Hydrogen is already an important feedstock supporting the chemical industry, and this makes the transition away from fossil fuels challenging.
- Green hydrogen could help decarbonize the chemical industry and beyond transform the industry toward “green” products manufacturing.
- What is the current status, and which technologies could support such a transition? What is the role of policy in this?

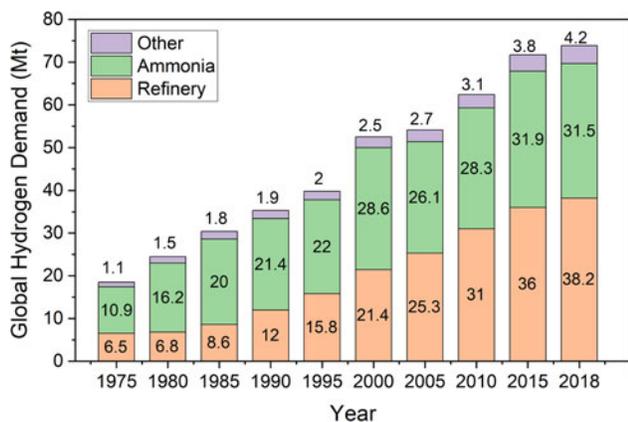


Figure 1. Global demand of pure hydrogen in refinery, ammonia, and other sectors for the period 1975–2018. Source: IEA. All rights reserved.¹

Common nitrogen-rich fertilizers including urea and ammonium nitrate are produced directly from ammonia. Urea is obtained after reacting ammonia with CO₂ originating from the steam reforming, while ammonium nitrate is produced through the catalytic oxidation of ammonia with nitric acid. As a carbon-free commodity, ammonia has been touted as a promising alternative to conventional hydrogen storage systems.² However, most of the hydrogen for its production comes from fossil fuels through reforming - which collectively accounts for 830 Mt CO₂/yr globally.^{1,3} The chemical industry, with 10% of the global energy consumption and 7% of the greenhouse gas emissions,⁴ is also the largest user of energy in the industry sector. Enabling the use of renewable hydrogen

could thus have a significant impact in decarbonizing the industry sector. Renewables for green hydrogen production include solar and wind coupled with water electrolysis, solar-thermal, and in a distant future direct photochemical hydrogen generation. However, at the moment, the amount of renewable hydrogen is far from meeting the global needs for hydrogen (Fig. 2).

In the refinery sector, which is one of the biggest consumers, hydrogen is used in upgrading the hydrocarbons. Hydrogen is used to remove sulfur, halides, oxygen, metals, and/or nitrogen impurities, and cracking of heavier to lightweight hydrocarbons to produce many value-added chemicals. Most of these processes need careful conditions with suitable catalysts, which dictate the efficiency of the process.

Many chemical industries also use hydrogen extensively to reduce the degree of unsaturation, taste, and/or odor in fats and oils via a hydrogenation process carried out in the presence of nickel catalysts.^{5,6} This process increases the melting point and enhances the resistance to oxidation with prolonged preservation. In the hydrogenation process, the amount of hydrogen consumed depends on the oil and the degree of hardness (measured by the reduction in iodine number - that is the amount of hydrogen gas equivalent to iodine absorbed), the purity of hydrogen, and the equipment. Assuming that high-quality hydrogen is used, the actual amount of gas required is often ~110% higher than the theoretical values.⁷

The hydrogenation of fats produces trans fats, which have adverse health effects,⁸ but recently, new chemistry has revealed that the formation of trans fats could be avoided by carefully manipulating the selectivity of the catalysts.⁹ It is expected that such selective catalytic hydrogenation processes will be further developed in the future and could help to lower the pernicious effects of saturated fats.¹⁰

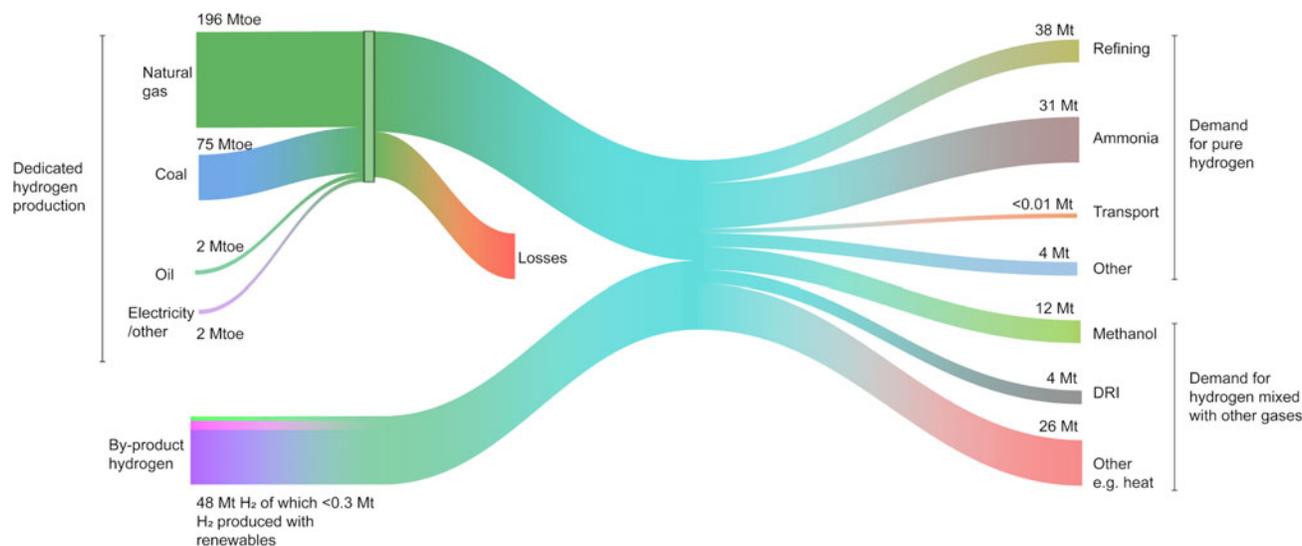


Figure 2. The flow of the global hydrogen production, supply, and demand in 2018 – units in Mt, Mtoe (Million tons of oil equivalent), and DRI (Direct Reduction of Iron). Source: IEA. All rights reserved.¹

At the moment, for all of the mentioned applications, most of the hydrogen is obtained through steam reforming of fossil fuels. In steam reforming, hydrocarbons are converted to carbon monoxide (CO) and H₂, commonly known as synthesis gas or syngas, using steam at high temperature (700–1000 °C).¹¹



However, if hydrogen is to become the fuel of the future, extensive development in advanced technologies for the production of green hydrogen and enabling energy policies are essential to shift our dependence from fossil fuels toward renewables and sustainable hydrogen.

Technologies for renewable hydrogen production

Hydrogen is often described as a clean and sustainable energy vector but in order to live up to this description, renewable methods using sustainable sources need to be the backbone of hydrogen production.¹² In this section, renewable methods to produce H₂ from water and biomass, along with their associated costs - in USD across the manuscript (Fig. 3), are reviewed in comparison to the production cost of hydrogen from steam methane reforming (1.9–2.6 \$/kg H₂) and the 2020 U.S. Department of Energy (DOE) target (2 \$/kg H₂).^{13,14}

For a more in-depth analysis, El-Emam and Ozcan published a comprehensive review on the technological, economic, and environmental aspects of renewable hydrogen production.¹⁵

Making hydrogen from biomass

Biomass currently covers 14% of the total primary energy consumption¹⁶ due to its abundance and ease of accessibility across many countries.¹⁷ Nowadays, as a CO₂ neutral precursor, biomass is considered as an important renewable resource for hydrogen production,¹⁸ although the carbon foot print associated with the use of biomass for hydrogen production may not be neutral. For example, 8.99×10^{-2} CO₂ eqv. g/s is emitted to produce 0.484 MJ/s H₂ from an annual consumption of 2.53×10^6 kg of biomass.¹⁹ The use of biomass for energy production is often a great concern with respect to land use. However, alternatives like lignocellulosic waste and crops waste have the potential to address this issue to some extent.²⁰ Other types of “low cost” biomass to produce hydrogen include bio-waste, biogas, industrial organic waste, sewage sludge, bio-oil, and biochar;^{21–23} and the usual hydrogen content in biomass is ~5–7 wt%.²⁴

Currently, the two main routes to produce hydrogen from biomass are through the thermochemical and biochemical process (Fig. 4).^{25,26} Thermochemical processes include pyrolysis, gasification, steam reforming, and supercritical gasification,²¹ whereas biochemical processes include bio-photolysis, bio-fermentation, and dark fermentation.²⁷ In the biochemical route, biomass can be converted into biofuels through various processes including anaerobic or aerobic digestion, fermentation, and acid hydrolysis.²⁸ Recently, emerging technologies like bio-electrochemical systems have also been used to convert waste treatment into energy production. In this method,

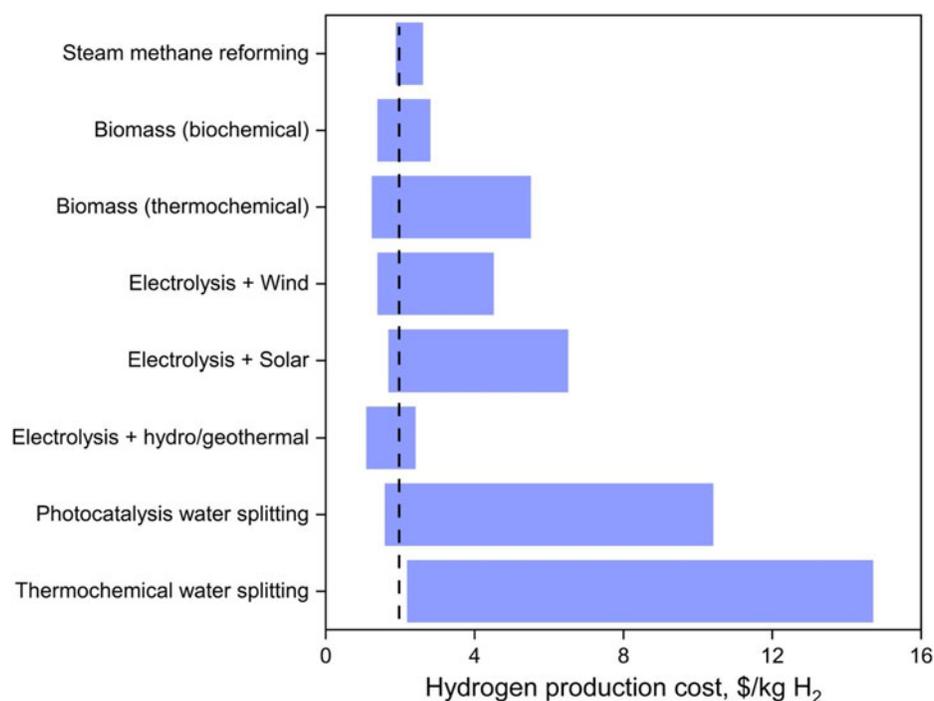


Figure 3. Average hydrogen production cost from various methods. The black dotted line represents the 2020 DOE target of 2 \$/kg H₂.

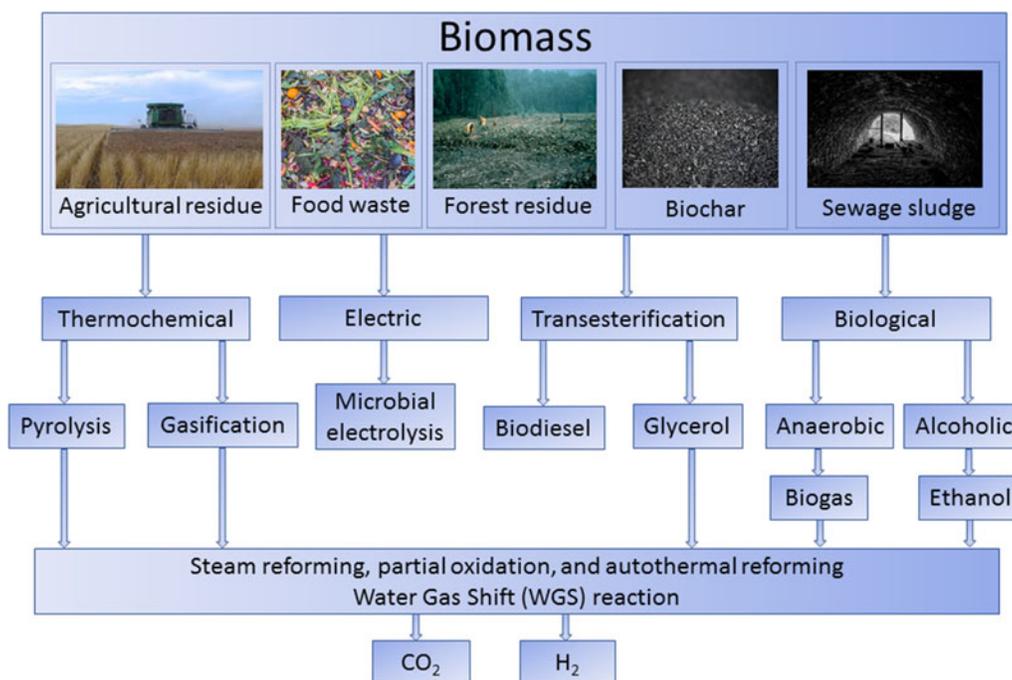


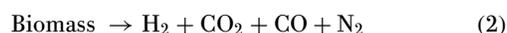
Figure 4. Hydrogen production by different methods from various types of biomass.

electrochemically active micro-organisms (e.g., *Shewanella oneidensis* and *Geobacter sulfurreducens*) are grown under electrochemical interactions with electrodes^{29,30} to catalyze and oxidize organic matter to generate CO₂, electrons, and protons.³⁰ The electrons are transferred to the anode, while the protons move through a membrane to the cathode, where they combine to release H₂.³¹ An example of such system produced ~4.5 l H₂/day from waste water.³²

Apart from bio-electrochemical systems, hydrogen production from biomass can be light-driven. Light-dependent processes include bio-photolysis and photofermentation. In bio-photolysis, water is split to produce hydrogen by some green algae under anaerobic conditions. Photofermentation is done by using a purple non-sulfur bacteria converting organic acids into H₂ and CO₂. In light-independent processes, i.e., dark fermentation, organic substrates are converted to H₂ in anaerobic condition (Table 1).³³ With a cost of hydrogen production ranging from 1.4 to 2.8 \$/kg H₂, biological routes to process biomass are promising but are currently at a very early experimental stage.

Relative to biological routes, thermochemical methods are more flexible and provide a simpler approach as there is no need for additional chemicals but instead heat and pressure are used to generate biofuels.⁴³ This can be done by pyrolysis and/or gasification (Table 2).^{44,45} Gasification is a well-developed process where hydrogen-rich fuel gas (CO, H₂, and CH₄) is produced at 700–1200 °C using gasification agents (O₂, CO₂, steam, and air).^{16,20} Gasification with air produces a low-quality gas (4–7 MJ/m³ HHV), whereas higher quality

gas (~10–18 MJ/m³ HHV) can be obtained under more oxidative conditions, i.e., pure O₂.⁵⁰ The gasification process using fluidized bed reactors have demonstrated high biomass conversion with H₂ content in gas ~55 vol.% and H₂ production of ~6.9 wt%.^{20,51} The cost of H₂ production by gasification from biomass is estimated to be ~1.77–2.05 \$/kg H₂,¹⁴ and the process can be generalized in the following equation:⁵²



H₂ can also be obtained via the pyrolysis of biomass at lower temperatures of 300–650 °C,^{20,52,53} but, at such temperatures, the hydrogen yield is lowered and of ~18 vol%.⁵² However, with suitable catalysts, e.g., Ni/Al₂O₃,²⁰ and elevated temperatures, the amount of produced H₂ can be increased to yields ~38 vol% at 600 °C and ~70 vol% at 900 °C. Recently, an effective two-staged pyrolysis process has been proposed,⁵⁴ where the biomass is initially heated to 950 °C to produce pyrolysis gases, and then further heated at 950 °C again. With a 10 wt % Ni-dolomite catalyst, the amount of hydrogen obtained in this two steps process was 59.14 vol%.⁵⁵ The cost of H₂ production from biomass pyrolysis has been calculated as 1.25–2.20 \$/kg H₂,¹⁴ and the process is generalized in the following equation:⁵²



Recently, other feedstocks like bioethanol, glycerol, sorbitol, and glucose have also been investigated as a potential source of hydrogen⁵⁶ through the conventional approach of steam

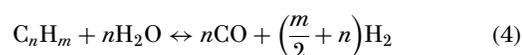
Table 1. Biological processes to produce hydrogen from biomass.

| Process | Reactions | Organisms | Key enzymes | Substrate | H ₂ yield | \$/kg H ₂ | Reactors | References |
|-------------------|---|---|----------------------------|---|--|----------------------------------|--|---------------|
| Biophotolysis | <p><i>Direct:</i> $2\text{H}_2\text{O} + \text{light} \rightarrow 2\text{H}_2 + \text{O}_2$</p> <p><i>Indirect:</i> $6\text{H}_2\text{O} + 6\text{CO}_2 + \text{light} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{CO}_2$ $\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + 2\text{CH}_3\text{COOH} + 2\text{CO}_2$</p> | <p><i>Chlamydomonas reinhardtii,</i> <i>Chlorella fusca,</i> <i>Scenedesmus obliquus,</i> <i>Chlorococcum littorale,</i> <i>Nostoc, Anabaena,</i> <i>Calothrix, Oscillatoria</i></p> | Nitrogenase or hydrogenase | Water, carbohydrate | 119.8 ml/l (direct biophotolysis) | 2.13 (direct) 1.42 (indirect) | Photobioreactor, flat plate photobioreactor | [14,33–36] |
| Photofermentation | <p>$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} + \text{light energy} \rightarrow 12\text{H}_2 + 6\text{CO}_2$</p> <p><i>Nitrogen-deficient process:</i> $\text{CH}_3\text{COOH} + 2\text{H}_2\text{O} + \text{light energy} \rightarrow 2\text{H}_2 + 2\text{CO}_2$</p> | <p><i>Rhodobacter capsulatus,</i> <i>Rhodobium marinum, R. sphaeroides</i></p> | Nitrogenase, hydrogenase | Sugar beet molasses, food waste, wastewater | 1 l/l with 28 g/l sugar-containing culture, 3.65 mol/mol mixed acids (acid and butyric acid) | 2.83 | Borosilicate glass bioreactors, fed batch | [14,35,37–39] |
| Dark fermentation | <p>$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} \rightarrow 12\text{H}_2 + 6\text{CO}_2$</p> | <p><i>Bacillus, Enterobacter, Clostridium, Thermotoga, Thermoanaerobacterium</i></p> | Hydrogenase | Wastewater mixed sludge, glucose, xylose | ~1.7 mol/mol glucose, 0.8 mol/mol xylose | 2.57 | Gas bioreactors, serum bottles, fluidized bed reactors | [14,40–42] |

Table 2. Hydrogen production strategies from pyrolysis and the gasification process.

| Methods | Brief description | Reactor and condition | Advantage | Disadvantage | Product yield |
|---|--|---|---|--|---|
| Air gasification ^{21,24,46} | Uses air as a gasifying agent to produce CO + H ₂ | Fluidized bed reactor/700–900 °C air with steam mixture | Can achieve maximum conversion | Removal of tar from the product is difficult | High H ₂ and gas yield at high temperature |
| Steam gasification ^{21,24,26,47} | Uses steam along with air to produce H ₂ -rich syngas | Fluidized bed gasifier/770 °C and steam to the biomass ratio of 1 | High H ₂ to CO ratio, suitable for large-scale industrial production | High tar content and CO ₂ emission | 19.4–42.6% H ₂ |
| Oxygen gasification ²⁴ | Supplies pure oxygen into gasifier for gasification | Circulating fluidized bed gasifier | Low tar content in the syngas produced | Purifying oxygen is an energy-intensive process | |
| Supercritical water gasification ^{21,24,26,48} | Uses supercritical steam as a gasifying agent. Also, at the supercritical condition, steam works as a catalyst toward the conversion | Tubular batch reactor/650 °C with a heating range of 30 °C/min | High conversion and H ₂ content without tar and coke formation | High energy input to pump the feed stock, strict operating condition, and difficult to recycle alkaline catalyst | 30–40% H ₂ |
| Fast pyrolysis ^{21,24,26,49} | Occurs at moderate temperature in the absence of oxygen with a high heat transfer rate to the biomass particle | Fluidized bed reactor, atmospheric pressure | Can produce high hydrogen content gas | Low hydrogen yield and high energy consumption | 12% gases (2–3 wt% of H ₂ to biomass), 72% bio-oil, 16% char |

reforming¹¹:



In this approach, the hydrogen content in syngas varies according to the gasification operating conditions, i.e. temperature, steam-to-biomass ratio, and catalysts. Steam gasification is prone to the formation of tar, which may affect the maintenance and operation cost due to pipeline blockage.⁵⁷ Therefore, catalysts are often used to promote tar cracking and reduce the operating temperature as well as increase the hydrogen selectivity from biomass.⁵⁸ Some of the common catalysts are alkaline earth catalysts (e.g., KOH, KHCO₃, Na₃PO₄, MgO, and NaOH),^{26,59} metal-based catalysts (e.g., Ni/Al₂O₃, Ni/Al, Ni/Zn/Al, Cu/Zn/Zr, Rh/Zr/Ce, Pt/Co/CeO₂, and Ru/SrO-Al₂O₃),^{60–67} and mineral catalysts (dolomite and olivine).^{68,69} The activity of the metal-based catalysts supported on Al₂O₃-MgO is in an order of Ru > Rh > Ir > Ni > Pt.⁷⁰ Although the noble metals such as Ru and Rh can effectively

promote gasification, these remain expensive. Traditional alkali metal catalysts have also been used effectively; however, challenges remain due to the high loading, easy scaling, blockage, and difficult recovery. As a result, Ni-based catalysts have been widely used especially due to their synergy with other metals.

For example, 100% carbon conversion and ~70 vol% H₂ yield have been reported with a Pt-Ni/CeO₂-SiO₂ catalyst.⁷¹ With an estimated cost of H₂ production up to ~5.5 \$/kg H₂,⁷² more scientific advancement is needed before biomass gasification technologies can be used at an industrial scale. The future efforts are expected to be on tar treatment, cost-effective catalysts, condition optimization, and large-scale implementation.

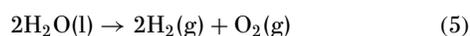
Making hydrogen by splitting water

Even though water is an abundant hydrogen source, water electrolysis accounts for only a small fraction of the global hydrogen production.⁷³ Depending on the energy source used, water electrolysis can be a completely sustainable and a clean way to generate hydrogen since no greenhouse gas is

emitted.⁷⁴ Hydrogen production from water splitting can be done by using various methods including electrolysis and photocatalysis.⁷⁵ However, the latter is far from mature. During the photocatalysis process, a light excited semiconducting electrode with a suitable excitation bandgap, e.g., TiO₂, is used to split water into hydrogen and oxygen.⁷⁶ Unfortunately, TiO₂ strongly absorbs light in the UV spectrum ($\lambda < 350$ nm) only, and not in the visible light range ($350 \text{ nm} < \lambda < 700 \text{ nm}$), and this results in a poor photocatalytic activity under sunlight. The development of high-performing photocatalysts under sunlight is therefore critical for photocatalysis to become a key method to produce H₂.⁷⁷ To date, many semiconductor photocatalysts and co-catalysts have been studied including doped TiO₂,⁷⁸ perovskites,⁷⁹ graphitic C₃N₄,⁸⁰ BiVO₄,⁸¹ and NiS.⁸² Although this approach is reported to have less environmental impact, the poor efficiency (10–18%)⁸³ and relative high cost are not attractive.⁸⁴ Early estimation would suggest a hydrogen production cost between 1.6 and 10.4 \$/kg H₂.⁸⁵

Exotic methods including sonolysis, where a sound wave between 20 and 40 kHz is used to split water through cavitation effects, have been reported.⁸⁶ Thermochemical water splitting from solar concentrators (>2000 °C) have also been proposed with relatively high efficiency (49% solar-to-fuel energy conversion efficiency).⁸⁷ Depending on the type of thermochemical cycles used (where heat sources and chemical reactions are combined to split water into hydrogen and oxygen),⁷⁵ the cost of H₂ production varies considerably from 2.8–4.1 \$/kg H₂ for the hybrid sulfur cycle,⁸⁸ to 8.0–14.7 \$/kg H₂ for the ZnO/Zn cycle,⁸⁹ and 2.2 \$/kg H₂ for the Cu-Cl cycle.⁷⁵

Electrolysis is a general term describing the process of driving a non-spontaneous electrochemical reaction by applying a voltage difference between two electrodes. In water electrolysis, gaseous hydrogen and oxygen are generated from water in the following equation:



This is an energy-demanding reaction with a change in Gibbs free energy of 237.2 kJ/mol at standard conditions.^{90,91} If this reaction is done in an electrochemical cell, a potential difference of 1.23 V is required at room temperature and standard pressure.⁹² Various electrochemical cell configurations and chemistry have been investigated to generate hydrogen through water electrolysis. These technologies are at various stages of maturity and include the proton exchange membrane (PEM),^{93,94} alkaline water (AW),^{95,96} anion exchange membrane (AEM),^{97,98} solid oxide electrolysis (SOE),⁹⁹ and microbial electrolysis cell (MEC)¹⁰⁰ technologies.

Table 3 summarizes the characteristics of these different approaches, and to date, AW electrolysis remains the most cost effective approach to generate hydrogen.^{104–106} PEM systems lead to the highest H₂ purity but unfortunately suffer from several limitations such as electrolyte contamination,^{107,108} and deterioration,¹⁰⁹ and slow oxygen evolution reaction (OER) kinetics.¹¹⁰ To speed up the OER kinetics,

various catalysts have been tested including Pt on carbon, ruthenium-based materials,¹¹¹ and non-noble metal catalysts.¹¹²

The price and source of electricity to power the electrolysis reaction are additional factors to consider. Several projects have demonstrated the technological viability of renewable hydrogen from wind and solar. However, advancements in direct and more efficient water electrolysis processes from renewable sources are needed to reduce cost and facilitate the uptake of renewable hydrogen.¹¹³

Over the past decades, there has been a rapid increase in installed capacity of wind energy coupled with a decrease in the associated costs.¹¹⁴ It is therefore of little surprise that researchers around the planet are looking into the utilization of wind energy to produce hydrogen.^{115–118} The calculated costs involved with H₂ production from wind energy vary widely based on several factors including if the wind-mills are grid-connected or isolated systems, the type of electrolyzers used, and wind penetration scenarios.¹¹⁹ For example, a Norwegian study calculated prices between 2.0 and 4.5 \$/kg H₂,¹¹⁵ a Danish study predicted a price of around 3.5 \$/kg H₂,¹¹⁹ whereas a South African study listed values between 1.4 and 39.5 \$/kg H₂.¹¹⁶ The annual hydrogen production volume also varies considerably based on the country's available wind energy capacity and the mean wind speed. In Fayzabad, Afghanistan, a 100 kW wind turbine system could produce up to 8.7×10^6 kg H₂/year,¹¹⁷ in South Africa, between 6.5×10^3 and 2.3×10^5 kg H₂/year could be generated,¹¹⁶ while in Brazil the projected hydrogen production from the surplus wind electricity was predicted to be of 2.2×10^{11} kg H₂/year.¹¹⁸

Producing hydrogen from photovoltaics (PV) was once the most expensive method (up to 78.6 \$/kg H₂) due to the high cost of the PV system.¹²⁰ However, installed solar capacity has increased drastically due to the recent sharp drop in price of solar PV systems.¹²¹ To date, solar is the most cost-competitive way to produce clean renewable hydrogen.¹²² In 2007, a study calculated that a PV electrolysis plant of 260 km² would be enough to provide an annual H₂ production of 2.2×10^8 kg at a cost of 6.5 \$/kg H₂,¹²³ and since then, the cost of solar hydrogen has fallen to less than 3 \$/kg H₂.¹²⁴ Solar hydrogen production capacity and the cost of course depend on multiple factors including the country and location (solar irradiation level), the type of electrolyzers, and the nature of the PV systems, i.e., grid-connected or autonomous.¹²² For example, it has been predicted that a 20 kW PV system receiving 299 MW/h of solar radiation would produce 3.73×10^5 kg H₂/year,¹²⁵ while a Japanese study projected a low production cost of 1.7–2.8 \$/kg using a PV and battery-assisted electrolyzers.¹²⁴ As compared with solar, wind energy has the advantage of being a “dual-use” technology where the land can still be used for other important activities such as farming and agriculture, or even solar farms. Hybrid wind-solar systems could be one solution in order to maximize the use of land and minimize the problem of intermittent solar irradiation.^{126–128} Floating systems could also provide alternatives to produce hydrogen while minimizing land impact.¹²⁹

Table 3. Materials, components, and characteristics of different electrolysis systems.

| | Alkaline ^{101,102} | PEM ^{101,102} | AEM ^{101,103} |
|---|--|--|--|
| Electrolyte | 20–30% KOH | PFSA | QAPS |
| Charge carrier | OH ⁻ | H ⁺ | OH ⁻ |
| Temperature range (°C) | 65–100 | 70–100 | 50–70 |
| Typical discharge H ₂ pressure (bar) | 25–30 | 30–80 | 30 |
| Separator | Asbestos, PAMa, ZrO ₂ -PPS, NiO, Sb ₂ O ₅ -PS | PFSA (e.g., Nafion) | QAPS (e.g., A-201) |
| OER catalyst | Ni ₂ CoO ₄ , La-Sr-CoO ₃ , Co ₃ O ₄ | Ir/Ru oxide | Co ₃ O ₄ |
| HER catalyst | Ni | Pt | CeO ₂ -La ₂ O ₃ |
| Typical current collector | Ni | Titanium | Ni |
| Cell sealant | Metallic | Synthetic rubber or fluoroelastomer | Synthetic rubber or fluoroelastomer |
| Anodic reaction | 2OH ⁻ → H ₂ O + 1/2O ₂ + e ⁻ | 2H ₂ O → O ₂ + 4H ⁺ + 4e ⁻ | 2OH ⁻ → H ₂ O + 1/2O ₂ + e ⁻ |
| Cathodic reaction | 2H ₂ O + 2e ⁻ → 2H ₂ + 2OH ⁻ | 4H ⁺ + 4e ⁻ → 4H ₂ | 2H ₂ O + 2e ⁻ → 2H ₂ + 2OH ⁻ |
| Conventional current density (mA/cm ²) | 200–500 | 800–2500 | 200–500 |
| Demonstrated durability (h) | 100,000 | 100,000–50,000 | NA |
| Hydrogen purity (%) | 99.3–99.9 | 99.9999 | 99.99 |
| Typical current efficiency | 50–70.8 | 48.5–65.5 | 39.7 |
| Demonstrated rated production (N m ³ /h) | 1–760 | 0.265–30 | 0.25–1 |
| Specific energy consumption (kWh N/m ³) | 4.5–7.5 | 5.8–7.3 | 5.2–4.8 |
| Demonstrated rated power (kW) | 2.8–3534 | 1.8–174 | 1.3–4.8 |
| System cost (\$/kg) | 1400–900 | 2200–1300 | NA |
| Technology status | Mature for large scale | Mature for small scale | R&D |

PAMa: polysulphone-bonded polyantimonic acid; PPS: ZrO₂ on polyphenylsulphone; Sb₂O₅-PS: polysulphone impregnated with Sb₂O₅ polyoxide; PFSA: perfluorosulfonated acid; QAPS: quaternary ammonia polysulfone; OER: oxygen evolution reaction; HER: hydrogen evolution reaction; NA: not available.

Alternatives including hydropower and geothermal may also have the potential to be used to produce hydrogen. Hydropower is often considered expensive due to the upfront capital cost of

building huge dams. However, a Canadian study found that despite the initial capital costs, hydropower H₂ production is cost competitive as compared with steam methane reforming

at 2.4 \$/kg H₂, and if the upfront investments are excluded (by using existing hydropower plants), the hydrogen cost goes down to 1.2 \$/kg H₂.¹³⁰ Geothermal energy is another source of sustainable energy, and a recent study demonstrated that geothermal powered electrolysis is a viable method for hydrogen production (1.1 \$/kg H₂) with a payback period of only 4–5 years.¹³¹

Storage and distribution of hydrogen

Effective methods to store hydrogen are essential to enable its widespread utilization in particular for industrial use where plants require a constant feedstock input. The main problem with storing hydrogen is its low volumetric density. Hydrogen is the lightest element, and at ambient condition, it is a gas with a low density of 0.0899 kg/m³.¹³² Even when liquefied at –253 °C, the density of H₂ is only 70.8 kg/m³, which is one-fifteenth of water’s density. Hydrogen is also a very small highly diffusive molecule and thus hydrogen leaks can easily occur.¹³³ Besides, the use of hydrogen is associated with difficulties in terms of materials’ compatibility. In particular, the dissociation of hydrogen molecules at the surface of metals and further hydrogen diffusion at metallic interstitial sites can lead to piping embrittlement and accidental fracture as a result of the reduced ductility and weakening of metals subjected to high purity/pressure hydrogen.^{134–136} The storage of hydrogen is also more delicate than other fuels, because hydrogen has higher laminar burning, buoyant, and propagation velocities that results in higher flammability than other fuels. In addition, hydrogen is also very sensitive to detonation due to its wide volume fraction range of ignition (4–74%) and detonation (18–59%).^{137–140}

Existing methods to store hydrogen are summarized in Fig. 5. Storing hydrogen in high pressure vessels (up to 700 bar in lightweight composite cylinder) is the most common method so far, but the resulting low volumetric storage density, high cost of the composite vessels (~\$13/KWh for 100,000 vessels per year),¹⁴¹ and their maintenance/safety are still a concern.¹⁴⁰ Cryogenic tanks are designed to store liquid hydrogen at –253 °C under ambient pressure (the pressure can increase to 10⁴ bar in a closed storage system due to the low critical temperature (–239.95 °C) of hydrogen).¹⁴² As a general observation and depending on the vessel design, conventional cryogenic tanks can store twice more hydrogen per volume as compared to 700 bar hydrogen gas tanks.¹⁴² However, with such a storage technology, it is inevitable to avoid the loss of hydrogen even with a perfect insulation because of heat leakage.^{143,144} The boiling losses of 0.4% per day for a 50 m³ double-walled vacuum-insulated spherical Dewar vessel have been reported.¹⁴⁵ In addition, hydrogen liquefaction is a very energy intensive process with at least 30% of the energy stored lost through the liquefaction of hydrogen.¹⁴⁶

Hydrogen can also be stored by materials physically or chemically. This includes microporous materials, interstitial metal hydrides, and complex hydrides. Microporous materials, including carbon materials,^{147–152} zeolites,^{153–158} and metal organic frameworks (MOFs),^{159–163} can absorb molecular hydrogen in their porous structures at low temperature.^{152,164,165} The hydrogen storage capacity then depends upon the specific surface areas and the applied pressure.^{142,152} Typically, the adsorption capacity of MOFs is <2 wt% at room temperature.¹⁶⁶ The advantage of porous materials is that they allow for hydrogen storage at higher temperatures, e.g., –150 °C, than feasible with cryogenic tanks for the similar volumetric hydrogen densities.¹⁴³

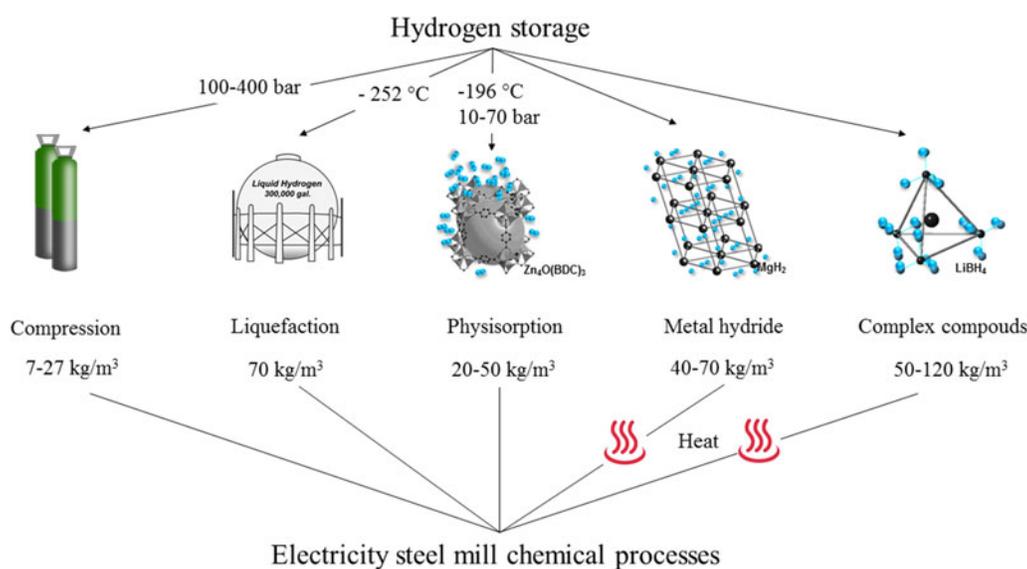


Figure 5. Hydrogen storage methods with their respective volumetric densities.

An alternative method to store hydrogen is in the use of materials storing hydrogen within their structure to form a hydride. Metal hydrides are usually formed by the reaction between metals or intermetallic compounds with hydrogen by the reversible reaction below¹⁶⁷:



where M is either a metal, an alloy, or an intermetallic compound, MH is the metal hydride formed, and Q is the heat generated during the reaction.¹⁶⁷

Interstitial metal hydrides are capable of absorbing large amounts of hydrogen (i.e., the volumetric density of LaNi₅ is 123 kg H₂/m³ of material; that is 1.74 times more than that of liquid hydrogen). In this process, hydrogen is stored in an atomic form after dissociation of molecular hydrogen at the surface of the interstitial metal.¹⁴⁷

Generally, existing binary hydrides along the periodic table of elements are too unstable or too stable to be relevant for practical application. However, it has been found that intermetallic compounds, e.g., TiFe, ZrV₂, and LaNi₅,^{166,168,169} formed by alloying at least two elements (one unstable with one stable hydride) can facilitate the hydrogen storage properties. Generally, the element forming a stable hydride are transition metals or rare earths like Ti, Zr, Y, and La. The unstable hydride elements (often absorbing hydrogen at high hydrogen pressure only) are transition metals including Cr, Mn, Fe, Co, and Ni. The formation of intermetallic alloyed by these two elements can lead to intermediate hydrogen sorption properties with reversibility. Interstitial metal hydrides show excellent and practical hydrogen storage properties since they can uptake and release a large amount of hydrogen safely at ambient temperature and moderate hydrogen pressures.¹⁷⁰ However, one of the major limitations of these interstitial hydrides is their weight, because their composition involves heavy elements, and this results in low gravimetric hydrogen storage capacities.

Better hydrogen storage materials, i.e., of higher gravimetric storage capacities, may exist in the form of complex hydrides. Complex hydrides are ionic compounds that release hydrogen when they decompose.¹⁷⁰ Complex hydrides are usually formed through the combination of alkali or alkaline earth metals, e.g., Li, Na and Mg, and [AlH₄]⁻, [NH₂]⁻ and [BH₄]⁻ groups. The theoretical gravimetric and volumetric densities of some of the complex hydrides are high, for example, the theoretical gravimetric capacity of LiBH₄ is 18.5% and the volumetric capacity is 121 kg H₂/m³ (70% more than the volumetric capacity of liquid hydrogen).¹⁷¹⁻¹⁷³ However, the multiple steps of hydrogen desorption, the release of impurities in the form of B₂H₆ from borohydrides or NH₃ from amides, and the poor hydrogen reversibility of these materials remain the main barrier for their practical applications. The poor reversibility is generally due to the formation of stable intermediate decomposition products during decomposition and extensive elemental disproportion.¹⁶⁶ Different strategies including those based on the potential to alter the properties of hydrogen in nano-

hydride materials are under current investigations to tackle these challenges.¹⁶⁶

Currently, hydrogen is delivered from production sites to the end-users including refueling stations by road or pipeline depending on the application, volume, and distance.¹⁷⁴ For small volumes, transport by road remains the most favorable option. In this case, hydrogen is compressed to 180–200 bar and delivered by tube trailers. Delivering liquid hydrogen is more economical over long distances due to the higher volumetric density. A 40 ton truck can carry 350 kg of gaseous hydrogen or 3500 kg liquid hydrogen,¹⁴³ and the delivery cost of compressed hydrogen gas is \$1/kg/100 km by tube trailers and \$0.1/kg/100 km for liquid hydrogen by trucks in the USA.¹⁷⁵ Hydrogen is also noncorrosive; therefore, this facilitates the design and construction of tank trailers. However, because of the extreme low temperature, additional space for safety and suitable thermal insulation must be considered.^{138,143}

Gaseous hydrogen can also be transported in pipelines like natural gas, especially when large volumes are to be transported over long distances. In this case, the cost of hydrogen transport is estimated to be of \$0.1/kg H₂ over 100 km.¹³⁸ However, this does not take into account the need to retrofit existing gas network. Conventional pipelines for natural gas are made of steel with a typical diameter of 25–30 cm and the operation pressure is 10–20 bar.¹⁴² Using such an infrastructure to transport hydrogen is not feasible in many cases without substantial modifications to reduce diffusion losses in sealing areas as well as materials and seals embrittlement.¹⁴³ In addition, the minimum power required to pump a gas through the pipe follows the equation below:

$$P = 8\pi l v^2 \eta \quad (7)$$

where l is the length of the pipe, and v and η are the velocity and dynamic viscosity of the gas. The volumetric density of hydrogen is 36% of the density of natural gas at the same pressure, and the viscosity of hydrogen is 80% of that of natural gas. Therefore, to pump the same amount of hydrogen, the power needed is 2.2 times that for natural gas.¹⁴²

The role of enabling policies

Today, hydrogen is mainly used for the production of ammonia and hydrocracking processes, with only a small portion used in the transport sector including in the nascent fleet of fuel cell vehicles. Uncertainties in technological development and price advantage of fossil fuel present a major challenge for the growth of renewable hydrogen at the industrial scale. Industry faces national and international competitive pressures, and existing economic models are highly sensitive to feedstock prices. Projections from the International Partnership for the Hydrogen Economy (IPHE) assume that hydrogen will continue to be produced from cheaper fossil fuels before renewable hydrogen can play a significant role. However, continuing declining prices of wind turbines,¹⁷⁶ solar PV,¹⁷⁷ and electrolyzers¹⁷⁸ suggests that the production of hydrogen via power-to-gas

(PtG) may become economically favorable in the next decade.¹⁷⁹ For example, case studies have found that renewable hydrogen is already cost competitive in small- and medium-scaled applications combining renewable wind energy with a PtG facility.¹⁷⁹ In this transition, it is often envisaged that carbon capture and storage may assist the production of low-carbon emission hydrogen from natural gas and coal, although currently not competitive.¹⁸⁰ Solutions still remain to be found to effectively capture and store carbon dioxide, without mentioning the social licence aspects of such a solution.¹⁸⁰

Additionally, non-economic barriers hindering the deployment of hydrogen technologies and infrastructures have also been identified.¹⁸¹ This includes (i) complex procedures and lack of information and assistance to enable projects, (ii) lack of public knowledge and awareness of the renewable hydrogen, (iii) social acceptance of the safety of hydrogen-related technologies and infrastructures, and (iv) lack of government initiatives to facilitate the use of hydrogen technologies and infrastructure construction. Existing safety regulations along hydrogen production, distribution, and storage are also limiting factors.¹⁸²

In recent years, many countries have announced ambitious initiatives and visions to utilize renewable hydrogen as an energy carrier and achieve the greenhouse gas emission targets following the Paris Agreement in November 2016.¹⁸³ However, implementation toward a hydrogen economy is still distant and in the light of the COVID-19 pandemic lobbying toward business as usual is more than ever prevalent. Currently, there are more than 19 hydrogen strategies and roadmaps around the world.¹⁸⁴ However, many countries aim to focus on hydrogen use across the transport sector and existing gas distribution and transmission networks, with little understanding of the potential of hydrogen in the industrial sector. The EU, France, and Norway in contrast have identified hydrogen as an industrial feedstock, and aims to focus their strategy in this area,¹⁸⁴ while the transport sector is to remain mainly battery-driven.

Policy and pilot projects that could enable the use of renewable hydrogen in industry are still lacking because of the relatively high cost of renewable hydrogen (approximately 5.30 \$/kg H₂).¹⁸⁵ Only a few countries offer subsidies, tax incentives, and rebates for investments in renewable hydrogen production. For example, in Norway, electricity used to electrolyse water for hydrogen production is tax exempt, and in the Netherlands, a subsidy of up to €750,000 supports hydrogen-related projects.¹⁸²

Many of the current demonstration and commercialization projects along renewable hydrogen plants are initiated by industry only, with the private sector expected to invest more than \$50 billion in hydrogen projects by 2030. For example, Shell and ITM Power planned to install a 10 MW electrolyser in its refining industry site in Germany in 2017. In many countries like the USA, Japan, and China, primary hydrogen investments remain toward the deployment of fuel cell vehicles and hydrogen refuelling stations. While the heavy industry sector is the largest consumer of hydrogen, this sector is more closely bound to emission reduction regulations, renewable energy mandates, and carbon markets, compared with other light industries.¹⁸⁶

Currently, there is no standard for low-carbon hydrogen, and green hydrogen is not recognized as a renewable fuel in many countries and thus not accountable toward the renewable target set in the mobility sector. It is therefore essential for organizations and policymakers to develop appropriate national and international standards, regulations, and relevant hydrogen certifications. This will allow renewable hydrogen to be supported by climate policies, in the same way as renewable technologies. The system “CertifHy” proposed in Europe to evaluate the environmental value of hydrogen could be a starting model to trade certified hydrogen. In this system, CO₂ emission levels (91 g CO₂/MJ H₂) of hydrogen produced from reforming natural gas are used as a reference point. Hydrogen produced with a 60% reduction from this level (i.e., 36.4 g CO₂/MJ H₂) is defined as “Premium Hydrogen,” while Premium hydrogen produced from renewable energy is defined as “Green Hydrogen.”¹⁸⁷

Government policies need to be designed as a long-term and fair competition platform for the hydrogen sector, introducing both incentives and regulations. When designing regulations relating to greenhouse gases reduction for industry, it is essential to acknowledge the significance and feasibility of clean hydrogen. It is conceivable to make use of a certain percentage of clean hydrogen in industrial processes mandatory with targeted reductions in use of steam methane-reforming hydrogen. Meanwhile, long-term high-risk mitigation implementations and incentives, such as the subsidy of a percentage of the high capital expenditure or compensation via products, could be effective in stimulating the large-scale production and supply of clean hydrogen. This can possibly reduce the cost of clean hydrogen for consumers, accelerating its mass deployment across industry.

Finally, public awareness and acceptance toward hydrogen are also important factors. It is apparent that many citizens are not educated on the potential of renewable hydrogen and its benefits for the environment.¹⁸¹ Even though the social acceptance of new technologies is considerably high in many European countries, hydrogen is still considered dangerous due to its high flammability. It is therefore important to demonstrate and implement a production of hydrogen that is safe to gain an increase in public support.

Summary and perspectives

As a crucial reactant for the chemical industry, the demand for hydrogen has grown considerably and will continue to rise in the foreseeable future. However, with most of the industrial hydrogen being sourced from fossil fuels, it is imperative that we start looking into sustainable production methods for hydrogen to succeed as a clean chemical feedstock and an energy carrier. Currently, only a small fraction of hydrogen is produced from renewable sources due to slow technological advances, lack of mass scale manufacturing of hydrogen technologies, and thus a high cost of green hydrogen relative to fossil fuels, and the lack of environmental government policies promoting

the use of clean hydrogen. A few emerging technologies look promising based on the 2020 DOE target and even appear cost competitive to steam methane reforming for hydrogen production. However, the calculated production costs often do not tell the whole story; for example, electrolysis via geothermal and hydropower has a low cost of 1.1–2.4 \$/kg H₂ but unfortunately their use is restricted by the geographic location of the energy source. Biochemically processed biomass also appears cost competitive at 1.4–2.8 \$/kg H₂, but as an emerging technology, its reliability and actual cost at an industrial scale still remains to be determined. So far, wind-powered water electrolysis appears to have the best chance to play a major role in renewable hydrogen production due to the maturity and decreasing cost of wind technology. Once produced, the last hurdle for hydrogen is its storage and transport due to the low density of the gas. Until new methods like solid-state storage become more established, conventional methods (compressed gas cylinders and liquefied hydrogen) will remain the norm to get hydrogen to its end applications. Advancements in technological processes, cost, and policies still need to be conjointly progressed before renewable hydrogen can become the mainstream.

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