A review of hydrogen as an energy vector

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Abstract

Hydrogen is known as a technically viable and benign energy vector for applications ranging from the small-scale power supply in off-grid modes to large-scale chemical energy exports. However, with hydrogen being naturally unavailable in its pure form, traditionally reliant industries such as oil refining and fertilisers have sourced it through emission-intensive gasification and reforming of fossil fuels. Although the deployment of hydrogen as an alternative energy vector has long been discussed, it has not been realised because of the lack of low-cost hydrogen generation and conversion technologies. The recent tipping point in the cost of some renewable energy technologies such as wind and photovoltaics (PV) has mobilised continuing sustained interest in renewable hydrogen through water splitting. This paper presents a critical review of the current state of the arts of hydrogen supply chain as a forwarding energy vector, comprising its resources, generation and storage technologies, demand market, and economics.

Keywords: Hydrogen economy; hydrogen supply chain; hydrogen carriers; hydrogen generation; hydrogen storage; renewable hydrogen.

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1. Introduction

The discovery of hydrogen dates back to 1671 when Robert Boyle (1627–1691) produced the gas while experimenting with iron and sulphuric acid ($Fe + H_2SO_4 \rightarrow Fe^{2+} + SO_4^{2-} + H_2$) [1]. He described the reaction and called this gas “inflammable solution of iron”. Almost a century later, in 1766, Henry Cavendish (1731–1810) produced the gas over mercury and recognised it as a distinct element [2]. He explained its properties but failed to conceptualise it correctly, describing it as “inflammable air from metals” as he thought the gas was released from the metal instead of the acid. Eventually, Antoine Lavoisier (1743–1794) recognised the nature of the gas (1783) and gave it its current name, “hydrogen”, composed of two Greek words "*hydro*" meaning water and "*genes*" meaning forming [3].

Hydrogen is the lightest of the known elements and the most abundant gas in the universe [4], accounting for around 90% of the visible universe. Hydrogen has the maximum energy content of conventional fuels per unit of weight, e.g. energy content of hydrogen is about 3x of that of gasoline [5]. The origin of the renewable energy that we receive from the sun or stars is hydrogen fusion. It is estimated that the sun’s supply of hydrogen is enough to sustain the fusion reaction for another 5 billion years [6].

Despite the abundance of hydrogen, obtaining hydrogen in elemental form is cumbersome. It is not the air constituent, and the pathways to obtain it are, as represented in Figure 1, through renewable assisted water splitting, thermochemical conversion of fossil fuels, and biological processes. The most straightforward pathway is water splitting but has not been traditionally favoured as a result of its high energy demand. The leading industrial approaches have been gasification and reforming for the generation of synthesis gas (syngas), i.e. a mixture consisting primarily of H_2 and CO, followed by water-gas shift (WGS) reactions ($CO + H_2O \rightleftharpoons CO_2 + H_2$) and carbon dioxide removal. Syngas is an intermediate high-value gaseous mixture that can be used as a feedstock for the synthesis of enormous hydrocarbons. Although gasification of coal, biomass, and oil are possible routes for syngas generation, natural gas steam reforming is the preferred state-of-the-art industrial pathway due to a high H_2/CO ratio of the produced syngas.

Hydrogen has been served as an intermediate in chemical processing. The most dominant application of hydrogen is for crude oil refining, upgrading of Fischer-Tropsch Gas-to-Liquid (FT-GTL) products as well as ammonia and urea production. Future applications of hydrogen will be in iron and steel making, chemical industries, transport, gas grid, etc.

Since the 2010s, a new industrial and academic interest has emerged in the hydrogen economy. The tipping point in some renewable technologies, especially photovoltaics (PV), has revolutionised the energy industry, including hydrogen. The increase in production scale, together with several other reasons such as the shift of global production to China and a reduction in silicon price resulted in a dramatic change in PV cell prices, to the extent that its market price has dropped below $1/W, beyond optimistic predictions made in the 2000s. At this price, PV technology has passed the parity price of fossil fuels in several jurisdictions [7].

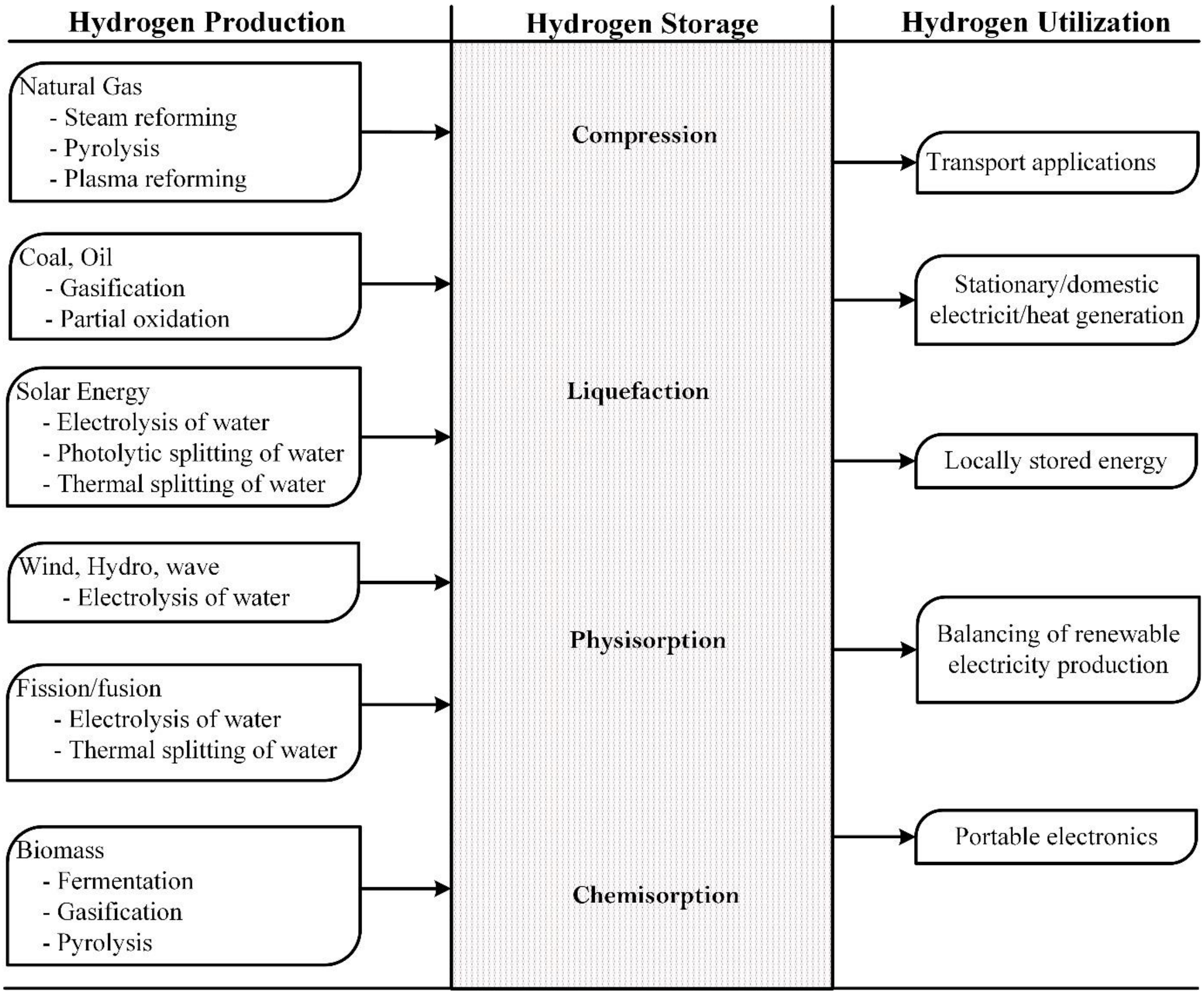


Figure 1: Hydrogen vector: sources, generation options, storage options and end-uses

The projection of renewable energy over-supply is the main driver, besides climate change and energy security concerns, for a renewed interest in water splitting technologies using renewable energies. This trend may be reinforced by fast-advancing emerging technologies beyond electrolysis such as solar thermal hydrogen generation [8, 9].

The global energy consumption is increasing at about 2.3% per annum [10], leading to increased CO_2 emission levels and consequent adverse impacts on the environment. A report from the UN’s Intergovernmental Panel on Climate Change (IPCC) introduces four pathways to capping the global temperature increase at 1.5°C [11]. CO_2 emissions from industry in pathways are projected to be 65–90% lower in 2050 relative to 2010. Such CO_2 emissions mitigations can be achieved through electrification of various sectors, use of hydrogen, product substitution, sustainable and green bio-based products, and carbon capture, storage and utilization (CCSU) in energy-intensive industries, i.e. iron and steel making, ammonia, ethylene, and methanol production.

Although hydrogen-based energy economy is costly and in its emerging stage, technological advancement can be seen in its favour where clean and reliable power supply is required with massive energy storage. Furthermore, hydrogen can be employed as a storage medium for intermittent renewable electricity and as an energy vector for off-grid areas requiring a power supply. Here, we use the term “energy vector” to refer to an energy-rich substance that facilitates the translocation and/or storage of energy—in form of gaseous, liquid, solid hydrogen, through hydrogen to chemicals, etc.— with the intention of using it at a distance in time and/or space from the primary production site. Hydrogen can create new connections between centralised or decentralised supply and demand points. This will potentially enhance the flexibility of the overall energy system.

This review elucidates the pertinent aspects of hydrogen as an energy vector including conventional and prospective technology, markets and economics. Cost-effective and carbon-neutral hydrogen production is key to enable a sustainable hydrogen economy while hydrogen storage and distribution are required for global hydrogen energy supply. Finally, we discuss hydrogen economics concerning production, transportation and uses.

2. Hydrogen demand market

2.1. Conventional demand market

Hydrogen has served as an intermediate chemical in chemical processing. The most critical usage of hydrogen has been in crude oil refining sector [12, 13], upgrading of Fischer-Tropsch Gas-to-Liquid (FT-GTL) products [14] and in the ammonia [15] and urea production. The consumption of hydrogen by region and end-use may vary significantly [16]. For example, in 2006, more than 95% of hydrogen in Japan was used for ammonia synthesis. In the same year, North, and Central and South American refineries used nearly 60% of hydrogen. Europe used 40% of hydrogen for ammonia production, about 50% of that in refineries and ca. 10% of the hydrogen for methanol synthesis, pipeline, cylinder and other uses. Around 45% of hydrogen in Africa and the Middle East was used in ammonia synthesis, ca. 25% in refineries and around 25% for methanol synthesis. Other parts of Asia, on the other hand, used 50% of hydrogen for ammonia synthesis, 35% in refineries, 10% for methanol synthesis and the rest 5% for other applications. In 2007, the global ammonia plants and chemical/refinery processes used ca. 89% of the produced hydrogen [17]. In 2009, China's annual hydrogen production was 10 million tonnes[5]. Petroleum refining, ammonia, and methanol synthesis plants were the three largest markets for hydrogen in China in 2017 and accounted for over 93% of its total hydrogen consumption [18].

Given a low liquefaction temperature of hydrogen, other applications include cooling in reciprocating and rotating equipment such as turbines and generators, for over half a century [19]. Here, we briefly explain the H_2 applications in the main industries.

2.1.1. Hydrogen in refining

Crude oil refining is an umbrella term comprising processes for separating petroleum cuts such as liquified petroleum gas (LPG), naphtha, petrol, diesel, kerosene and fuel oil. Given the market quality requirements and standards of petroleum cuts, particular treatment processes are essential for removing polluting elements including mercury, sulphur, nitrogen and aromatics, and also for breaking long hydrocarbon chains into shorter chains. Hydrotreatment and hydrocracking are two vital hydroprocessing components of any crude oil refinery (shown schematically in Figure 2) and are explained next.

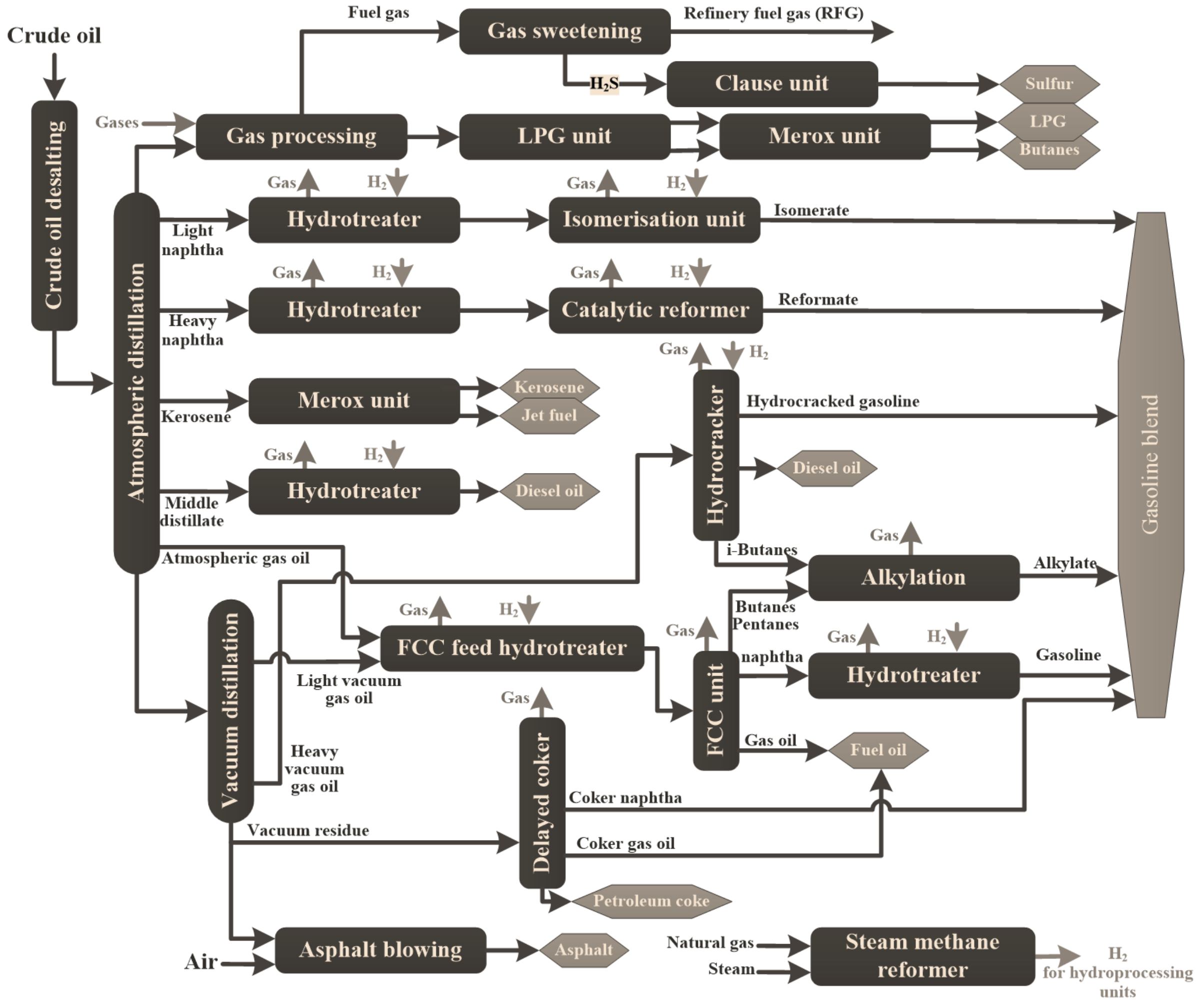


Figure 2: Schematic of a crude oil refinery and hydroprocessing units for hydrotreating and hydrocracking [20]

2.1.1.1. Hydrotreatment

The hydrogenolysis refers to a type of hydrogenation that converts C-X bonds, with C representing carbon and X representing any of sulphur (S), nitrogen (N), oxygen (O), to C-H and H-X bonds. In refining of fossil feedstocks, hydrotreatment is a necessary process to (*i*) increase the hydrogen content of products, (*ii*) remove sulphur, nitrogen, oxygen and metals, and (*iii*) saturate olefinic and aromatic bonds of a given feedstock (boiling range) in the presence of a catalyst [21, 22]. Consequently, not only is the cleanliness of the fuel improved but also cetane number, density, and smoke point are enhanced. Demand for efficient hydrotreating processes has shown an increasing trend as environmental regulations have become more stringent. These processes operate at high temperatures and high pressures. For instance, the Shell hydrotreating process for the production of ultra-low-sulphur diesel (sulphur content <10 ppm) operates at 350–390°C and 60–90 bar [23]. Some hydrotreaters are built for treating specific components. For instance, hydrodesulphurization (HDS) and hydrodenitrogenation (HDN) plants are employed for removing sulphur and nitrogen, respectively [24].

Applications of hydrotreatment are beyond fuel and chemical refining, such as in vegetable oil saturation. Since the invention of hydrogenation by Wilhelm Normann (1870–1939) in 1901 and the following patent in 1903 [25], the food industry has used it for converting liquid vegetable oils to solid or semi-solid form by complete or partial hydrogenation (saturation) of its unsaturated fatty acids.

2.1.1.2. Hydrocracking

The residues of atmospheric and vacuum distillation columns of a refinery [26] (see Figure 2, [20]) have average carbon numbers higher than that of crude oil itself. Due to their low C/H ratios and high viscosity, such fluids are not generally friendly fuel sources [27]. Therefore, they require hydrogenation to break the large chains and to improve the C/H ratio and the molecular weight [28, 29]. If hydrotreatment is called light hydroprocessing, hydrocracking should be then called severe hydroprocessing. Unlike the hydrotreatment that aims to remove pollutants from a feedstock, the primary objective of hydrocracking is to break the R-C-C-R´ bonds of heavy hydrocarbon chains (with R and R´ representing any hydrocarbon) to R-C-H and H-C-R´ bonds, thereby reducing the molecular weight and viscosity of undesirable hydrocarbons to a desired boiling range such as that of diesel. Hydrogen demand of refineries is partially met by recovering it from refining byproducts, mainly via fluid catalytic cracking (FCC) and catalytic reforming (CR), see Figure 4 and Section 3.4 for details.

2.1.2. Hydrogen for ammonia and urea production

Though refineries are the current primary users of hydrogen—and that trend will increase as more stringent rules for quality of refinery products are imposed—ammonia currently has the secondary role in the hydrogen economy. Ammonia is a remarkable chemical product to store energy and a hydrogen carrier for the hydrogen economy. Ammonia was first obtained from the coal gas industry. Haber and Bosch designed a process to produce ammonia from nitrogen and hydrogen. In this process, hydrogen reacts with nitrogen with a molar ratio of 3:1 to produce one mole of ammonia in three fixed bed reactors in series and with different lengths [30]. In 2014, the global industrial production of ammonia was 176 million tonnes. Ammonia is the primary feedstock for the production of a large class of nitrogen-containing chemicals [31]. Given its widespread applications (see Figure 3), its primary uses are for fertiliser (≈80%), fibre and explosive production [32].

The basic urea process was developed in 1922 and is known as Bosch-Meiser process [33]. In this process, ammonia reacts with CO_2 to produce ammonium carbamate ($H_2N\text{-}COONH_4$). The reaction is fast exothermic and occurs at high pressure and temperature. Ammonium carbamate is then decomposed through a slow endothermic to form urea. Ammonium nitrate, the other important chemical derived from ammonia, is produced via the reaction of ammonia with nitric acid [34].

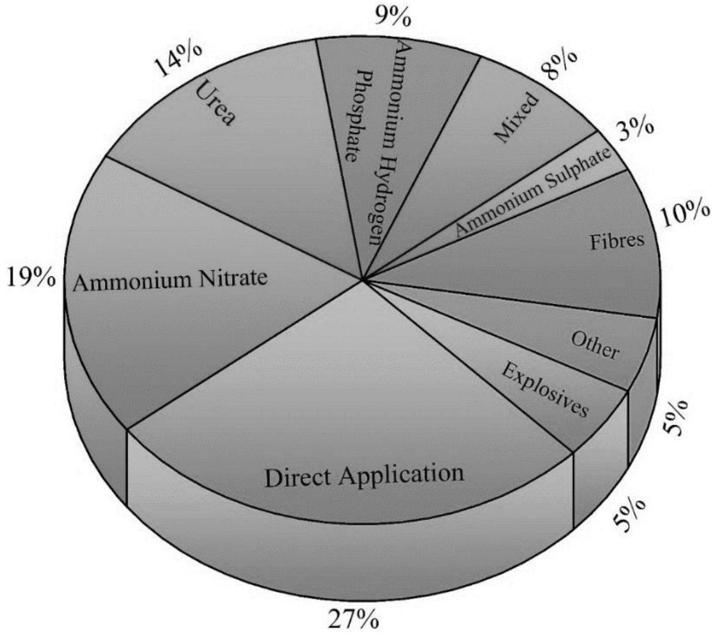


Figure 3: Distribution of ammonia consumption market (data source: [32])

2.2. Future demand market

The two-degree scenario of the International Energy Agency [10] projects more than 300 Gt (giga tonnes) of avoided CO_2 emissions up to 2050, requiring a revolution in energy systems. Most of the contribution is required by industry (about 150 Gt), followed by transport (around 140 Gt). The challenge to meet the goals in all sectors is immense, especially in electricity generation [35]. Hydrogen can play a vital role in the shift to a net-zero-emission future because of its cleanness and flexibility to act as a fuel in various applications as well as energy storage.

The global demand for hydrogen is expected to increase by 4–5% per year during the next five years. This is because of the demand for crude oil refining, and methanol and ammonia synthesis. Asia is expected to lead the demand growth because of its domestic economies growth. By 2030 and under business-as-usual scenario assumptions, it is anticipated that the hydrogen consumption in the refining sector will increase by more than twice of that in 2005 [36]. Thereby, a substantial reduction of the CO_2 footprint of conventional fuels and biofuels during the upgrading and refining processes will be achieved if the hydrogen is decarbonised.

The hydrogen generation market value is anticipated to be \$154.74 billion in 2022 compared to \$115.25 billion in 2017 [5].

As already discussed, hydrogen has historically been an intermediate product in the chemical industry. The necessity of environmental reform, however, has made hydrogen an attractive solution for sustainable energy management. Advantages of deploying hydrogen-based renewable fuels include (i) no emissions when it is combusted at the point of end-use, with the exception of minor NO_x production if combusted with air; (ii) diversity of energy sources to drive production processes [37, 38]; (iii) high flexibility in end-uses including central and local electric power generation, portable power, shipping, rail transport, vehicles, combined heat and power (CHP) generation for industrial processes and buildings, and chemical industries [20, 33, 39-41]. Through diversification of transportation fuel base, hydrogen technologies offer increased security of fuel supply chains. Combined with captured CO_2, synthetic hydrocarbons for power plants or transportation applications can be produced, without generating the need for capital-intensive infrastructure upgrades. Despite many benefits, hydrogen suffers from low volume intensity. It has the highest mass-specific energy density among chemical fuels with LHV and HHV range of 120 and142 MJ/kg, respectively, while the value for gasoline is 36.4–49.6 MJ/kg [42]. Nevertheless, it’s low volumetric energy density (10.7–12.7 MJ/m^3[43]) creates storage and transportation challenges.

Recently, many countries have become interested in introducing renewable hydrogen to improve the overall sustainable energy scenario. For example, around 376 hydrogen filling stations had been installed around the world by the end of 2018 [44]. For complete combustion of a unit of mass of hydrogen in an internal combustion engine (ICE), 34 units of air are required. This is 130% above the 14.7:1 air/fuel ratio needed for gasoline [45]. Depending on the technique used to measure the hydrogen to ICEs, the power output can vary from 85% (intake manifold injection) to 120% (high-pressure injection) for gasoline ICE. Recently, a Japanese consortium of major automakers and energy firms declared that by 2020 they would install 160 hydrogen filling stations across Japan [46]. Korea has set a goal of 310 hydrogen refuelling stations across the state by 2022 [47]. By the end of 2017, about 6,364 hydrogen fuel-cell vehicles (HFCVs) were sold globally since 2013 when such vehicles were commercially available. Among all automakers, Toyota has been the most successful one, accounting for more than 77% of the sales of hydrogen cars. By 2021, it is anticipated that at least 11 automakers will have rolled out HFCVs, including Toyota, Lexus, Hyundai, Kia, Honda, Mercedes-Benz and BMW; other competitors in this space are Tata Motors, Pininfarina

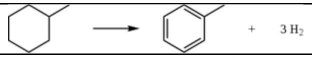
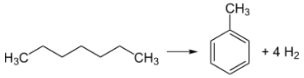
S.p.A. (owned by Mahindra & Mahindra), Riversimple and the RONN Motor Group [48]. Experts also believe that by the end of 2032 there will be around 5000 hydrogen refuelling stations around the world and the aggregate capacity of hydrogen will be around 3MM kg/day [49].

One of the CO_2 mitigation options in the industry [50] is fundamental changes in the current process technologies. This can be achieved by use of renewable hydrogen as a reducing agent in the iron and steel industry [31, 51, 52], e.g. HYBRIT concept by SSAB, [53, 54], replacement of the basic oxygen furnace route in steel production industry via hydrogen, usage of hydrogen in the chemical industry, etc. A Course 50 research project in Japan aims to introduce the hydrogen-enriched coke oven gas into the blast furnace that can reduce carbon emissions [55]. Another future application of hydrogen will be in air transport. The future of air transport via hydrogen-fuelled aircraft is discussed in [56, 57]. Different strategies to evaluate hydrogen's feasibility in the air transport sector including hydrogen production, storage, engines configurations and aircraft configurations were discussed. Other future hydrogen applications are for light-duty passenger vehicles, Non-individual/public vehicles, trains and trams, ferries and smaller boats, power and heat [5].

3. Hydrogen production

Table 1 summarises hydrogen generation pathways, including their source of energy, hydrogen source, process, technology, reaction kinetics and temperature range. In the next subsections, we are going to briefly discuss the current state of the art of these generation pathways.

Table 1: Hydrogen generation pathways: sources, approaches and technologies

Source of process energy	**Hydrogen source**	**Approach**	**Process**	**Technology**	**Reactions**	**Temperature range (°C)**	**Ref.**
Fossil fuels	Carbonaceous material (fossil, waste or biomass)	Thermochemical	Natural gas reforming	Steam methane reforming	$C_nH_m + n\,H_2O \rightleftharpoons (n + {}^{m}\!/_{2})\,H_2 + n\,CO$ $CH_4 + H_2O \rightleftharpoons 3\,H_2 + CO$ WGS: $CO + H_2O \rightleftharpoons H_2 + CO_2$	700–1100	[58]
				Partial oxidation	$CH_4 + \frac{1}{2}O_2 \rightleftharpoons 2H_2 + CO$	Thermal: >1200 catalytic: 800–900	[58]
				Autothermal reforming	$CH_4 + H_2O \rightleftharpoons 3\,H_2 + CO$ WGS: $CO + H_2O \rightleftharpoons H_2 + CO_2$ $CH_4 + \frac{1}{2}O_2 \rightleftharpoons 2H_2 + CO$	950–1100	[58]
				Tri-reforming	$4CH_4 + O_2 + 2H_2O \rightarrow 10\,H_2 + 4CO$ $2CH_4 + O_2 + CO_2 \rightarrow 3\,H_2 + 3CO + H_2O$		[59]
			Natural gas pyrolysis	Kværner process	$C_nH_m \rightarrow n\,C + {}^{m}\!/_{2}\,H_2$ $CH_4 \rightarrow 2\,H_2 + C$	1600	[60, 61]
Fossil fuels, biomass, and wastes			Coal/biomass/liquid fuel/waste gasification		$3C\,(coal) + O_2 + H_2O \rightarrow H_2 + 3CO$ WGS: $CO + H_2O \rightleftharpoons H_2 + CO_2$	>700	[62]
			Coal/biomass/liquid fuel//waste pyrolysis	Gasifier	Complex set of reactions	400–700	[63]
Fossil fuels (typically)	Water or hydrocarbons	Chemical byproducts	Chlorine production	Chloralkal process	$2\,NaCl + 2\,H_2O \rightarrow Cl_2 + H_2 + 2\,NaOH$ --- Cathode: $2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$ Anode: $2\,Cl^- \rightarrow Cl_2 + 2\,e^-$	<90	[64]
			Dehydrogenation of naphthenes			~400	[65]
			Dehydrocyclisation				[66]

Bacteria	Hydrocarbons	Biological	Dark fermentation		(1) $C_6H_{12}O_6 + 2\ H_2O \rightarrow 2\ CH_3COOH + 2HCOOH + 2\ H_2$ (2) $C_6H_{12}O_6 + 2\ H_2O \rightarrow 2\ CH_3COOH + 2\ CO_2 + 4\ H_2$ (3) $C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$ (4) $3C_6H_{12}O_6 \rightarrow 4CH_3CH_2COOH + 2CH_3COOH + 2CO_2 + 2H_2O$		[67]
Bacteria and light			Photofermentation		(1) $2CH_3COOH$ + Light $\rightarrow 2CO_2 + 4H_2$ (2) $CH_3CH_2CH_2COOH + 3H_2O$ + Light $\rightarrow 4CO_2 + 10H_2$ (3) $HCOOH$ + Light $\rightarrow CO_2 + H_2$		[68]
			Hybrid of dark and photo fermentation	Single-stage or sequential	Dark fermentation of sucrose followed by photofermentation of fatty acids		[68-70]
Electricity			Electrohydrogenesis (microbial fuel cells)		$C_{12}H_{22}O_{11} + 13H_2O \rightarrow 12CO_2 + 48H^+ + 48e^-$		[71]
Light	Water	Photocatalysis	Photoelectrochemical (artificial photosynthesis)		$2H_2O$ + light $\rightleftharpoons 2\ H_2+O_2$		[72, 73]
Electricity		Electrolysis	Electricity based	High-pressure electrolysis	$2H_2O \rightleftharpoons 2\ H_2+O_2$		[74]
Electricity				Low-pressure electrolysis	$2H_2O \rightleftharpoons 2\ H_2+O_2$		[74]
Thermal/electricity		Thermo-electrolysis	Combined electrical and thermal	Power and high-temperature electrolysis	$2H_2O \rightleftharpoons 2\ H_2+O_2$	100–1000	[75, 76]
Thermal (any source)		Thermolysis	Very high temperatures	Concentrating solar thermal	$2H_2O \rightleftharpoons 2\ H_2+O_2$	>2200	[77]
Non-renewable or renewable carbonaceous fuels Alternatively, solar thermal		Thermochemical	Two-step metal oxide cycles (1) Reduction $MO_{ox} \rightarrow MO_{red} + {}^1/{}_2O_2$ (T>1300 °C) (2) MO_{red} +H2O $\rightarrow MO_{ox} + H_2$ (T<1000 °C)	Iron oxide cycle	(1) $M(II)Fe_2(III)O_4 \rightarrow M(II)O + 2Fe(II)O + ½O_2$ (Reduction) (2) $M(II)O + 2Fe(II)O + H_2O \rightarrow M(II)Fe_2(III)O_4 + H_2$ (Oxidation) M: Fe, Zn, Mn, Ni, Co (1) $Fe_3O_4 \rightarrow 3FeO + ½O_2$ (Reduction) (2) $3FeO + H_2O \rightarrow Fe_3O_4 + H_2$ (Oxidation)	(1) ~1600 (2) ~600	[76, 78-81]

				Zinc-zinc oxide cycle	(1) Dissociation: $ZnO \rightarrow Zn + 1/2\ O_2$ (2) Hydrolysis: $Zn + H_2O \rightarrow ZnO + H_2$	(1) ~2000 (2) ~330	[82]
				SnO2/SnO based cycle	(1) $SnO_2 \rightarrow SnO + 1/2\ O_2$ (2) $SnO + H_2O \rightarrow SnO_2 + H_2$	(1) 1500 (2) 530	[83]
				Cerium(IV) oxide-cerium(III) oxide cycle	(1) Dissociation: $2CeO_2 \rightarrow Ce_2O_3 + 0.5\ O_2$ (2) Hydrolysis: $Ce_2O_3 + H_2O \rightarrow 2CeO_2 + H_2$	(1) ~2000 (2) ~430	[84]
			Three-step cycles	Sulphur-iodine cycle	(1) $I_2 + SO_2 + 2\ H_2O \rightarrow 2\ HI + H_2SO_4$ (120 °C); Bunsen reaction The HI is then separated by distillation or liquid/liquid gravitic separation. (2) $2\ H_2SO_4 \rightarrow 2\ SO_2 + 2\ H_2O + O_2$ (830 °C) The water, SO_2, and residual H_2SO_4 must be separated from the oxygen byproduct by condensation. (3) $2\ HI \rightarrow I_2 + H_2$ (450 °C)		[85]
			Four-step cycles	Copper-chlorine cycle	(1) $2\ Cu + 2\ HCl(g) \rightarrow 2\ CuCl(l) + H_2(g)$ (2) $2\ CuCl_2 + H_2O(g) \rightarrow Cu_2OCl_2 + 2\ HCl(g)$ (3) $2\ Cu_2OCl_2 \rightarrow 4\ CuCl + O_2(g)$ (4) $2\ CuCl \rightarrow CuCl_2(aq) + Cu$	(1) 430–475 (2) 400 (3) 500 (4) ambient-temperature electrolysis	[86]
		Hybrid thermochemical-electrochemical	Single-step	Hybrid sulphur cycle (with H_2SO_4 as byproduct)	(1) $S(s) + O_2(g) \rightarrow SO_2(g)$ (2) $SO_2(aq) + 2\ H_2O(l) \rightarrow H_2SO_4(aq) + H_2(g)$	???	[87]
			Two-step	Hybrid sulphur cycle	(1) $H_2SO_4(aq) \rightarrow H_2O(g) + SO_2(g) + ½\ O_2(g)$ (2) $SO_2(aq) + 2\ H_2O(l) \rightarrow H_2SO_4(aq) + H_2(g)$	(1) >800 (thermochemical)(2) 80–120 (electrochemical)	[87]

3.1. Fossil-fuel-based thermochemical hydrogen production

Currently, around 96% of hydrogen is generated from fossil fuels [5, 88], i.e. 49% from natural gas, 29% from liquid hydrocarbons, and ca. 18% from coal [18]. About 4% of hydrogen is produced from water electrolysis and other byproduct sources of hydrogen. The common routes of hydrogen production are from fossil fuels include hydrocarbon reforming, coal gasification, hydrocarbon pyrolysis and plasma reforming, all of which are thermochemical processes. In China, for instance, steam reforming of natural gas and coal are the two main ways of producing hydrogen in the ammonia and methanol synthesis[18].

3.1.1. Reforming

In the hydrocarbon reforming, a gaseous hydrocarbon fuel is converted into hydrogen via certain reforming techniques. Based on the reactant, hydrocarbon reforming can be classified as steam reforming, partial oxidation or autothermal reforming [89].

3.1.1.1. Steam reforming (SR)

Steam reforming (SR) is the most comprehensive endothermic catalytic process for the generation of hydrogen-rich syngas from light hydrocarbons. Most often, the feed is natural gas, and the process is called steam methane reforming (SMR). SR process consists of three steps: reforming or syngas generation, water-gas shift (WGS) reaction to increasing hydrogen content (i.e. H_2/CO) ratio of syngas, gas purification (CO_2 separation). The natural gas feed is endothermically converted with steam into syngas in a catalytic tube reactor. The endothermic steam methane reforming reactions are favoured by elevated temperatures. The syngas H_2/CO ratio of an SMR is above 3. The heat requirement of the reformer is supplied by, e.g. burning natural gas. Process heat, as well as flue gas stream from the reformer, are used for the steam generation. If the natural gas feedstock contains organic sulphur compounds, a desulphurisation unit must be installed before the reforming step to avoid poisoning the reforming catalyst [88]. Generally, to obtain the purified H_2 and to prevent catalyst coking, the gas mixture is heated to high temperature. Afterwards, the gas mixture is transferred to a heat recovery system and then is fed into a WGS reactor where the steam and CO are converted to CO_2 and H_2. At that point, the gaseous mixture is transferred either through a CO_2 removal unit and methanation process or through a pressure swing adsorption process to obtain a pure hydrogen product [90]. An essential factor for characterising the SR process is the hydrogen to carbon atom ratio of the feedstock materials. The lower this ratio is, the higher carbon dioxide emissions are formed [91]. A membrane reactor can be used to replace both reforming and WGS reactors to achieve an overall higher reaction rate [92]. In the last two decades, researchers are working to find an alternative solution to conventional reformers such as membrane reactors and fluidised-bed membrane reactors. Among them, micro-membrane reactors attract significant attention concerning the scientific and technological point of view due to their characteristics and application.

Recently, most of the research related to SR is mainly focused on catalyst performance to increase the hydrogen yield by the resistance to catalyst sintering and minimising the effect of the carbon deposition and sulphur poisoning. Several studies are focused on experimental estimation to quantify the performance of both noble and non-noble metal-based catalyst and their interactions on metal-support. Among them, the Ni-based catalyst demonstrated the expected outcome because of the low cost and their specific features.

There are many review articles available on SR; among them, we found Ref. [93] critically reviewed and summarised all the aspects of SR including catalyst, membrane, reaction kinetics and challenges.

The heat efficiency of hydrogen production from natural gas reforming on an industrial scale is around 70–85% [94]. The heat requirement of the SR can also be supplied by concentrated solar thermal energy [95-98]. Solar thermal reforming is one of the first solar-derived fuel routes investigated since the early 80s in the U.S. [99].

3.1.1.2. Partial oxidation (POX)

POX can be classified as thermal and catalytic partial oxidation. In the thermal partial oxidation (TPOX) process, the raw material in the presence of oxygen is converted to syngas at 1300–1500°C and 3–8 MPa [100]. Feedstocks to the TPOX can be methane, heavy feedstock such as oil residues and coal [90]. In this process, after sulphur removal, pure oxygen is used for partial oxidisation of hydrocarbon feedstock, and the produced syngas is further treated in the same manner as the SR process. Compared to the SR, more CO is produced in the POX route. The conversion of CO with steam, therefore, complements the process into H_2 and CO_2. Due to the lower H:C content of the heavy feedstock compared to methane, a more significant fraction of the produced hydrogen comes from steam [90]. The cost of the air separation unit and the associated costs of the desulphurization steps make such plants extremely capital intensive [88]. The cost of an oxygen plant can be 19.1 million $/325 tonne O_2/day with a scaling factor of 0.7 [101].

TPOX typically finds that produce syngas from natural gas by using Fischer–Tropsch synthesis. However, at a small scale, the low adiabatic flame temperature can hinder the reaction kinetics, process stabilities and efficiency. To overcome these, most research works have been done based on principles of excess enthalpy combustion that were introduced by Weinberg [102]. Usually, the upper flammability limit is essential to maximise the H_2 production in TPOX. It can be achieved by recirculation of heat and product, using a catalyst. But, in super adiabatic combustion (SAC), the combustion of the reactant mixture takes place above the adiabatic temperature, which is a viable option for TPOX [103]. Combustion inside a porous medium (PM) and porous inert medium (PIM) are always favourable for SAC by internal heat recirculation to produce H_2 and syngas. Comprehensive reviews concerning the fundamentals of combustion in PM, PIM and application can be found in Refs.[104, 105].

Catalytic partial oxidation (CPOX) process operates at 700–1000°C with feedstock transformed from methane to naphtha (e.g. conventional natural gas, flare gas, shale gas) [90]. CPOX offers a potential solution to overcoming heat transfer, and high external heat energy consumption problems experienced in reforming technologies. Due to the exothermicity of the chemical reactions, syngas with a molar ratio of H_2: CO close to 2 with little CO_2 are produced. Consequently, it is difficult to control the reactor temperature. CPOX is much faster than the TPOX process. Comprehensive reviews of CPOX including reaction kinetics, thermodynamics, membrane, catalyst and application, are given in Refs. [106, 107].

CPOX benefits from high reaction rates, energy-efficient and highly selective in a single reactor, which helps to decrease the capital and operating costs to produce hydrogen. Methane has an added significant interest in producing hydrogen through this process. Usually, in this process, heat is supplied by controlled combustion of feedstock (e.g., methane), and its thermal efficiency is around 60–75% [108]. The hydrogen yield in this process varies significantly with the choice of the catalyst [109].

3.1.1.3. Autothermal reforming (ATR)

ATR is a combination of the endothermic SR and the exothermic CPOX reactions. In the ATR method, steam and oxygen are fed into the adiabatic reformer, because the oxidation and reforming reactions coincide. This process has been used to increase the hydrogen production rate with low carbon monoxide content. ATR requires no external heat, is more straightforward and less expensive than SR of methane, because although SR has higher efficiency and low CO content, due to the endothermic process, the required energy must be transferred from outside. Also, ATR can be started up and shut down very quickly while producing a more substantial amount of hydrogen than standalone POX [110]. Using suitable catalysts, heavier hydrocarbons than methane may be converted into hydrogen onboard automobiles via the ATR process [111].

To prevent coke generation in the ATR of biodiesel fuel required more oxidative reactions compared to conventional diesel fuels because of carbonaceous deposits, along with the adsorption of sulphur-containing substances, as the major reason for catalyst deactivation [112]. The recent updates about ATR design, challenges, application are given in Refs.[113, 114].

It is expected that the ATR is an attractive route for syngas production for the GTL fuel industry due to its favourable syngas composition (H_2/CO ratio of around 2) for the FT synthesis, relative compactness and lower fixed capital cost [30, 101, 115-122]. The list of reactions governing the reforming techniques is available in [33, 89].

3.1.2. Gasification

Gasification is a process whereby dense liquid or solid fuels including coal, petroleum waste and biomass are partially oxidised with oxygen and steam under high temperature and pressure in a gasifier reactor to form syngas [89]. After impurities are removed from the syngas, the CO content of the syngas reacts with steam in the WGS reactor to produce additional hydrogen and CO_2 [62]. However, due to the relatively higher carbon content of coal, it emits a significant amount of CO_2 and other contaminants to the atmosphere in comparison to other hydrogen production routes. Besides, topological and ecological changes are the critical adverse effects of coal mining. Carbon capture, storage, and utilisation (CCSU) technologies are being developed for the management of the highly concentrated CO_2 stream [123], but they lead to higher hydrogen production cost [33, 124]. Usually, coal-based hydrogen generation has a higher production cost than natural gas reforming. However, it has been observed that coal-based hydrogen generation could also be economically viable with co-generation of electricity [125]. Extended reviews of gasification using coal, biomass and other solid fuels are given in Refs. [62, 126-128], where they emphasise on recent advances based on current research across the world including supply and utilisation of solid fuels, challenges, process optimisation and modelling and different gasifier.

3.1.3. Pyrolysis

By definition, pyrolysis is the decomposition of organic substances in the absence of oxygen at 500–800°C as well as short vapour residence times of 3–1500 s [89, 129]. Usually, the light liquid hydrocarbons (with a boiling point of 50–200°C) produce hydrogen and carbon, whereas a substantial residual fraction (at a boiling point of higher than 350°C) produces hydrogen in two steps such as hydrogasification and cracking of methane [124]. Compared with SR, this process requires less energy to produce hydrogen, and the thermal energy demand of this process can be provided by the combustion of hydrogen (~15–20%), which helps to reduce the significant amount of CO_2 emission from this process [130]. Moreover, pyrolysis does not require a WGS reactor. Instead, the CO_2 removal process can be installed for CO_2 capture, storage, and utilisation. As a result, the total capital investment of pyrolysis for large plant becomes lower than that for the SR or POX processes, which helps to reduce the hydrogen production cost ≈25–30% [88]. From the current and sustainable environmental aspect, it will be more convenient to produce carbon and hydrogen through catalytic dissociation of natural gas rather than SR combined with CO_2 impounding.

3.1.4. Plasma reforming

The reaction mechanism of plasma reforming is similar to conventional reforming. In this process, however, free radicals and energy are fed through plasma (produced with electricity or heat) for the reforming reaction [131]. Commonly, this process has been developed to support ATR, POX and SR syngas generation routes. Plasma devices, known as plasmatrons, produce high temperatures (e.g., >2000°C) and require a very high degree of temperature control. The generation of heat is independent of reaction kinetics, and the optimum operating conditions can be controlled over a wide range of gas compositions and feed rates [91]. Gas streams with a high hydrogen content can be generated in plasma reformers from various hydrocarbon feedstocks (e.g. natural gas, oil, gasoline, biomass, diesel, jet fuel, etc.) with high conversion efficiencies of ca. 100% [91]. The plasma conditions (i.e., high temperature, and a high degree of dissociation and ionisation) can be utilised to accelerate thermodynamically favourable reactions without the need for a catalyst or to supply the required energy of endothermic reforming processes.

Plasma reforming can be generally divided into two categories according to the average gas temperature, such as thermal (or equilibrium) and non-thermal plasma reforming. Thermal plasmas have been applied for dry reforming of methane (DRM), and the results show that greenhouse gases (GHGs) conversions achieved with thermal plasma can reach over 80% and carbon deposition is restrained. Non-thermal plasmas, including corona discharge, gliding arc, dielectric barrier discharge (DBD), atmospheric-pressure glow discharge (APGD), microwave discharge and spark discharge have been investigated to generate syngas. Generally, CH_4 and CO_2 conversions achieved with non-thermal plasmas are lower than those of catalysis and thermal plasma; more details can be found in Ref. [132].

The advantages of plasma reformers are compactness and low weight, minimal cost, high conversion efficiencies, the flexibility of operation with a variety of fuels including heavy hydrocarbons and “dirty” hydrocarbons, and fast response time. As a result, plasma reforming can be employed for stationary and/or mobile applications [133]. High-pressure operation and reliance on electrical energy are the main drawbacks.

3.2. Biomass-based thermochemical hydrogen production

Biomass can be considered a potential alternative fuel source that can help to meet future energy demands. Biomass can be found from a wide range of sources such as crops and crop residue, wood from forest and forest residue, industrial residue, grass, animal waste, municipal solid waste, sawdust, aquatic plants and algae, waste paper, corn, and many others [134]. It has been stated that biomass could fill the energy demand by more than 25% by the year 2050 [125]. Unlike fossil fuels, the CO_2 emissions from biomass are recycled from the air through plant photosynthesis. Bioenergy equipped with CCS technology is known as BECCS and is used to improve its life cycle impacts. BECCS intends to achieve very low or even negative emissions (i.e. the net effect is the removal of GHG from the air). However, this is limited by the geographical, technical and economic barriers of the CCS implementation. There are two main processes by which hydrogen has been produced from biomass: thermochemical and biological. The thermochemical process is usually much faster than the biological process and offers a higher stoichiometric yield of hydrogen. Biomass can be mixed with fossil fuels in integrated gasification combined cycle processes for concurrent hydrogen and power generation [62].

Thermochemical conversion of biomass is very similar to that of fossil fuels, using gasification or pyrolysis. Both processes produce CO and CH_4, which can be processed for excess hydrogen production through SR and WGS. Apart from these generation routes, combustion, liquefaction, and supercritical fluid extraction are less preferred methods due to their relatively low hydrogen yield and strict operating requirements [125].

3.2.1. Biomass gasification

Biomass gasification systems can use both biomass and coal as fuel feedstock and generate high amounts of gaseous product and small quantities of char. Gasification usually comprises combustion and pyrolysis processes that produce the required heat for endothermic pyrolysis reactions. Gasification is carried out at a high temperature to increase the hydrogen yield. At the end of the gasification process, a mixture of CH_4, H_2, CO and CO_2 is produced. In this system, air or oxygen is introduced into combustion or POX processes. In this process, thermal efficiency is low because of the moisture content of the biomass, which must be vaporised. That may be accomplished without or with a catalyst and in a fluidised bed or fixed bed reactor; usually, the former has superior performance [135]. Sometimes superheated steam has been utilised to reform dry biomass to obtain high hydrogen yields. Ideally, oxygen is chosen in gasification plants, but an air separation unit is not economically viable for small-scale plants. That limits the gasifiers to using air, resulting in substantial dilution of the product and also the production of NO_x. WGS and separation process are sometimes employed to generate pure hydrogen. The gasification process requires a massive amount of feedstock because most gasification reactors are built on a large-scale. Based on the lower heating value, gasification can achieve efficiencies in the range of 35–50% [108]. Biomass logistics (collection and transportation) for the gasification plant is costly. Besides, the complexity of the removal of tars from biomass gasification process limits the commercialisation of biomass-based hydrogen production [88].

3.2.2. Biomass pyrolysis

Biomass pyrolysis is another promising method of hydrogen production. In biomass pyrolysis, the biomass feedstock is heated and gasified at pressure and temperature in the range of 0.1–0.5 MPa, 500–900°C, respectively [125]. Usually, this process occurs in the absence of air or oxygen, so the chance of dioxin formation can be almost eliminated. As a result, no carbon oxides are formed and there is no need to further employ secondary reactors such as WGS or preferential oxidation (PrOx). The main attractions of biomass pyrolysis process are compactness and relative simplicity, fuel flexibility and clean carbon byproduct and low CO and CO_2 emissions [91]. Based on the operating conditions, the method can be either fast pyrolysis or conventional/slow pyrolysis. Fast pyrolysis occurs at high temperature, with short residence time. High-temperature gas and low-temperature tar are produced in this process. In the slow pyrolysis scheme, on the other hand, the primary product is charcoal. Hence that process is not considered a potential method to produce hydrogen. The products of fast pyrolysis may be gaseous, solid (char), or liquid (tar and other organics). If the reactor is not appropriately designed for this process, there is a potential risk of carbon outgrowth. However, along with reduced CO and CO_2 emissions, biomass pyrolysis produces a significant amount of solid carbon, necessitating a smart approach for confiscation[88, 125].

3.3. Biological hydrogen production

The biological process offers carbon-neutral hydrogen production. There are three main biological process methods for producing hydrogen: direct and indirect bio-photolysis, photo and dark fermentation, and metabolic processing.

Bio-photolysis is similar to the photosynthesis of plants and algae and is used for hydrogen generation. In indirect bio-photolysis, a water molecule is split into oxygen and hydrogen ion via photosynthesis by green algae. These hydrogen ions react with the hydrogenase enzyme to generate hydrogen. Usually, these enzymes are susceptible to oxygen. However, due to the light saturation effect, the overall hydrogen production rate is decreased. Hence, mutants are extracted from microalgae to control the pigment content with a smaller amount of chlorophyll and help to increase the level of oxygen tolerance, so that the yield of hydrogen is increased [136]. Indirect bio-photolysis uses hydrogenase and nitrogenase enzymes to produce hydrogen, but the hydrogen production rate is comparable to that of hydrogenase enzymes by green algae [136]. Hydrogen production by algae via bio-photolysis could be considered as an environmentally sustainable and economically feasible method from both water and CO_2 utilisation perspectives [88]. However, due to the low hydrogen yield, a significant active surface area is required to collect sunlight. That and the absence of waste utilisation are the main limitations of this method.

Fermentation is a desirable method to produce hydrogen because of the utilisation of waste materials. Moreover, hydrogen production is cheaper with concurrent waste treatment. Dark fermentation utilises mostly anaerobic bacteria on carbohydrate-rich substrates and under anoxic condition. This process is relatively simple, as it does not need any light sources; hence it can produce hydrogen at any time with limited space. Photofermentation requires solar energy with an anoxygenic condition and organic acids. Because of the presence of nitrogenase, some photosynthetic bacteria can convert organic acids into H_2 and CO_2. The hydrogen yield is typically greater under sunlight than in dark conditions. However, due to the lower solar energy conversion efficiency, anaerobic photo-bioreactors require large areas and the scarcity of organic acids confines this method to competing with dark fermentation [88].

Metabolic processing is an emerging technology that combines bacterial metabolism with electrochemistry to produce hydrogen [137]. It can produce a high hydrogen yield as well as pure organic materials from complex organics of, e.g. dark fermentation. However, it requires an external energy supply to boost the energy of the generated electrons. Consequently, the cost of hydrogen production also increases [138].

3.4. Impure hydrogen as a byproduct of chemical processes

Hydrogen can also be an impure byproduct of a chemical process. Two examples are discussed here.

3.4.1. Hydrogen as a refinery byproduct

Part of the hydrogen demand of refineries is provided via their byproduct streams, mainly from CR and FCC units. Naphtha— an intermediate product of refineries— with molecular weight and properties close to gasoline has a poor octane number. CR isomerises paraffin (linear hydrocarbons) into cyclic naphthenes and iso-paraffins (i.e. branched alkanes). It also aromatises paraffin and naphthenes to aromatics, a process that produces a significant amount of hydrogen (see Figure 4).

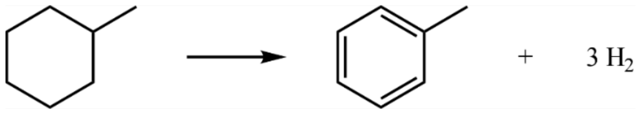
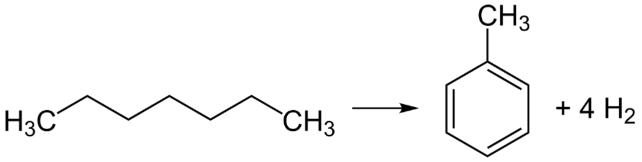
Dehydrogenation of naphthenes [65]	
Dehydrogenation and aromatisation of paraffin [66]	

Figure 4: Example of oil refining intermediate reactions that produce H_2 as a byproduct

In refineries, some secondary components are not required but can be installed when the economics of the refinery justifies. FCC is one of such secondary units for generating products with a much more exceptional boiling range through the cracking of long-chain molecules (e.g., gas oil). Unlike hydrocracking, which is of interest in locations with a high diesel demand (e.g. in Asia), FCC is installed when the demand market for additional distillate fuels and gasoline is high (such as in the U.S.). The light-end gas streams leaving the FCC unit —such as methane and ethane—contains some H_2 that can be separated via several approaches to be fed into hydroprocessing units.

3.4.2. Hydrogen as a byproduct of the chlorine production process

The primary approach used for chlorine and caustic soda production is the chloralkali process ($2\ NaCl + 2\ H_2O \rightarrow Cl_2 + H_2 + 2\ NaOH$), in which hydrogen is produced as a byproduct in the cathode [64]. The chloralkali process plays a critical role in the chemical industry, where its products are used in more than 50% of those industries [139]. This process has been practised since the 19th century, with three evolutions: the diaphragm cell process, the mercury cell process, and the membrane cell process. Though the first two processes are the oldest and most widespread across the world, they can have significant environmental impacts (e.g., mercury discharge) [140]. The hydrogen from this industry finds applications in several sectors.

3.5. Hydrogen production via water splitting

Although hydrocarbon SR is a widely used and economical route for industrial hydrogen production [141], it produces significant amounts of CO_2 emissions owing to its carbonaceous feedstock. However, for hydrogen production purposes SR could be of interest in the short term if it is efficiently developed to diminish CO_2 emissions or through a CCS process [141]. Hydrogen production by steam reforming of methanol [142, 143] also provides a cheap route but emits large amounts of CO_2.

High-temperature processes provided with the heat from nuclear reactors or solar concentrators can be employed to split water. Biological processes using microbes can also produce hydrogen in the presence of sunlight [144]. Additionally, hydrogen production by photocatalysis [145] and photoelectrochemical cells [20] in the presence of sunlight are potential future methods to produce hydrogen[146]. Photobiological photoelectrolysis processes are still at their early stage of development; whereas the former has low conversion efficiency [147], the cost and practical issues are the primary barriers for the latter. Hydrogen production by fermentation approach is an environmentally safe process. There is enormous potential as a sustainable development strategy, but challenges and limitations including low H_2 yield, production of GHGs, and side reactions that convert H_2 into byproducts before it is harvested remain to be addressed [148-150].

While hydrocarbons currently dominate feedstock to produce hydrogen, the generation of hydrogen from renewable sources would be a leading priority in future because of its clean and sustainable characteristics for the environment. Excluding biomass conversion, water splitting is the most desired approach for renewable-based hydrogen generation. The water splitting is exothermic hydrolysis of water into hydrogen and oxygen. The overall reaction of the cycle is:

$$H_2O \rightarrow H_2 + \tfrac{1}{2} O_2 \qquad \Delta H_{298} = 242\ \mathrm{kJ/mole} \qquad (1)$$

In the following section, we briefly discuss the available water-splitting processes currently practised around the world as shown in Table 1.

3.5.1. Electrolysis

Water electrolysis is an established technology, based on the introduction of direct electric current to the water. The hydrogen purity from this technology is very high ca. 99.999 vol% once the product stream has been dried and oxygen impurities have been separated. Importantly, electrolytic hydrogen production is appropriate for direct use in low-temperature fuel cells, which are sensitive to impurities of the hydrogen stream, in contrast to biomass- and fossil fuels-derived hydrogen. In the water electrolysis process, the direct electric current passes through anode and cathode immersed in water. Hydrogen is produced on the surface of the cathode. In water electrolysis, the electricity is the only energy source, and it is distinguished from direct photocatalysis of the water dissociation reaction or photo-assisted electrolysis. Besides the flexibility of integration with different solar power generation technologies and engineering maturity, another advantage of electrolysis is other renewable sources of power can be used when sunlight is not available. Since electricity is the energy source to the electrolyser, the electrolytic facilities do not require occupying space when solar capture is optimal. Also, unforeseeable safety impacts are lowered by the possible distance between the electrolyser and the solar thermal plant. However, the high consumption of electricity by an electrolyser leads to increases in the hydrogen production costs [88]. This cost could be minimised, and it would be competitive, only if the required input energy was supplied from renewable energy sources.

Figure 5 illustrates three key electrolyser technologies: the best-known alkaline electrolyser (AE), proton-exchange membrane (PEM) electrolysers and solid oxide electrolyser (SOE). Each alternative has advantages and challenges for development and integration with renewable sources of energy. According to the International Energy Agency (see Figure 5), SOEs have the highest potential for efficiency gains among commercial configurations.

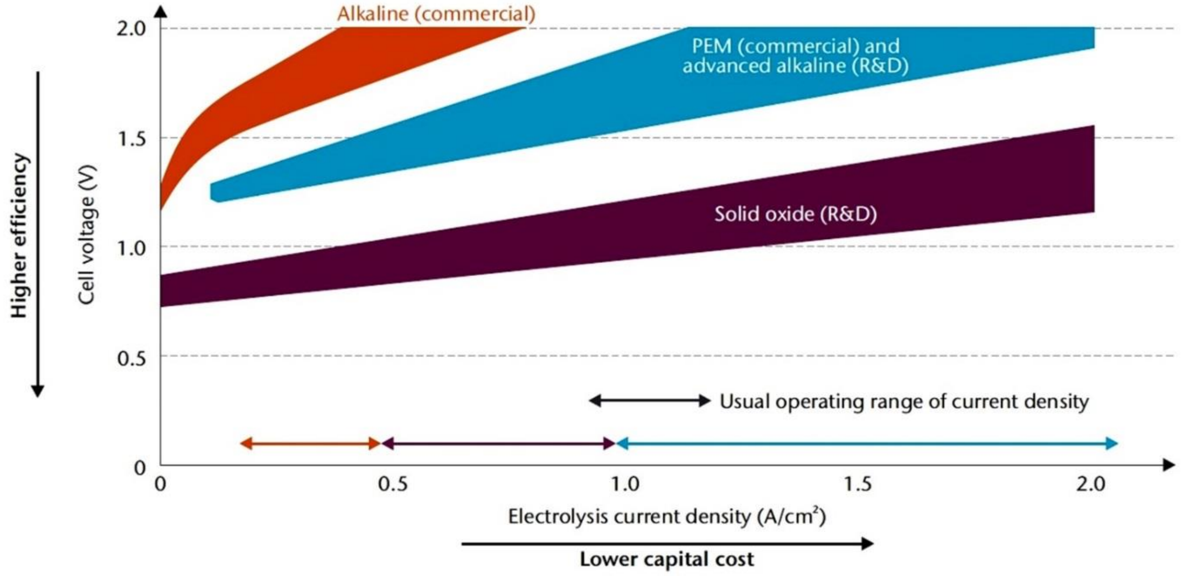


Figure 5: Development potential for main electrolyser technologies (Source: IEA (2015) Technology Roadmap Hydrogen and Fuel Cells. All rights reserved.) [55]

3.5.2. Thermo-electrolysis

In thermo-electrolysis H_2 is produced from steam with high efficiency and high purity. From the thermodynamic points of view, it is beneficial to run the electrolyser at high temperatures (700–1000°C) where a significant fraction of the required power is delivered as thermal energy so that the primary energy demand is significantly reduced. In contrast, for low-temperature electrolysis (70–80°C), a more significant quantity of electrical energy is required to dominate the endothermic reaction. Moreover, at high-temperature conditions, the reaction kinetics of the electrolyser increase and, as a result, electrical losses in the cell decrease. This is due to the lower polarisation losses from the electrode reactions as well as lower ohmic resistance in the electrolyte[76]. SOE is used for electrolysis of water in a gaseous state at high temperatures, whereas research into the use of AE at high temperature (200°C) is somewhat limited so far [151]. At high temperatures, there is an impediment for AE, predominantly at high current densities, which is the lower stability of the materials such as electrodes and diaphragms. Suitable materials are currently available, but their durability still needs to be proved [151]. At high heating values (HHV), the efficiency of SOE is higher than 95%, with promising stacks output (e.g., high yield of hydrogen and syngas) at high current densities. However, SOE suffers from significant degradation at high current densities, such as an increase of cell resistance and the occurrence of structural corrosion at both electrodes. Overall, with this process, the hydrogen production cost will be competitive compared to low-temperature electrolysis because of lower electricity consumption and longer lifespan. Currently, around

80% of the estimated hydrogen and syngas production price depends on electricity, and the investment costs (such as stack and balance) tend to have minor significance [151].

3.5.3. Thermolysis

Thermolytic water splitting is a process whereby a higher temperature is used to break down water into hydrogen and oxygen. In this process, water is usually decomposed at ~2500°C and the challenge is the stability of materials at this high temperature and the scarcity of sustainable heat sources [38]. Another drawback of this process is the lack of a useful gas separation technique of the explosive mixture. The existing semi-permeable membrane based on ZrO_2 and other high-temperature materials can be employed at the thermolysis temperature. However, gas separation is only possible when the gas mixture temperature decreases, and the gas mixture can then be effectively separated by palladium membranes [152]. Different chemical reagents have been suggested to lessen the operating limitations of thermolysis. This leads to the final category of hydrogen generation pathways through water splitting called thermochemical processes (Table 1) which warrant a separate section.

3.5.4. Thermochemical water splitting

The most direct reaction to split water is the single-step thermal dissociation of water; however, its adverse thermodynamics makes the process one of the most challenging for practical implementation. The need for a high-temperature heat source (~2500°C) for dissociation of water and the necessity of a useful technique to separate these gases at high temperatures while avoiding an explosive mixture are significant obstacles to technical success. Therefore, thermochemical cycles that avoid the separation issue while permitting operation at moderately elevated temperatures is considered a feasible alternative. Several thermodynamic cycles have been studied, with most of the current research works focusing on two-step reactions, i.e. thermal reduction and re-oxidation of materials containing cerium and iron oxides.

Indeed, over 300 water-splitting cycles have been reported so far [91]. Typically, water can be split by a two-step process that relies on the reduction and subsequent re-oxidation of metal oxides (MOs), that helps to decrease the temperature to about 1000°C [153]. Two-step cycles can be categorized into volatile and non-volatile. Overall, the former has greater oxygen conversion ability than the latter because reduction is thermodynamically more feasible as a result of the higher entropy changes during gas-solid phase transitions [154]. On the other hand, multistep cycles are metal oxide in aggregation with harsh acids or bases. Most processes significantly reduce the operating temperature to around 900°C, but high pressure is required. By proper sizing and optimisation of the system, it would be possible to enhance thermal efficiency, and proper estimation of the relationships between thermodynamic losses, capital costs, and thermal process efficiency may help to reduce the hydrogen production cost [91]. These processes are elaborated in the next sections.

3.5.4.1. Two-step cycles

The concept of using metal oxide-based redox (reduction-oxidation reaction) materials in two-step cycles was first considered in the late 1970s [155, 156]. The general concept of the process shown in Figure 6.

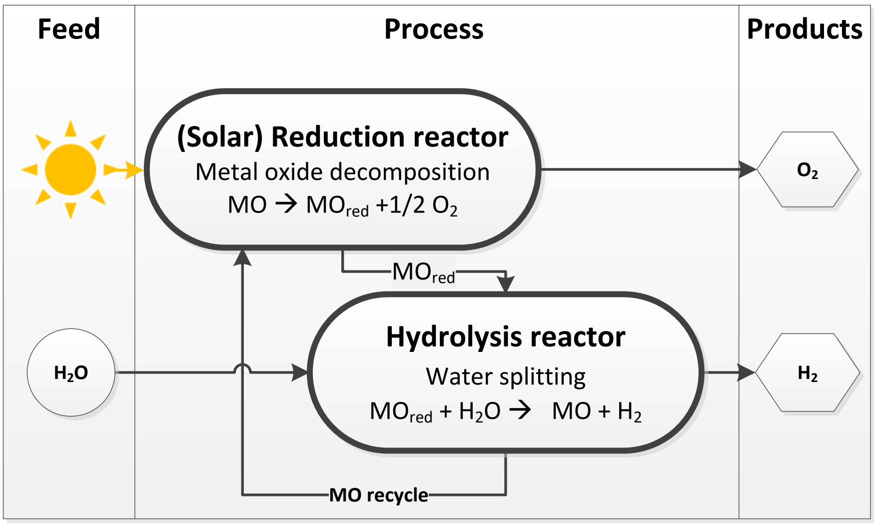


Figure 6: Two-step thermochemical water splitting (MO: metal oxide) [78, 155, 156]

MO in Figure 6 denotes metal-based redox material, which is either reduced (MO_{red}) to produce oxygen or oxidised (MO_{ox}) to produce hydrogen. Sometimes, MO_{red} denotes an elemental metal. The first step, as shown in Figure 6, is the solar-driven endothermic dissociation of metal oxide to the elemental metal or a lower-valence metal oxide [157].

The processing temperatures of each step depend forcefully on the applied material and are reviewed herein. The thermal reduction typically happens at much higher temperatures than the water splitting, $T_{red} > T_{ox}$ [158, 159]. The thermochemical conversion efficiency is therefore defined as the ratio of the fuel net heating value, ΔH_{fuel}, to the net thermal input, Q_{TC}:

$$\eta_{\mathrm{conv}} = \frac{\Delta H_{\mathrm{fuel}}}{Q_{\mathrm{TC}}} \tag{2}$$

Typically, the thermal efficiency of more than 36% implies annual solar to the fuel efficiency of 20% for H_2 production using a metal oxide solar thermodynamical approach [160]. In 2008, Diver and Kolb performed a screening analysis of potential solar thermochemical hydrogen production via various cycles to support the U.S. DOE-funded hydrogen production program

[161], as shown in Table 2. They assessed numerous thermochemical concepts including multistep, relatively low-temperature cycles, e.g., hybrid Cu-Cl, two-step and non-volatile metal oxides cycles and high-temperature cycles such as ZnO/Zn.

Table 2: Estimated thermochemical and annual efficiency of various solar thermochemical H_2 production routes[161]

Cycle name	Temperature (K)	Thermochemical efficiency (HHV) (%)	Annual efficiency (%)
Copper chloride	873	44	21
Zinc oxide	2073	45	17
Two-step MO_x	2073	52	25
Hybrid sulphur	1123	50	22

Based on the comparison by Diver and Kolb, non-volatile metal oxide cycles may be suitable for higher conversion efficiencies compared to low-temperature electrolysis [161]. Redox materials, however, should fulfil a wide variety of properties [157]: thermodynamics is an essential condition. In addition, it is a prerequisite for water splitting purposes that the materials have a less noble character than H_2 in their lower oxidation state. For the reverse reaction from high oxidation state to low oxidation state (known as the regeneration of the redox material), the energetic expense of the reverse reaction has to be minimum. It is thermodynamically advantageous to perform the regeneration at the highest possible temperatures (Figure 7). Change of solid-state entropy during the redox reaction ($\Delta S_{\mathrm{redox}}$) is equal to $S_{\mathrm{red}} - S_{\mathrm{ox}}$. The window of the thermodynamically favourable temperature of water splitting and thermal reduction is widened, if $\Delta S >> 0$. According to Figure 7, a high entropy gain is advantageous. This is due to the fact that the change of Gibbs free energy with respect to temperature (dG/dT) corresponds to the entropy of reaction. Nevertheless, most redox material systems show negative changes in entropy. This makes the $\Delta S_{\mathrm{redox}}$ a further penalty for the thermodynamics of two-step cycles. Besides these considerations, the temperature spans of real gas splitting reactors are limited due to very slow rates at splitting temperatures lower than 973 K as well as irreversible material degradation problems caused at reduction temperatures above 1973 K.

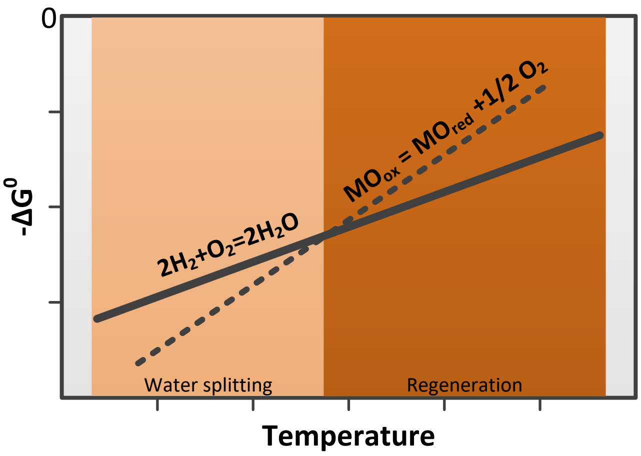


Figure 7: Free enthalpy of idealized $MO_{ox} \leftrightarrow MO_{red} + 1/2\ O_2$ redox reaction compared to H_2/H_2O equilibrium.

Other important criteria include microstructural stability, available reaction surfaces of the redox materials, atomic mobility, along with the type of solid-state transformation reaction. Particular multivalent MO systems are advantageous for nucleation as the change of oxidation states might be completed within one parent structure. For instance, CeO_2 crystallises in a fluorite-type structure and is condensed to $CeO_{1.65}$ w/o a structural dissociation of the fluorite base structure.

One possible drawback arising from high atomic mobility, nevertheless, is quick sintering and coarsening of the redox materials. According to Miller et al. [162], high surface areas are beneficial for the gas/solid redox reactions, but the sintering impacts eased by high atomic mobility neutralize the small particle size of the starting redox material. Therefore, microstructural design techniques should be employed to keep high surface areas of porous bodies of redox material. The role of material science is not restricted to introducing suitable redox agents, and research has been focused on the microstructural stability of the substances, on the kinetics and the reaction kinetics of atomic diffusion, rate and the type of transformation on catalysts' stability and activity, which are briefly reviewed here.

Zinc oxide cycle

Volatile redox pairs used in two-step cycles show a phase transition in the reduction phase. This is due to the lower boiling point of the reduced species compared with the reduction temperature (Zn melts at 692 K and boils at 1180 K). It appears that the most favourable volatile candidate redox pairs for the thermochemical splitting of water are as follows:

Thermal reduction at 2173 K:

$$ZnO_{(s)} \rightarrow Zn_{(g)} + \frac{1}{2}O_2 \qquad (3)$$

Water splitting at 773 K:

$$\mathrm{Zn_{(s)} + H_2O_{(g)} \rightarrow ZnO_{(s)} + H_{2(g)}} \tag{4}$$

Many articles have focused on ZnO/Zn cycles, e.g., [82, 158, 163]. Such cycles theoretically can produce a significant amount of H_2 i.e. 12.3 mmol H_2 per gram of ZnO; nevertheless, high H_2 productivity is restricted by the partial recombination of O_2 and Zn during gas cooling after the reduction phase. The quenching of the gases causes significant technical challenges, particularly for the reactor design.

Iron oxide cycle

The quenching drawback of volatile materials has motivated research into non-volatile materials, e.g., Fe_3O_4/FeO or dropped ferrites such as that introduced by [156, 164, 165]. In iron oxide cycle, water reacts with FeO (wüstite) to form hydrogen and Fe_3O_4 (magnetite). In the next step, Fe_3O_4 is thermally reduced to form oxygen and wüstite again according to the reactions listed below:

Water splitting:

$$\mathrm{3\ FeO + H_2O \rightarrow Fe_3O_4 + H_2} \tag{5}$$

Thermal reduction:

$$\mathrm{Fe_3O_4 \rightarrow 3\ FeO + \frac{1}{2} O_2} \tag{6}$$

Thermodynamically, reaction (5) is slightly exothermic, continues at temperatures lower than 1273 K and at the pressure of 1 bar. Reaction (6) is highly endothermic and proceeds at temperatures higher than 2573 K in the air [159]. The temperature reaction (6) is higher than the melting points of FeO (1643 K) and Fe_3O_4 (1808 K), bringing about a liquid FeO and Fe_3O_4 phase, which has led to the occurrence of sintering phenomena and a rapid decrease in material performance. Mixed robust solutions of M_3O_4/MO (M = alkaline earth metal or transient metal) and Fe_3O_4/FeO can be reduced at lower temperatures compared to pure iron oxide system. In such systems, iron is partially substituted in Fe_3O_4 by a transition metal, e.g., cobalt (Co), zinc (Zn), manganese (Mn), or nickel (Ni) , forming mixed iron oxides or ferrites with the formulae of $(Fe_{1-x}Mx)_3O_4$, while the $(Fe_{1-x}M_x)_{1-y}O$ (reduced phase) is still capable of carrying out the hydrolysis reaction. MFe_2O_4 (M = Co, Mn, Cu, Ni, or Zn) is presently considered as the most promising non-volatile cycles since it provides substantial reactivity with water and a reasonable theoretical yield of about 4.3 mmol H_2/g of Fe_3O_4 [166]. Several studies have investigated the water-splitting capability of ferrites.

Kaneko et al. [167] studied a Zn-ferrite $ZnFe_2O_4$ system in which $ZnFe_2O_4$ breaks down in a solar reactor under argon atmosphere. The deposition reaction started at a temperature of 1500 K, and its rate increased at elevated temperatures, forming solid $Zn_xFe_{3-x}O_4$, gaseous Zn, and oxygen. In an atmospheric medium, it was also observed that $ZnFe_2O_4$ can be decomposed at ca. 1800 K, forming ZnO and Fe_3O_4. The ZnO was separated from Fe_3O_4 and deposited on the solar reactor wall. This observation suggested that Zn vaporises from $ZnFe_2O_4$ and recombines instantly with oxygen present in the air to form ZnO [168]. Tamaura et al. [169] also studied the mechanism of hydrogen production with a $ZnO/Fe_3O_4/H_2O$ system at temperature range of 973–1073 K, where they observed that a nonstoichiometric spinel product was formed that contains lower zinc content than the stoichiometric $ZnFe_2O_4$. However, the authors disregarded the process. The reason is that the separated Fe_3O_4 and ZnO should be amassed and then mixed after each reduction step that makes the reactor design and process operation complicated. Siegel and co-workers [170, 171] investigated a monolithic ring structure consisting of ferrite and yttrium-stabilized zirconia (YSZ) phase assembly, with a series of material screenings, i.e., Mn, NiMn, Ni, and Co-ferrite powders. They observed promising performance with Ni- and Co-ferrite materials, where 36 cycles could be carried out with a $Co_{0.67}Fe_{2.33}O_4$/YSZ monolith under T_{red} (reduction temperature) of 1673 K and T_{ox} (splitting temperature) of 1373–1673 K. No substantial degradation of the hydrogen produced in a cycle was seen. For comparison, a monolith containing pure $Co_{0.67}Fe_{2.33}O_4$ was also examined, where hydrogen was produced only in the first cycle, confirming the need for YSZ to avoid deactivation of the ferrite. Furthermore, Miller et al. substituted the YSZ with other support materials such as titanium oxide (TiO_2), aluminium oxide (Al_2O_3), hafnium oxide (HfO_2) and yttrium-doped hafnium oxide (Y-HfO_2). Monoliths containing $Co_{0.67}Fe_{2.33}O_4/TiO_2$ and $Co_{0.67}Fe_{2.33}O_4/Al_2O_3$ formed only tiny quantities of hydrogen thru water-splitting reactions. Mixtures of $Co_{0.67}Fe_{2.33}O_4$/Y-HfO_2 and $Co_{0.67}Fe_{2.33}O_4/HfO_2$ produced hydrogen during repeated cycling; nonetheless, the amount of the produced hydrogen was still less than that obtained with the $Co_{0.67}Fe_{2.33}O_4$/YSZ monolith. These studies highlighted that the support structure plays an essential role in the reduction and splitting reactions [162].

Gokon et al. [172] studied a ceramic foam device coated to examine splitting the cycle of Fe_3O_4 or $NiFe_2O_4$ powder supported on monoclinic ZrO_2 (Fe_3O_4/m-ZrO_2 and $NiFe_2O_4$/m-ZrO_2). Ten repeated cycles were undertaken with a $NiFe_2O_4$/m-ZrO_2 foam device at T_{red} of 1673–1723 K and T_{ox} of 1373 K. Scheffe and Weimer [173] investigated $CoFe_2O_4$ deposited on Al_2O_3 supports using atomic layer deposition to form nanoscale films on particles of different substrates. Multilayers of Fe_2O_3 and CoO were deposited consecutively onto porous Al_2O_3 substrates to form a 5 nm film on the substrate. Reduction temperature of $CoFe_2O_4$ on Al_2O_3 was 1473 K, i.e., ca. 200 K lower than $CoFe_2O_4$ coated on ZrO_2, forming cobalt aluminate ($CoAl_2O_4$) and hercynite ($FeAl_2O_4$). While the reaction of H_2O and $FeAl_2O_4$ is less thermodynamically favourable than H_2O and FeO, it was demonstrated that water to produce H_2 is possible if non-equilibrium conditions are kept. A substantial amount of H_2 was produced at T_{red} of only 1473 K, whereas $CoFe_2O_4$ produced slight or no quantity of H_2 until the same reduction temperature was reached.

Ceria

The capability of ceria for storing and releasing oxygen is well established. Otsuka et al. [174] proposed ceria as a potential material for water-splitting applications. More recently, ceria has received considerable attention as a material capable of use in two-step cycles. Ceria exists in both Ce^{+3} and Ce^{+4} oxidation states. The complete two-step cycle can be shown as follows:

Thermal reduction:

$$2\,\mathrm{CeO_2} \rightarrow \mathrm{Ce_2O_3} + \frac{1}{2}\mathrm{O_2} \tag{7}$$

Water splitting:

$$\mathrm{Ce_2O_3} + \mathrm{H_2O} \rightarrow 2\,\mathrm{CeO_2} + \mathrm{H_2} \tag{8}$$

Abanades and Flamant [175] were among the first to study the water-splitting in a solar reactor in lab-scale ceria. The splitting process was conducted via a fixed bed reactor. Complete conversion of the Ce_2O_3 to CeO_2 was observed due to the high reactivity of water with the reduced cerium oxide. The thermal reduction was done at T_{red}=2273 K and P_{red}=100–200 mbar. These high temperatures essential for the reduction resulted in practical design issues for reactors, to avoid ceria evaporation and high energy loss. Whereas the reduction process starts at about 1673 K under oxygen-deficient conditions, other researchers have concentrated on partially-reduced ceria systems. In this case, only a fraction of the cerium atoms mutate their oxidation state.

Thermal reduction:

$$\mathrm{CeO_2} \rightarrow \mathrm{CeO_{2-x}} + \frac{x}{2}\mathrm{O_2} \tag{9}$$

Water splitting:

$$\mathrm{CeO_{2-x}} + x\,\mathrm{H_2O} \rightarrow \mathrm{CeO_2} + x\,\mathrm{H_2} \tag{10}$$

However, because this cycle is nonstoichiometric, low specific hydrogen yields may be expected. Ceria suffers sintering that commonly occurs at high temperatures, along with the problem that storage and release of oxygen happen at the surface. These adverse properties of ceria are mitigated through modification via doping with oxides that show very similar crystal structure as proposed to decrease the ceria grain growth, as well as to render the material more amenable to reduction [176]. Kaneko et al. [177] studied thermochemical two-step cycle at 1273–1673 K using ceria doped with transition metals (Ni, Fe, Mn, Cu). They reported yields of ca. 0.08 mmol H_2/ gram of material for CeO_2-NiO and CeO_2-MnO. CeO_2-Fe_2O_3 performed better than non-doped CeO_2, while Cu did not better the splitting properties of ceria.

Perovskites

An alternative thermochemical two-step cycle has been introduced using materials with a perovskite ($CaTiO_3$) structure. Evdou et al. [178] used thermogravimetric oxidation/reduction experiments to study the redox potential of perovskite materials with the general formula of $La_{1-x}Sr_xMO_3$ (M = Fe or Mn and x = 0; 0.3; 0.7; 1). Partial oxidation of methane was used to obtain a more efficient and isothermal condition process rather than the two-step cycle, as follows:

CH_4-Reduction:

$$\mathrm{MO_{ox}} + \beta\mathrm{CH_4} \rightarrow \mathrm{MO_{red}} + \beta_1\mathrm{CO} + \beta_2\mathrm{CO_2} + \beta_3\mathrm{H_2} + \beta_4\mathrm{H_2O} \tag{11}$$

Thermogravimetry at 1173 K and by changing O_2/He and CH_4/He intake indicated that the materials could lose and take up oxygen reversibly from their lattice up to 1.7 wt% for $LaFeO_3$ and up to 5.5 wt.% for $SrMnO_3$ per minute. This means that 0.25 and 1.7 mmol of O_2/g were respectively released. The extent of reaction associated with the materials was seen to be five times greater than that observed with ceria, and they exhibited superior kinetics thru the reduction and oxidation cycles. Stability was kept during 80 complete cycles.

3.5.4.2. Three-step cycles

Sulphur-iodine cycle

The sulphur-iodine (S-I) cycle is a favourable thermochemical water splitting process first reported in the mid-1970s by General Atomics (GA) [179]. This thermochemical cycle comprises three successive reactions (shown in Figure 8) to produce hydrogen.

Exothermic hydrolysis at 393 K:

$$\mathrm{I_2(l+g)} + \mathrm{SO_2(g)} + \mathrm{2H_2O(g)} \rightarrow \mathrm{2HI(g)} + \mathrm{H_2SO_4(l)} \tag{12}$$

Endothermic oxygen production at 1123 K:

$$H_2SO_4(g) \rightarrow SO_2(g) + H_2O(g) + \frac{1}{2}O_2(g) \tag{13}$$

Endothermic hydrogen production at 723 K:

$$2HI(g) \rightarrow I_2(g) + H_2(g) \tag{14}$$

The requisite temperature of each step usually depends on reactor technology. For example, Kubo et al. [180] adopted 1223 K in step 2, and Schultz [179] reported an even lower temperature. However, it is difficult to differentiate the cycle type by these temperature differences. The thermochemical cycles could be coupled with the output heat of power generators that use solar, nuclear, or geothermal energy [181]. The presence of iodine-based compounds in the S-I cycle creates some important engineering challenges, such as the need for extra safeguards to handle the mixture of flammable I_2 and H_2 at 723 K. Additionally, the separation of HI, I_2 and H_2 is a complex multiple-stage process, and the distillation of azeotropic HI would drastically increase the cycle energy costs [181].

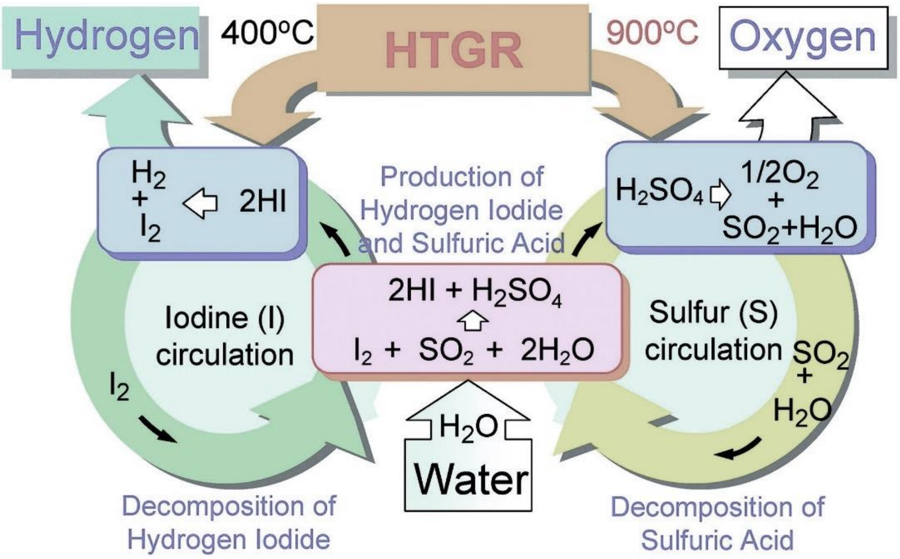


Figure 8: The S-I cycle thermochemical for hydrogen production (Image: adopted with permission from the Royal Society of Chemistry [182])

3.5.4.3. Four-step cycles

Copper-chlorine (CU-Cl) cycle

The Cu-Cl cycle is a promising thermochemical alternative for producing hydrogen because of its lower temperature requirement around 803 K. In 1976, Dokyia and Kotera [183] proposed an electrolytic process of the Cu-Cl cycle for hydrogen production as two- and three-step cycles. The number of significant steps characterises the different Cu-Cl cycle types and their type of grouping. For example, Rosen et al. [184] described a conceptual loop encompassing five steps whereas Lewis et al. [185, 186] defined four- and five-step Cu-Cl cycles. In another study, Ewan and Allen suggested a merely thermal reaction pathway to produce hydrogen with low yield [187]. The chemical reaction of four-step cycles is as follows:

Exothermic chlorination at 723 K:

$$\mathrm{2Cu(s) + 2HCl(g) = 2CuCl(molten) + H_2(g)} \tag{15}$$

Disproportionation in the HCl (aq), at 303–353 K:

$$\mathrm{4CuCl(s) = 2Cu(s) + 2CuCl_2(aq)} \tag{16}$$

Endothermic oxychlorination at 648 K (n_f, the quantity of free water in a mole is 30–50):

$$\mathrm{CuCl_2(aq)} + n_f\mathrm{H_2O(l) = CuOCuCl_2(s) + 2HCl(g)} + \left(n_f - 1\right)\mathrm{H_2O(g)} \tag{17}$$

Endothermic decomposition at 803 K:

$$\mathrm{CuOCuCl_2(s) = 2CuCl(molten)} + \frac{1}{2}\mathrm{O_2(g)} \tag{18}$$

The Cu-Cl cycle has gained significant attention because it can be coupled with solar thermal energy and relatively lower temperature is required [186, 188]. Due to the multiple steps of water dissociation, it requires multiple chemical reactors and auxiliary equipment in comparison to metal redox cycles. As a result, it may incur high hydrogen production costs in small-scale projects. To offset such costs, large-scale hydrogen production is suggested. Also, to collect and store the heat in working fluids is a complex engineering problem, because fluids differ in characteristics such as volatility, toxicity, melting point, liability to decompose at high temperatures, and need for different materials in working fluid vessels [181].

3.5.4.4. Hybrid thermochemical-electrochemical cycles

Two-step hybrid sulphur cycle

The sulphur-based thermochemical cycle is called the “hybrid sulphur cycle” or “Westinghouse cycle” and has received significant attention due to its lower operating temperature (about 353 K) during the electrolysis of aqueous SO_2 solution. The hybrid sulphur cycle, initially proposed by Brecher et al. [189], is a two-step cycle to decompose water (Figure 91 left). It is a hybrid cycle since it combines the thermal decomposition of $\mathrm{H_2SO_4}$ with an electrochemical step which substitutes the Bunsen reaction (equation 12) and the HI decomposition reaction of the S-I cycle, and can be shown as follows:

Thermochemical at >723 k:

$$\mathrm{H_2SO_4 \rightarrow H_2O + SO_3} \tag{19}$$

Thermochemical at 1173–1273 K:

$$SO_3 \rightarrow SO_2 + \tfrac{1}{2}O_2 \tag{20}$$

Electrolysis at 353 K:

$$SO_2 + 2H_2O \rightarrow H_2 + H_2SO_4 \tag{21}$$

The required voltage for the electrolysis is significantly lower than that required for electrolysis, hence the electrical power consumption is lower. Water and sulphur dioxide react electrolytically to generate hydrogen and sulphuric acid. The produced sulphuric acid is first decomposed (vaporised to produce sulphur trioxide and steam), which is then further decomposed at high temperature into oxygen and sulphur dioxide. The advantage of this process compared to direct water electrolysis is its lower electric power needs.

Single-step hybrid sulphur cycle

An alternative to the described two-step hybrid sulphur cycle is a once-through process (Figure 9 right) [87]. The governing equations are:

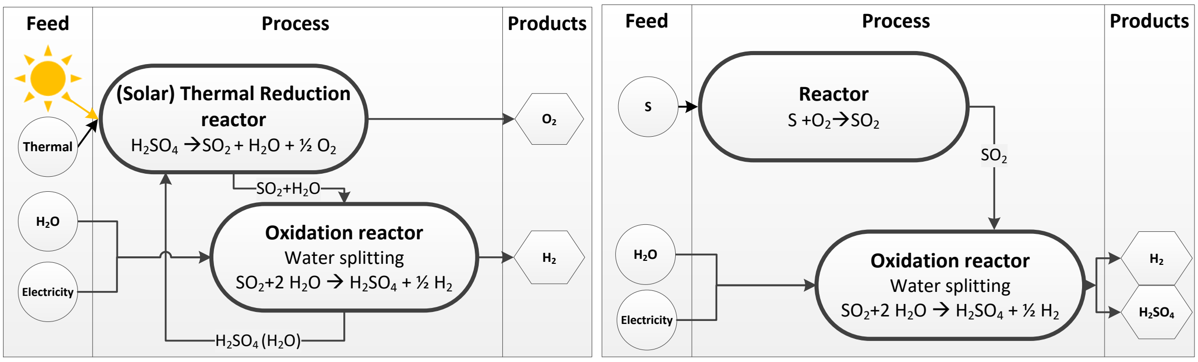
Thermochemical:

$$S\ (s) + O_2(g) \rightarrow SO_2(g) \tag{22}$$

Electrolysis:

$$SO_2(aq) + 2H_2O\ (l) \rightarrow H_2SO_4(aq) + H_2(g) \tag{23}$$

Further to the operability advantage of the single-stage process, it offers better economics in locations with access to sulphur as it consumes sulphur and produces sulphuric acid as a byproduct. Therefore, this process can be of interest to crude oil refineries where substantial amounts of sulphur are produced, while they also have significant hydrogen demand.



Original (looping) hybrid sulfur process **Once-through hybrid sulfur process**

Figure 9: Schematic of conventional two-step (left) and alternative once-through (right) hybrid sulphur cycles [87]

3.5.5. Photocatalysis

In this approach, photoelectrochemical (PEC) light-collecting systems are used to power the water electrolysis process. When it is exposed to sunlight, a semiconductor photo-electrode which is submerged in aqueous electrolyte solution produces enough electricity to split water. Depending on the solar intensity and the type of semiconductor material, the current density varies in the range 10–30 mA/cm^2 and the required voltage for electrolysis is about 1.35 V [91]. In this process of splitting water, several prerequisites are apparent. First, the energy rating of the semiconductor materials ought to overlap the energy levels of the oxygen and hydrogen reduction reactions. Second, the semiconductor system should be stable under photoelectrolysis circumstances. Finally, the charge removed from the semiconductor surface has to be fast enough to avoid corrosion issues, which helps to reduce energy loss. This process is presently the least-cost and most-efficient method of producing renewable hydrogen. The production technology is still in the experimental stage but has already shown a promising efficiency and hydrogen generation costs [190].

4. Hydrogen transmission and distribution

Depending on the hydrogen amount and distance, hydrogen can be transported from production facilities to retailers via various means. For instance, as illustrated in Figure 10, the hydrogen to refuelling stations could be supplied by each of these means:

1) hydrogen can be transported from a centralised hydrogen production facility via gaseous trucks (hydrogen pressure levels for gaseous truck transport range over 35 MPa to 50 MPa), liquefied trucks, or pipelines (Table 3)[55];

2) alternatively, it can be produced at the local refuelling station via reformers (i.e. SR, POX, etc.) or small-scale electrolysers.

For small quantities and short distances, delivery of gaseous hydrogen via tube trailers is usually the best option [191]. For long distances and average hydrogen amounts, on the other hand, liquid tankers are preferred. Typical tankers capacity is 400 to 4000 kg of liquid hydrogen; however, boil-off can occur during liquid hydrogen transport. Liquid H_2 can also be transported by train or by ship, provided that appropriate railway lines, waterways, together with loading terminals are available. Pipelines are the best option to transport hydrogen for large amounts over long distances. Extensive experience in hydrogen transport via pipeline grids already exists, e.g. in 2016 worldwide hydrogen transport via pipeline was more than 4500 km, the share of Europe amounted up to 1600 km, while in the U.S. nearby 2608 km were in place [192]. Injecting hydrogen into gas transmission grid and downstream separating/purifying to extract pure hydrogen from the natural gas is an alternative of delivering hydrogen to end-users and markets [192]. Hydrogen-rich town gas or coke-oven gas was distributed to households in the USA, Germany, and England via gas pipelines.

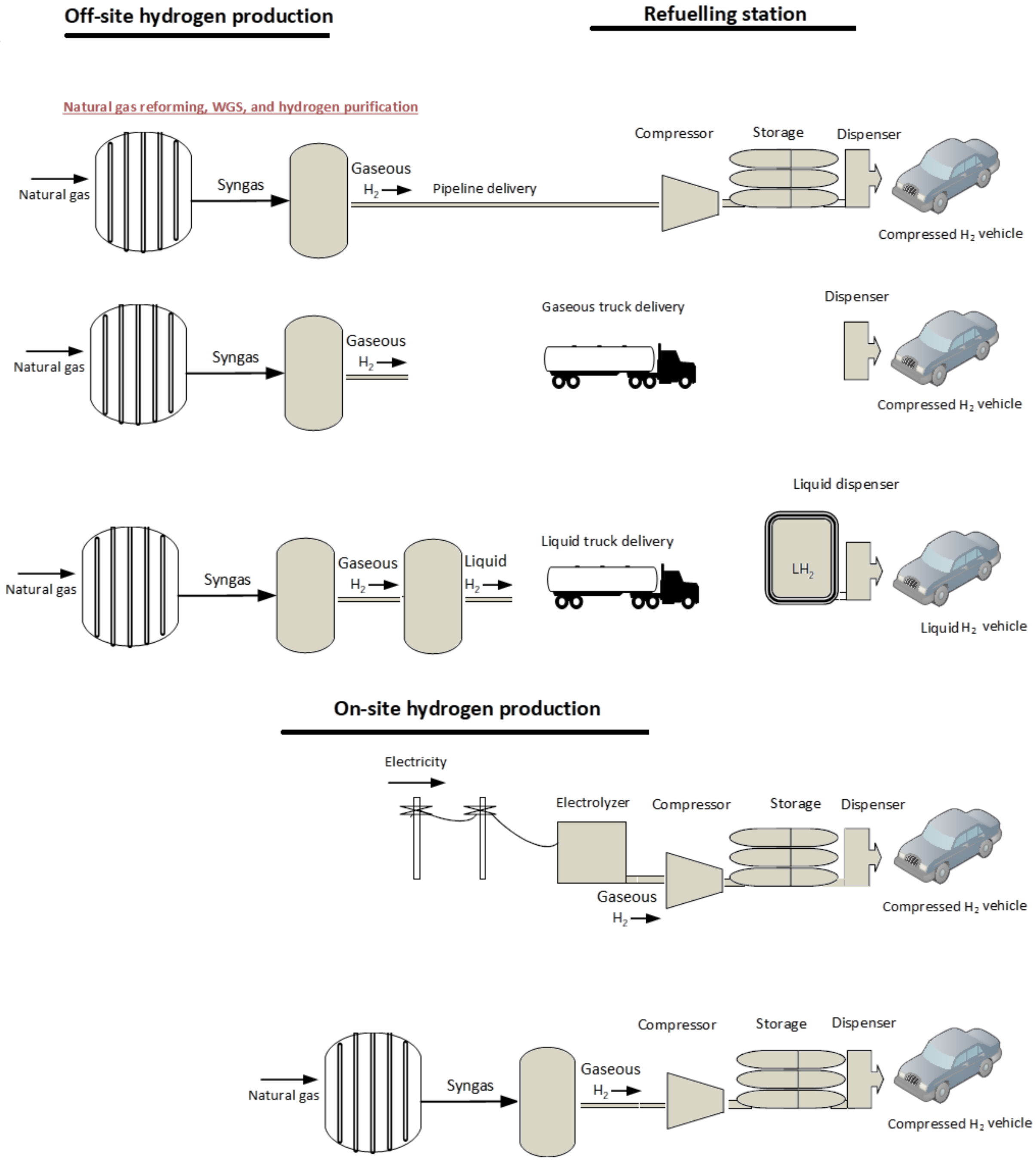


Figure 10: Hydrogen transport from production facilities to refuelling stations

Each of on-site or off-site hydrogen generation approaches has its pros and cons. Off-site, large-scale hydrogen generation suggests economies of scale (i.e. lower generation cost) but results in higher transmission and distribution costs. On the other hand, the opposite of this statement is true for on-site (decentralised) hydrogen production. While transmission and distribution costs are lowered, smaller-scale hydrogen generation imposes costs at the hydrogen generation stage. To find the optimal network configuration (including production, transmission and distribution) necessitates a detailed analysis considering the full range of impacting factors including existing hydrogen production and transmission and distribution infrastructure, availability of resources for hydrogen production, distance of hydrogen production place and end-users, and demand of the retail (refuelling) stations. Nevertheless, economies of scale of off-site hydrogen generation facilities potentially outweigh the additional costs incurred from longer transmission and distribution distances. A trade-off does exist between fixed capital investment and variable costs of hydrogen transmission and distribution options: gaseous hydrogen carriers has the lowest fixed investment cost and high variable costs because of the lower transport capacity (Table 3). On the other hand, in the case of pipelines transport, fixed investment cost is high, and the variable cost is low. The variable costs of pipeline transport are low when the pipeline network is fully utilised.

Table 3: Overview of hydrogen transmission and distribution options (L: low, M: medium, H: high) [55]

Hydrogen delivery option	Capacity	Transport distance	Energy loss	Fixed costs	Variable costs	Deployment phase
Hydrogen pipelines	H	H	L	H	L	Medium to long term
Gaseous tube trailers	L	L	L	L	H	Near term
Liquefied truck trailers	M	H	H	M	M	Medium to long term

It is estimated that liquid hydrogen delivery via tankers can cost around €0.13/kg, which is close to the U.S.-DOE estimate of €0.15/kg [191]. Tube trailers may contain 300 kg of gas at 200 bar and are used for small deliveries and short distances to cut the high cost of carrying small amounts of hydrogen. The cost of hydrogen transport via tube trailers (excl. compression) over a distance of 100 km is approximately €0.6/kg. The cost of hydrogen transport with tube trailer including compression could reach €2.2/kg [191]. Hydrogen transportation pipelines are typically 10–12” in diameter and operate at 10–20 bar [191]. Cost of transporting 5 bm^3 H_2/year via pipeline is €0.261 /kg, while this cost is reduced to €0.185 /kg for a capacity of 10 bm^3 H_2/year [191]. On the other hand, transporting 30 bm^3 H_2/year via pipeline costs €0.139/kg. In [193], hydrogen delivery costs as a function of the delivery pathway (i.e. pipeline, pipeline-tube trailer, and tube trailer), dispensed gas pressure (350 bar and 700 bar), and year (2005, 2011, 2013, 2020) is given. The projected hydrogen delivery cost for 350 and 700 bar gas and for all delivery pathways in 2020 is expected to reach \$2/kg H_2 delivered and dispensed.

5. Key hydrogen storage and conversion options

Use of hydrogen for energy storage for short-, medium- or long-term is referred to as time-shifting with hydrogen [5]. Hydrogen can be utilised as a chemical energy storage medium [37, 194, 195]. The energy captured from renewables (e.g. wind and PV solar cells) can be stored as hydrogen to produce electricity and/or heat, on-demand for off-grid locations. The primary advantage of H_2 storage over other energy storage alternatives such as batteries is its potential for seasonal and long-term storage. Energy can be stored in large quantities such as terawatt-hours, for a long time and in different forms. The lower heating value (LHV) of pure hydrogen is ca. 120 MJ/kg, compared to around 40 MJ/kg of petroleum products and approximately 50 MJ/kg of methane. The energy density of various energy storage options is provided elsewhere (Table 3.1 in [196]). Although the LHV of hydrogen is extremely favourable, the issue lies with its low volumetric energy density of 0.0823 kg/m^3 at ambient conditions (298 K and atmospheric pressure) [70]. Therefore, improving its volumetric energy density is a necessary step towards facilitating optimal hydrogen storage. The possible options are compression, liquefaction, and storing hydrogen in liquids and solid materials, all of which are briefly discussed in the next sections.

5.1. Gaseous hydrogen

Compression of hydrogen is the most straightforward storage system. Its advantages include ease of operation at ambient temperature along with its simple storage and retrieval. Compressing hydrogen rises its density to nearly 23.32 kg/m^3 at 350 bar (common pressure of fuel-cell buses) and to 39.22 kg/m^3 at 700 bar (common pressure of commercial fuel-cell passenger cars) [146]. Cryo-compression to the pressure of 200 bar and 100 K results in a density of ca. 39.52 kg/m^3 [146], matching that of compression to 700 bar and 25°C, while partially trading one technical difficulty (cryogenic temperature) for another (high pressure).

Storing compressed hydrogen is nowadays a commercial fact in fuel cell vehicles and refuelling stations. The commonly named type IV storage tank can be used in vehicles and has a cylindrical composite structure together with wound carbon fibre on hydrogen-impermeable liner [197, 198]. The tanks are commercially available, the low weight meets key targets, do not require internal heat exchange, well-engineered, and safety-tested [199]. The tanks also meet the standard that is adopted in several states for pressure ranges of 350–700 bar. These tanks are usable for cryo- compression. From the electrical energy storage viewpoint, storing compressed hydrogen is technically viable. There are two primary issues with compressed hydrogen storage. First, it requires an energy-demanding compression facility which imposes a substantial load on the energy system. Secondly, its operating pressure is much higher than conventional electrolysers and fuel cells, requiring pressure adjustment. Other drawbacks are large physical volume, high cost of ca. \$500–600 per kg H_2, some safety issues such as the rapid loss of H_2 in accidents.

Glass microspheres could also be utilised for storing hydrogen in gaseous form onboard a vehicle [199]. This storage approach is described by three main steps:

- Charging: hollow glass spheres are filled with H_2 at a high temperature of ca. 300°C and pressure range of 350–700 bar and via permeation in the high-pressure vessel;
- Filling: glass microspheres are cooled down to ambient temperature and then moved to a low-pressure tank onboard the vehicle;
- Discharging: glass microspheres are heated up to nearly 200–300°C for an under the controlled release of hydrogen to run the vehicle;

The glass microspheres slowly leak hydrogen at room temperature. The advantages of glass microspheres are: storage density of 5.4 wt.% hydrogen, safe operation as hydrogen is stored at a relatively low pressure onboard which are appropriate for conformable tanks leading to low container costs. The disadvantages of glass microspheres for hydrogen storage are: the high pressure required for filling, heat supply at temperatures greater than the PEM fuel cell (nearly 70–80°C), too much breakage during cycling and the intrinsically low volumetric density that can be attained.

Table 4 compares the foremost merit factors of glass microspheres and composite tanks. Generally speaking, it is likely to build safe systems, but costs should be minimized. The overall system disadvantage with glass microspheres systems is the high-temperature requirement while composite suffer from a high-pressure necessity.

Table 4: Merit factors of gaseous hydrogen storage: glass microspheres and composite tanks [199]

Parameter	**Glass microspheres**		**Composite tanks**	
	value	**comment**	**value**	**comment**
Energy density	+	Up to 5 wt.% H_2, conformable	-	Only partially-conformable
Temperature	-	High T needed	+	No heat exchanger needed
Pressure	+	Low onboard pressure possible	-	high-pressure compressors needed
Safety	+	Inherently safe	+	Existing codes and standards

Robustness	-	Breakable spheres	+	Extensively tested
Cost	NA	Needs to be determined	-	\$500–600/kg H_2

For large-scale hydrogen storage, the succedent alternatives are available for future considerations [200]:

- Storage in buried steel pipes;
- Underground storage (favourably in salt formations),
- Aboveground spherical or cylindrical steel tanks.

Technical, operational, economic, and site-specific parameters for the above storage options are given in [200]. Qualitative assessment of opportunities for hydrogen caverns of several European countries is listed in [200].

Underground storage of hydrogen in depleted oil wells and salt caverns is a mature and well-established practice [5]. Examples of gaseous hydrogen caverns are [17]:

- Clemens Dome, lake Jackson, U.S., by ConocoPhillips (storage capacity: 580,000 m^3);
- Moss Bluff salt dome, U.S., by Praxair (maximum permitted capacity: 566,000 m^3);
- Teesside, UK, by Sabic Petrochemicals (storage capacity: 3 × 70,000 m^3).

At the beginning of 2013, nearly 688 underground storage facilities were operational with a working capacity of 377 bm^3 (i.e. 10.3% of 2012 the global gas consumption) and are anticipated to reach 557–631 bm^3 by 2030 [201]. These underground facilities have been located in four regions: North America (414 sites in the U.S. plus 59 ones in Canada), Europe (144 sites), the Commonwealth of Independent States (51 facilities), Asia-Oceania (18 sites) and Iran and Argentina with one site each. In Europe, the total gas storage capacity in 2013 was 99 b m^3 with 21.5% in Germany, 16.3% in Italy, 12.9% in France, etc.

Qualitative overview of different underground hydrogen storage options including depleted oil/gas fields, salt caverns, aquifers and linked/unlinked rock caverns concerning technical feasibility, safety, capital and operational cost is given in [55]. Salt caverns are of most interest option for hydrogen storage. In another study, Bai et al. reviewed ways and mechanisms, the feasibility and the necessities of underground hydrogen storage and its perspectives in China [202].

5.2. Liquid hydrogen

The disadvantage of compressed gaseous hydrogen is a low volumetric energy density which increases transportation costs, particularly for long-distance delivery. A comparison of various

H_2 storage options regarding volumetric and gravimetric energy intensity is shown in Figure 11. For obvious reasons, the techno-economic goal is to achieve the highest intensity for both volume and weight (upper right of Figure 11). Among the current H_2 storage options, liquid-state hydrogen has the highest energy intensity.

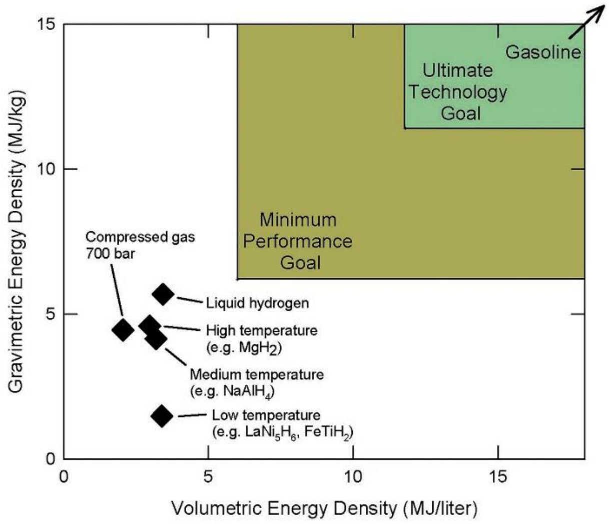


Figure 11: Volumetric and gravimetric energy intensity comparison of various hydrogen storage options (Image: courtesy of J. F. Herbst [203])

Storage of liquid hydrogen is technically feasible on a small scale and has been trialled in vehicles. However, it has been surpassed by compressed gaseous hydrogen storage. The potential role of liquid hydrogen storage in energy systems is not yet well recognized, but cryogenic hydrogen storage (in order of 100 GWh [55]) at the scale of many cubic meters of liquid is widely used in the space industry. Liquefied hydrogen is feasible in the case of large-scale export of hydrogen. Kawasaki Heavy Industry (Japan) has been moving forward with the building of small carriers of liquefied hydrogen, primarily at the 200-tonne scale [74].

Liquid hydrogen option suffers from the inevitable losses arising from boil-off as a result of the flow of heat into the reservoir from the outdoor. Additionally, hydrogen liquefaction needs an extremely load, i.e. about 35% of the LHV of the liquefied hydrogen [18]; therefore, it is better for centralised liquefaction facilities with their associated economies of scale. Other challenges are the system total volume and weight, the need for super-insulated cryogenic containers, costly tank and the ortho-para conversion [204].

Other storage alternatives include storing hydrogen in other liquids including rechargeable organic liquids, Borohydride ($NaBH_4$) solutions, or anhydrous ammonia NH_3 [199]. Some rechargeable organic liquids can be utilised for storing hydrogen in liquid form. The process can be described via three steps:

1) an organic liquid such as methylcyclohexane (C_7H_{14}) is dehydrogenated catalytically to generate hydrogen onboard vehicle;

2) the dehydrogenated product (toluene C_7H_8) is sent from the tank to a central processing facility and simultaneously feed the tank with fresh hydrogen-rich liquid;

3) to re-hydrogenate the hydrogen depleted liquid, it is brought back to the initial species and then sent it to the filling refuelling station.

$$C_7H_{14}\ (l) \Leftrightarrow C_7H_8\ (l) + 3H_2\ (g)\ \ T_{\text{dehyd}} = 300 - 400\ ℃ \tag{24}$$

The reaction (24) gives a volumetric and gravimetric energy storage density of about 43 kg H_2/m^3 and 6.1 wt.% H_2, respectively. The methylcyclohexane in the liquid state involved in the reaction (24) should be handled carefully as it is colourless liquid and reacts violently with strong oxidant compounds which can cause fire and explosion. Thereby, there is a need to accomplish comprehensive toxicity and safety studies for this hydrogen storage medium.

Borohydride ($NaBH_4$) the liquid solution can also be used for hydrogen storage [199]. The catalytic hydrolysis reaction is given by the following equation:

$$NaBH_4(l) + 2H_2O(l) \rightarrow 4H_2\ (g) + NaBO_2(s) \tag{25}$$

Theoretically, a maximum hydrogen storage density of 10.9 wt.% H_2 can be obtained in this case. The key advantage of using $NaBH_4$ solutions for hydrogen storage is that safe and under-control onboard generation of hydrogen can be obtained. The key challenge of this method is that $NaBO_2$ should be regenerated to borohydride off-board. The cost of $NaBH_4$ regeneration should reduce from ca. \$50 /kg to as low as \$1/kg.

Table 5 compares the merit features for LH_2, $NaBH_4$ solutions and the organic liquids to store hydrogen. LH_2 can meet the aviation sector fuel demand, while hydrogen storage in organic liquids and $NaBH_4$ solutions could be appropriate for refuelling purposes of private and fleet vehicles.

Table 5: Merit features for liquid H_2 storage methods [199]

Parameter	**LH_2**		**Organic liquids**		**$NaBH_4$ solutions**	
	value	**comment**	**value**	**comment**	**value**	**comment**
Pressure	+	low pressure	+		+	
Temperature	-	30–40% losses	-	$T_{\text{dehyd}}: 300 - 400℃$	+	
Safety	-	Public perception	-	Toxicity	?	
Energy density	+	100 wt.% H_2	+	6.1 wt.% H_2	+	10.9 wt.% H_2
Cost	-	Infrastructure	-	Infrastructure	-	Regeneration costs

5.3. Solid hydrogen

Hydrogen storage in solid substances is an efficient as well as safe method to store energy for either mobile or stationary applications [199]. In a comprehensive study, He et al. [205] have demonstrated the critical role of advanced materials in the development of efficient hydrogen carriers. Four key groups of suitable solid materials for hydrogen storage are:

- Rechargeable hydrides (alloys & intermetallics, nanocrystalline);
- Carbon and other high-surface-area (HSA) materials (activated charcoals, graphite nanofibers, clathrate hydrates, nanotubes, MOFs, Zeolites);
- Thermal chemical hydrides (ammonia borane, aluminium hydride);
- H_2O-reactive chemical hydrides (encapsulated NaH, LiH and MgH_2 slurries, CaH_2, $LiAlH_4$, etc.).

Hydrogen, in its molecular form, can be stored by physical adsorption process on the surface of some porous solid materials. In 2013, Dalebrook et al. [206] reviewed various methods of absorption and desorption of hydrogen. They categorised them as physisorption storage on zeolites, metal-organic frameworks (MOFs) and chemical storage in amines, formic acid, etc. In the physisorption approach, hydrogen, in its molecular form, is absorbed and then desorbed reversibly.

Carbon-based solid materials including graphite, carbon foams, activated carbon, and carbon nanotubes have received remarkable attention in the hydrogen storage sphere owing to their properties such as chemical stability, high surface area, and low weight [207, 208]. The theoretical surface area of graphene, as a single layer of graphite, is about 2630 m^2/g [209, 210], thereby it is a suitable material for physisorption storage. In addition, microporous organic polymer materials are of interest for energy storage as a result of tailored porosity and high specific surface area. Lately, polymers of intrinsic micro-porosity (PIMs) [211] and hyper-cross-linked polymers (HCPs) [212] have been considered for hydrogen storage based on physisorption at low temperatures. Covalent organic frameworks (COFs) present much more delicate control over porosity and crystallinity properties than PIMs and HCPs [213]. Innovative nano-porous materials, for instance, MOFs, have also been considered for hydrogen storage purposes [214-216]. Because of their variable building blocks, MOF materials have high porosity, well-defined hydrogen occupation sites high surface area, and adjustable and uniform pore sizes. These properties make MOFs favourable alternatives for storing hydrogen based on physisorption.

Storing hydrogen in complex hydrides or chemical metal hydrides gives a high volumetric density and low absorption pressure thru hydrogen uptake. The group of materials collectively recognised as metal hydrides (MHs) encompass a diverse class of materials including elemental metals, stoichiometric non-metallic species, and alloys. MHs can dissociate hydrogen molecules at their surface and absorb hydrogen atoms into the inner crystals structure. Absorption and desorption phenomena occur over a wide range of temperatures and pressures.

The advantages of MH storage are:

(i) The decoupling of energy and power ratings makes it more valuable than batteries for long-term storage purposes [217];

(ii) The ability to be tuned for low pressures make it suitable for direct coupling to electrolysers and near-atmospheric operating pressures;

(iii) Outstanding safety owing to the low pressure and fairly slow kinetic rates of hydrogen release; and

(iv) High volumetric storage density. For instance, the $LaNi_5H_6$ contains only 1.4 wt% hydrogen but has a 100%-dense volumetric capacity of almost 115 kg/m^3 at ambient temperature and pressures below 10 bar [218] that is comparable to 70.8 kg/m^3 at 1 bar and 20.3 K for liquified hydrogen. A list of MH materials and their mass and volume intensities is shown in Figure 12.

Comprehensive studies of hydrogen storage in solid materials are available in numerous review papers and books that have been published within the past decades [219-221]. Light-weight metals including Li, Na, and Mg form hydride materials with high gravimetric hydrogen storage capacities. The release of hydrogen, nevertheless, needs high temperatures, above 650°C for Li for example, as a result of the high enthalpy of formation. Magnesium hydride suggests the highest potential with ca. 7.6 wt.% and good reversibility property, but the desorption process is kinetically restricted. Webb [222] investigated the use of MgH_2 to enhance hydrogen sorption by adding catalytic materials along with the mechanical amendment of the material [222]. MgH_2 has the best combination of affordability and hydrogen yield [199]. The key research and development task is to lower the processing cost of the spent hydroxide back to the starting hydride. This process is an energy-intensive process, and there are uncertainties about the possibility of cost reduction for vehicle applications.

Alloying of various metals can change the enthalpy of hydrides. This method has been investigated for its potential applicability to hydrogen storage. The most useable alloys for this purpose are AB_5 intermetallic compounds —e.g., $LaNi_5$— for hydrogen storage capacity of around 1.4 wt.%, and equilibrium pressure of <2 bar at ambient temperature [219]. AB_2 compounds are obtained from the Laves phases with a storage capacity of < 2 wt.% [78]. Body-centred cubic (BCC) alloys, on the other hand, have the maximum storage capacity of up to 4 wt.% with a reversible capacity of above 2wt.% [223-225].

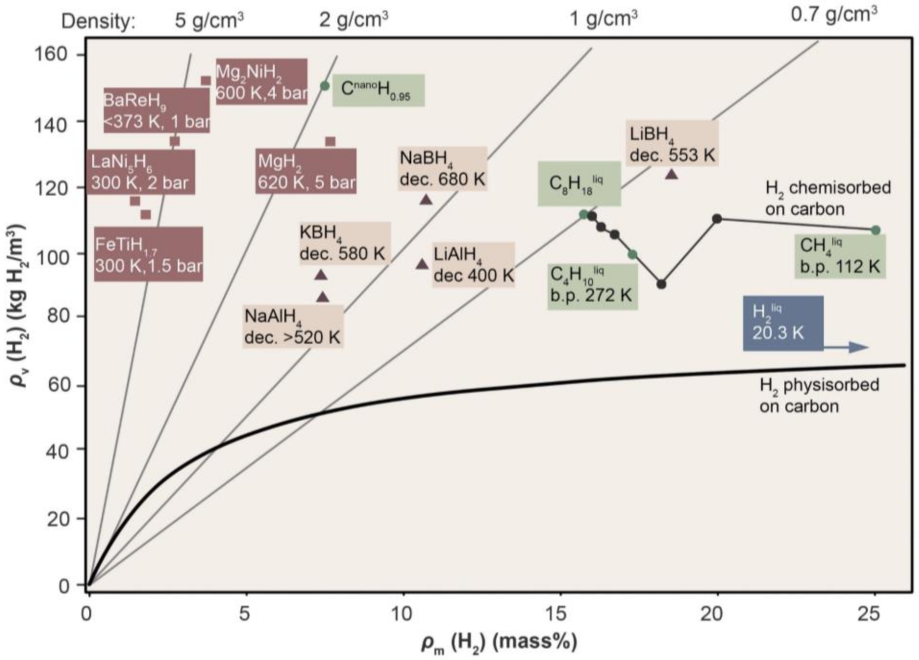


Figure 12: Comparison of volumetric storage capacity vs. storage density of metal hydride and other storage materials (Image source: [208] with permission from Nature)

Ammonia borane NH_4BH_4 is a chemical hydride that could also be utilised to store hydrogen [199]. Table 6 represents the decomposition reactions, the associated temperatures and storage density (wt.% H_2). NH_4BH_4 is decomposed in four steps giving a very high hydrogen yield. Since the reactions shown in table 6 are not reversible, an offboard regeneration process is required.

Table 6: Decomposition reactions, storage density and temperature for thermal chemical hydrides [199]

Reaction	Storage density (wt.% H_2)	Decomposition temperature (°C)
$NH_4BH_4 \rightarrow NH_3BH_3 + H_2$	6.1	<25
$NH_3BH_3 \rightarrow NH_2BH_2 + H_2$	6.5	<120
$NH_2BH_2 \rightarrow NHBH + H_2$	6.9	>120
$NHBH \rightarrow BN + H_2$	7.3	>500

Table 7 compares the most plausible (state-of-the-art) hydrogen storage methods and compares system weights, volumes and density of those technologies [199]. The pros of solid hydrogen storage in contrast to gaseous and liquid hydrogen storage methods are lower pressure requirement (i.e. greater energy efficiency), lower volume, and higher purity hydrogen output.

Compressed hydrogen and liquid storage approaches are the most commercially feasible storage options.

Table 7: Hydrogen storage technology and estimates for weights, volumes and density for storing 3 kg H_2 in vehicular compressed gas at 70 bar, cryogenic liquid, and metal hydride [199]

Technology	Volume (litres)	Weight (kg)	Density (Wt. % H_2)
Compressed H_2 at 70 MPa	100	50	6
LH_2	90	40	7.5
Low-temperature metal hydride	55	215	1.4

5.4. Fuel cells

The history of hydrogen-fuelled vehicles backed to 1807 when Francois Isaac de Rivaz made the first hydrogen car of the world [226]. The use of hydrogen instead of fossil fuels in vehicles has received much attention to reducing GHG emissions of the transport sector. Hydrogen can be utilised in ICEs. ICEs using hydrogen (H_2-ICE) are so similar to ICEs working with other fuels. The key dissimilarity is the H_2 storage system, i.e. much heavier bigger and more complex than a diesel or gasoline tank. H_2-ICEs are not anymore considered as a realistic option for the future of road transport. Thus, hydrogen-fuelled vehicles, i.e. FCEVs (fuel cell electric vehicles) are pure electrical. H_2-ICEs have the same efficiency as the diesel-fuelled ICEs which is in the range of 24%. FCEVs can be used for an extensive driving range and can be fuelled in minutes. The primary power source of FCEVs is the fuel cell system fuelled with hydrogen. So, a hydrogen storage system is required to store the needed quantity of hydrogen onboard the vehicle. The solution selected by nearly all original equipment manufacturers is a composite (plastic cylinders or carbon fibre wrapped metal) storage system— type IV hydrogen storage tanks—to store hydrogen at 700 bar. The overall efficiency of FCEVs is 2x as high as that of an ICE. The amount of stored hydrogen onboard an FCEV is much lower than an H_2-ICE, leading to a driving range of over 500 km. In fuel cells, the oxidation and conversion of hydrogen-enriched fuel to useful energy takes place. The exhaust stream is water vapour and thereby has almost no environmental impact. The electrical efficiency of fuel cells is higher than open-cycle gas turbines and is in the range of 32% to up to 70% (at HHV). The efficiency of fuel cells is lowest at high loads and increases with decreasing power output [55]. Under transient cycles, a fuel cell module can achieve its highest efficiency. Various types of fuel cell do exist and are distinguished by their operating temperature and membrane type. Fuel cells can be grouped to the alkaline fuel cell, PEM fuel cell, molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), and SOFC. Operating temperature of alkaline and PEM fuel cells are low and around 80°C. The operating temperatures of MCFC, PAFC and SOFC are higher of up to 600°C for solid oxide fuel cells (SOFC). So, MCFC, PAFC and SOFC fuel cells are more suitable for CHP applications. PEM fuel cells are the most suitable option for fuel cell electric vehicles. In the period 2008 to 2013, the global fuel cells market grew by nearly 400% [55].

5.5. Alternative hydrogen carriers

One of the critical challenges of the hydrogen supply chain is the scarcity of devoted storage and distribution infrastructure, as along with the fact that the allocated infrastructure is not feasible without high hydrogen production quantity. One potential first step is to focus on hydrogen production while simultaneously ensuring that the produced hydrogen has multiple potential uses beyond merely supplying a 100% hydrogen network. This hydrogen can then be used as a motivator and stepping stone for dedicated infrastructure, as well as for producing of value-added chemicals including methane, ammonia, methanol, FT-GTL fuels, etc. which are briefly discussed in the next sections.

5.5.1. Synthetic methane

The most traditional approach of the hydrogen conversion is currently the methanation process where hydrogen reacts with CO_2 to produce methane via the Sabatier-reaction or biological processes bringing about an extra energy conversion loss of 8% [227]. Müller et al. [228] stated that about 95% of the CO_2 could be converted to methane in a demonstration plant. The methanation reaction is highly exothermic leading to high conversion losses when the produced heat is not entirely used.

The CO_2 used in the process can be recycled CO_2 from a power plant or industrial process flue gases, or else it can be directly captured from the atmosphere. It can then be injected into the nearest natural gas network for public and industrial use.

Synthetic methane production is an attractive option for locations with substantial investment in natural gas infrastructure and where it is economically viable to continue to use natural gas. The critical issue of integrated electrolysis and methanation processes is the process efficiency. The diagram in Figure 13 illustrates the typical round-trip efficiency of power to water electrolyser (~3/4), methanation process (~4/5), and natural gas turbine (~3/5), yielding an overall efficiency of less than 40% [229].

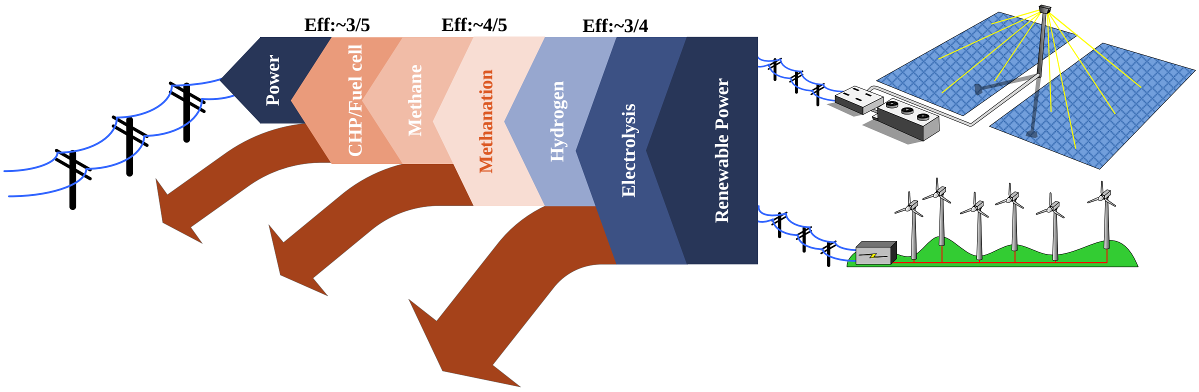


Figure 13: Illustrative diagram of the renewable power methane concept (Image source: [230])

The first large power-to-methane plant was constructed by ETOGAS for Audi AG in Werlte, Germany. This plant's CO_2 intake comes from a waste-biogas plant and intermittent renewable electricity to produce synthetic methane to feed directly into the local natural gas grid [144]. In 2014, KIT began a research project entitled by HELMETH (integrated High-temperature ELectrolysis and METHanation for effective power to gas conversion) and was financed by the European Union (EU). The aim of the project demonstrating the concept of a highly efficient power-to-gas (PtG) process by integrating a high-temperature electrolyser such as solid oxide electrolysis cell technology with CO_2-methanation [144].

As explained by the German Association for Electrical, Electronic and Information Technologies [231], large-scale storage of electricity at sufficient potentials in Europe can be carried out by the electrolysis water splitting and underground storage of the produced hydrogen in geologically feasible locations subject to its public acceptable [200]. This energy conversion and storage approach is PtG, and in this method, energy and electricity can be stored at TWh-scale for weeks or months. PtG may be in the form of power-to-hydrogen (PtH_2) or power-to-methane ($PtCH_4$ [33, 232]).

Sustainable CO_2 sources are required for hydrogen methanation. Existing natural gas infrastructure including pipelines, compressor station, and storage facilities can be used to distribute hydrogen and/or synthetic methane to end-users and potential markets. Hydrogen can be injected into the natural gas transmission pipelines in limited quantities depending on natural gas flow variations as well as the allowed maximum hydrogen content of natural gas (admixture up to 10 vol% does not cause adverse effects in most cases [201]). Limitations on the hydrogen concentration in the gas network during transport, storage, distribution, measuring and control and end-user appliances are given in [55]. In case of adding hydrogen into the natural gas grid, gas turbines, compressing stations, and CNG tanks (e.g. used in CNG vehicles) do not need any further adjustment if the blend share is lower than 2% by volume. The potentials of the PtG technology for the integration of renewable power into the German energy system is addressed from an economic point of view [200]. Net present value (NPV) of the entire PtG infrastructure was maximized. In total, eight different scenarios were considered, i.e. four diverse hydrogen applications in industry, re-electrification, mobility, and natural gas grid injection, and two time horizons in 2025 and in 2050.

Table 8 represents the performance of various storage types including underground storage, PtH_2, $PtCH_4$, and power to power for large-scale energy storage. Hydrogen pressure levels range for underground storage is from 2–18 MPa [55]. Power to power refers to situations where electricity is converted into H_2 via water splitting electrolysers, stored in a UGS cavern or a pressurised tank and then re-electrified when required using a hydrogen gas turbine or a fuel cell. The maturity of all the storage type is at the demonstration stage. For underground storage, the lifetime is the highest among all storage types while the investment cost is the least one.

Table 8: Performance of various large-scale hydrogen storage [55].

Storage type	Energy efficiency (%)*	Investment cost ($/Wh)**	Lifetime (years)	Maturity
UGS	90–95, including compression	~0.008	30	D
PtCH4	~58 excluding gas turbine (HHV); ~21 including gas turbine (PtP)	2.6 (with AE)–4.1 (with PEM), excluding gas turbine; 3.5 (with AE)–5 (with PEM), including gas turbine (PtP)	2.28– 6.85 (stack lifetime electrolyser)	D
HENG	~73 excluding gas turbine (HHV); ~26 including gas turbine (PtP)	1.5 (with AE)–3 (with PEM), excluding gas turbine; 2.4 (with AE)–4 (with PEM), including gas turbine (PtP)	2.28– 6.85 (stack lifetime electrolyser)	D
PtP	29 (HHV, with AE) – 33 (HHV, with PEM)	1.9 (with AE)–6.3 (with PEM) plus ~0.008 (for storage)	2.28– 6.85 (stack lifetime electrolyser)	D

Notes:

- Capacity scale of all storage options (i.e. UGS, PtCH4, HENG, PtP) is in the range of GWh to TWh
- HENG: hydrogen-enriched natural gas (hydrogen is blended in the natural gas grid)
- UGS: underground storage
- PtP: power-to-power (including underground storage)
- AE: alkaline electrolyser
- PEM: PEM electrolyser
- D: demonstration

* = Unless otherwise stated, efficiencies are based on LHV.
** = Investment costs are based on the energy output.

Earlier the syngas production pathways for H_2 generation were elaborated. However, pure hydrogen is one of the ultimate products from syngas. Syngas is an intermediate gas which can be used for the synthesis of a wide range of hydrocarbons such as methanol, dimethyl ether and synthetic fuels. We discussed syngas generation through reforming, gasification and pyrolysis. An alternative approach is co-electrolysis of H_2O and CO_2, which produces syngas with desired compositions [233-236]. If the thermal and electrical demand for this electrolysis is supplied by renewable resources (e.g., solar [237]), it can then lead to renewable fuels and chemicals which also act as renewable hydrogen carriers. Nevertheless, this pathway suffers from low overall process efficiency, and the feasibility of the process depends on the demand exerted by market conditions.

5.5.2. Methanol

Methanol is taken into account as one of the best hydrogen carriers due to its easy storage and transportation in liquid form in conventional tankers [238]. Methanol can be used as an intermediate chemical which can be utilised for the production of propylene, MTBE, DME, acetic acid, ethylene, hydrogen, etc. [239]. Usually, the electricity consumption in methanol synthesis is higher than the methanation process since extra compressor power is needed for the recycle stream. Nevertheless, methanol production does have lower losses because it is less exothermic. Methanol gives the impression to be a promising storage choice because its volumetric energy density is higher than both methane and hydrogen. Methanol can be combusted in gasoline engines [227]. Methanol is conventionally produced from a syngas feed ($\mathrm{CO_2 + 3H_2 \rightarrow CH_3OH + H_2O}$). Since the required CO_2 content of the syngas feed to the reactor should be high, the methanol process is perceived as a CO_2 utilisation process alternative — a way in which CO_2 can be recycled rather than directly emitted. As such, CO_2 utilisation thru methanol synthesis has received much attention in recent years [240]. When H_2 is obtained from renewables, the methanol process has double the benefit — it not only offers a suitable hydrogen carrier but also reduces or delays CO_2 emissions. In 2011, approximately 17 Mtonnes of methanol was used as fuel and for energy applications. From 2012 to 2016, on the other hand, the global methanol consumption more than doubled (it is increased from ca. 20 Mtonnes in 2012 to 38 Mtonnes in 2016), translating to roughly 37% of annual growth across the world [241].

Rihko-Struckmann et al. [242] investigated the CO_2 utilisation potential in membranes based on process simulations with the assumption of equilibrium conversion. They reported that almost 27% of CO_2 is converted in the membrane reactor (operating at 250°C and 5 MPa) and the unreacted CO_2 is removed from the raw product gas stream and recycled back to the reactor. Consequently, the total CO_2conversion reached ca. 96.8%. In another study, Jadhav et al. [243] stated that equilibrium conversion efficiency could be attained with copper catalysts. Methanol is produced at 300°C and about 70 bar from CO_2 in a reactor with a $Cu/ZnO/Al_2O_3$catalyst. The ceramic is mainly adapted to the highly exothermic reaction. A pilot plant with a capacity of 100 tonnes per year has been constructed by Mitsui Chemicals in Japan, a process that began in 2009. In China, Wei and co-workers have reported an innovative catalyst (ZrO_2 doped CuZnO) for CO/CO_2 hydrogenation to produce methanol. The ZrO_2-doped CuZnO catalyst exhibited high selectivity and high activity towards both CO_2 and CO hydrogenation [244].

5.5.3. Fischer-Tropsch Gas-to-Liquid (FT-GTL)

Historically, liquid fuels have been preferred to both solid and gaseous fuels, as a result of high energy density, ease of transportation and, more importantly, the reliance of internal combustion engines on them, meaning almost the entire transport industry. The Fischer-Tropsch (FT) process invented by Fischer and Tropsch in the early 20th century in Germany for reducing the country's overseas dependence on liquids for transportation. This technology converts syngas into "syncrude", i.e., a liquid blend of hydrocarbons, in the FT reactor in the presence of cobalt or iron catalysts [245]. This syncrude is then upgraded in the subsequent upgrading and separation processes (pure hydrogen is needed for hydrotreating and hydrocracking of the FT reactor effluent stream [14]) to end-products including LPG, naphtha, diesel, kerosene, and wax [246]. Therefore, FT-GTL is an alternative hydrogen carrier which converts H_2 into high-chain GTL products instead of separating it from syngas. Depending on the hydrogen source (water, biomass, or fossil fuels), and the utility energy source, GTL fuels can be within the entire range of 0–100% renewable.

5.5.4. Ammonia (NH_3)

As hydrogen energy carriers, both methane and methanol have outward potentials; methane due to the existing natural gas transmission and distribution infrastructure, and methanol because of its liquid state at ambient conditions and easiness of transportation. Nevertheless, both methane and methanol contribute to CO_2 emissions. Ammonia is, however, a carbon-free compound, has a high hydrogen density and is not a GHG. Thereby, ammonia is a favourable alternative to hydrogen which can be transported in gas, liquid or solid form; it is transportable even dissolved in water.

The invention of the Haber-Bosch process for the production of ammonia from hydrogen and nitrogen mixture has been instrumental to the development of modern civilisation [247]. Ammonia is a naturally rare chemical, found in trace amounts in nitrogenous animal and vegetable matters. Traditional agriculture received a limited source of nitrogen from waste organic matter. It is estimated that without the well-known Haber-Bosch process and without the access to synthetic nitrogen assets, agriculture could deliver only half of its products relative to the current output [247] by requiring four times more land [248]. The increased agricultural output is key to sustain the food supplies to a population increasing from 1.8 billion (as measured at the time of the Haber-Bosch process invention in 1913) to 7.7 billion (2018) [249].

Today, ammonia is considered as a hydrogen carrier due to its high hydrogen content of 3:1 (H:N) and better storage properties as compared to those for hydrogen. At standard temperature and pressure conditions (STP), ammonia, similarly to hydrogen, is a gas. However, the boiling point of ammonia is -33.34°C, and it freezes at -77.7°C to white crystals, as compared to those of hydrogen being -252.9°C and -259.1°C, respectively. Furthermore, it can substantially dissolve in water (47% w/w at 0°C, 31%w/w at 25°C, and 18% w/w at 50°C), which it is advantageous for storage and transportation [250].

The use of ammonia as a potential energy carrier has some advantages and include the availability of mature well-established technologies for its production and transportation and the fact that the process of ammonia production is well studied (i.e., Haber-Bosch process). Although ammonia synthesis reactions are exothermic, in practice, the ammonia production from mixture of hydrogen and nitrogen incurs a small energy loss of ca. 1.5 GJ/tonne compared to the nearly 28.4 GJ/tonne energy stored in ammonia [251]. Ammonia storage is more convenient than the hydrogen storage; for instance, up to 50,000 tonnes of ammonia could be stored in insulated tanks at -33 °C and 1 bar, and in quantities below 1500 tonnes it can be stored in low-pressure tanks [80]. Ammonia can be stored in liquid form. A standard storage tank with a capacity of 60,000 m^3 filled with ammonia holds nearly 211 GWh energy, which is equivalent to the annual production of about 30 wind turbines on land [140].

Ammonia has already been utilised in solid oxide fuel cells. It can also be used in alkaline fuel cells and polymer electrolyte membrane (PEMFC). However, before feeding ammonia to a fuel cell, it has to be split into hydrogen and nitrogen constituents [252]. Dunn et al. [253] have shown that ammonia-based thermochemical storage, along with concentrating solar power (CSP) facilities are technically achievable.

6. Hydrogen economics

6.1. Hydrogen supply chain and associated challenges

Hydrogen itself should not be viewed as the ultimate “problem” or “objective”. Instead, it is an energy vector around which considerable infrastructure should be constructed, especially for long-distance transport and export purposes. Hydrogen is of interest due to its properties; actually, hydrogen can be utilised within the context of a wholly carbon-neutral energy system. Nevertheless, its production is still more expensive than the current production routes from fossil fuels; hydrogen storage and transportation to end-users are both more difficult and more expensive as well. Hence, consideration of techno- and socio-economically viable and environmentally benign processes for hydrogen production is fundamental to establishing a hydrogen-based economy for future energy systems [254].

For the “hydrogen economy” to be genuinely viable, research into technological advances to overcome these barriers is required. Innovations in policy that will incentivise the push for zero-carbon energy exports are also needed. Figure 14 classifies H_2 development challenges into three categories: production/generation, storage/carrier, and conversion. In the following section, these techno-economic challenges are addressed, and possible pathways are discussed concisely.

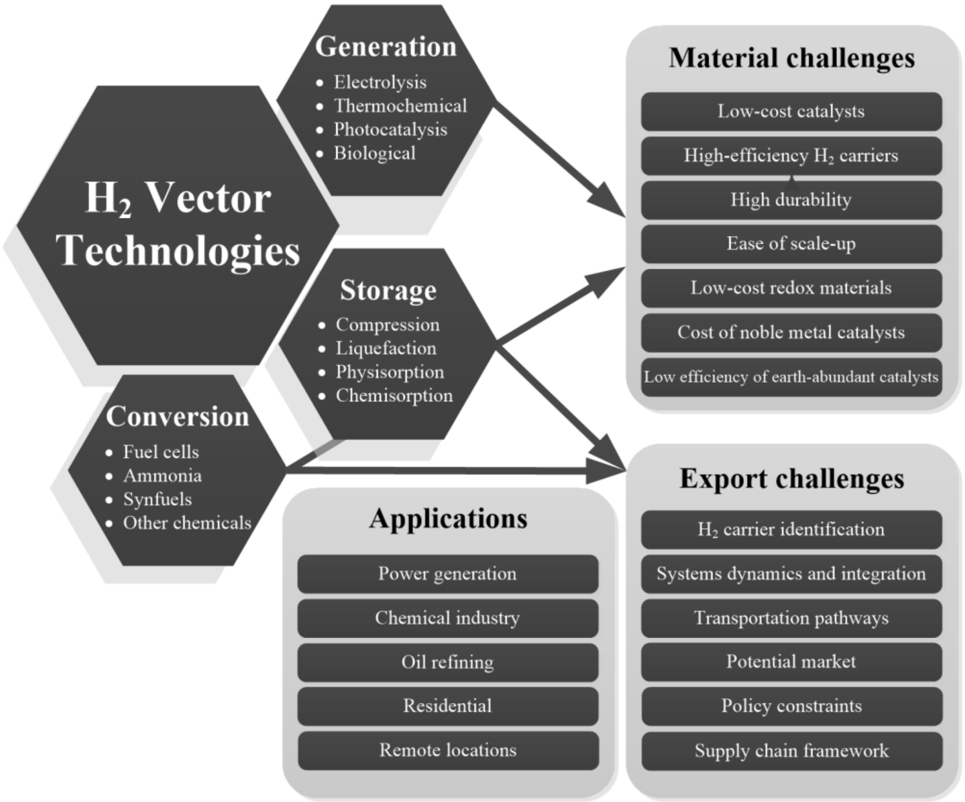


Figure 14: Core technologies and challenges in H_2 production and use

One of the opportunities for cost reduction is in material improvement. The catalysts currently used for H_2 generation and storage are expensive and based on relatively scarce materials (i.e., Pt, Ru, Ir), leaving little opportunity to reduce cost, thus significantly limiting their practical application. One core research area targets replacing the expensive materials with transition metal oxides catalysts, such as MnO_x, NiO_x, FeO_x, and CoO_x, as replacements for noble MO water-oxidation catalysts, for example, IrO_2 and RuO_2. The advantage of using transition MO catalysts is that they are found in abundance on Earth and are therefore inexpensive compared with noble MO oxide water-oxidation catalysts. The key challenges are to do with achieving comparable electrochemical performance, as non-noble MOs need considerably higher mass loadings (mg/cm^2) than the currently implemented great materials (µg/cm^2).

The policy requirements and the status and prospective for the deployment of hydrogen infrastructure in the EU to allow widespread deployment of renewable-driven hydrogen as a fuel and energy storage medium is addressed in Ref. [255]. Several technological and nontechnological barriers exist that prevent private investors and industries from engaging in hydrogen infrastructure deployment. Covering policy, public support, and financial measures are required in the early stages of hydrogen infrastructure build-up. The U.S. current status of hydrogen infrastructure, initial costs of deploying hydrogen infrastructure, market trends, hydrogen production, transmission, distribution, and refuelling infrastructure, transmission and distribution barriers, and material of construction of compressors, storage and liquefaction facilities, gaseous tube trailers, and liquid tanker trucks were discussed in Ref. [256]. The Japanese strategic road map and the strategic energy plan for hydrogen and the situation of building a hydrogen infrastructure in Japan are introduced in Ref. [257].

6.2. Cost analysis for H_2 production

Hydrogen likely plays a significant role in the energy sector for the mid-term to long-term future, and one should be able to produce it thru environmentally benign and cost-effective methods. There have been ongoing attempts to develop quantitative methods for the analysis of hydrogen infrastructure. There are specific requirements for the development of model-based system analysis tool to compare and assess various hydrogen pathways and the potential of their integration into national/international energy systems, in addition to the optimisation of existing hydrogen infrastructure. Early attempts lacked a suitable geographical representation of critical infrastructure facets, including the location and distribution of hydrogen production sites and demand centres. Added to these are missing components and features such as the transport distances involved, costs, and modes, or the regional distribution of renewable sources and the possibility of synergies with national electricity networks, which in the total lead to nonrigorous modelling results.

The dominant challenges currently hindering such development are storage and high infrastructure costs. From a techno-economic perspective, SR is currently the most plausible method. However, there is significant concern about increases in the price of natural gas and about CO_2 emissions [258], which make the development of sustainable and benign alternatives a necessity. In 2005, Kreutz et al. [259], conducted a comprehensive study of the performance, costs, and prospects of converting coal (using already mature technology and assumption of the price of coal as 1.26 $/GJ at LHV) to H_2 and electricity, with CCS. Their calculation showed that the costs for about 91% decarbonised energy (through quench gasification at a pressure of 70 bar) were ca. $1.0/kg for hydrogen and around 6.2 ¢/kWh for electricity; the reported costs were 19% and 35% higher corresponding energy costs with CO_2 venting, respectively.

In 2007, Ball et al. [260] developed an innovative modelling approach “MOREHyS” that considered the temporal set-up and geographic of an infrastructure for a hydrogen-based transport system in the German context and up to 2030, combined with impacts on the national energy system. MOREHyS was developed based on an open-source model called BALMOREL and standing for Baltic model of regional energy market liberalisation, which was primarily established to support analysis of the energy sector of the Baltic Sea region, with specific focus on the electricity and CHP sectors [261], but was further extended over time [262]. Within MOREHyS modelling approach, the complete hydrogen and electricity sectors — beginning with the resources and moving through several energy conversion steps to the supply of the final energy forms — were modelled, taking into account the technical (such as installed capacity, conversion efficiency, and byproducts), economic (including investments, fixed and variable costs) and ecological (e.g., emission factors) characteristics, as shown in the schematic in Figure 15. The results of that study demonstrated that because the infrastructure (gas and coal) was being developed, the fossil hydrogen production dominated but was highly sensitive to price ratios of feedstock. The authors predicted that specific costs of hydrogen supply would drop from around 11 c/kWh at the starting point down to 7 c/kWh around 2030, which would be competitive when the oil prices are beyond 50–70 $/barrel.

In that modelling approach, each technology class was defined via techno-economic parameters; thus, MOREHyS was recognized as a technology-based model (i.e. bottom-up) of the energy system. The objective function of the optimisation problem was sequentially performed on a year-by-year basis, undertaken to minimise the cost of the whole region each year. The decision variables of the model are the amount of electricity, heat and hydrogen production at each time step, area, and technology type; capital investment of new generation capacity per area and technology type; power transmission and new investments in power transmission capacities; and the quantity of hydrogen transported between as well as within all hydrogen areas.

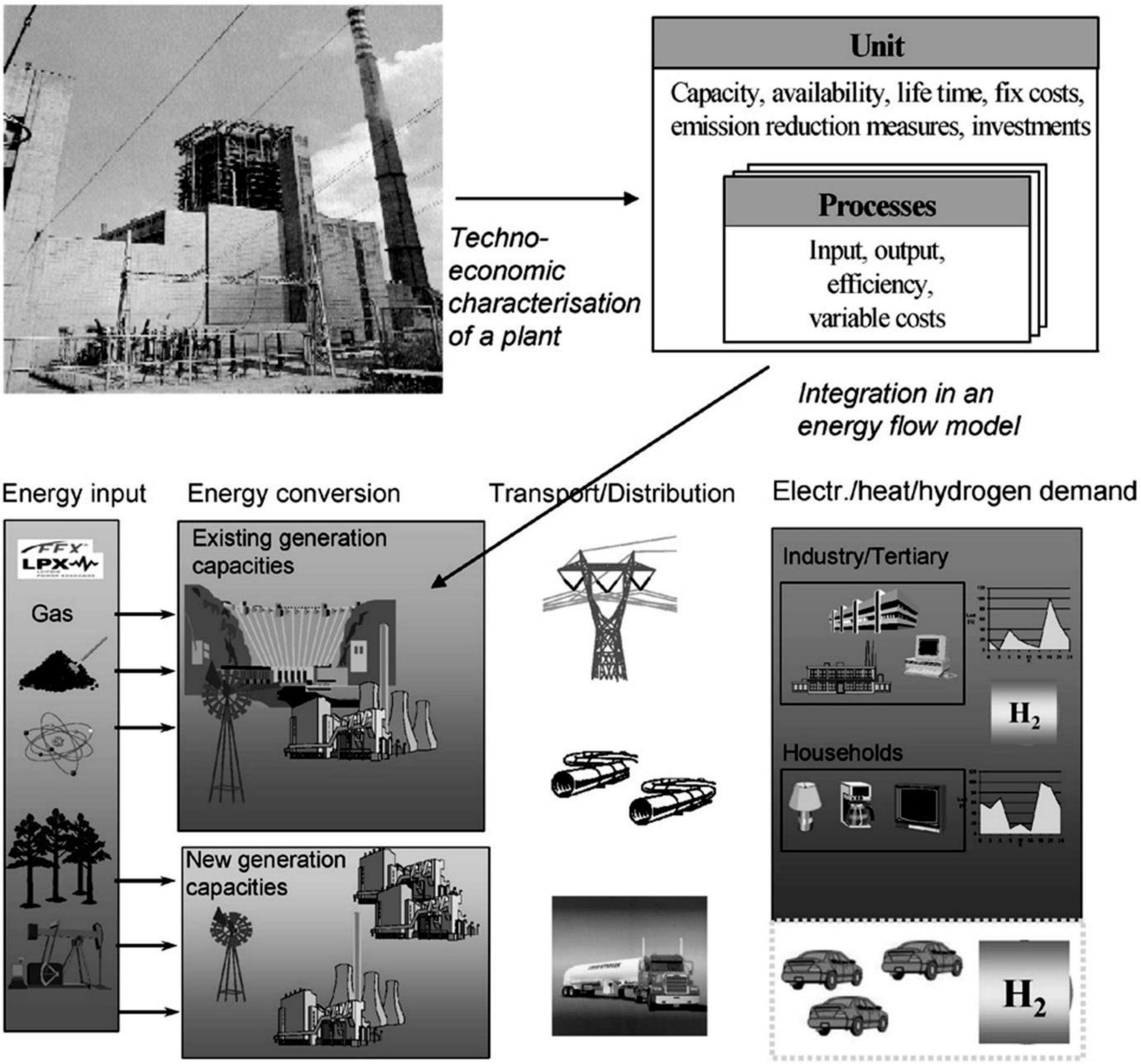


Figure 15: Methodologies used in the MOREHys modelling approach (Image source: [260] with permission from Elsevier)

In the optimisation problem, the existing technologies together with their fixed and variable costs competed against new generation, transportation/transmission technologies with their additional amortised investments. Dynamics between the considered years were introduced by transferring the optimisation results (i.e., endogenously optimal capacities of production and transportation/transmission) from the previous year’s step to the start of the subsequent year.

Therefore, individual optimisation time periods were interlinked thru capacity accumulations together with the annual decommissioning of the old capacities of the model. As the optimisation model had forethought only within a year but not beyond it, it was realised that decision-making could be short-sighted [260]. Another weakness of this model is the central, one-dimensional optimisation approach assuming the same target function for all of the applicants. The model identified the likely economic and environmental advantages of a hydrogen infrastructure build-up by evaluating the global optimum of the whole energy system rather than the optimal decision variables for each company. Consequently, the optimal decision variables were not inevitably the same as the decisions for individual players.

Zerrahn and Schill [263] critically reviewed and compared the different model to explore the role of power storage in the energy value chain with high shares of renewables. Based on their findings, they introduce a new open-source model called DIETER (the Dispatch and Investment Evaluation Tool with Endogenous Renewables). The model is designed to determine cost-minimising combinations of generation, demand-side management (DSM), and power storage capacities as well as their optimal dispatch. This model also includes the arbitrage value of power storage and system values related to the provision of dispatchable capacity and reserves. Based on this model, they optimise the hydrogen supply chain for Germany by technology choices (between alkaline and PEM electrolyser) for providing H_2 at German fuel stations. This includes onsite generation, as well as central electrolysis plus transport in gaseous or liquid form, or via liquid organic hydrogen carriers (LOHC). In doing so, they were explicitly taking into account power system fallout. These differ between technologies because of different characteristics and find a trade-off between energy efficiency and power system flexibility, which plays out differently at varying levels of renewable penetration and H_2 demand.

For a 30-year time frame, Talebian, Herrera [264] modelled hydrogen supply chain for light-duty passenger vehicles in British Columbia, Canada. This model considers water electrolysis and SR(with and without CCS) hydrogen generation and also includes current provincial emissions mitigation policies, different capacity options for all components of the supply chain, covering the on-site production and capacity expansion for central production and storage facilities as well as minimum storage requirement for fueling stations. Their results showed that electrolysis is not competitive with SR, even implementing carbon control policies unless there is a significant cost reduction of the electrolyser.

A techno-economic analysis is performed by Nguyen et al. [265] for large scale hydrogen production by water electrolysis across Canada, including Germany and California in flat and wholesale electricity markets. In this analysis, they consider Alkaline and PEM electrolyser with compressed and underground gaseous hydrogen storage with a capacity of ca. 50 tonnes per day. There are many spikes in the wholesale electricity market because of seasonal fluctuation due to changing climate conditions or variation of fuel prices. So, they developed an operational strategy to minimise the hydrogen production cost. From this analysis, it was found that avoiding operation during peak periods can reduce the electricity cost up to 30% in the Ontario and California wholesale electricity markets. Also, the lowest levelised cost of hydrogen was found when deployment of the plants is in the Ontario wholesale electricity market. Hydrogen production cost in Ontario combined with underground storage was found to be the cheapest in the three wholesale electricity markets. Compared to steam methane reforming (without carbon capture), the electrolytic hydrogen cost is 6%–27% higher. However, this cost becomes comparable to steam methane reforming once carbon capture and storage are included in the analysis. Besides, the integration of water electrolysis under the current flat-rate pricing scheme across Canada remains expensive and requires reduction of both energy and demand charge rates to be economically viable.

In 2010, Mansilla [266] performed a techno-economic analysis of the final hydrogen production cost of alkaline water electrolysis, which can potentially be used for the production of sustainable hydrogen. They simplified their model assumptions by using only sensitivity parameters for the study (i.e., load factor, maintenance, discount rate, thermal energy cost, construction duration, plant life, labour, and electrical energy). In that study, the thermal energy cost was calculated based on the conversion of electricity to heat as 1.8 €/kg of hydrogen. Hence, the hydrogen production cost was seen to be highly sensitive to electricity consumption and stack replacement. In the end, the study highlighted that in modelling, assumptions play a vital role in evaluating the hydrogen production cost compatible with each scenario.

Shaner et al. [267] also conducted a techno-economic study on photoelectrochemical (PEC) and photovoltaic-electrolytic (PVE) solar hydrogen generation to produce 10 tonne H_2 per day. They used unconcentrated, and 10× concentrated PEC systems versus unconnected and grid supplemented PVE systems. They found that, with the same overall plant efficiency of 9.8%, non-grid-connected PVE system base-case and the unconcentrated PEC system capital expenditures for the nominated capacity were respectively \$260 MM (371 \$/m/S^2, 12.1 \$/kg of H_2) and \$205 MM (\$293 /m/S^2 of solar collection area, levelised cost of hydrogen product

(LCH) \$11.4 H_2/kg) . In addition, the 10× concentrated PEC base-case system resulted in a capital cost of \$160 MM (\$428/m/s^2, \$9.2 /kg of H_2) with an efficiency of 20%, and the grid supplemented base-case PVE system capital investment was reported as \$66 MM (\$441/m/s^2, \$6.1 /kg of H_2), while grid electrolysis system and solar-to-hydrogen efficiencies are 61% and 9.8%. The authors used a benchmark PEM-based grid-connected electrolyser and presumed the system efficiency of about 61% and the grid electricity price of \$0.07/kWh so that the LCH reduced to \$5.5/kg of H_2. Based on this observation, they reported that increasing the system efficiency could positively influence the cost reductions for the whole system. Shaner et al. also concluded that at the time of the investigation, the cost of solar hydrogen production was deemed to be higher than that derived from SR priced at 1.39 \$/kg of H_2.

The adoption of renewable-derived hydrogen against the use of fossil fuel-derived hydrogen (without/with CCS) to a great extent depends on its economic attractiveness. The relationships between electricity price, natural gas price, CO_2 price, yearly full-load hours, and the resulting levelised cost of hydrogen are represented in [55]. Under optimistic assumptions for the electrolysers' techno-economic parameters, electrolytic hydrogen is significantly more costly than hydrogen from the reforming of natural gas, except if natural gas or CO_2 prices are high and very cheap renewable electrical energy is available. Natural gas reforming equipped with CCS is a promising option for hydrogen production, if the CO_2 price is above \$50/tonne CO_2. Also, at low prices of natural gas, renewable-derived hydrogen would be only cost-competitive if low-carbon, low-cost electricity is available for over 80% of the year. It is important to mention that, looking merely at hydrogen production costs is not sufficient and costs for hydrogen transmission and distribution should be considered in order to estimate the competitiveness of renewable-derived hydrogen.

The Commonwealth Scientific and Industrial Research Organisation (CSIRO) of Australia provided an evaluation of the cost of hydrogen production via PV and electrolysis as approximately \$18.70/kg of H_2 [268]. The estimated prices were based on an assumption of a \$2300/kW system cost applicable for large-scale hydrogen production, a non-tracking PV cells system with a capacity factor of 20.5% and a weighted average capital cost of ca. 6.4%. In line with advances in technologies, CSIRO also projected a significant cost reduction for hydrogen production of \$9.10/kg of H_2 by 2030. Recently, CSIRO estimated grid-connected hydrogen production by water electrolysis for alkaline, \$4.78-5.84/kg of H_2 and PEM, \$6.08-7.43/kg of H_2. For PEM, they make comparison based on electricity input, among them, grid-connected estimation shows lowest levelised cost of hydrogen, \$6.60/kg of H_2 with an average capacity factor of 0.85, \$11/kg of H_2 co-located PV and wind with a capacity factor of 0.30 and \$26/kg of H_2 curtailed renewable energy with a capacity factor of 0.10. This estimation includes electricity price, capacity factor, plant size, capital cost and efficiency; more details can be found in Ref. [269]. Typically, around 2% of global hydrogen production is produced by water electrolysis, but for low-carbon hydrogen, it has a significant prospect. There is a challenge, especially surplus energy from renewables or clean sources; the number of hours is deficient. Besides, if we want to mitigate all the current hydrogen demand by water electrolysis, it requires electricity demand of 3600 TWh, which is higher than the annual electricity generation of the European Union [270]. Currently, there are significant variations in hydrogen production costs in a different geographical region, and their future economy depends on many factors that will also continue to vary, including prices for fossil fuels, electricity, carbon and policy. SR without CCS is now the most economical option for hydrogen production in most parts of the world, for example, \$1/kg of H_2 in the Middle East. Among low-carbon options, electrolysis requires electricity prices of \$ 10–40/MWh and full load hours of 3000–6000 to become cost-competitive with SR with CCS; depends on local gas prices [270]. Electrolysis would be a feasible option where useful renewable resources or nuclear power plants are available, primarily if they currently depend on relatively high-cost natural gas imports. The conversion of hydrogen to ammonia benefits from existing infrastructure and demand; it also does not need carbon as an input. For synthetic liquid fuels from electrolytic hydrogen, however, electricity costs of \$20/MWh translate into costs of \$ 60–70/bbl without taking account of any capital expenditure or CO_2 feedstock costs. For synthetic methane, the equivalent figure is \$10–12/MBtu. Carbon pricing or the same policies would be needed to reduce the cost gap between synthetic hydrocarbons and fossil fuels [270].

6.3. H2A Model

The U.S. Department of Energy (DOE) Hydrogen Fuel Cell and Infrastructure Technologies program developed a H2A model to estimate the levelised hydrogen selling price needed to reach a determined internal rate of return (IRR) by analysing a discounted cash flow rate of return; or, in other words, to find a minimum selling price of hydrogen. H2A stands for a hydrogen analysis which was first developed in 2003 to establish consistent and transparent sets of financial parameters and methodologies for different pathways of hydrogen production. When comparing hydrogen techno-economic studies, one often finds differences in analyses which were because of different assumptions, such as feedstock costs or IRRs, and not actual system discrepancies. Hence, the H2A model aims to give a common framework to enhance the understanding of the discrepancies among analyses [271]. In this model, the information (feedstock, utility prices, and physical property data) about feedstocks (commercial and industrial natural gas, commercial and industrial electricity, diesel fuel, gasoline, methanol, ethanol, and biomass) and their projections for every year between 2000–2025 are incorporated based on the yearly energy perspective developed by the DOE's Energy Information Administration [47, 111]. Between 2025 and 2035, the values can be extrapolated by merely using the 2015 to 2025 growth rate.

In 2016 the DOE conducted a comprehensive techno-economic analysis on five diverse hydrogen production pathways. These analyses provided insight projections for capital expenditures, energy and fuel/feedstock usage, land usage, indirect capital costs, and labour requirements for each hydrogen production alternative. This information was later used as input data into the H2A discounted cash flow model, as shown in Figure 16, to project the production cost of H_2 ($/kg of H_2).

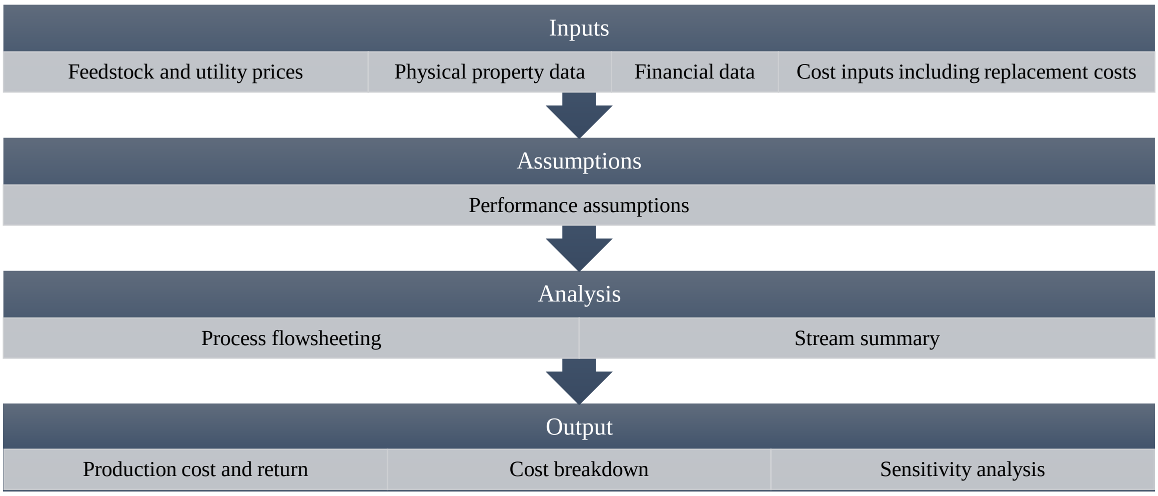


Figure 16: Analysis tool of H2A production cash flow

In developing the H2A model, the DOE incorporated standard economic assumptions which were considered essential for producing consistent and comparable outcomes across technology options. Table 9 lists a set of fundamental economic parameters initially chosen by the H2A. These assumptions were deliberated within the conditions of industry collaborators who contributed to the development of the H2A model. However, the parameters may be freely changed according to users' circumstances.

Table 9: The assumptions and technologies of choice in the H2A model

Technology	Input assumptions/parameters
• PEM • High-temperature SOEC • Dark fermentation of biomass for hydrogen production • Hydrogen production via monolithic piston-type reactors with quick swing reforming and regeneration reactions • Reformer-Electrolyser-Purifier (REP) developed by Fuel Cell Energy, Inc.	• Reference year dollars: often presented in 2007\$ • Debt versus equity financing: 100% equity • After-tax IRR: 10% real • Inflation rate: 1.9% • Effective total tax rate: 38.9% • Depreciation period and schedule: Modified Accelerated Cost Recovery System (MACRS) • Central plant production: 20 years • Forecourt production (i.e. in distributed production facilities): 7 years • Delivery components: typically5 years with a few exceptions • Economic analysis period: ▪ Central plant production: 40 years ▪ Forecourt production: 20 years ▪ Delivery components model: 20 years o Decommissioning costs were assumed equal to salvage value

Thereby five technologies (listed in Table 9) were analysed and summarised in the latest hydrogen production report issued by the DOE. Quantitative cost analyses were conducted primarily for two production scenarios, Forecourt and Central. Forecourt production is used for facilities that produce approximately 1,500 kg H_2/day, whereas central production is used for facilities that produce 50,000 kg H_2/ day. The future case analyses consider cost trends for various parameters (such as feedstock or energy costs) which are used to project H_2 costs at far future date (nominally 2025). Feedstock and energy costs were obtained from the Energy Information Administration's 2009 Annual Energy Outlook projections (out to 2070) and were further extrapolated into future years using Pacific Northwest National Laboratory's Global Change Assessment Model (GCAM) for the discounted cash flow analysis.

It is worth noting that H_2 production technology is rapidly advancing and periodic updates to the analyses will undoubtedly be required to reflect the cost impacts of improvements. Results for four of the five H_2 production system studies are shown in Figure 17 based on levelised cost of H_2 (\$/kg of H_2). The levelised costs were computed using DOE's H2A Production tool, a discounted cash flow model that uses feedstock and energy costs, thermal requirements, and capital and maintenance costs as input parameters specific to each case. All costs are presented in 2007\$. The range of H_2 production costs for projected current case studies was shown as \$2.58–\$51.02 per kg of H_2.

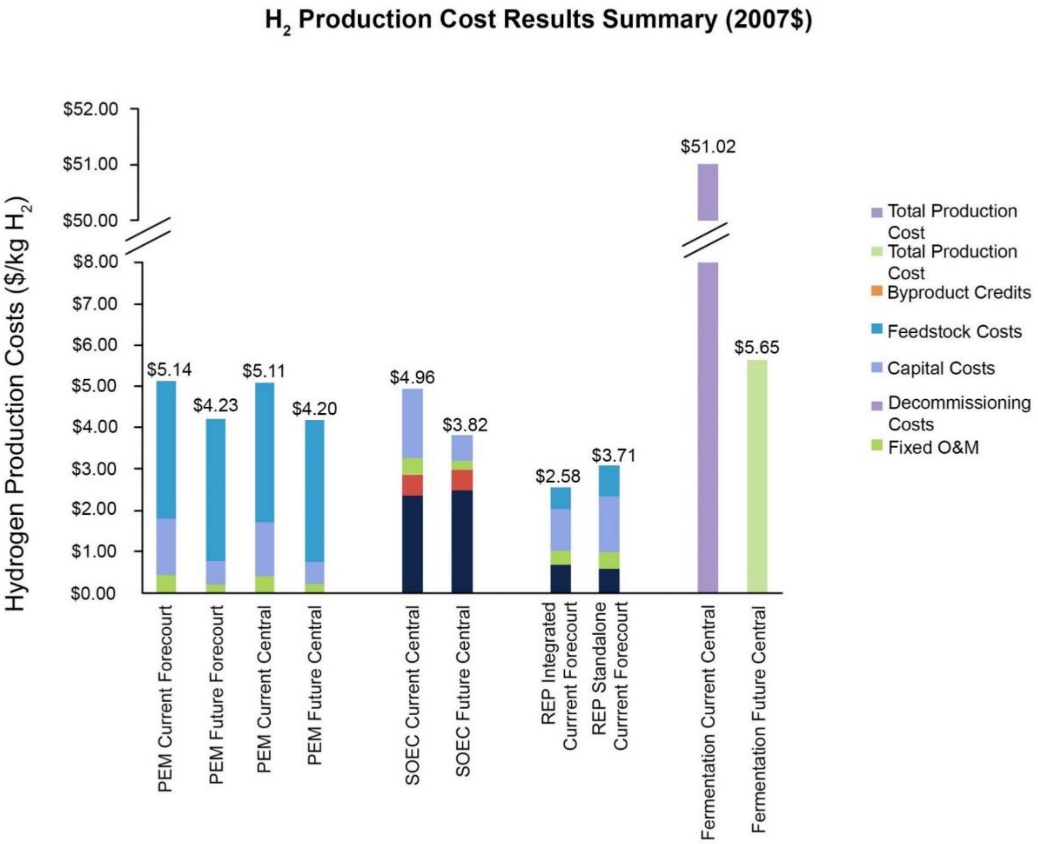


Figure 17: H$_2$ production cost summary levelised based on 2007$, for the presented production pathways (Image: Courtesy of the U.S. Department of Energy (DOE)/NREL/ALLIANCE [49])

It is worth noting that the projected current fermentation hydrogen cost was calculated as relatively higher ($51.02 per kg of H$_2$) compared with other technologies because the production method was not yet mature. The range of costs for hydrogen production from the projected current cases tightened to $2.58–$5.14 per kg of H$_2$. The costs of hydrogen production using high-temperature SOE was estimated at $3.82 for future central and $ 4.96 for current central. This system often operates at high stack temperature (≈800 ºC) and relatively high outlet gas pressure close to 300 psi. In this comparison, heat to warm the stack inlet temperature is provided from a generic heat source, and steam is used as a sweep gas on the oxygen-generating side of the cells (cathodes) to lower the oxygen partial pressure and improve performance.

The sensitivity analysis for variables including effective electricity price over the lifetime of the plant, uninstalled fixed capital cost, stack service lifetime, the average price of heat over the life of the plant, thermal usage, plant capacity, and electrical usage consistently revealed that electricity price was the primary cost driver. The hydrogen production cost also seemed to be sensitive to changes relative to the uninstalled capital cost and stack service lifetime [49].

Steam reforming, currently deemed the least expensive process for producing hydrogen, was considered through the reformation of natural gas in a REP. The REP technology is a product of Fuel Cell Energy Inc. and derives from the company's existing MCFC technology, which usually generates electricity for large applications. The REP is essentially an MCFC stack operated in reverse (i.e., by electrolysis). In short, natural gas first undergoes SR in a separate SR reactor and the reformed gas is then sent into the REP unit, where the CO_2 is effectively transported across the electrolyte, splitting a water molecule as part of the reaction. Therefore, H_2 is generated both from the SR and from water electrolysis. Due to the production of CO_2 during SR, which is pumped across the MCFC electrolyte (at high concentration >95%), H_2 exits the REP unit. This process is considered less environmentally friendly.

Nonetheless, the long-term direction is toward renewable pathways such as water electrolysis using renewable electricity. At present, the cost is one of the most significant challenges for renewable-derived hydrogen production. To be used in transportation FCs, hydrogen should be cost-competitive with conventional fossil fuels and technologies on a per-distance basis. As such, the DOE has set the cost of hydrogen — irrespective of the production pathway— to be less than about $4/kg equivalent to one-gallon gasoline.

In 2009, the DOE reported that approximately 78% of the hydrogen cost through water electrolysers comes from the cost of electricity. The capital cost accounted for 17% and all other costs combined accounted for 5% of the hydrogen production cost. The DOE hydrogen program, however, reported that a significant improvement of almost 67% in production efficiency had been achieved compared with 62% in the year 2006. This trend was also confirmed for the system's capital cost, which reduced from $665/kW to $460/kW in 2009. The DOE also estimated the effect of electricity price on the hydrogen production cost by water electrolysis, as shown in Figure 18.

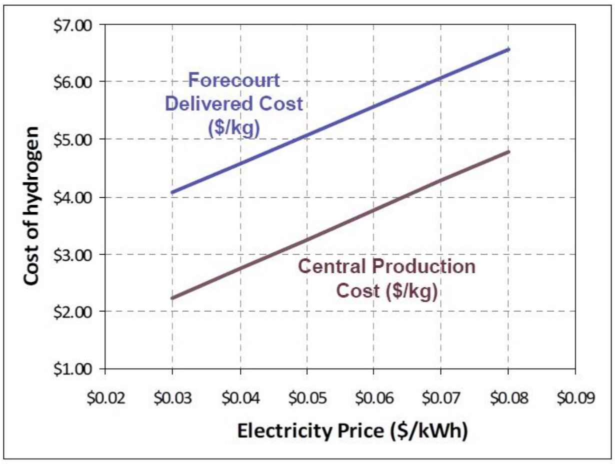


Figure 18: Cost of hydrogen production vs. electricity price (Image: Courtesy of the U.S. Department of Energy (DOE)/NREL/ALLIANCE [272])

From the final report (2013–2016) of cost analysis for hydrogen production pathways issued by the DOE [49], the significant parameters used to advance the H2A model for baseline cases are shown in Table 10. Also, the hydrogen cost breakdown details for the cases conducted is shown in Table 11. The main cost driver for the production of hydrogen through electrolysis is recognised as electricity feedstock [49].

Table 10: Input parameters of the H2A production cases for PEM electrolysers (costs in 2007$ and 2012$) [49]

Parameter	**Projected current forecourt**	**Projected future forecourt**	**Projected current central**	**Projected future central**
Plant capacity (kg/day)	1500	1500	50000	50000
Total uninstalled capital (2012$/kW)	940	450	900	400
Stack capital cost (2012$/kW)	385	171	423	148
Balance of plant (BOP) capital Cost (2012$/kW)	555	279	477	252
Total electrical usage (kWh/kg)	54.6	50.3	54.3	50.2
Conversion efficiency (LHV of H_2) (%)	61	66	61	66
Stack electrical usage (kWh/kg)	49.2	46.7	49.2	46.7
Conversion efficiency (LHV of H_2) (%)	68	71	68	71
BOP electrical usage (kWh/kg)	5.4	3.6	5.1	3.5
Electrolyser power consumption (MW)	3.4	3.1	113	105
Average electricity price over plant lifetime (2007¢/kWh)	6.12	6.88	6.22	6.89
Electricity price in start-up year	5.74	6.59	5.74	6.59
Outlet pressure from electrolyse (psi)	450	1000	450	1000
Installation cost (% of uninstalled capital cost)	12	10	12	10
Replacement intervals(years)	7	10	7	10
Replacement cost of major equipment	15	12	15	12
Plant lifetime (years)	20	20	40	40
Stack current (mA/cm^2)	1500	1600	1500	1600
Capacity factor (%)	86	86	97	97

Table 11: H_2 production costs breakdown in 2007$/kg H_2 for PEM electrolysers baseline cases

Component	Projected current forecourt	Projected future forecourt	Projected current central	Projected future central
Stack capital cost	0.42	0.16	0.48	0.17
BOP capital cost	0.61	0.25	0.53	0.26
Indirect capital cost and replacement cost	0.32	0.16	0.32	0.10
Decommissioning	0.02	0.01	0.00	0.00
Fixed operations and maintenance	0.42	0.18	0.40	0.20
Electricity feedstock	3.34	3.46	3.38	3.46
Variable operation and maintenance	0.01	0.01	0.10	0.01
Total production cost (2007$/kg H_2)	5.14	4.23	5.12	4.20

The DOE provided a series of suggestions for integration of the electrolysis process with renewable energy to lessen the cost of hydrogen production. For instance, through the initial research results, it was observed that switching between direct coupling and power converters could improve the overall energy capture of a PVE system by ca. 10%. Also, the study of the long-term effects of operating an electrolyser stack connected with a wind turbine simulator providing a highly variable profile suggested that over some 10,000 hours of operation there was no significant difference in electrolyser decay rate versus an always powered operation profile [273].

7. Conclusion

Hydrogen is a universal chemical energy carrier with technically diverse production, storage, distribution and end-use pathways. It finds applications in power generation, transportation, chemical industry and district energy systems. Steam reforming of natural gas is known as the most plausible method for hydrogen production. Nevertheless, the increases in the price of natural gas and about CO_2 emissions makes the development of sustainable and benign production routes inevitable. Up to the present time, there are no commercial applications of biomass gasification to produce hydrogen. Nevertheless, this can be a feasible option in the future once the technological barriers are vanquished.

While it is several decades since the concept of “hydrogen economy” was conceived, it is only in recent years that hydrogen value chain shows commercial justification for applications beyond chemical industry, for general energy purposes. The major factors driving this include the dramatic fall in the cost of solar and wind technology and the steady improvement in the economic status of hydrogen technologies and supporting infrastructure. In addition, the active interest in developing a global demand and a supply chain as demonstrated by Japan, South Korea and China (even Germany) helps to drop the cost of the hydrogen value chain.

Hydrogen production from water electrolysis is likely to be an economically competitive option in the near future, primarily when the energy is sourced from renewables and supported by governments' policies on the carbon tax and renewable subsidies. The study of storage options also demonstrates that liquid hydrogen may be preferable to compressed hydrogen. Solid-state hydrogen storage in some materials such as metal hydride or complex hydride could be an option for stand-alone or stationary use; this option may be preferable as it allows the decoupling of power and energy ratings requires only low operating pressure and incorporates increased high volumetric energy intensity and safety. The exact nature of the challenges to be overcome depends on the qualities of the storage material, specifically the overall weight of the storage facility, the degeneration with cycles, and the costs.

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List of abbreviations

AE	Alkaline electrolysers
ATR	Autothermal reforming
BCC	Body-centred cubic
BECCS	Bioenergy equipped with CCS technology
BOP	Balance of plant
CHP	Combined heat and power
COE	Cost of energy
COF	Covalent organic framework
CPOX	Catalytic partial oxidation
CCS	Carbon capture and storage
CCSU	Carbon capture, storage, and utilisation
CR	Catalytic reforming
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CSP	Concentrating solar power
DOE	Department of Energy

EU	European Union
FC	Fuel cell
FCC	Fluid catalytic cracking
FT	Fischer-Tropsch
GA	General Atomics
GCAM	Global change assessment model
GHG	Greenhouse gases
GTL	Gas to liquid
HCP	Hyper-cross-linked polymers
HDN	Hydro-de-nitrogenation
HDS	Hydrodesulphurization
HENG	Hydrogen-enriched natural gas
HFCV	Hydrogen fuel-cell vehicles
HHV	High heating value
HSA	High surface area
ICE	Internal combustion engine
IPCC	Intergovernmental Panel on Climate Change
IRR	Internal rate of return
LCH	levelised cost of hydrogen product
LHV	Low heating value
LPG	Liquefied petroleum gas
MACRS	Modified accelerated cost recovery system
MCFC	Molten carbonate fuel cell
MH	Metal hydride
MO	Metal oxide
MOF	Metal-organic framework
NPV	Net present value
PAFC	Phosphoric acid fuel cell
PEC	Photoelectrochemical
PEM	1) Proton-exchange membrane; 2) Polymer electrolyte membrane
PEMFC	Polymer electrolyte membrane (PEM) fuel cells
PIM	Polymers of intrinsic microporosity
POX	Partial oxidation
PrOx	Preferential oxidation
$PtCH_4$	Power-to-methane
PtG	Power to gas
PtH_2	Power-to-hydrogen
PtP	Power-to-power (including underground storage)
PV	Photovoltaic
PVE	Photovoltaic-electrolysis
REP	Reformer-Electrolyser-Purifier
SR	Steam reforming
SOFC	Solid oxide fuel cells
SOE	Solid oxide electrolyser
SR	Steam reforming
SRNL	Savannah River National Laboratory
SYNGAS	Synthesis gas
TPOX	Thermal partial oxidation
UGS	Underground storage
WGS	Water-gas shift

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