

## 1

## Introduction

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*We find ourselves on the cusp of a new epoch in history, where every possibility is still an option. Hydrogen, the very stuff of the stars and our own sun, is now being seized by human ingenuity and harnessed for human ends. Charting the right course at the very beginning of the journey is essential if we are to make the great promise of a hydrogen age a viable reality for our children and a worthy legacy for the generations that will come after us.*

Jeremy Rifkin [1].

Hydrogen is being considered as an important future energy carrier, which means it can store and deliver energy in a usable form. At standard temperature and pressure (0 °C and 1013 hPa), hydrogen exists in a gaseous form. It is odourless, colourless, tasteless, non-toxic and lighter than air. The stoichiometric fraction of hydrogen in air is 29.53 vol%. Abundant on earth as an element, hydrogen is present everywhere, being the simplest element in the universe representing 75 wt% or 90 vol% of all matter. As an energy carrier, hydrogen is not an energy source itself; it can only be produced from other sources of energy, such as fossil fuels, renewable sources or nuclear power by different energy conversion processes. Exothermic combustion reaction with oxygen forms water (heat of combustion  $1.4 \times 10^8$  J kg<sup>-1</sup>) and no greenhouse gases containing carbon are emitted to the atmosphere.

Selected physical properties of hydrogen based on Van Nostrand are presented in Table 1.1 [2].

The energy content of hydrogen is 33.3 kWh kg<sup>-1</sup>, corresponding to 120 MJ kg<sup>-1</sup> (lower heating value, LHV), and 39.4 kWh kg<sup>-1</sup>, corresponding to 142 MJ kg<sup>-1</sup> (upper heating value, UHV). The difference between the UHV and the LHV is the molar enthalpy of vaporization of water, which is 44.01 kJ mol<sup>-1</sup>. UHV is obtained when as a result of hydrogen combustion water steam is produced, whereas LHV is obtained when the product water is condensed back to liquid.

Because of its high energy-to-weight ratio, hydrogen has commonly been used in a number of applications for the last 100 years and a lot of experience has been gained since its production and use, with it becoming the fuel of choice. Hydrogen application for transportation has a long history. One of the first demonstrated

**Table 1.1** Selected physical properties of hydrogen.

Parameter	Value	Unit
Molecular weight	2.016	Mol
Melting point	13.96	K
Boiling point (at 1 atm)	14.0	K
Density solid at 4.2 K	0.089	g cm <sup>-3</sup>
Density liquid at 20.4 K	0.071	g cm <sup>-3</sup>
Gas density (at 0 °C and 1 atm)	0.0899	g l <sup>-1</sup>
Gas thermal conductivity (at 25 °C)	0.00044	cal·cm s <sup>-1</sup> cm <sup>-2</sup> °C <sup>-1</sup>
Gas viscosity (at 25 °C and 1 atm)	0.0089	cP
Gross heat of combustion (at 25 °C and 1 atm)	265.0339	kJ g <sup>-1</sup> mol <sup>-1</sup>
Net heat of combustion (at 25 °C and 1 atm)	241.9292	kJ g <sup>-1</sup> mol <sup>-1</sup>
Autoignition temperature	858	K
Flammability limit in oxygen	4–94	%
Flammability limit in air	4–74	%

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applications took place in the eighteenth century in Paris. The first manned flight (Jacques Charles and Nicolas Robert) had been demonstrated in a balloon called “hydrogen gas aerostat” for about 45 min, covering a distance of about 21 km.

A car with an internal combustion engine (ICE) that used a mixture of hydrogen and oxygen for fuel was invented by Francoise Isaac de Rivaz from Switzerland in January 1807 and it was the first internal combustion-powered automobile. The main application of hydrogen in the twentieth century was noted for nuclear submarines, airships and launching systems from the 1960s, and the first experimental investigations of liquid hydrogen for propulsion was started in the United States in 1945. Later it became a fuel of choice for rockets and launchers. The development of fuel cells was a major milestone in successful hydrogen application in the transportation sector. At present hydrogen-powered cars based on the polymer electrolyte membrane fuel cell (PEMFC) are being demonstrated worldwide. Fuel cell usage allows significant advantages such as energy-efficient drive train, silent mode of operation and high efficiency in well-to-wheel assessment.

When compared with other fuels such as methanol, petrol, diesel or kerosene, it is obvious that hydrogen yields much higher energy per unit weight than any other fuel. Hydrogen has a high energy-to-weight ratio (about three times more than gasoline, diesel or kerosene) and can be hazardous to handle. The flammability range is highest for hydrogen, but as long as it stays in an area that is properly ventilated there is no risk of reaching this limit. In addition, hydrogen has a relatively high ignition temperature of 858 K, as opposed to an ignition temperature of 501 K for gasoline. Hydrogen ignites very easily and burns with a wide range of mixtures with oxygen or air as compared to any other fuel.

When compared with most hydrocarbons, hydrogen has a much wider flammability range, from 4 (lower flammability limit, LFL) to 75 vol% (upper flammability limit, UFL) in air (4–95 vol% in oxygen) and detonability limits of 11–59 vol% in

air [3, 4]. Flammability limits of hydrogen increase with temperature. The lower limit drops from 4 vol% at Normal Temperature and Pressure (NTP (20 °C, 1 atm)) to 3% at 100 °C; detonability limits expand with the scale of a mixture [5]. Hydrogen has very low minimum ignition energy (MIE) of 0.017 MJ in air and 0.0012 MJ in oxygen at 25 °C and 1 bar [6]. For comparison, MIE values for most combustibles are in the range of 0.1–0.3 MJ and values for oxygen are at least an order of magnitude lower [6] (Table 1.2).

Because of its low density, hydrogen does not collect near the ground but dissipates in air, as opposed to gasoline and diesel fuel. Hydrogen and methanol have been evaluated by Adamson and Pearsons [7] with regard to safety, economics and emissions. Comparative risks analysis in case of accident in enclosed and ventilated areas showed that both hydrogen and methanol are safer than petrol, but in certain situations hydrogen may be of higher risk than methanol. The fraction of heat radiated from the flames is certainly an important factor in case of fire. As can be seen in the Table 1.2, hydrogen and methanol, due to lower values of heat in radiative form, are less likely to catch fire than petrol. Hake *et al.* [8] compared different fuels and fuel storage systems of exemplary passenger cars with regard to the safety features of gasoline, diesel, methanol, methane and hydrogen. Hydrogen could be risky depending on the infrastructure, which is not the case with diesel or gasoline. Although hydrogen's physical properties are well established, actual risks and hazards can only be determined with real systems and long-operating experience. The present lack of operating experience with hydrogen systems has been recognized as a significant barrier to their application. Several international efforts have been initiated to develop regulations, codes and standards (RCS). For example, the European Union has used the EIHP2 (European Integrated Hydrogen Project phase 2) project methodology to outline inputs for regulatory and standardization activities on

**Table 1.2** Selected properties of hydrogen compared with other fuels.

Fuel	Gravimetric energy density		Volumetric energy density		Flammability limits	Explosive limits	Fraction of heat in radiative form
	MJ kg <sup>-1</sup>	kWh kg <sup>-1</sup>	MJ l <sup>-1</sup>	kWh l <sup>-1</sup>	vol%	vol%	
Hydrogen compared 200 bar	120	33.3	2.1	0.58	—	—	—
Hydrogen liquid	120	33.3	8.4	2.33	4–75	18.3–59.0	17–25
Methanol	19.7	5.36	15.7	4.36	6–36.5	6–36	17
Petrol	42	11.36	31.5	8.75	1–7.6	1.1–3.3	30–42
Diesel	45.3	12.58	35.5	9.86	—	0.6–7.5	—
Kerosene	43.5	12.08	31.0	8.6	—	0.7–5	—

Source: By permission of Wiley VCH.

a European and global level, thus allowing safe development, introduction and daily operation of hydrogen-fuelled vehicles on public roads and their associated hydrogen refuelling stations [9]. A generic risk-based maintenance and inspection protocol for hydrogen refuelling stations has also been developed. A study has been undertaken to define the potential for the introduction of environmentally friendly hydrogen technologies in stand-alone power systems (H-SAPS). Barriers and potential benefits of promoting new technological applications on a wide scale and the market potential for SAPS have been widely analysed in select cases of existing small- and medium-sized systems with power rating from 8 to 100 kW (Gaidouromantra, Kythnos Island, Greece/PV-diesel-battery/ $\sim 8$  kW; Fair Isle, UK/wind-diesel/ $\sim 100$  kW; Rauhelleren, Norway/diesel/ $\sim 30$  kW; Rambla del Aqua, Spain/PV-battery/ $\sim 11$  kW) [10]. On the basis of the analysis, several interesting observations have been made. In order to introduce hydrogen energy technologies in autonomous power systems, a renewable energy source should be incorporated and in addition it should always be overdimensioned to cover power demand and use an excess electricity to produce hydrogen. It was shown that the replacement of conventional power sources with hydrogen is probably more economically viable in power systems having year-round load demand than those having seasonal power demand (power systems with seasonal power demand require seasonal energy storage; thus water electrolyser and hydrogen storage should be overdimensioned). The cost of fossil fuels in remote locations is higher (due to the increasing costs of fuel transportation); therefore the replacement of conventional power equipment by hydrogen energy equipment is expected to be beneficial from the financial point of view. Furthermore, such systems can successfully be used in short to medium market niche applications and have certain environmental advantages, especially in remote communities [10]. It is expected that hydrogen may play a considerable role in the future global energy systems. As stated by MacCurdy [11], "The degree of civilization of any epoch, people, or group of peoples, is measured by ability to utilize energy for human advancement or needs." Growing interest of hydrogen in transportation sector has been recognized and hydrogen-powered fuel cell vehicles (FCVs) are demonstrated successfully in Asia, the United States and Europe. Hydrogen-fuelled cars are reported to be about 1.5–2.5 times more efficient than gasoline-advanced cars on a TtW basis (tank to wheels) and produce no emissions, thus offering good performance; a distance of 500 or more kilometres can be refuelled within a few minutes [12]. A very famous example is the BMW seven series with a compressed hydrogen tank and with more than 35 years of experience in hydrogen usage (Figure 1.1).

As transitioning to hydrogen fuels and fuel cells still remains a challenge, there may be a need for an intermediate phase, where both hydrogen and conventional fuels are used together in the same vehicle. As stated, "The solution to meet this transitional requirement is the manufacturing of bi-fuel vehicles running on both hydrogen and gasoline using current internal combustion engine technologies ... This bi-fuel approach will stimulate the creation of a hydrogen-refuelling network thus allowing for a full transition to a hydrogen powered vehicle economy" [13]. It



**Figure 1.1** B class fuel cell car from Daimler with compressed hydrogen tank. (By permission of Wiley VCH.)

is estimated that cars with a bi-fuel system will increase their autonomy range by using hydrogen and will be able to cover a distance of approximately 200–300 km on hydrogen and up to 500 km on gasoline. A comparison between several vehicles on the market and the bi-fuel prototype by Alset Technology LLC is given in Table 1.3.

The deployment of completely new infrastructure for transportation is one of the key challenges on the technical, economic and financial fronts. The rechargeable vehicles market (battery electric vehicles, BEVs and plug in electric vehicles, PHEVs), which started a few years ago, will require new infrastructure,

**Table 1.3** Comparison between several vehicles on the market and bi-fuel prototype vehicle by Alset.

Model	Engine	Capacity (l)	Power		Torque (Nm)	Specific power	
			HP	kW		HP l <sup>-1</sup>	kW l <sup>-1</sup>
BMW Hydrogen 7	V12 bivalent	6.0	260	191.23	390	43.3	31.87
Ford Focus C-Max	4cyl-inline monovalent	2.2	112	82.32	?	49.8	37.42
Quantum Prius H2-Hybrid	4cyl-inline hybrid	1.5	71	52.18	111	47.4	34.78
Ford Shuttle E-450	V10 monovalent	6.8	272	199.0	1110	40.0	29.39
Alset H2 Bi-Fuel 1.0	4cyl-inline bivalent	2.0	150	110.25	390	75.2	55.125

Source: Adapted from [13].

with contribution from both the private and public sectors and from different locations. France is one of the leading countries in the market for electric vehicles, aspiring towards 10% market share by 2020 [14]. For the development of the future hydrogen economy, an efficient and safe way of storing hydrogen in different applications, mobile, stationary and portable, is mandatory. Several means of hydrogen storage include compressed hydrogen gas (CGH<sub>2</sub>), liquid cryogenic hydrogen (LH<sub>2</sub>) and solid state hydrogen storage (SSH<sub>2</sub>). Onboard hydrogen storage is one of the key fundamental barriers for commercialization of hydrogen-fuelled light vehicles. Hydrogen storage activities are currently focused on low-pressure material-based technologies allowing *per saldo* driving range above 500 km per vehicle. This means that a mass of more than 5 kg of hydrogen has to be carried, which requires meeting rigorous structural demands with regard to hydrogen tanks, costs, safety and performance requirements in order to be competitive with comparable vehicles available on the market. The current US Department of Energy (DoE) targets for onboard hydrogen storage systems for light-duty vehicles require that in 2017 hydrogen gravimetric and volumetric capacities reach a level of 5.5 wt% and 0.04 kg l<sup>-1</sup>, respectively, corresponding to usable specific energy of 1.8 kWh kg<sup>-1</sup> from hydrogen [15]. Selected DoE Technical Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles (complete system including tanks, materials, valves, regulators and pipes) are presented in Table 1.4.

The vision on how hydrogen could be introduced in the energy system played a major role in the HyWays (the European Hydrogen Energy Roadmap) project [16]. It was highlighted that if hydrogen is introduced into the energy system, the costs to reduce one unit of CO<sub>2</sub> will decrease by 4% by 2030 and 15% by 2050. About 85% of the reduction of emissions is related to road transport, with the projection that CO<sub>2</sub> emissions from road transport will reduce by 50% by 2050 (Figure 1.2).

Introducing hydrogen technologies into the transport sector (cars, light-duty vehicles, heavy trucks) will also have a significant impact on non-CO<sub>2</sub> emissions into the atmosphere. The projections for the emission levels of CO, NO<sub>x</sub>, volatile organic components (VOCs) and particulate matter (PM – solid or liquid particles found in the air) are that the levels will be reduced by more than 70% for NO<sub>x</sub> and other pollutants [17]. The main markets for hydrogen end-use applications are passenger transport, light-duty vehicles and city buses. About half of the transport sector is expected to make a fuel shift towards hydrogen. Heavy-duty transport (trucks) and long distance vehicles are expected to switch to alternative fuels. The involvement of hydrogen in the residential and tertiary sector is expected to be limited to remote areas and specific niche applications, where a hydrogen infrastructure is already present [16]. The main challenges in introducing hydrogen into the energy system still remain the same: cost reduction for end-use application with the main focus on road transport; also, policy support continues to be an issue – the key finding of HyWays was that hydrogen is not high enough on the policymakers' agendas and more demonstration projects are needed in order to increase the awareness about hydrogen perspectives.

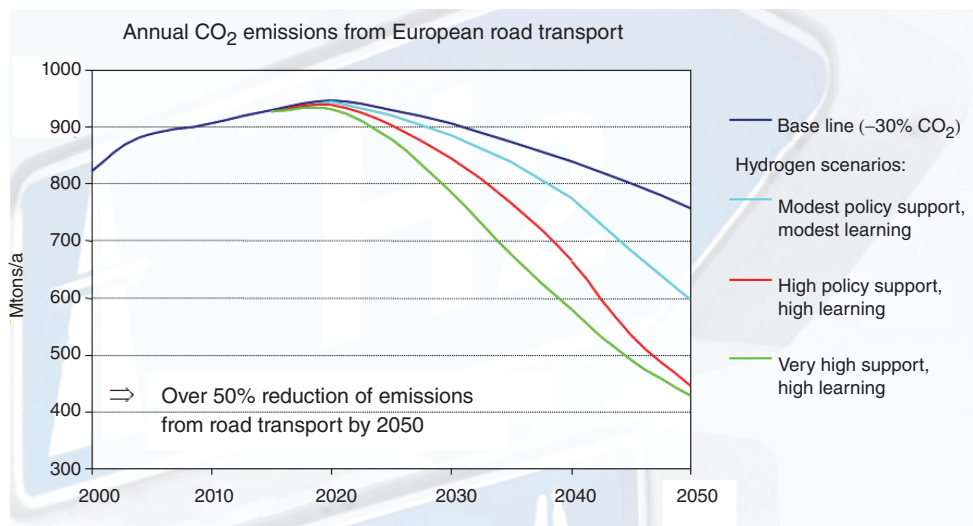
**Table 1.4** Selected DoE technical targets for onboard hydrogen storage systems for light-duty vehicles [15].

Storage parameter	Units	2010	2017	Ultimate
System gravimetric capacity	kWh kg <sup>-1</sup>	1.5	1.8	2.5
Usable specific energy from H <sub>2</sub>	kg H <sub>2</sub> /kg system	0.045	0.055	0.075
System volumetric capacity	kWh l <sup>-1</sup>	0.9	1.3	2.3
Usable energy density from H <sub>2</sub>	kg H <sub>2</sub> /l system	0.028	0.040	0.070
Storage system costs	\$/kWh net	4	TBD	TBD
Fuel cost	\$/gge <sup>a)</sup> at pump	3–7	2–4	2–4
System fill time (5 kg)	min	4.2	3.3	2.5
	kg H <sub>2</sub> /min	1.2	1.5	2.0
Minimum full flow rate	G s <sup>-1</sup> kW <sup>-1</sup>	0.02	0.02	0.02
Operating ambient temperature	°C	–30/50 (sun)	–40/60 (sun)	–40/60 (sun)
Minimum/maximum delivery temperature	°C	–40/85	–40/85	–40/85
Operational cycle life (1/4 tank to full)	Cycles	1000	1500	1500
Fuel purity	% H <sub>2</sub>	99.97% dry basis SAE J2719 and ISO/PDTS 14687-2		

a) gge, gasoline gallon equivalent =  $1.3 \times 10^8$  J.

A summary of the deployment phases, targets (targets for 2020 together with the European Hydrogen and Fuel Cell Platform have been elaborated on) and required main actions until 2050 are shown in Figure 1.3 [17]. Snapshot 2020 refers to the point where production volumes are significantly increased (breaking level at least 100 000 units per year) and snapshot 2030 refers to the maximum growth point where hydrogen and fuel cells are fully competitive with other technologies on the market.





**Figure 1.2** Annual CO<sub>2</sub> emission levels from European road transport; current status and predictions until 2050 based on several hydrogen scenarios on policy support (modest, high and very high). (HyWays and ECN [17].)

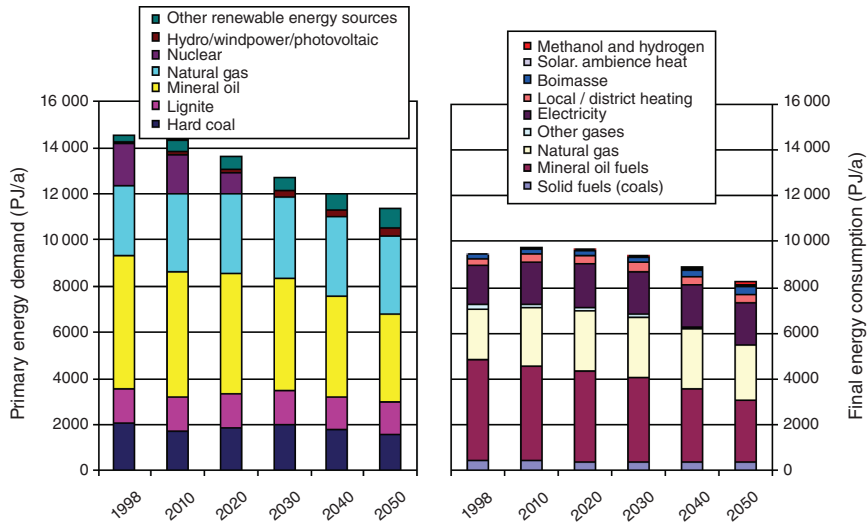
	2010	2015	2020	2030	2050
<b>Phases</b>	<ul style="list-style-type: none"> <li>Technology development with focus on cost reduction</li> </ul>	<ul style="list-style-type: none"> <li>Pre-commercial technology refinement and market preparation</li> <li>Start of commercialization</li> </ul>	<b>HFP Snapshot</b> <ul style="list-style-type: none"> <li>Materialization of first impacts               <ul style="list-style-type: none"> <li>New hydrogen supply capacities partially based on low carbon sources</li> <li>Improvement in local air quality</li> <li>More than 5% of new car sales H<sub>2</sub>&amp;FC</li> </ul> </li> </ul>	<b>HyWays Snapshot 2030</b> <ul style="list-style-type: none"> <li>Hydrogen &amp; FC are competitive               <ul style="list-style-type: none"> <li>Creation of new jobs and safeguarding existing jobs (net employment effect of 200 000 - 300 000 labor years)</li> <li>Shift towards carbon-free hydrogen supply</li> <li>More than 20% of new car sales H<sub>2</sub> &amp; FC</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>H<sub>2</sub> &amp; FC dominant technologies high impact               <ul style="list-style-type: none"> <li>80% of light duty vehicles &amp; city buses fuelled with CO<sub>2</sub> free hydrogen</li> <li>Reaching more than 80% CO<sub>2</sub> reduction in passenger car transport</li> <li>In stationary end-use applications, hydrogen is used in remote locations and island grids</li> </ul> </li> </ul>
<b>Targets</b>	<ul style="list-style-type: none"> <li>LHPs facilitate initial fleet of a few 1 000 vehicles by 2015</li> <li>PPP "Lighthouse Projects"</li> <li>Increase R&amp;D budgets to 80 M€/year</li> <li>Financial support for large scale demonstration projects</li> </ul>		<b>Vehicles</b> <ul style="list-style-type: none"> <li>2.5 million of fleet</li> <li><b>Cost</b> <ul style="list-style-type: none"> <li>H<sub>2</sub>: 4 kg<sup>-1</sup> (50€/barrel)</li> <li>FC: 100 € kw<sup>-1</sup></li> <li>Tank: 10 € kWh<sup>-1</sup></li> </ul> </li> </ul>	<b>Vehicles</b> <ul style="list-style-type: none"> <li>25 million of fleet</li> <li><b>Cost</b> <ul style="list-style-type: none"> <li>H<sub>2</sub>: 3 € kg<sup>-1</sup> (50€/barrel)</li> <li>FC: 50 € kw<sup>-1</sup></li> <li>Tank: 5 € kWh<sup>-1</sup></li> </ul> </li> </ul>	
<b>Required policy support actions</b>	<ul style="list-style-type: none"> <li>Develop H<sub>2</sub> specific support framework               <ul style="list-style-type: none"> <li>Create/support early markets</li> <li>Implement performance monitoring framework</li> <li>Long term security for investing stakeholders</li> <li>Education and training programmes</li> <li>Harmonisation of regulations codes and standards</li> </ul> </li> </ul>		<ul style="list-style-type: none"> <li>H<sub>2</sub> specific support framework               <ul style="list-style-type: none"> <li>In place before 2015 at MS level</li> <li>Deployment supports, e.g. tax incentives of 180 M€/year</li> <li>Public procurement</li> <li>Planning and execution of strategic development of hydrogen infrastructure</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>Gradual switch from hydrogen specific support to generic support of sustainability (2020 →)</li> </ul>	<ul style="list-style-type: none"> <li>Incentives provided through general support schemes for sustainability</li> </ul>
	2010	2015	2020	2030	2050

**Figure 1.3** A summary of the deployment phases, targets and main actions until 2050. (HyWays and ECN [17].)

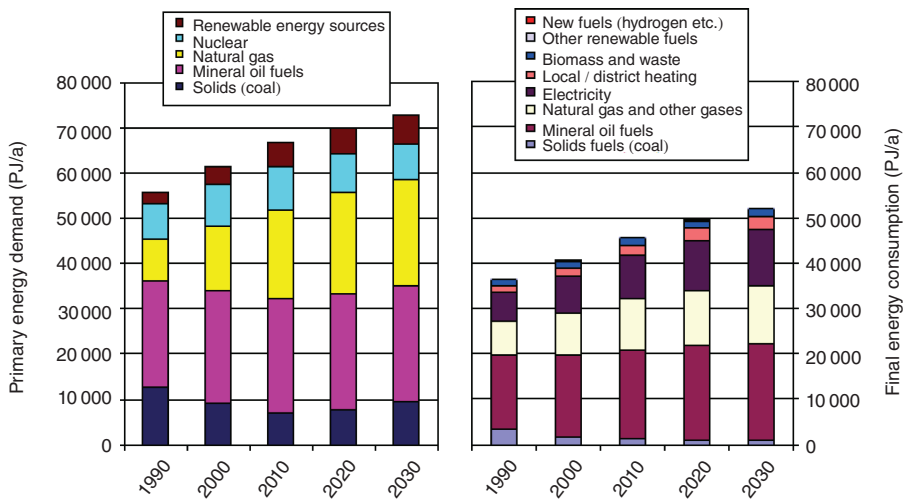
On the basis of the HyWays project findings, several key R&D areas for mobile and stationary hydrogen and fuel cells have been formulated. They include significant cost reduction for the H<sub>2</sub> drive train (improvement of PEM fuel cells and its periphery components, onboard storage, hydrogen ICE integration and system optimization), cost reduction for the hydrogen production chains, system integration for hydrogen systems and intensified development of RCS for



hydrogen. Last but not the least, it is of importance to comply with long-term sustainability requirements (production of hydrogen from renewable power sources, fossil fuels with carbon capture and storage – CCS, nuclear power and with closed fuel cycle) [17]. The main challenges that have been listed by the US DoE [18] can be summarized as follows: hydrogen is currently more expensive than gasoline and hydrogen storage systems for automotives cannot meet driving range expectations (above 300 miles) presently without occupying additional space. Given the technology status, the risk of hydrogen delivery infrastructure is still high. Within the scope of the German HyTrust project a current state of public acceptance in hydrogen technology in the mobility sector has been analysed. On the basis of results from interviews, focus groups, conferences and representative surveys, it can be stated that the German population has a very positive attitude towards hydrogen-powered cars, viewing them as a possibility of being mobile without harming the environment. People have no safety concerns regarding hydrogen or hydrogen cars, but they expect that the hydrogen that is used for Fuel Cell Electric Vehicles (FCEV) is produced from electricity based on renewable sources. What is interesting is that there are no safety concerns towards hydrogen and hydrogen-powered vehicles in the population because there is a basic trust in the German technology system [19]. Detailed analysis on prospects for hydrogen in different energy scenarios has been performed [8], and the relevant cases were based on (i) the study commission of the German Parliament “Nachhaltige Energieversorgung unter den Bedingungen der Globalisierung und der Liberalisierung” (Final Report of the Study Commission of the German Parliament in 2002), (ii) scenario study of the European Energy and Transport Trends to 2030 in 2003 and (iii) and the “World Energy Outlook 2002” of the International Energy Agency (IEA) in 2002. The three bodies estimated prospects for hydrogen in future energy systems differently. In Germany it is assumed that hydrogen will be introduced into the final energy carrier market after 2020, reaching about 2% of the total consumption of all fuels by 2050. Hydrogen usage will focus on the transportation market for fuel cells in passenger cars and buses. Around 25% of the hydrogen is to be used for electricity production. To sum up, the role of hydrogen is assumed to be very small for the next five decades. According to the European Commission (EC), the demand for new energy carriers such as hydrogen will grow, but will be insignificant till 2030 as a result of no significant market share for new vehicle technologies such as FCEV. This is also due to the lack of sufficient infrastructure for the supply and distribution of hydrogen. On the other hand, the world energy outlook of the IEA sees prospects for hydrogen use in power generation. It is assumed that global energy use will increase steadily through 2030. Global primary energy demand is projected to increase by 1.7% per year from 2000 to 2030, reaching an annual level of 650 EJ. In that scenario, hydrogen from reformed natural gas converted in fuel cells for electricity generation is expected to emerge as a new source of power generation, especially after 2020. All three scenarios are discussed below (Figures 1.4–1.6).



**Figure 1.4** Primary energy demand and final energy consumption and hydrogen in Germany [8].



**Figure 1.5** EU-15 baseline scenario of primary energy demand and final energy consumption [8].

## 1.1

### Overview on Different Hydrogen Production Means from a Technical Point of View

Hydrogen production is the main step towards transitioning to a hydrogen economy, wherein hydrogen will replace fossil fuels. Hydrogen can be produced by processing a multitude of primary energy resources such as fossil fuels (coal, crude

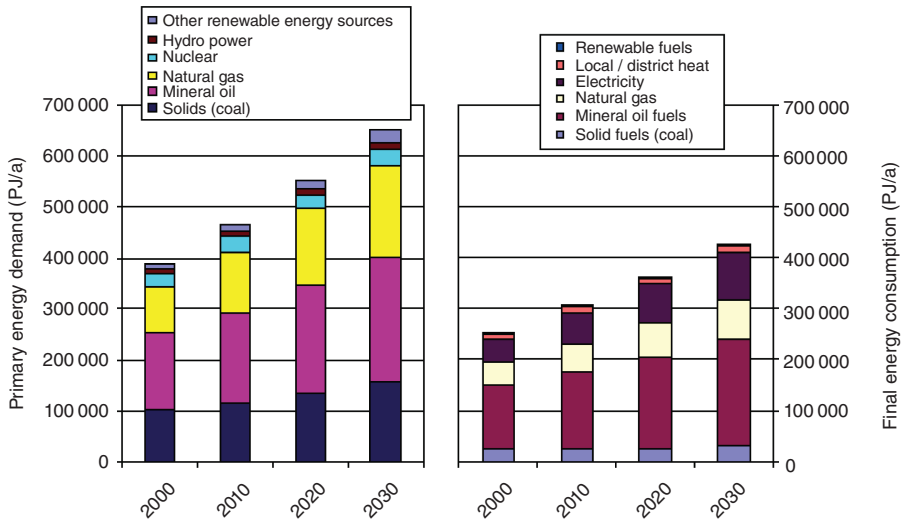
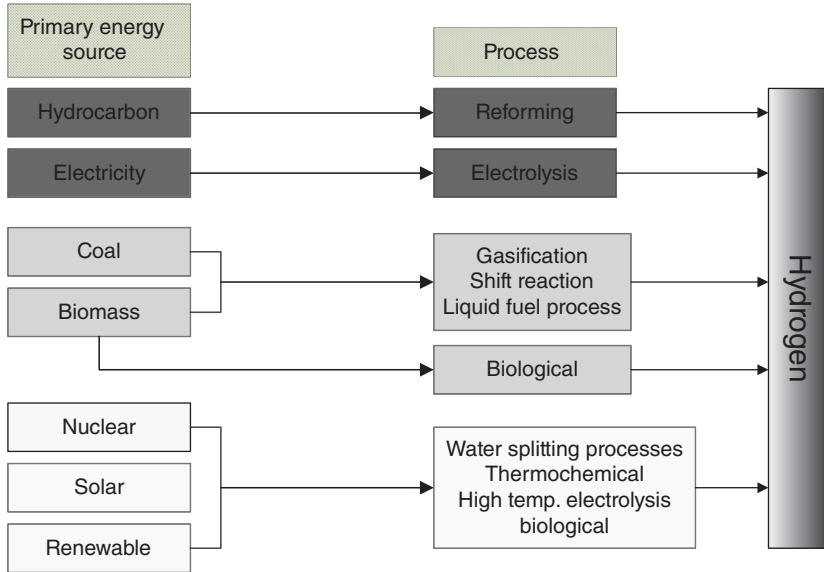


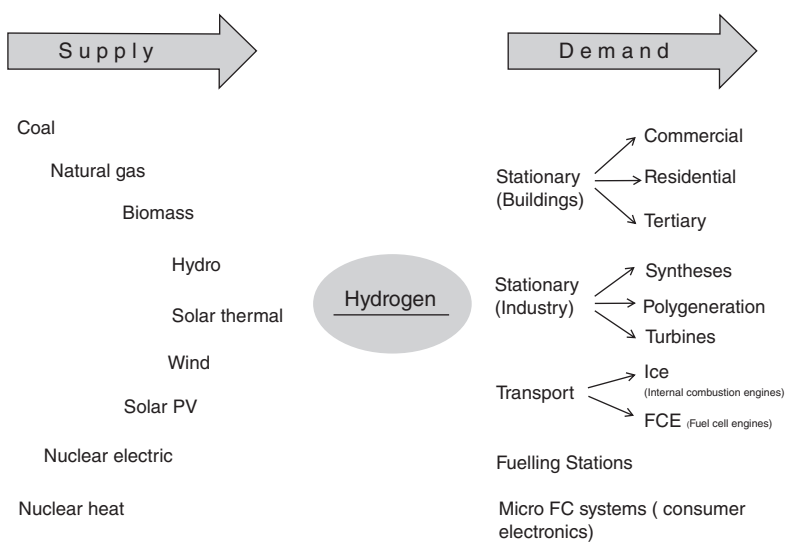
Figure 1.6 World of primary energy demand and final energy consumption by fuel [8].

oil, natural gas, etc.), nuclear fuels (e.g. deuterium, thorium, uranium), geothermal (heat that is stored in underground streams or in hot rocks beneath the earth) as well as solar, wind and tidal energy. These energy sources can also be classified into two groups: renewable (which are non-exhaustible and provide continuous energy supply such as solar or wind energy) and non-renewable, where resources are exhaustible and limited such as fossil fuels. The aim of this section is to give a short overview on the current ways of producing hydrogen such as reforming processes, electrolysis or gasification as well as methods that are in the R&D stage. The major hydrogen production technologies are those producing hydrogen from fossil fuels, from biomass or from water. As can be seen in Figure 1.7, hydrogen can be produced from fossil fuels by steam reforming of natural gas, thermal cracking of natural gas, partial oxidation (POX) of heavy fractions or coal gasification; from biomass by burning, fermenting, pyrolysis, gasification followed by liquefaction or biological production; from water by electrolysis, photolysis, thermochemical processes, thermolysis and combinations of biological, thermal and electrolytic processes. More details on different hydrogen production routes can be found, for example, in [20–26].

Hydrogen can be used in ICE as well as converted to electricity to power electric motors by means of fuel cells, mainly PEMFC. In transportation hydrogen is used in passenger cars, buses and light-duty vehicles. A general illustration of the supply → demand chain as well as the classification of end-users of hydrogen is presented in Figure 1.8.



**Figure 1.7** General pathways of hydrogen production. (By permission of Wiley VCH.)



**Figure 1.8** Hydrogen by means of different sources and its potential application in stationary, transportation and portable sectors [20]. (By permission of Wiley VCH.)

## 1.1.1

**Reforming**

Reforming processes, especially steam reforming, in combination with fossil fuels are the dominant processes for hydrogen production today. Typical feedstock is natural gas, but liquid hydrocarbons such as gasoline can also be used. Three reforming methods that are briefly presented here are catalytic steam reforming (CSR), POX and autothermal reforming (ATR). The chemistry of fuel processing methods, state of the art of catalyst technology for fuel processing applications, fuel processing reactors and balance of plant components has been described in detail by Kolb [27]. Steam reforming of natural gas is currently the cheapest, technically and commercially well-established way to produce hydrogen and is mainly used in the petrochemical and chemical industries. The cost of hydrogen production from steam reforming strongly depends on the costs and availability of natural gas feedstock.

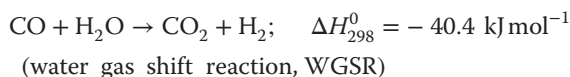
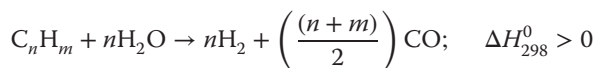
Steam reforming is highly endothermic – high reaction temperatures, typically above 600 K, and pressure of about 2–3 MPa [28] are needed for gas phase conversion in the presence of Fe- or Ni-based catalysts supported on  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$ .

The efficiency of steam reforming is around 65–70% [20]. Steam reforming of light hydrocarbons is also a well-established industrial process. One of the benefits of using methanol is that the reforming reaction can be carried out at a lower temperature – endothermic steam reforming can be carried out at around 300 °C over a Co–Zn catalyst [29], whereas about 800 °C is required for hydrocarbons. Theoretically, steam reforming of methanol can produce 75% hydrogen concentration at 100%  $\text{CO}_2$  selectivity; in practice, it is more than 70% with various catalysts [30]. Higher temperatures (850–1500 °C) are required for the steam reforming of ethanol because of its C–C bond [31]. POX reforming is an exothermic reaction that uses a substoichiometric amount of oxygen, generally from air, to convert the fuel to a  $\text{H}_2$ -containing stream. The substoichiometric amount of  $\text{O}_2$  used results in significant production of carbon monoxide (CO). The process is much faster than steam reforming and can occur with or without the presence of catalysts. The non-catalytic Texaco process operates at temperatures in the range of 1200–1500 °C and pressure above 3 MPa. Catalytic POX uses lower temperatures of around 1000 °C, but for production of pure hydrogen it is less efficient and more costly than steam reforming. Catalysts include supported nickel (NiO–MgO), nickel-modified hexa-aluminates, platinum group metals Pt, Rh, Pd/alumina on ceria-containing supports or on titania [20]. In case of POX, only fuel and feed air is required for the reaction; there are no evaporation processes with the typical by-product methane. The disadvantage of the POX process is catalyst deactivation due to coke deposition and CO. ATR or oxidative steam reforming combines the endothermic steam reforming process with the exothermic POX reaction; therefore it is called autothermal. In such combination, the energy generated by the POX reaction provides the energy for the steam reforming reaction. These systems can be very productive and fast

starting and have been demonstrated with methanol, gasoline and natural gas. ATR has several advantages such as improved heat integration, faster start-up and lower operating temperatures. As in the case of the POX product stream, the autothermal reformat stream contains CO and the  $H_2$  is further diluted by the nitrogen added from air. Among various onboard processing methods for liquid fuels oxidative methanol reforming (OMR) is regarded as the most promising for supplying hydrogen to PEMFCs in a vehicle. The OMR reaction is a combination of POX with steam reforming at a ratio where the overall reaction is thermally neutral or modestly exothermic. It has been confirmed that the high activity of the process of methanol conversion and the high selectivity of hydrogen production are enhanced by the presence of a Pd–ZnO catalyst [32].

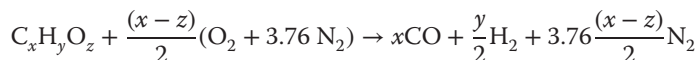
Respective reforming reactions in a general way are as follows [27]:

Steam reforming:

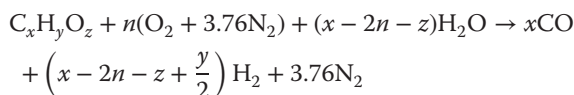


WGSR increases the hydrogen concentration of reformat. It occurs in two stages, as high temperature shift (HTS) at around 350 °C and as low temperature shift (LTS) at around 200 °C. Ideally, WGS reactions should reduce the CO level down to less than 5000 ppm.

POX:



ATR:



### 1.1.2

#### Electrolysis

This section presents main state-of-the-art alkaline and PEM water electrolyzers and a review of manufacturers worldwide. Detailed information on the relevant technologies including operational principles, characteristics, applications and limitations and challenges will be presented in the respective parts of the book. Chapter 2 provides dedicated information on water electrolysis technologies: both alkaline and PEM based. Chapter 3 provides detailed information on high-temperature steam electrolysis. Despite more than 100 years of experience in alkaline electrolysis systems and thousands of installed plants all over the world, only a few systems or industries that provide the state of the art on

this technology remain. Several examples are given in Table 1.7. According to Carmo *et al.* [33] and Mergel *et al.* [23], this could be because of the cost of electrical energy. Electrolytic hydrogen costs are not being able to compete with the production costs for hydrogen by conventional steam reforming of fossil fuels. Challenges of alkaline electrolyser technology concern system lifetimes and maintenance costs. There is currently increased interest with regard to PEM electrolysis technology and over the past 20 years new companies have appeared on the market and new projects have been established in the field. The efficiency of PEM technology could reach a level from 55% to 70%. Key worldwide players in PEM electrolysers area are provided in Tables 1.5 and 1.6 [33]. PEM water electrolysis is still rather expensive due to platinum-based family catalysts and proton exchange membrane. Nevertheless, PEM electrolysis is well suited to be coupled with wind and solar energy.

**Table 1.5** Realized alkaline water electrolyser manufacturers [33].

Manufacturer	Rated power (kW)	H <sub>2</sub> production rate (Nm <sup>3</sup> h <sup>-1</sup> )	Specific energy consumption (kWh Nm <sup>-3</sup> )	Maximum pressure (bar)	Location
Brown Boveri (KIMA)	165 000	33 000	—	—	Aswan – Egypt
De Nora	150 000	30 000	4.6	atm	Nangal – India
Norsk Hydro	140 000	28 000	4.1	atm	Ryukan – Norway
Norsk Hydro	135 000	27 000	4.1	atm	Ghomfjord – Norway
Que Que	105 000	21 000	—	—	Zimbabwe
Electrolyser Inc.	76 000–10 5000	15 200–21 000	4.9	atm	Trail – Canada
Lurgi	22 500	4500	4.3	3	Cuzco – Peru
IHT	511.5–3534	110–760	4.65 to 4.3	32	Switzerland
NEL Hydrogen Technologies – Statoil	43–2 150 \$10–500	4.3	atm	Norway	—
ELT (Barisic)	13.8–1 518	3–330	4.6 to 4.3	atm	Germany
Linde	N.a.	5–250	N.a.	25	Germany
AccaGen	6.7–487	1–100	6.7 to 4.87	10 (optional 30 and 200)	Switzerland
Idroenergy	3–377	0.4–80	7.5 to 4.71	1.8–8	Italy
Hydrogenics	54–312	10–60	5.4 to 5.2	10 (optional 25)	Canada
Teledyne Energy Systems	N.a.	2.8–56	N.a.	10	USA
H2Logic	3.6–213	0.66–42.62	5.45 to 5	4 (optional 12)	Denmark
Claind	N.a.	0.5–30	N.a.	15	Italy
Erredue	3.6–108	0.6–21.3	6 to 5.1	2.5–4	Italy
PIEL, division of ILT Technology	2.8–80	0.4–16	7 to 5	1.8–18	Italy
Sagim	5–25	1–5	5	10	France
Avalence	2–25	0.4–4.6	5.43 to 5	448	USA

Source: By permission of EFCF Luzern 2013, [www.efcf.com](http://www.efcf.com).



**Table 1.6** Main PEM water electrolyser manufacturers [33].

Manufacturer	Rated power (kW)	H <sub>2</sub> production rate (Nm <sup>3</sup> h <sup>-1</sup> )	Specific energy consumption (kWh Nm <sup>-3</sup> )	Maximum pressure (bar)	Location
Proton Onsite	1.8–174	0.265–30 (concept: 90)	7.3 to 5.8	13.8–15 (optional 30)	USA
ITM Power	3–40	0.6–7	4.9–5.5	15	UK
Giner	20	3.7	5.4	85	USA
H-TEC Systems	1.5–20	0.3–3.6	5–5.5	30	Germany
Hydrogenics	7.2	1	7.2	7.9	Canada
Siemens	N.a.	20	N.a.	50	Germany
Treadwell Corp.	N.a.	1.2–10.2	N.a.	75.7	USA

Source: By permission of the EFCF Luzern 2013, [www.efcf.com](http://www.efcf.com).

### 1.1.3

#### Gasification

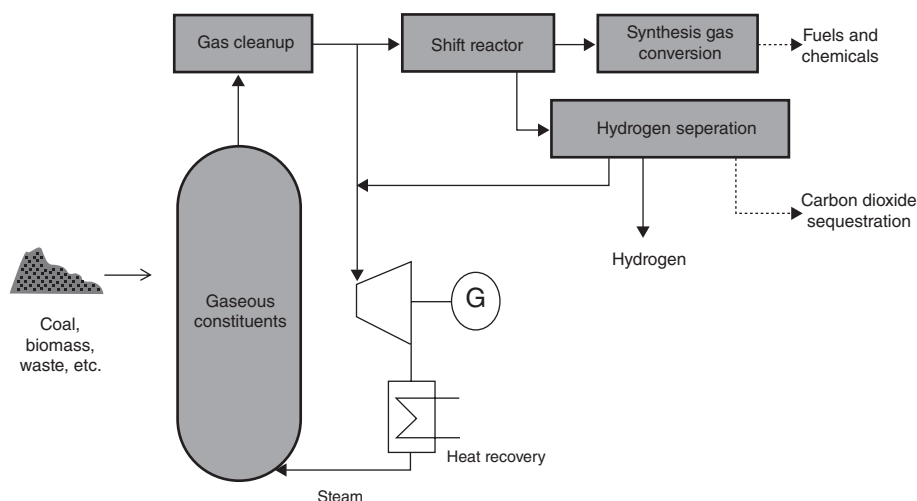
Systems based on gasification can utilize coal, petroleum coke, biomass and municipal and hazardous wastes. In principle the process is similar to POX of heavy oils and involves three main steps: conversion of coal feedstock in the presence of oxidant (typically oxygen or air and steam) to syngas at high temperatures of 1000–1500 °C in a gasification reactor, catalytic shift reaction and purification of the produced hydrogen, typically from residual carbon and ash. Depending on the gasification technology, some water, CO<sub>2</sub> and CH<sub>4</sub> could be present in the syngas including traces of components such as hydrogen cyanide (HCN), hydrogen chloride gas (HCl), hydrogen sulphide (H<sub>2</sub>S) and carbonyl sulphide (COS). Generated syngas can either be used directly to produce electricity or be further processed to pure hydrogen to be used for hydrocracking of petroleum or ammonia production (Figure 1.9).

During the pyrolytic process the biomass is heated at 370–550 °C at 0.1–0.5 MPa in the absence of air to convert it into liquid oils, solid charcoal and gaseous compounds. A variety of different types of biomass have been pyrolytically processed for hydrogen generation. They include, for example, pelletized peanut shells [34–36], post-consumer residues such as plastics, trap grease, mixed biomass and synthetic polymers [37] as well as bagasse, switchgrass and a nutshell mixture composed of 40% almond nutshells, 40% almond prunings and 20% walnut shells [38].

### 1.1.4

#### Biomass and Biomass-Derived Fuels Conversion

Biomass and biomass-derived fuels are renewable energy sources that can be used to produce hydrogen in a sustainable way. Generally speaking, four main types of

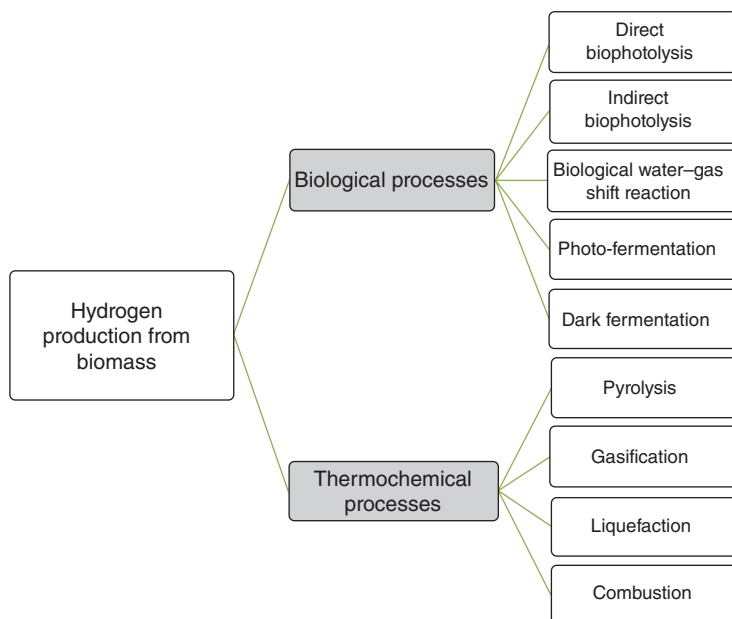


**Figure 1.9** Gasification-based energy conversion options. (By permission of Wiley VCH.)

biomass feedstock can be distinguished: (i) energy crops including herbaceous, woody, industrial, agricultural and water, (ii) agricultural residues and waste, (iii) forest waste and residues and (iv) industrial and municipal wastes [39]. The use of a variety of biomass instead of fossil fuels for hydrogen generation may reduce  $\text{CO}_2$  emissions to the atmosphere, because the  $\text{CO}_2$  released when the biomass is gasified has previously been absorbed from the atmosphere and fixed by photosynthesis in the growing plants. It is estimated that about 12% of today's world energy supply comes from biomass, and the contribution from developing countries is significant higher, about 40–50% [39]. A wide range of technologies exists for transforming biomass into hydrogen, as can be seen in Figure 1.10 [20]. Processes can be divided into thermochemical and biological (fermentation) routes, relevant in both the near term and the mid term. In the long term hydrogen can be produced using photobiological processes, such as photosynthesis in cyanobacteria and algae.

Hydrogen can be produced via purely biological routes through the fermentation of biomass using microorganisms, or directly from cyanobacteria, purple bacteria and microalgae. All biological hydrogen production processes depend on the presence of hydrogen-producing enzymes (nitrogenase, Fe hydrogenase and NiFe hydrogenase). Algae and some microbial fermentations use photosynthesis to produce hydrogen. Other fermentation processes and direct production of hydrogen from cyanobacteria can take place in the absence of light. In Table 1.7, the advantages and disadvantages of different biological routes for hydrogen production are listed.

Research on biomass fermentation for hydrogen is increasing rapidly, especially on thermophilic bacteria and hydrogenases. Photobiological processes appear promising, but are not likely to become commercially available for some years [12].



**Figure 1.10** Technologies for hydrogen production from biomass [20]. (By permission of Wiley VCH.)

Photobiological hydrogen production is based on photosynthesis in bacteria and green algae. Hydrogen production in photobiological systems is presently limited by low energy conversion efficiencies. Markov *et al.* [40] have reviewed the state of the art of the development of bioreactors, dividing them into two categories based on the nature of hydrogen-evolving reactions. One category consists of photobioreactors based on hydrogen photoproduction and includes three types: (i) photobioreactors incorporating cyanobacteria, (ii) photobioreactors incorporating green algae and (iii) photobioreactors incorporating purple bacteria. To the second category belong bioreactors based on dark anaerobic hydrogen production with three types: (i) “water gas shift reaction” bioreactors incorporating purple bacteria, (ii) anaerobic fermentation bioreactors incorporating chemotrophic bacteria and (iii) bioreactors with immobilized enzymes. Biological processes for hydrogen generation are still at an early stage of development, mainly on a laboratory scale; however, there is intensive research under way to find ways to improve hydrogen yield and hydrogen production rates.

### 1.1.5

#### Water Splitting

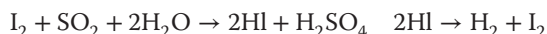
Hydrogen can also be produced by splitting water and here three processes can be distinguished: electrolysis, photochemical processes and thermochemical cycles. Electrolytical water and steam splitting processes will be discussed in detail in

**Table 1.7** Advantages and disadvantages of different biological processes for hydrogen production depending on the type of microorganism [20].

Type of microorganism	Advantages	Disadvantages
<b>Green algae</b>		
<i>Chlamydomonas reinhardtii</i>	Can produce H <sub>2</sub> from water	Require light for H <sub>2</sub> production
<i>Chlamydomonas moevussi</i>	Solar conversion energy increased by 10-fold as compared to trees, crops	O <sub>2</sub> can be dangerous for the system
<i>Scenedesmus obliquus</i>		
<b>Cyanobacteria</b>		
<i>Anabaena azollae</i>	Can produce H <sub>2</sub> from water	Uptake hydrogenase enzyme needs to be removed to stop degradation of H <sub>2</sub>
<i>Anabaena CA</i>	Nitrogenase enzyme mainly produces H <sub>2</sub>	Require sun light
<i>Anabaena cylindrica</i>	Has the ability to fix N <sub>2</sub> from atmosphere	About 30% of O <sub>2</sub> is present in gas mixture with H <sub>2</sub>
<i>AnabaenaCarlabilis</i>		CO <sub>2</sub> is present in the gas
<i>Nostoc muscorum</i>		O <sub>2</sub> has inhibitory effect on nitrogenise
<i>Nostoc sponglaeforme</i>		
<i>Westiellopsis prolifica</i>		
<b>Photosynthetic bacteria</b>		
<i>Rhodobacter sphaeroides</i>	Can use different materials such as whey, distillery effluents	Require light for H <sub>2</sub> production
<i>Rhodobacter capsulatus</i>	Can use wide spectrum of light	Fermented broth causes water pollution problem
<i>Rhodobacter sulidophilus</i>		
<i>Rhodopseumodomonas sphaeroides</i>		
<i>Rhodopseumodomonas paluxtris</i>		
<i>Rhodopseumodomonas capsulate</i>		
<i>Rhodospilillum rubnum</i>		
<i>Holabacterium halobium</i>		
<i>Chlorobium limicola</i>		
<i>Chloroflexu aurantiacus</i>		
<i>Thiocapsa roseopersicina</i>		
<b>Fermentative bacteria</b>		
<i>Enterobacter aerogenes</i>	Can produce H <sub>2</sub> all day long without light	Fermented broth is required to undergo further treatment before disposal; otherwise it causes water pollution problem
<i>Enterobacter cloacae</i>	Can utilize different carbon sources such as starch, cellobiose, sucrose, xylose	CO <sub>2</sub> present in the gas
<i>Clostridium butyricum</i>	Different types of raw materials can be used	
<i>Clostridium pasteurianum</i>	Produces valuable metabolites such as butyric acid, lactic acid as by-products	
<i>Desulfovibrio vulgaris</i>	Anaerobic process, therefore no oxygen limitation problems	
<i>Magashaera elsdonii</i>		
<i>Citrobacter intermedius</i>		
<i>Escherichia coli</i>		

the respective chapters of the book. In case of thermochemical cycles, water is decomposed directly into hydrogen and oxygen through numerous endothermic and exothermic chemical reactions at temperatures oscillating above 2500 °C in order to obtain significant dissociation rates. Light is used to light up a semiconductor-based photocatalyst immersed in an aqueous electrolyte or water [41, 42]. Hydrogen can be generated using the nuclear energy of thermochemical cycles (e.g. sulphur–iodine or UT-3) and hybrid cycles with the electrolytic and thermochemical steps. This process requires a large amount of heat or electricity to generate hydrogen, which can be supplied by nuclear energy. It is estimated that one of the most promising thermochemical cycles for massive-scale hydrogen production is the sulphur–iodine (S–I) cycle (originally developed by General Atomic) with thermal to hydrogen efficiency of 52% and adiabatic UT-3 cycle (calcium–bromine cycle) developed at the University of Tokyo with efficiency of around 50% [20].

The sulphur–iodine cycle (S–I cycle) is probably the most studied thermochemical cycle. It consists of two successive reactions taking place at 180 and 400 °C, respectively [43]



This hydrogen production way is particularly interesting for the concentrated solar power (CSP) technologies.

In the feasibility study for a commercial plant, the UT-3 cycle in Japan showed a hydrogen capacity of 20 000 Nm<sup>3</sup> h<sup>−1</sup>. Japan Atomic Energy Research Institute (JAERI) aimed at connecting a nuclear system with a chemical process producing hydrogen. High-temperature steam electrolyzers using nuclear energy are able to generate hydrogen without the corrosive conditions associated with thermochemical processes and greenhouse gas emissions associated with hydrocarbon processes [44]. In general, there are more than 300 water splitting processes reported in the literature allowing a temperature reduction from 2500 °C, but they usually work at higher pressures. Some examples are the Ispra Mark process, sulphur acid decomposition and the SynMet process of ZnO reduction and methane reforming in a solar reactor developed at the Paul Scherrer Institute. Thermochemical cycles coupled to a solar energy source work at lower temperatures (around 1200–1800 °C) and have been investigated in various research studies by using a laboratory demonstrator on a pilot scale over years. The German Aerospace Center (DLR) is working since the 1970s on directly using solar energy, including photovoltaics and solar thermal, and on iron-based thermochemical cycle processes [45]. After successful solar thermochemical hydrogen production in pilot tests (HYDROSOL-2) at the DLR, Cologne, the process was introduced in the Spanish Plataforma Solar de Almeria (PSA) in Tabernas. A demonstration of the process by operating a solar receiver–reactor has shown repeatable hydrogen production in multiple cycles and is summarized by Neises [46]. The author also discussed investigations on the two-step thermochemical cycle using silicon carbide honeycombs coated with a zinc ferrite redox system. Another concept is

based on the photoelectrochemical cell (PEC cell). In the PEC cell, oxidation and reduction take place on locally separated electrodes. One of the main key challenges, apart from complicated and expensive architecture of the devices, is the requirement for an efficient photocatalyst. It should be cheap, easy to produce and non-toxic. Moreover, it should not contain scarce or expensive chemical elements. The potential of various photocatalysts has been reviewed by Ashokkumar [47], whereas a review and recent developments in photocatalytic water splitting for  $H_2$  production using titanium oxide can be found in [48]. A very interesting material class in this context includes perovskite-type-related oxynitrides, which offer the possibility to absorb visible light and to be adapted to the numerous requirements by defect engineering and substitution. It has been demonstrated that the activity of  $LaTiO_2N$ , which is used as a photoanode in PEC cells, can be improved by substitution and that modifications in the microstructure and in the particle size influence its performance [49].

## 1.2

### Summary Including Hydrogen Production Cost Overview

The most significant part of the hydrogen economy is hydrogen production in a sustainable, efficient and environmentally friendly way. The key challenge of different hydrogen production methods from various sources is to reduce costs. “Low-cost hydrogen will foster a new era of energy sustainability, based on hydrogen” [50]. Table 1.8 presents US DoE estimated targets and costs of producing hydrogen by selected technological processes [18].

Table 1.9 depicts an overview of hydrogen production costs from different processes taking into account numerous literature sources.

Table 1.10 concentrates exclusively on hydrogen production costs from electrolysis.

From Tables 1.9 and 1.10 it can be observed that the cost windows of steam reforming of light hydrocarbons and electrolysis slightly overlap, making electrolysis competitive with steam reforming in some specific situations. However, these two tables also highlight large disparities in hydrogen production costs. They can be explained on the basis of the different assumptions made by the authors of the mentioned studies. Factors of influence that have been identified are essentially:

- Maturity of the technology (pilot plant, industrial plant)
- Investment, operation, maintenance and replacement costs of the different equipments
- Size of the production plant
- Cost of energy source (coal, electricity, natural gas, etc.)
- Efficiency, capacity factor, and lifetime of the plant
- Purity of produced hydrogen.

**Table 1.8** DoE technical targets for hydrogen production from a variety of feedstock.

<i>Distributed production of hydrogen from bioderived renewable liquids</i>					
Parameters	Units	2006	2012	2017 target	
Production unit energy efficiency	%	70.0	72.0	65–75	
Capital costs (uninstalled)	\$	1.4 M	1.0 M	600 K	
Total hydrogen costs	\$/gge	4.40	3.80	<3.00	
<i>Distributed hydrogen production from natural gas</i>					
Parameters	Units	2003	2006	2010	2015
Production unit energy efficiency	% (LHV)	65.0	70.0	72.0	75.0
Production unit capital costs (uninstalled)	\$	12.3 M	1.1 M	900 K	580 K
Total hydrogen costs	\$/gge H <sub>2</sub>	5.00	3.00	2.50	2.00
<i>Distributed water electrolysis hydrogen production</i>					
Parameters	Units	2003	2006	2012	2017 target
Hydrogen costs	\$/gge	5.15	4.80	3.70	<3.00
Electrolyser capital cost	\$/gge (\$/kW)	NA	1.2 (665)	0.70 (400)	0.30 (125)
Electrolyser energy efficiency	% (LHV)	NA	62	69	74
<i>Central wind water electrolysis</i>					
Parameters	Units	2006	2012	2017 target	
Hydrogen costs (plant gate)	\$/gge	5.90	3.10	<2.00	
Electrolyser capital cost	\$/gge (\$/kW)	2.20 (665)	0.80 (350)	0.20 (109)	
Electrolyser energy efficiency	% (LHV)	62	69	74	
<i>Biomass gasification/pyrolysis hydrogen production</i>					
Parameters	Units	2005	2012	2017 target	
Hydrogen costs (plant gate)	\$/gge	<2.00	1.60	1.10	
Total capital investment	\$M	<194	150	110	
Energy efficiency	%	>35	43	60	
<i>Solar-driven high-temperature thermochemical hydrogen production</i>					
Parameters	Units	2008	2012	2017 target	
Hydrogen costs (HTTC)	\$/gge H <sub>2</sub>	10.00	6.00	3.00	
Heliostat capital cost	\$/m <sup>2</sup>	180	140	80	
Process energy efficiency	%	25	30	>35	
<i>Photochemical hydrogen production</i>					
Parameters	Units	2003	2006	2013	2018 target
Usable semiconductor bandgap	eV	2.8	2.8	2.3	2.0
Chemical conversion process efficiency	%	4	4	10	12
Plant solar to hydrogen efficiency	%	NA	NA	8	10
Durability	h	NA	NA	1000	5000



**Table 1.8** (Continued)

<i>Distributed production of hydrogen from bioderived renewable liquids</i>					
Parameters	Units	2006	2012	2017 target	
<i>Photolytic biological hydrogen production from water</i>					
Parameters	Units	2003	2006	2013	2017 target
Utilization efficiency of solar light energy	%	10	15	15	20
Efficiency of incident light energy to H <sub>2</sub> from water	%	0.1	0.1	2	5
Duration of continuous photoproduction	Time units	NA	NA	30 min	4 h
O <sub>2</sub> tolerance (half life in air)	Time units	1 s	1 s	10 min	2 h
<i>Dark fermentation hydrogen production</i>					
Parameters	Units	2003	2006	2013	2018
Yield of H <sub>2</sub> production from glucose	mol H <sub>2</sub> /mol glucose	2	2	4	6
Feedstock cost	cents/lb sugar	13.5	13.5	10	8
Duration of continuous production	Time units	17 d	17 d	3 mo	6 mo
<i>Photosynthetic bacterial hydrogen production</i>					
Parameters	Units	2003	2006	2013	2018
Efficiency of incident solar light energy to H <sub>2</sub> from organic liquids	%	1.9	1.9	3.0	4.5
Molar yield of carbon conversion to H <sub>2</sub> (depends on nature of organic substrate)	% of maximum	42	42	50	65
Duration of continuous photoproduction	Time units	6 d	6 d	30 d	3 mo

Source: Adapted from [18].

According to [43], 45–50 million tons of hydrogen are produced each year. The majority of this production comes from reforming of light hydrocarbons or oxidation of heavy hydrocarbons as depicted in Figure 1.11.

It has been noticed that hydrogen production from electrolysis represents a very small part of the total production (4%). The amount of hydrogen produced by the other technologies mentioned previously can be considered negligible.

Among all these different production means, some of them are practical from an industrial point of view (although of different maturity levels) and present the advantage to produce clean hydrogen and solve the environmental issues related to the production of hydrogen from reforming of light hydrocarbons or oxidation of heavy hydrocarbons. Water electrolysis, thermochemical transformation of biomass, photosynthetic microorganisms, photoelectrolysis of water and thermochemical cycles could be distinguish here. It is worth pointing out once again that electrolysis can be considered a sustainable way to produce hydrogen only if

**Table 1.9** Overview of hydrogen production from different processes.

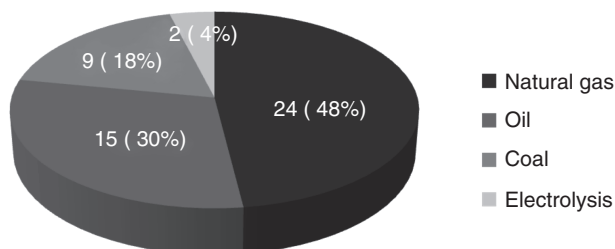
Process	Production costs (€/kg <sub>H<sub>2</sub></sub> )	Comments	Sources
Steam reforming of light hydrocarbons	[1.06; 2.08]		[28, 51, 52]
Partial oxidation of heavy hydrocarbons	[0.72; 1.41]	According to [53] hydrogen production cost from coal may drop down to 0.54 €/kg in the future thanks to R&D efforts (standardization of plant design and execution concept, improvements in reliability, gas cooler designs, etc.)	[28, 51–53]
Thermochemical transformation of biomass	[1.03; 5.39]	These costs are based on evaluations and mainly differ due to assumptions on biomass cost and on the use of either a pilot plant or an industrial plant	[51, 54, 55]
Photosynthetic microorganisms	[0.40; 9.47]	These costs are based on evaluations and disparities mainly depend on assumptions on hydrogen storage capacity, requirement for compression or cost of photobioreactor	[56]
Photoelectrolysis of water	[1.07; 13.5]	These costs are based on evaluations and disparities mainly depend on assumptions on the process used, efficiency, plant lifetime and photoelectrochemical reactor cost	[42]
Thermal dissociation of water	—	The high temperature required for the dissociation reaction to take place requires very resistant materials. Because of these requirements this hydrogen production method is still in the research phase; as such, no solid estimate of costs can be made	—
Thermochemical cycles	[2.66; 9.40]	These costs estimates are based on the cadmium oxide and sulphur–iodine cycles. Disparities can be attributed to assumptions such as cost of electricity, capital cost and capacity factor	[57, 58]

the electricity used comes from renewable sources. Similarly, for thermochemical cycles to be qualified as a clean hydrogen production mean, the heat required must come from a renewable source or must be wasted heat from an industrial process.

Consequently, it is important to realize that local considerations play an important role in the final cost of the produced hydrogen (costs to import the required equipment, local costs of energy, etc.).

**Table 1.10** Overview of hydrogen production costs from electrolysis.

Electrolysis technology	Production costs (€/kg H <sub>2</sub> )	Comments	Sources
Alkaline and PEM	[1.94; 8.60]	These costs mainly differ due to assumptions on: <ul style="list-style-type: none"> <li>– The size of the electrolyser (from 100 W to several megawatts)</li> <li>– The origin and cost of electrical energy (direct coupling with wind electricity, PV electricity, grid electricity, etc.)</li> </ul> The efficiency of the electrolyser (technology, system design, etc.)	[59–64]
High temperature	[2.00; 3.5]	These costs are based on evaluations with nuclear energy as electricity and heat sources. Variations in costs depend on the nature of the nuclear reactor and assumptions on performances and durability	[65–67]

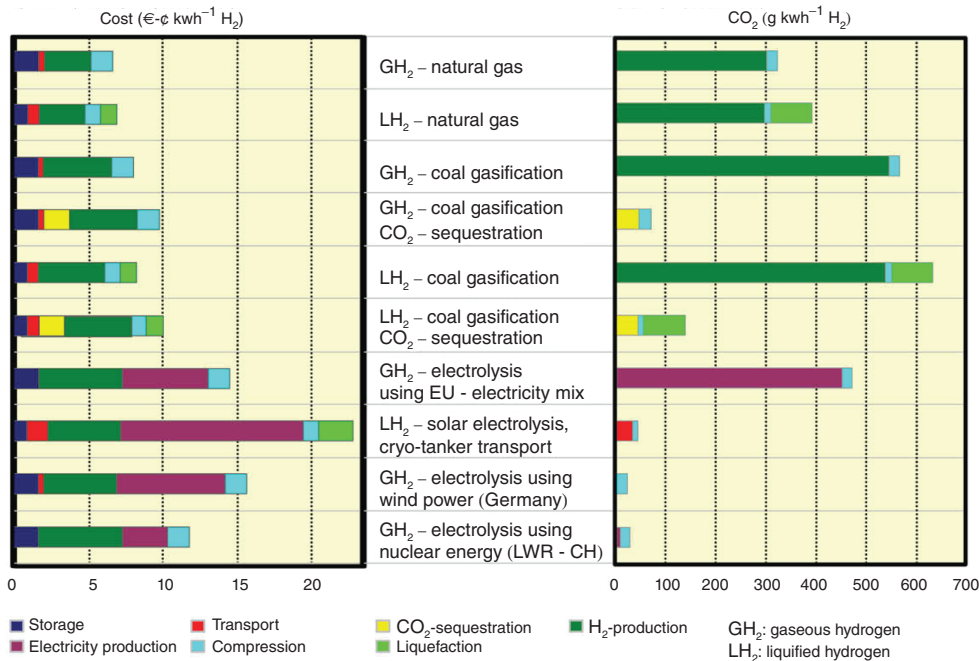
**Figure 1.11** Estimated world hydrogen production in million tonnes per year in 2008.

Furthermore, it is worth mentioning that the difficulty in comparing different production means rises from the fact that the obtained product (hydrogen) may have different characteristics in terms of pressure and purity. Some industrial processes may require very pure hydrogen, which, for example, cannot come directly from a steam reforming installation without a purification step. Similarly, some applications may require pressurized hydrogen. For example, in order to reduce the tank size in hydrogen vehicles, hydrogen is stored at high pressure, requiring a compressor to reach 350 or 700 bars. Consequently, comparing different means of hydrogen production would require the definition of a common functional unit that comprises not only a unit of mass of hydrogen (e.g. 1 kg) but also specifications in terms of pressure and purity.

In addition to costs it is essential to also consider a contribution of primary energy conversion processes to greenhouse gases emissions, which at the end

lead to climate change. No doubt  $\text{CO}_2$  is the most dominant gas with the maximum influence on climate changes, followed by methane ( $\text{CH}_4$ ),  $\text{N}_2\text{O}$  and fluorine gases (hydrofluorocarbons – HFCs, perfluorocarbons – PFCs and sulphur hexafluoride –  $\text{SF}_6$ ). Global warming potentials (GWPs) of different greenhouse gases as a function of time (20, 100 and 500 years horizon) have been summarized by Stolten *et al.* [68]. When looking at the  $\text{CO}_2$  emission status, the majority comes from the energy sector at 37% with a significant share of electricity generation, which accounts for a share of 30%. Eleven percent of emissions comes from the residential sector and about 31% is generated by industry (19%), trade and commerce (4%) and agriculture (8%) [68].

As shown in Figure 1.9 [69], hydrogen production from natural gas and especially from coal (about  $550 \text{ g CO}_2/\text{kWh H}_2$ ) generates a significant amount of  $\text{CO}_2$ . The  $\text{CO}_2$  capture and sequestration (CCS) process can significantly reduce the level. Emissions from nuclear or solar energy tend to zero level. Because of the maturity level of the industry, hydrogen production from natural gas has the lowest costs; slightly higher costs can be observed for hydrogen generated from coal, whereas the expenses associated with generating energy from renewable fuels are rather high as the technologies are still not fully developed to enter market levels. Because of the current goal to reduce greenhouse and hazardous emissions only

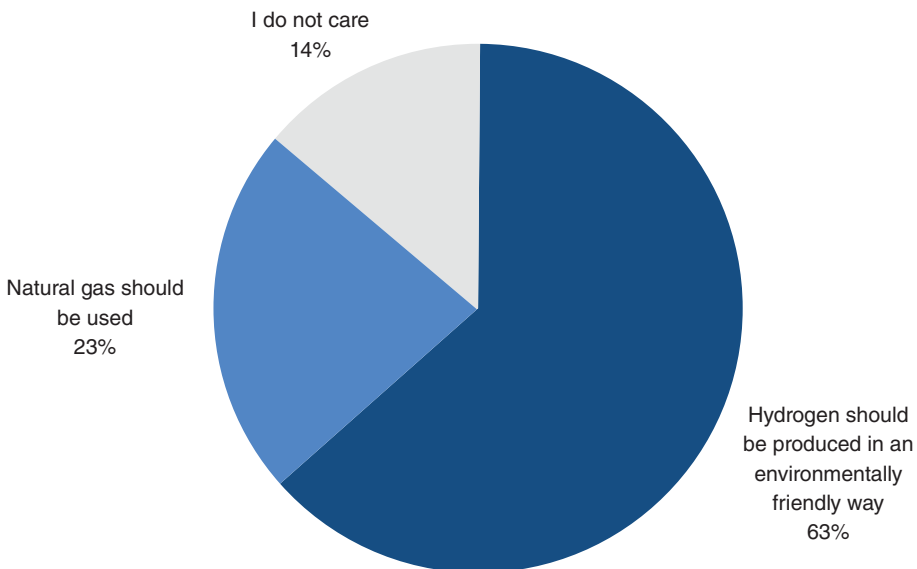


**Figure 1.12** Hydrogen costs and  $\text{CO}_2$  emissions per  $\text{kWh H}_2$  from selected hydrogen production from non-renewable (natural gas, coal) and renewable sources (solar and nuclear) [69].

renewable or carbon-reduced energy carriers can be viewed as a long-term option for the future energy sector (Figure 1.12).

Hydrogen production based on renewable energy sources significantly increases costs when compared with conventional fuels. In Germany, for example, hydrogen produced from biomass is tax free, that from regenerative electricity is tax exempt, whereas hydrogen as fuel is taxed at the mineral oil tax rate for natural gas, which is 13.9 €/MWh, and this rate will continue until 2020 [8]. As can be seen in Figure 1.13, almost two-thirds of Germans encourage the production of hydrogen in an environmentally friendly way. The general opinion is that hydrogen must be green from the beginning in order to contribute to reducing CO<sub>2</sub> emissions in the transport sector. A majority would also prefer hydrogen production in a decentralized way [19].

On the basis of the analysis of hydrogen energy technologies in autonomous power systems [70] it seems that autonomous systems not interconnected to the main grid power systems will be the first market application, where hydrogen can be technically and economically feasible and viable for short-term use. The study has shown that the most suitable way for the production of hydrogen for autonomous power systems is water electrolysis based on renewable energy sources, then reforming of biofuels, followed by the reforming of fossil fuels.



**Figure 1.13** Expectations of the Germans with regard to the environmentally friendly production of hydrogen (Survey 01/2013,  $n = 1012$ ) [19]. (By permission of the EFCF Luzern 2013, [www.efcf.com](http://www.efcf.com).)

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