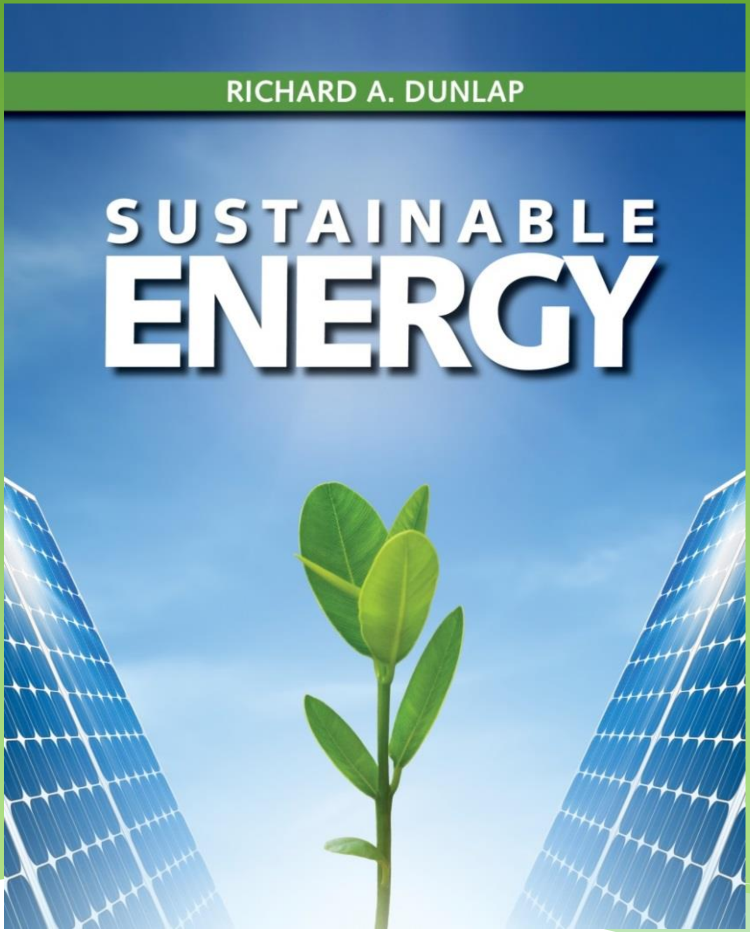
Sustainable Energy



Chapter 20

- Hydrogen

CENGAGE Learning

Learning Objectives

- The basic properties of hydrogen as a gas and as a liquid.
- Methods for hydrogen production.
- The factors that must be considered when storing gaseous or liquid hydrogen.
- The use of hydrogen as a fuel in internal combustion engines.
- The properties and types of fuel cells.
- The design of fuel cell vehicles.
- The viability of hydrogen as a fuel and efficiency considerations for its use.

Hydrogen

Hydrogen is a mechanism for storing energy and is not a primary energy source like oil.

Hydrogen is produced by certain endothermic chemical processes by supplying energy.

The energy supplied to produce the hydrogen can be recovered by burning the hydrogen or reacting it in a fuel cell.

The combustion of hydrogen

The combustion of hydrogen produces water and heat according to the reaction

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (20.1)$$

The energy produced by burning hydrogen is compared with that from burning gasoline.

Table 20.1: Specific and volumetric energy densities of gasoline and hydrogen at STP.

fuel	energy per kg (MJ)	energy per m^3 (MJ)
gasoline	44.5	34,800
hydrogen	142	11.8

Comparison of hydrogen energy with other transportation fuels

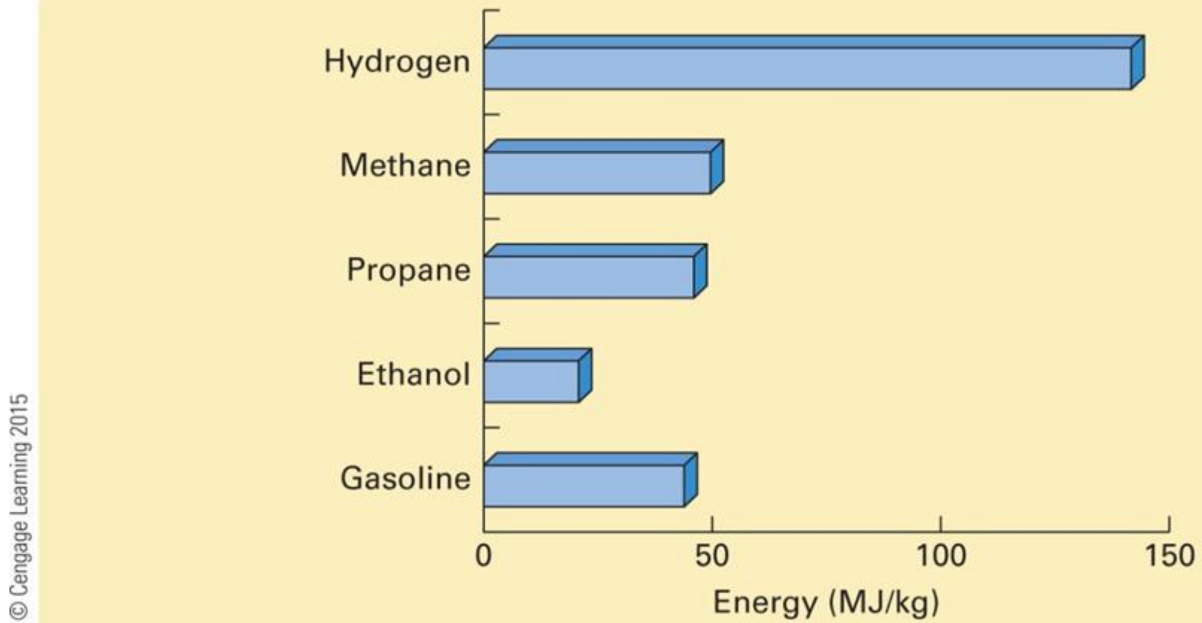


Figure 20.1: Energy content (per kg) of various fuels.

Production of hydrogen

Hydrogen can be produced by several methods:

- Electrolysis
- Thermal decomposition of water
- Chemical reactions
- Biological processes

Electrolysis

Electrolysis is the reduction of water according to the reaction

$$2H_2O + \text{energy} \rightarrow O_2 + 2H_2 \qquad (20.2)$$

Typically energy is supplied by an electric current

Electrolysis is typically about 70% efficient

Electrolysis cell

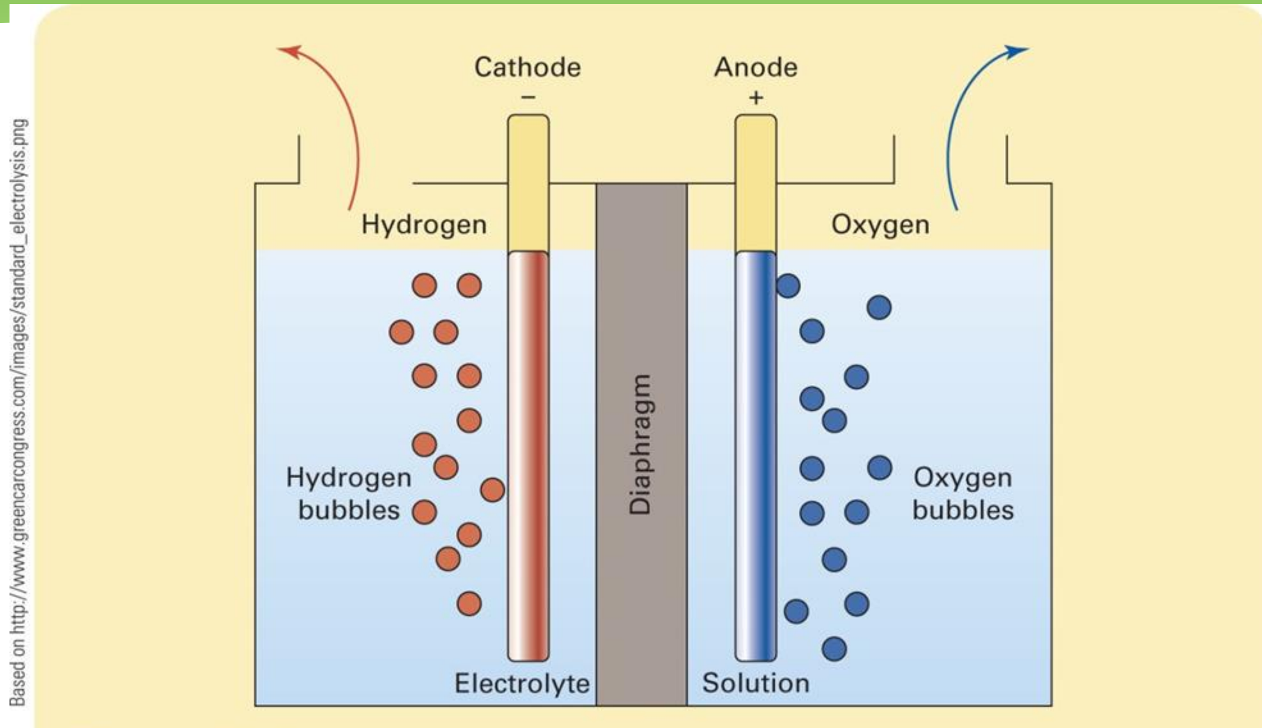


Figure 20.2: Basic electrolysis cell.

Electrical conductivity of the water is typically increased by dissolving an ionic compound

Thermal decomposition of water

Decomposition of water can be accomplished using thermal rather than electrical energy - Typically a catalyst facilitates the process.

Typical thermal decomposition reaction
Begin by heating sulfuric acid

$$\text{heat} + H_2SO_4 \rightarrow (1/2)O_2 + SO_2 + H_2O \qquad \textbf{(20.5)}$$

Combine the sulfur dioxide with iodine and water

$$\text{heat} + SO_2 + I_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \qquad \textbf{(20.6)}$$

Hydrogen iodide is decomposed to produce hydrogen

$$\text{heat} + 2HI \rightarrow H_2 + I_2 \qquad \textbf{(20.7)}$$

Chemical reactions

Hydrogen can be produced by high temperature reactions involving water such as the reaction of water with methane

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (20.8)$$

Or the reaction of with carbon

$$H_2O + C \rightarrow H_2 + CO \quad (20.10)$$

Biological processes

Certain biological process may produce hydrogen as a by-product.

Research is required to develop efficient and environmentally conscientious processes.

Hydrogen storage

Because hydrogen has a very low density, its volume must be reduced in order to store and transport it efficiently.

Methods for hydrogen storage

- Compressed hydrogen gas
- Liquid hydrogen
- Metal hydrides

Density pressure relationship

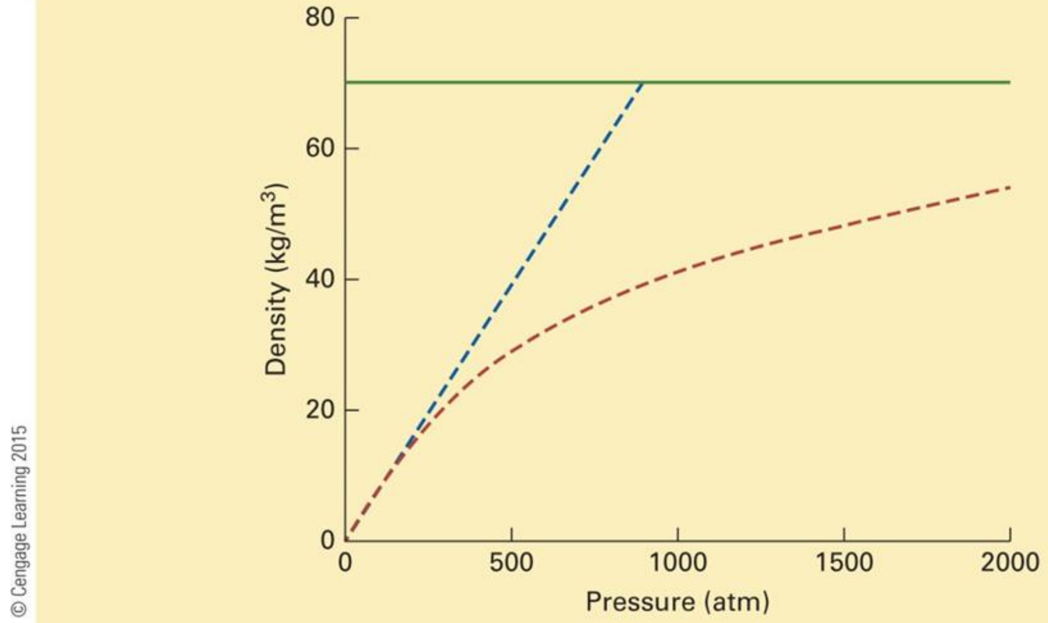


Figure 20.3: Density-pressure relationship for hydrogen gas showing the density of liquid hydrogen (red line) and the ideal gas law relationship (blue line) [1 atm = 101.325 kPa (kilopascals)]. The green line shows the density of liquid hydrogen.

Ideal gas law

At low pressures hydrogen follows the ideal gas law

$$PV = nRT \qquad (20.11)$$

or

$$\rho = \frac{MP}{RT} \qquad (20.12)$$

As the density increases atom-atom interactions cause the ideal gas law to break down and the density does not increase with pressure as rapidly.

Liquid hydrogen

Hydrogen may be liquefied by lowering the temperature below 20.3 K.

The density of LH_2 is greater than the density of CHG at any pressure.

Hydrogen spin states

The spins of the spins of the nuclei (protons) of the hydrogen atoms in a hydrogen molecule can align antiparallel or parallel.

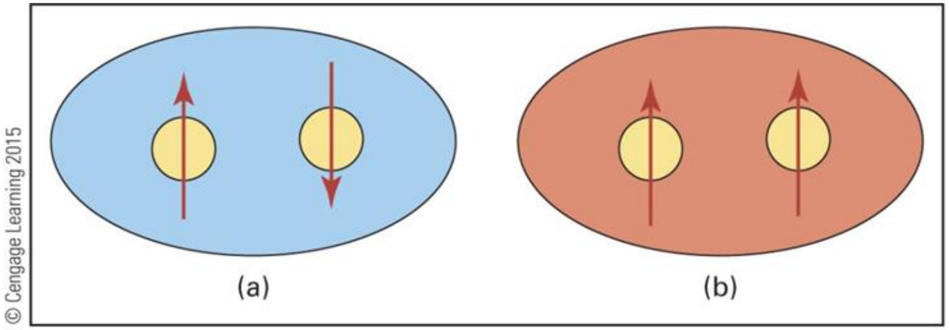


Figure 20.4: (a) Parahydrogen (ground state) and (b) orthohydrogen (excited state), showing the alignment of proton spins.

Ground and excited hydrogen states

The antiparallel alignment (parahydrogen) is the ground state and the parallel alignment (orthohydrogen) is the excited state.

At room temperature thermal energy causes a mixture of about 20% parahydrogen and 75% orthohydrogen.

Cooling the hydrogen quickly to the liquid state yields a non-equilibrium excess population of orthohydrogen
The orthohydrogen gradually converts to parahydrogen, giving up energy and causing some of the hydrogen to boil away.

Catalysts can be used to avoid this situation.

Loss rate of liquid hydrogen

Table 20.2: Loss rates for typical liquid hydrogen storage tanks of different volumes.

volume (m^3)	loss rate (%/day)
0.1	2
50	0.4
20,000	0.06

The loss rate decreases with increasing tank size (due to decreasing surface to volume ratio)

Metal hydrides

Hydrogen can be stored in a metal by the formation a metal hydride

$$2M + H_2 \rightarrow MH_2 \qquad (20.13)$$

A common metal for this process is Ti yielding TiH_2

Drawbacks of this approach are

- Difficult to get hydrogen into and out of metal quickly
- Excessive weight of metal

Comparison of different hydrogen storage mechanisms

Table 20.3: Storage capabilities for a 0.1-m^3 volume for hydrogen in different forms and a comparison with gasoline. Total masses include the mass of a suitable storage container.

fuel	fuel mass (kg)	total mass, typical (kg)	energy per volume ($MJ/0.1m^3$)	energy per mass (MJ/kg)
CHG (35 MPa)	2.0	100	280	2.8
CHG (70 MPa)	3.5	150	500	3.3
LH_2	7.2	100	1000	10
TiH_2	18	450	2550	5.7
gasoline	72	85	3500	41

Hydrogen internal combustion vehicles

Internal combustion vehicles using hydrogen as a fuel are being investigated by BMW and Mazda.

These use modified gasoline engines and are dual-fuel (hydrogen-gasoline).

They use different approaches to fuel storage.

Table 20.4: Specifications of two hydrogen internal combustion engine (ICE) vehicles.

manufacturer	model	fuels	hydrogen range [km (mi)]	gasoline range [km (mi)]
BMW	Hydrogen 7	LH_2/gasoline	200 (124)	480 (298)
Mazda	RX-8 RE	CHG/gasoline	100 (62)	530 (329)

BMW Hydrogen 7

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Figure 20.6: BMW Hydrogen 7 powered by a two-fuel internal combustion engine that runs on gasoline or hydrogen (LH_2).

Mazda RX-8 RE

© BG Motorsports/Alamy

Figure 20.7: Mazda RX-8 RE, powered by a two-fuel internal combustion engine that runs on gasoline or hydrogen (CHG).

Fuel cells

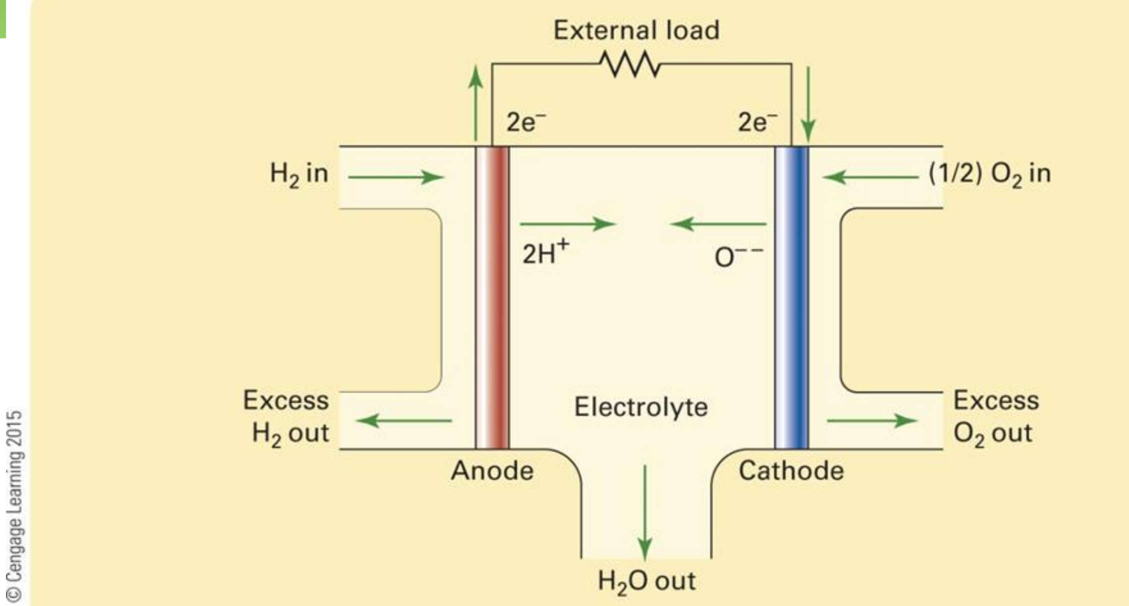

Figure 20.8: Schematic diagram of a generic hydrogen fuel cell.

Fuel cells combine hydrogen and oxygen and produce electricity directly without combustion

Air typically used as the source of oxygen

Operation of a fuel cell

Hydrogen is ionized at the anode by the reaction

$$H_2 \rightarrow 2H^+ + 2e^- \quad (20.14)$$

The two excess electrons travel through the external circuit to react with oxygen at the cathode

$$2e^- + (1/2)O_2 \rightarrow O^{--} \quad (20.15)$$

Water is formed in the electrolyte by the reaction

$$2H^+ + O^{--} \rightarrow H_2O \quad (20.16)$$

Types of fuel cells

Table 20.5: Properties of the common varieties of fuel cells.

type	electrolyte	operating temperature (°C)	power density (kW/m^2)	typical power output (kW)	lifetime (10^3 h)	efficiency (%)
phosphoric acid	H_3PO_4	~200	0.2	< 200	40	40
alkaline	KOH	−40 to 60	0.25	0.3 to 12	20	70
molten carbonate	K_2CO_3 or Na_2CO_3	~800	0.15	< 2000	40	60
solid oxide	ZrO_2	600–1000	0.3	100	40	60
solid polymer	PEM	60–80	0.5	50–250	40	80

Different fuel cell designs use different electrolytes and are suitable for different applications

Phosphoric acid fuel cells

Earliest design of fuel cells from mid-1800s

- Low power density
- Relatively low efficiency
- Good for stationary applications to produce backup emergency electricity

Alkaline fuel cells

- High efficiency
- Small size
- Expensive
- Produces drinkable water
- Used by NASA on spacecraft

Molten carbonate and solid oxide fuel cells

Similar operating characteristics

- Need to be operated at high temperature
- Can use methane (natural gas) as a source of hydrogen
- Emits CO_2 when running on methane

Solid polymer fuel cells

- High power density
- High efficiency
- Operates at low temperature
- Good range of power output for vehicle use
- Used almost exclusively for vehicles

Fuel cell vehicles

Many automobile manufacturers developing fuel cell vehicles.

These vehicles use electricity produced from hydrogen to run electric motors and are "hybrids" using batteries or supercapacitors as an additional energy source.

Comparison of some fuel cell vehicles

Table 20.6: Specifications of some hydrogen fuel cell vehicles.

make	model	hydrogen storage	mass [kg (lb)]	power at wheels [kW (hp)]	supplementary energy storage	range [km (mi)]
Ford	Focus FCV	25 MPa CHG (250 atm)	1727 (3800)	65 (80)	NiMH battery	280 (170)
Honda	FCX Clarity	34.5 MPa CHG (345 atm)	1625 (3575)	95 (127)	Li-ion battery	430 (260)
Kia	Borrego FCEV	69 MPa CHG (690 atm)	2250 (4950)	109 (146)	supercapacitor	680 (420)

Kia Borgeo fuel cell SUV

Figure 20.12: The Kia Borrego utilizes supercapacitors as a secondary energy source.

Hydrogen infrastructure

Use of fuel cell vehicles requires the commercial availability of hydrogen

World's first hydrogen fueling station in Iceland

Figure 20.16: Hydrogen fueling station. This facility in Reykjavík, Iceland opened in 2003 and was the world's first public hydrogen fueling station.

Hydrogen fueling stations in NW U.S. and SW Canada

Figure 20.14: Hydrogen fueling station locations in British Columbia and the U.S. Northwest.

Hydrogen fueling stations in Europe

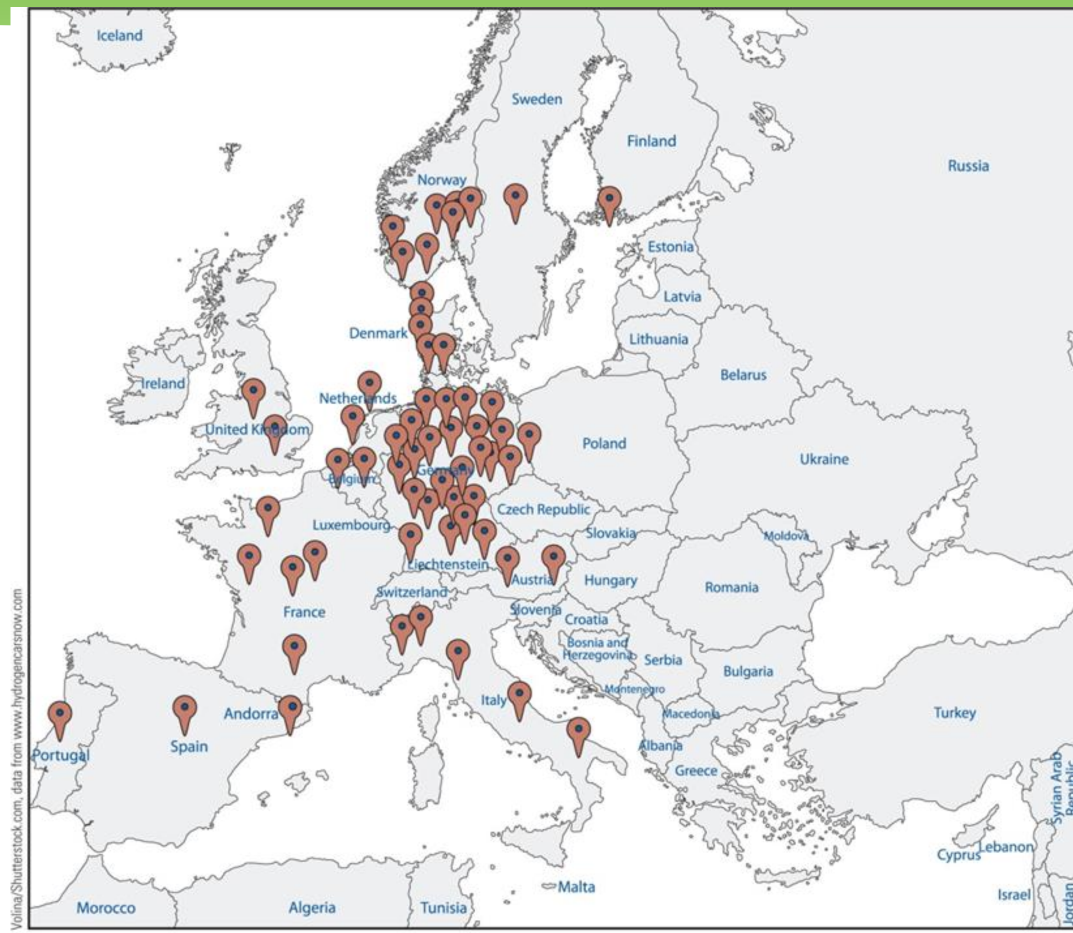

Figure 20.15: Hydrogen fueling station locations in Europe.

Transportation efficiencies

Four possible transportation technologies have been considered in detail

- Fossil fuel ICE vehicles (e.g. gasoline)
- Battery electric vehicles
- Hydrogen ICE vehicles
- Hydrogen fuel cell vehicles

Analysis of net efficiency Gasoline ICEs

Table 20.7: Efficiency analysis for gasoline-powered internal combustion engine vehicle showing net efficiency for conversion of primary energy (gasoline) to mechanical energy delivered to the vehicle's wheels.

process	efficiency (%)
fossil fuel → mechanical energy	17
net efficiency	17

Based on data from R. A. Dunlap, *Energy and Environment Research* "A simple and objective carbon footprint analysis for alternative transportation technologies" 3 (2013): 33–39.

Fossil fuel burned to produce mechanical energy in a heat engine

BEVs

Table 20.8: **Efficiency analysis for battery electric vehicle showing net efficiency for conversion of primary energy (oil of coal) to mechanical energy delivered to the vehicle's wheels.**

process	efficiency (%)
fossil fuel → electricity	40
electricity → mechanical energy	85
net efficiency	34

Based on data from R. A. Dunlap, *Energy and Environment Research* "A simple and objective carbon footprint analysis for alternative transportation technologies" 3 (2013): 33–39.

As most electricity (at least in the U.S.) is produced by burning fossil fuels, the net efficiency from primary energy source to mechanical energy (at the wheels) can be analyzed.

Hydrogen ICEs

Table 20.9: Efficiency analysis for hydrogen-powered internal combustion engine vehicle showing net efficiency for conversion of primary energy (oil or coal) to mechanical energy delivered to the vehicle's wheels.

process	efficiency (%)
fossil fuel → electricity	40
electricity → hydrogen gas	70
hydrogen gas → CHG or LH_2	80
CHG or LH_2 → mechanical energy	17
net efficiency	4

Based on data from R. A. Dunlap, *Energy and Environment Research* "A simple and objective carbon footprint analysis for alternative transportation technologies" 3 (2013): 33–39.

Following the energy conversion steps from primary energy to mechanical energy for a hydrogen ICE vehicle

Fuel cell vehicle

Efficiency analysis for a hydrogen fuel cell vehicle

Table 20.10: Efficiency analysis for hydrogen fuel cell-powered vehicle showing net efficiency for conversion of primary energy (oil or coal) to mechanical energy delivered to the vehicle's wheels.

process	efficiency (%)
fossil fuel → electricity	40
electricity → hydrogen gas	70
hydrogen gas → CHG	80
CHG → electricity	70
electricity → mechanical energy	90
net efficiency	14

Based on data from R. A. Dunlap, *Energy and Environment Research* "A simple and objective carbon footprint analysis for alternative transportation technologies" 3 (2013): 33–39.

Summary of efficiencies

- BEVs about twice typical gasoline vehicle
- Fuel cell vehicle similar to gasoline vehicle
- Hydrogen ICE substantially lower than gasoline

Carbon footprint analysis

Current U.S. electricity production methods

fuel	% electricity
coal	44.9
natural gas	23.4
petroleum	1.0
non-fossil	30.7

Carbon production per unit energy for different fossil fuels

fossil fuel	kg(CO_2)/MJ
coal (~pure carbon)	0.11
natural gas (methane, CH_4)	0.055
heavy hydrocarbons (>6 C/molecule)	0.069

Note: The combustion of carbon produces energy by the production of CO_2

The combustion of a hydrocarbon produces energy by the combustion of carbon to produce CO_2 and the combustion of hydrogen to produce H_2O

Carbon footprint analysis

Using current U.S. electricity generation

technology	$kg(CO_2)/(MJ)_p$	$(MJ)_p/(MJ)_w$	$(MJ)_w/km$	$kg(CO_2)/km$
gasoline ICE	0.069	5.9	0.6	0.24
H_2 ICE	0.063	25	0.6	0.94
H_2 fuel cell	0.063	7.1	0.6	0.27
BEV	0.063	2.9	0.6	0.11

Summary

- Hydrogen is an energy storage mechanism not a primary energy source
- Most commonly produced by electrolysis of water
- Hydrogen has a very high energy content per unit mass
- Its low density makes storage and transportation a challenge
- Can be stored as CHG, LH_2 or as a metal hydride
- CHG is the most common approach to storage
- Hydrogen ICE and fuel cell vehicles are under development
- Hydrogen ICE vehicles have low net efficiency and large carbon footprint
- Fuel cell vehicles are similar to gasoline vehicles in efficiency and carbon footprint