New Energy Sources

Hydrogen as a renewable energy source:

In the history of internal combustion engine development, hydrogen has been considered at several phases as a substitute to hydrocarbon-based fuels.

Hydrogen produces only water after combustion. It is a non-toxic, non-odorant gaseous matter and also can be burn completely . When hydrogen is burned, hydrogen combustion does not produce toxic products such as hydrocarbons, carbon monoxide, and oxide of sulfur, organic acids or carbon dioxides shown in Eq., except for the formation of NOx

Therefore, all the research and development (R&D) activities were carried out of the laboratory curiosity mainly with an objective to evaluate the suitability of hydrogen as an engine fuel.

- Hydrogen has some peculiar features compared to hydrocarbon fuels, the most significant being the absence of carbon. The burning velocity is so high that very rapid combustion can be achieved. The limit of flammability of hydrogen varies from an equivalence ratio (φ) of 0.1 to 7.1 hence the engine can be operated with a wide range of air/fuel ratio

- Hydrogen has since been used extensively in the space pro-gram since it has the best energy-to-weight ratio of any fuel. Liquid hydrogen is the fuel of choice for rocket engines, and has been utilized in the upper stages of launch vehicles on many space missions including the Apollo missions to the moon, Skylab, the Viking missions to Mars and the Voyager mission to Saturn.

Combustive Properties of Hydrogen

The properties of hydrogen are detailed in . The properties that contribute to its use as a combustible fuel are its:

wide range of flammability

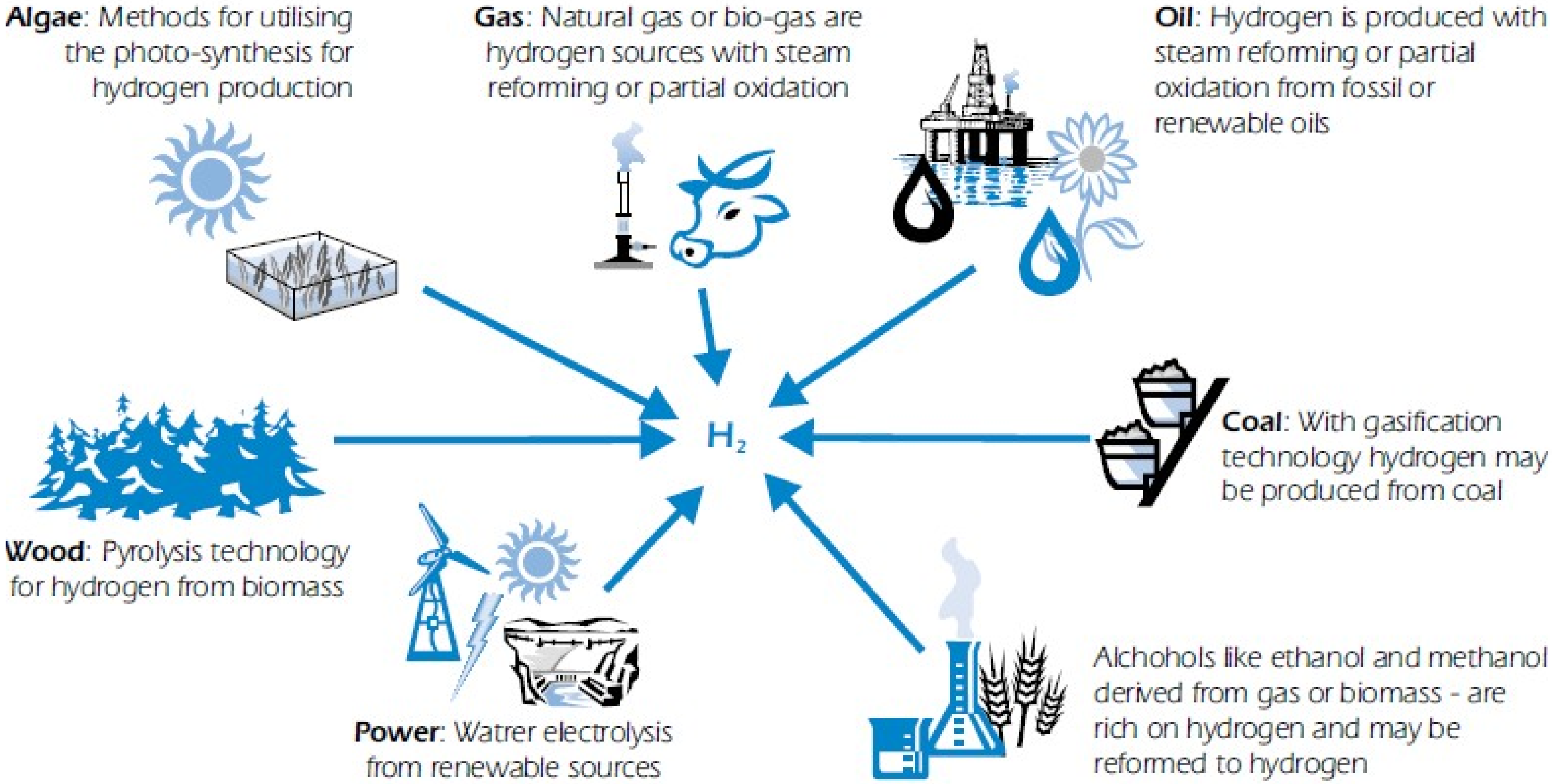
- low ignition energy
- small quenching distance
- high autoignition temperature
- high flame speed at stoichiometric ratios
- high diffusivity
- very low density

Properties	Diesel	Unleaded gasoline	Hydrogen
Formula	CnH1.8*n* C_8–C_{20}	CnH1.87*n* C_4–C_{12}	— H_2
Auto-ignition Temperature (K)	530	533–733	858
Min. ignition energy (mJ)	—	0.24	0.02
Flammability limits(vol. % in air)	0.7–5	1.4–7,6	4–75
Stoichiometric air fuel ratio on mass	14.5	14.6	34.3
Limits of flammability (equivalence ratio)	—	0.7–3,8	0.1–7,1
Density at 16 ◦C and 1.01 bar (kg/m^3)	833–881	721–785	0.0838
Net heating valve (MJ/kg)	42.5	43.9	119.93
Flame velocity (cm/s)	30	37–43	265–325
Quenching gap in NTP air (cm)	—	0.2	0.064
Diffusivity in air (cm^2/s)	—	0.08	0.63
Octane number		92–98	130
Cetane number	44-55	13–17	—

Production:

- Hydrogen can be produced from a variety of feedstocks. These include fossil resources, such as natural gas and coal, as well as renewable resources, such as biomass and water with input from renewable energy sources
- A variety of process technologies can be used, including chemical, biological, electrolytic, photolytic and thermo-chemical
- Each technology is in a different stage of development, and each offers unique opportunities, benefits and challenges
- Local availability of feedstock, the maturity of the technology, market applications and demand, policy issues, and costs will all influence the choice and timing of the various options for hydrogen production

Some feedstock and process alternatives



Source: Hydro.

Several technologies are already available in the marketplace for the industrial production of hydrogen. The first commercial technology, dating from the late 1920s, was the electrolysis of water to produce pure hydrogen. In the 1960s, the industrial production of hydrogen shifted slowly towards a fossil-based feedstock, which is the main source for hydrogen production today.

International Energy Agency (IEA) Hydrogen Implementing Agreement (HIA) focuses on the following hydrogen production activities:

- H_2 from fossil energy sources.
  - Large scale, with CO_2 capture and storage (in collaboration with the IEA Green House Gas Implementing Agreement programme – GHG)
  - Small scale, with distributed generation
- H_2 from biomass.
- Photo-electrolysis (photolysis).
- Photo-biological hydrogen production (biophotolysis).

HYDROGEN FROM FOSSIL FUELS

- Hydrogen can be produced from most fossil fuels. The complexity of the processes varies, and in this chapter hydrogen production from natural gas and coal is briefly discussed.

- Since carbon dioxide is produced as a by-product, the CO2 should be captured to ensure a sustainable (zero-emission) process. The feasibility of the processes will vary with respect to a centralised or distributed production plant.

Production from natural gas

Hydrogen can currently be produced from natural gas by means of three different chemical processes:

- Steam reforming (steam methane reforming – SMR).

Steam reforming involves the endothermic conversion of methane and water vapour into hydrogen and carbon monoxide.

The heat is often supplied from the combustion of some of the methane feed-gas.

The process typically occurs at temperatures of 700 to 850 °C and pressures of 3 to 25 bar.

The product gas contains approximately 12 % CO, which can be further converted to CO2 and H2 through the water-gas shift reaction .

$$CH_4 + H_2O + \text{heat} \rightarrow CO + 3H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2 + \text{heat}$$

- Partial oxidation (POX).

Partial oxidation of natural gas is the process whereby hydrogen is produced through the partial combustion of methane with oxygen gas to yield carbon monoxide and hydrogen

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 + \text{heat}$$

- Autothermal reforming (ATR) Autothermal reforming is a combination of both steam reforming and partial oxidation

Production from coal

Hydrogen can be produced from coal through a variety of gasification processes (e.g. fixed bed, fluidised bed or entrained flow). In practice, high-temperature entrained flow processes are favoured to maximise carbon conversion to gas, thus avoiding the formation of significant amounts of char, tars and phenols.

$$C(s) + H_2O + heat \rightarrow CO + H_2$$

Capture and storage of CO_2

Carbon dioxide is a major exhaust in all production of hydrogen from fossil fuels. The amount of CO_2 will vary with respect to the hydrogen content of the feedstock. To obtain a sustainable (zeroemission) production of hydrogen, the CO_2 should be captured and stored. This process is known as de-carbonisation.

HYDROGEN FROM SPLITTING OF WATER

Hydrogen can be produced from the splitting of water through various processes. This paper briefly discusses water electrolysis, photo-electrolysis, photo-biological production and high-temperature water decomposition.

Water electrolysis

Water electrolysis is the process whereby water is split into hydrogen and oxygen through the application of electrical energy, as in equation

$$H_2O + \text{electricity} \rightarrow H_2 + \tfrac{1}{2}O_2$$

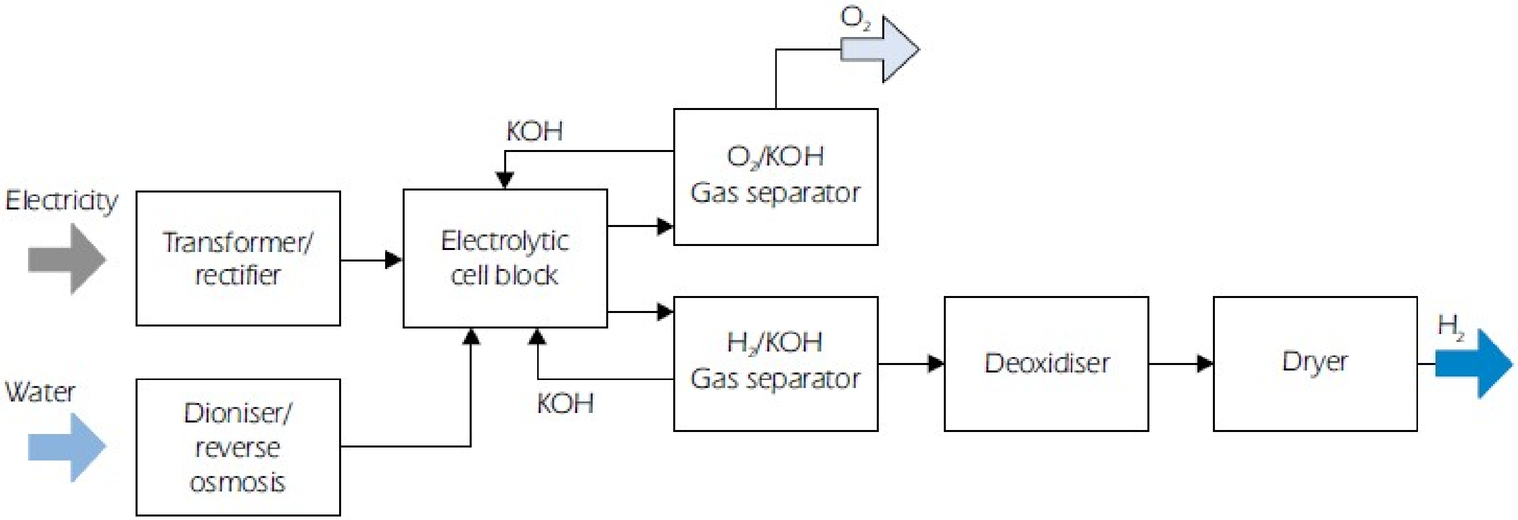
Alkaline electrolysis

Alkaline electrolysers use an aqueous KOH solution (caustic) as an electrolyte that usually circulates through the electrolytic cells. Alkaline electrolysers are suited for stationary applications and are available at operating pressures up to 25 bar. Alkaline electrolysis is a mature technology, with a significant operating record in industrial applications, that allows remote operation.

The following reactions take place inside the alkaline electrolysis cell:

Electrolyte:	$4H_2O \rightarrow 4H^+ + 4OH^-$
Cathode:	$4\ H^+ + 4e^- \rightarrow 2H_2$
Anode:	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
Sum:	$2H_2O \rightarrow O_2 + 2H_2$

Process diagram of alkaline electrolysis



Polymer electrolyte membrane (PEM) electrolysis

The principle of PEM electrolysis is presented in equations

PEM electrolysers require no liquid electrolyte, which simplifies the design significantly. The electrolyte is an acidic polymer membrane.

PEM electrolysers can potentially be designed for operating pressures up to several hundred bar, and are suited for both stationary and mobile applications

$$\text{anode: } H_2O \rightarrow \tfrac{1}{2}O_2 + 2\,H^+ + 2e^-$$

$$\text{cathode: } 2H^+ + 2e^- \rightarrow H_2$$

With relatively high cost, low capacity, poor efficiency and short lifetimes, the PEM electrolysers currently available are not as mature as alkaline electrolysers. It is expected that the performance of PEM electrolysers can be improved significantly by additional work in materials development and cell stack design.

High-temperature electrolysis

High-temperature electrolysis is based on technology from high-temperature fuel cells. The electrical energy needed to split water at 1000 °C is considerably less than electrolysis at 100 °C. This means that a high-temperature electrolyser can operate at significantly higher overall process efficiencies than regular low-temperature electrolysers.

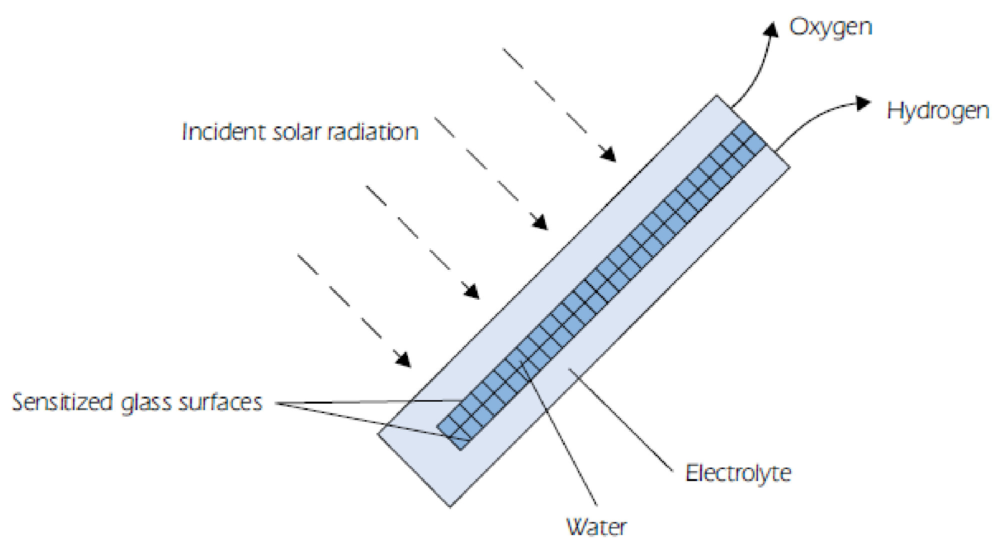
typical technology is the solid oxide electrolyser cell (SOEC).

Photo-electrolysis (photolysis)

Photovoltaic (PV) systems coupled to electrolysers are commercially available. The systems offer some flexibility, as the output can be electricity from photovoltaic cells or hydrogen from the electrolyser.

Direct photo-electrolysis represents an advanced alternative to a PV-electrolysis system by combining both processes in a single apparatus. This principle is illustrated in Figure

Photoelectrolysis of water is the process whereby light is used to split water directly into hydrogen and oxygen. Such systems offer great potential for cost reduction of electrolytic hydrogen, compared with conventional two-step technologies.

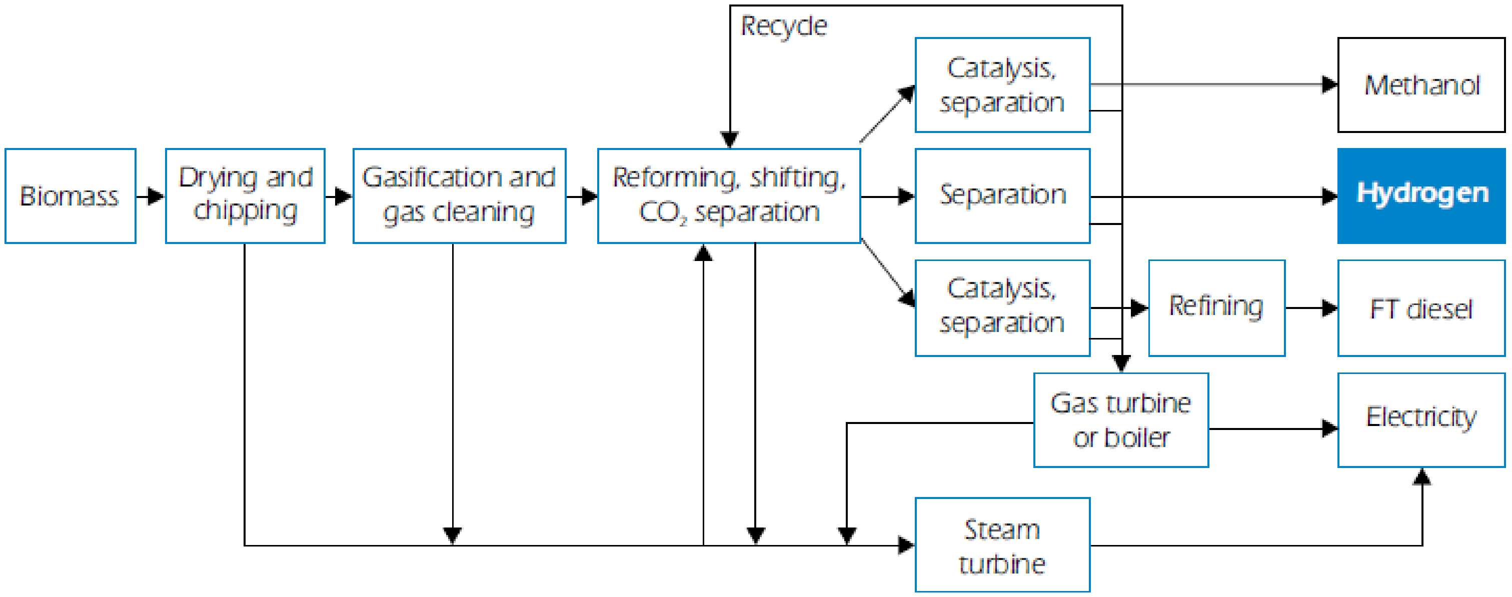


High-temperature decomposition

High-temperature splitting of water occurs at about 3000 °C. At this temperature, 10% of the water is decomposed and the remaining 90% can be recycled. To reduce the temperature, other processes for high temperature splitting of water have been suggested:

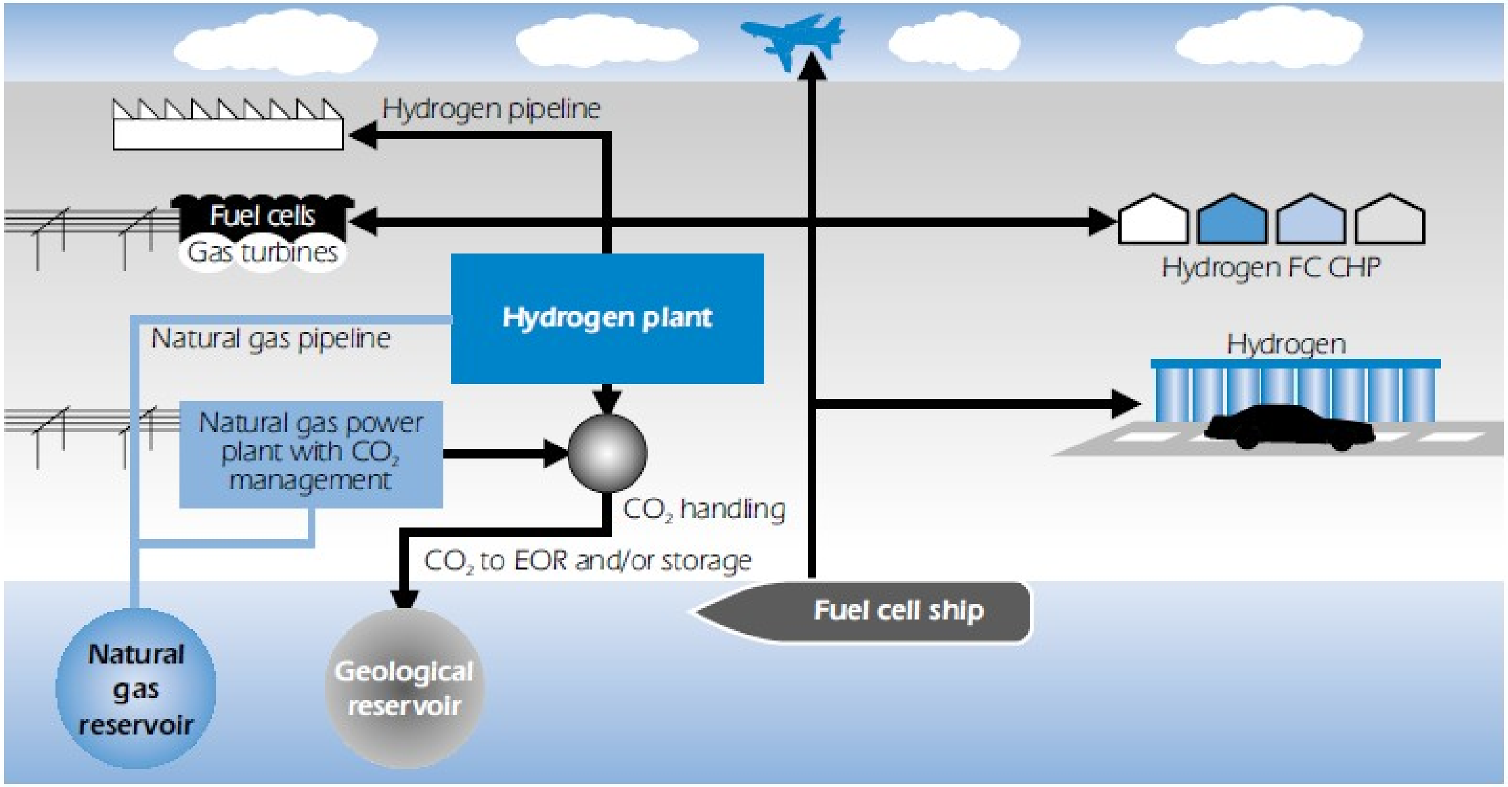
BIOMASS TO HYDROGEN

In biomass conversion processes, a hydrogen-containing gas is normally produced in a manner similar to the gasification of coal,



Generic flow sheet for methanol, hydrogen or FT diesel production
via biomass gasification

CENTRALISED HYDROGEN PRODUCTION



HYDROGEN STORAGE R&D: PRIORITIES AND GAPS

Hydrogen storage can be considered for onboard vehicular, portable, stationary, bulk, and transport applications,

GASEOUS HYDROGEN

The most common method to store hydrogen in gaseous form is in steel tanks, although lightweight composite tanks designed to endure higher pressures are also becoming more and more common.

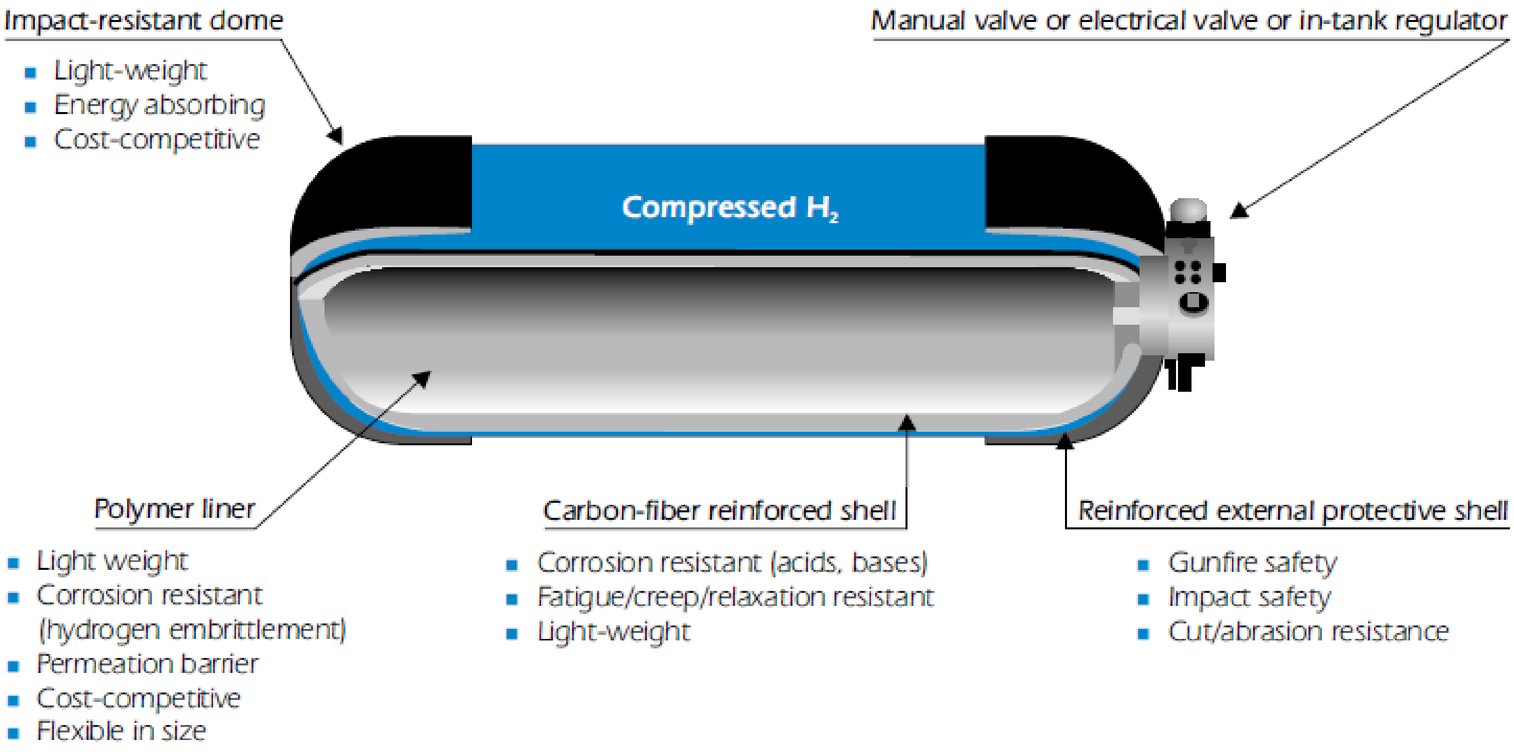
Cryogas, gaseous hydrogen cooled to near cryogenic temperatures, is another alternative that can be used to increase the volumetric energy density of gaseous hydrogen.

A more novel method to store hydrogen gas at high pressures is to use glass microspheres.

Composite tanks

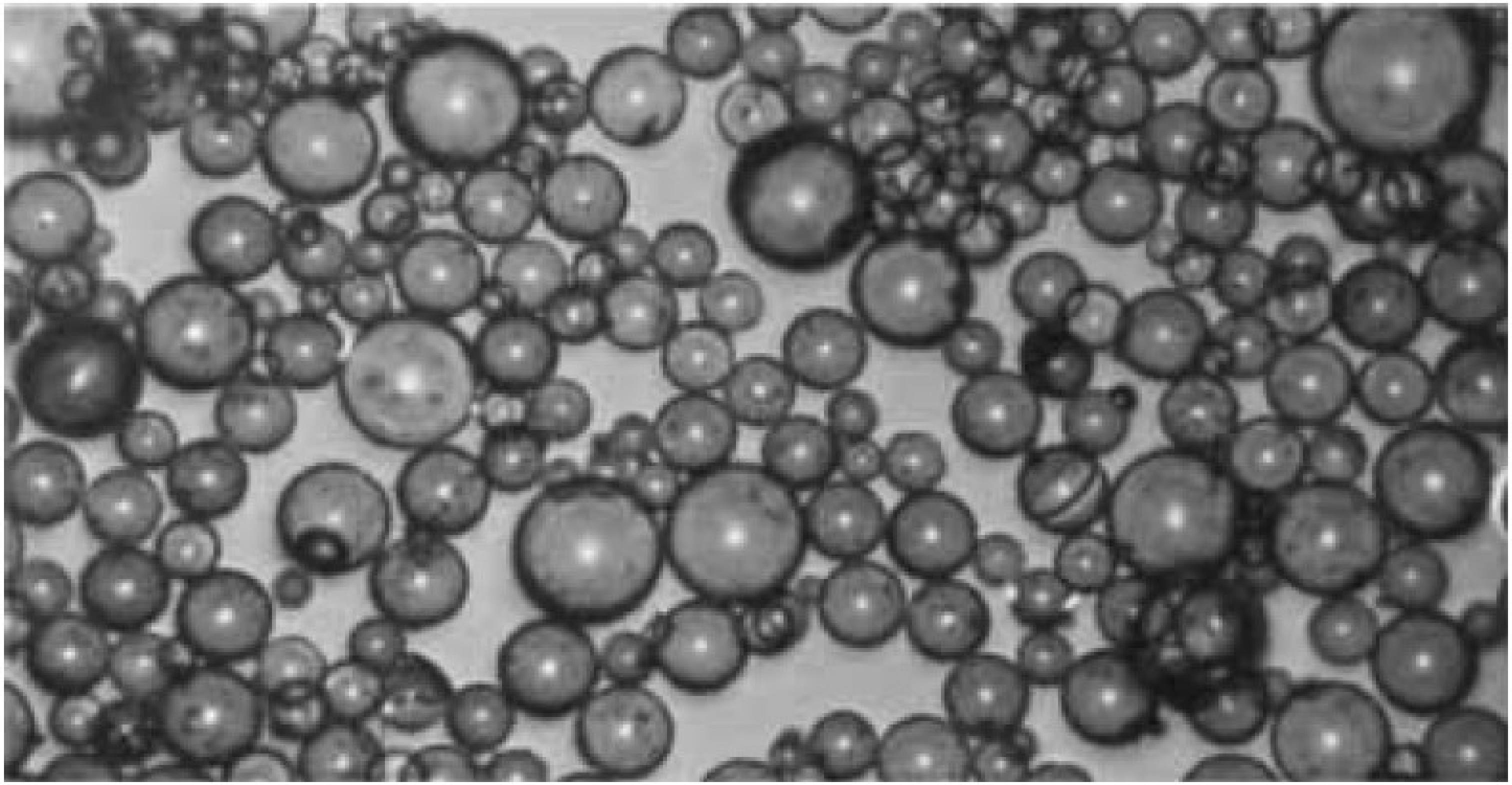
Schematic of a typical compressed H_2 gas composite tank

C-fibre-wrapped H_2 storage composite tank is shown in Figure



Glass microspheres

The basic concept for how glass microspheres can be used to store hydrogen gas onboard a vehicle can be described by three steps: charging, filling and discharging. First, hollow glass spheres are filled with H_2 at high pressure (350-700 bar) and high temperature (ca. 300 °C) by permeation in a high-pressure vessel. Next, the microspheres are cooled down to room temperature and transferred to the low-pressure vehicle tank. Finally, the microspheres are heated to ca. 200-300 °C for controlled release of H_2 to run the vehicle



LIQUID HYDROGEN

The most common way to store hydrogen in a liquid form is to cool it down to cryogenic temperatures (–253 °C).
Other options include storing hydrogen as a constituent in other liquids, such as NaBH4 solutions, rechargeable organic liquids, or anhydrous ammonia NH_3.

SOLID HYDROGEN

Overview of solid hydrogen storage options

Carbon and other HSA materials*	*Chemical hydrides (H_2O-reactive)*
• Activated charcoals • Nanotubes • Graphite nanofibers • MOFs, Zeolites, etc. • Clathrate hydrates	• Encapsulated NaH • LiH & MgH_2 slurries • CaH_2, $LiAlH_4$, etc
Rechargeable hydrides	*Chemical hydrides (thermal)*
• Alloys & intermetallics • Nanocrystalline • Complex	• Ammonia borozane • Aluminum hydride

* HSA = high surface area

There are four main groups of suitable materials: carbon and other high surface area materials; H2O-reactive chemical hydrides; thermal chemical hydrides; and rechargeable hydrides.