Five minute guide
Hydrogen
Hydrogen is not currently viewed as a significant energy vector (transfer, storage or secondary energy source), although substantial quantities are produced and consumed in various industrial processes.

Advantages

- Decarbonised gas energy into urban centres
- Very low greenhouse gas at point of use (trace NO\textsubscript{x} in air)
- Efficient, zero emissions CHP (Combined Heat & Power)
- Seasonal and diurnal resilience and security
- Power 2 Gas (P2G) able to provide grid services
- Stores constrained or intermittent renewables
- Distributed seasonal energy storage easier than electrical systems
- Potential natural gas transition fuel to zero carbon system
- Future low carbon nuclear based hydrogen production
- Safety considerations similar to natural gas or petroleum
- Rapid vehicle refuelling and ~400km range

Challenges

- Overall cycle efficiency improvements required
- Immature infrastructure development
- Public perception of safety is historically influenced
- Storage technologies under development (eg: Graphene)
- Well ventilated siting and careful design required
- Cost of fuel cells and other hydrogen equipment
- Regulatory and policy development
Characteristics of hydrogen

Uniquely identified by Henry Cavendish in 1776, it was named ‘Water Maker’ or Hydrogen by Antione Lavoiser in 1783.

Generally encountered as molecular hydrogen (H₂), it is an energy vector (means of transfer and storage) rather than a primary energy source.

By volume, gaseous hydrogen contains a third of the energy of the same volume of Methane.

On a weight basis it contains three times the energy of Methane.

Consequently cryogenic liquid (LH₂) or compressed gaseous hydrogen (CGH₂) is the preferred form in most practical applications.
Hydrogen can be derived, stored and converted through various processes, each of which represents different levels of carbon intensity, efficiency and end use functionality.
Hydrogen safety and public perception

In common with hydrocarbon fuels like petroleum or natural gas, hydrogen needs to be carefully managed in appropriately designed infrastructure, facilities and products.

Rapid buoyant dispersion
Hydrogen is 14.5 times more buoyant than air, whereas methane is only 4 times more buoyant and petroleum vapour is less buoyant, so hydrogen disperses and dilutes most rapidly. Care needs to be taken to allow adequate ventilation of potential overhead gas pockets.

Similar lower explosive limit to common fuels
In the event of a leak, the lower explosive limit is the first threshold to be reached. This threshold for hydrogen is similar to natural gas at 4.1% hydrogen in air and better than the 1.2% limit of petroleum in air. Although hydrogen does have much larger range between the lower and higher explosive limits, this is not an overriding factor in most real life situations where dilution and dispersion keep the gas/air ratio low.

Public perception and historical legacy
Events such as the LZ129 Hindenburg airship disaster in 1939 remind us of the need to carefully design and manage inherent hydrogen risks (although it is hypothesised that hydrogen was not the causal factor). Equally the Abbeystead explosion in 1984 reminds us that methane must also be treated carefully, as does the Buncefield petroleum fire in 2005.

Flame visibility and smell
Light emitted from burning pure hydrogen is in the ultraviolet range and is not visible to the human eye, however it does burn with a coloured flame in the presence of combustion process contaminants. Petroleum based flame is highly visible and natural gas is visible to a lesser degree. Similar to methane, pure hydrogen cannot be detected by smell. Hydrogen flame detectors are readily available and research into additives which generate a visible flame and odorise the gas are under development.

Radiant heat
Combustion of hydrogen produces less radiant heat than comparable hydrocarbons, reducing its propensity to ignite adjacent materials, but also meaning that the flame is less noticeable to people or thermal detection systems.

Energy density and leakage
Hydrogen has about a third of the energy density of methane, but due to the small molecular size of hydrogen it has a greater propensity to leak by a factor of three, so the net energy loss is about the same.
Benefits and evolving solutions

Microbial Biomass Conversion
Dark fermentation of biomass using microorganisms produces hydrogen and carbon dioxide. Alternatively Microbial Electrolysis Cells (MECs) combine biomass, microorganisms and a small electrical input to increase hydrogen yield. This approach has long-term potential to use wastewater.

Photobiological
Micro-organisms such as micro-algae or cyano-bacteria absorb sunlight to produce hydrogen. Alternatively photo-synthetic microbes photo-ferment biomass to produce hydrogen. These processes currently have a low hydrogen yield and are inhibited by concurrent oxygen generation. Further research is anticipated to increase effectiveness.

Photo Electro Chemical (PEC)
The PEC process uses semiconductors immersed in a water based electrolyte or a photo-reactive slurry to convert solar energy into chemical energy in the form of hydrogen and oxygen as a by-product. This developing technology can be applied in a similar manner to photovoltaic panels at various scales, both centralised and distributed.

Thermo Chemical Water Splitting
Using high temperatures generated from solar (Solar Thermochemical Hydrogen, STCH) or nuclear energy, water splitting cycles produce hydrogen and oxygen from water. Typically dual stage cerium oxide (2000/400°C) or copper chloride hybrid (500/400°C), but ~300 process variants are at various technology readiness levels.

HTE + Concentrated Solar Power (CSP)
High Temperature Electrolysis works on the basis that electrolysis of water can be more efficiently achieved at high electrolyte temperatures in the range of ~100-850°C. In a CSP or parabolic solar system the electricity generated can be more effectively converted into hydrogen by sequestering some of the process heat.

HTE + Nuclear
High Temperature Steam Electrolysis (HTSE) can take advantage of heat input at ~100-850°C derived from high temperature nuclear reactors to increase hydrogen electrolysis efficiency. This approach may be particularly relevant with respect to waste heat from small modular reactors which could be accessible to gas networks.
Benefits and evolving solutions

Steam Methane Reformation (SMR)
This mature process delivers ~95% of current production. $\text{C}_n\text{H}_m$ (eg: Methane) at ~3-25 bar reacted with high temperature steam (700-1000°C), then ‘water-gas-shift’ carbon monoxide and ‘Pressure Swing Absorption’. Generally large scale centralised, oxygen free production.

$$\text{CH}_4 + \text{H}_2\text{O} (+ \text{heat}) \rightarrow \text{CO} + 3\text{H}_2$$
then
$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 (+\text{heat})$$

Autothermal Reformation (ATR)
Basically the same as SMR, although it uses oxygen together with steam or carbon dioxide and is exothermic. Output temperature of 950-1100°C. Smaller, but less efficient than SMR.

$$2\text{CH}_4 + \text{O}_2 + 2\text{H}_2\text{O} (+ \text{heat}) \rightarrow 3\text{CO} + 3\text{H}_2 + 3\text{CO} + \text{H}_2\text{O} (+\text{heat})$$

or,
$$4\text{CH}_4 + \text{O}_2 + 2\text{H}_2\text{O} (+ \text{heat}) \rightarrow 2\text{CO} + 10\text{H}_2 (+\text{heat})$$

Partial Oxidisation (POX)
Endothermic partial oxidisation of natural gas followed by ‘Water-Gas-Shift’. Faster and smaller than SMR, but produces less hydrogen per unit of gas feedstock.

$$\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 (+ \text{heat})$$
then,
$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 (+\text{heat})$$

Low Temperature Plasma Reformation
Partial oxidation plasma pyrolysis of methane. This process is at an early technology readiness level but is showing promising low energy reformation potential.

Reformer Electrolyser Purifier (REP)
A developing technology which reforms and purifies in one step, combining electrolysis and using waste heat to support an efficient endothermic conversion. More efficient than SMR and scalable for centralised of distributed use.

Electrolysers
Electrolysers split water into hydrogen and oxygen using electricity input. The carbon footprint of the hydrogen depends upon the carbon footprint of the source electricity and electrolysis efficiency.

Polymer Electrolyte Membrane (PEM) is based on a solid polymer electrolyte operating at 70-90°C, while an Alkaline Electrolyser uses a Sodium or Potassium Hydroxide or solid alkaline electrolyte at 100-150°C and the Solid Oxide Electrolyser uses a solid ceramic electrolyte operating at about 700-800°C.
Transmission & distribution

The small molecular size of hydrogen and its particular chemical properties present transmission and distribution challenges and trade-offs.

Transmission Pipelines are suited to large volume, long distance GH2 transport. Reuse of steel natural gas pipelines is a challenge due to propensity for hydrogen embrittlement. CGH2 transmission by pipeline already exists for industrial purposes. Lower volumetric energy density of CGH2 compared with natural gas means that flow volumes and consequent gas velocity are higher in hydrogen based systems for comparable energy transfer.

Distribution Pipelines are suited to large volume, medium distance GH2 transport. Replacement of cast iron natural gas mains with polyethylene (PE) means that natural gas distribution networks are substantially hydrogen ready. Challenges with sulphur containing odourisers (eg: Mercaptans) ‘poisoning’ fuel cell catalysts.

High Pressure Tube Trailers are suited for low quantity delivery to discrete demand centres. Relatively large heavy goods vehicles require access space at a discharge location.

Metal Hydrides are suited for small quantities of H2 absorbed in the Metal Hydride with a high volumetric energy density. Containerised modules are transported by road, rail or marine transport.

Cryogenic Road Tankers are suited for medium quantity delivery to discrete demand centres. Relatively large heavy goods vehicles require access space at discharge location. Energy losses through gradual warming of the cryogenic LH2 results in ‘boil off’ of gaseous H2 (Pressure Regulated) unless actively cooled (Temperature Regulated).

Cryogenic Rail Tankers are suited for medium quantity delivery to discrete demand centres over long distances on the rail network from one industrial centre to another. Boil off or cooling energy losses.

Cryogenic Barges/Ships are suited for large quantity delivery over long distances similar to LNG carriers enabling international transport of LH2.
**Storage**

H₂ is a useful energy storage medium covering the needs of diurnal to seasonal timelines.

**Line-stack Storage in Pipelines**
The system pressure in conventional gas pipelines is increased within limits to store gas. CGH₂ has a third of the volumetric energy density of natural gas, so the energy equivalent ‘line-stack’ storage capacity for a given pipeline is less.

**Underground Storage**
In a similar manner to natural gas, pressurised GH₂ is stored underground in suitable geology such as salt caverns. The large volumes of gas facilitate seasonal storage of energy.

**Cryogenic LH₂ Storage**
LH₂ storage is an energy dense way of storing hydrogen, but it does have higher ‘round trip’ losses associated with liquefaction combined with time proportional ‘boil off’ or cooling requirements (it boils at -253°C) which are less suited to long term or inter-seasonal storage.

**Physisorption and Chemisorption**
Various Metal Hydrides and Graphene provide an opportunity to chemically absorb hydrogen for later release. Graphene can also absorb hydrogen within its physical structure.

**Chemical Conversion to Methanol, Ammonia and Methane**
Hydrogen can be used as a feedstock to produce chemicals such as Methanol and Ammonia as an energy storage vector. These chemicals have desirable energy characteristics, but are less desirable in other respects. Alternatively it can be combined with carbon dioxide to produce Methane which can be injected into the natural gas network.
End use applications – static fuel cells

Proton Exchange Membrane FC (PEMFC)
These polymer electrolyte based stacked systems are the same as used in vehicles. They are able to flex their power output. Current systems use small quantities a Platinum catalyst which are easily poisoned by sulphur and carbon monoxide so they need advanced fuel processing systems.

Solid Oxide FC (SOFC)
Although these are quite efficient, they operate at high temperatures (500-1000°C), have long start-up and stop times as well as having inflexible power output. They use a solid oxide electrolyte.

Molten Carbonate FC (MCFC)
Molten lithium and potassium carbonate in a ceramic matrix forms the electrolyte operating at ~650°C. They are large industrial systems with low power density and require stack replacement at about 50% life due to the aggressive chemistry.

Phosphoric Acid FC (PAFC)
Liquid phosphoric acid at 180-250°C is used as the electrolyte in conjunction with platinum catalysts (40x more than PEMFC).

<table>
<thead>
<tr>
<th>Conversion Efficiency</th>
<th>Losses</th>
<th>Unit Life</th>
<th>Power Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEMFC</td>
<td>6-10% +1% per annum</td>
<td>10 Years</td>
<td>0.75 – 2.0 kW Electrical 0.75 – 2.0 kW Thermal</td>
</tr>
<tr>
<td>SOFC</td>
<td>10% +1-2.5% per annum</td>
<td>3-10 Years</td>
<td>0.75 – 250 kW Electrical 0.75 – 250 kW Thermal</td>
</tr>
<tr>
<td>MCFC</td>
<td>+0.5% per annum</td>
<td>15-20 Years (FC overhaul at 50% life)</td>
<td>100 – 400 kW Electrical 110 – 450 kW Thermal</td>
</tr>
<tr>
<td>PAFC</td>
<td>+1.5% per annum</td>
<td>10 Years</td>
<td>300+ kW Electrical 450 kW Thermal</td>
</tr>
</tbody>
</table>

Source: H2FC Supergen
Hydrogen in transport

Hydrogen vehicles have near zero tail pipe emissions other than water vapour and trace NOₓ. Range and refuelling time are comparable to hydrocarbon fuelled vehicles.

As hydrogen vehicle technologies improve in both efficiency (supply and fuel cells) and capacity (mobile storage) they hold potential to satisfy the medium range requirements between that which is provided by battery electric vehicles and plug-in hybrid electric vehicles.

Fuel cell electric vehicles (FCEVs) and battery electric vehicles (BEVs) have a comparable drive train and high torque performance at low speeds, while also delivering significant range.

Refuelling of hydrogen vehicles is much more rapid than recharging battery electric vehicles meaning that they are well suited to commercial fleets which do not have long periods of downtime in their duty cycle (e.g. forklifts operating in a 24hr warehouse).

On-site production of hydrogen from sources of renewable distributed generation is able to accommodate fluctuating power input or draw off-peak electricity from the grid.

Well to Wheel (WTW) Emissions vs Vehicle range and projected performance improvement to 2050

Source: IEA Technology Roadmap