3 Hydrogen Production

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3.1 Introduction

Hydrogen does not exist naturally and must be produced by breaking down compounds such as water or methane. For this reason, it is considered as an energy carrier rather than a primary source of energy. Numerous technologies have been developed to produce hydrogen from a wide range of feedstocks. From an energy security perspective, this means that if a feedstock such as natural gas has restricted availability, production could switch to another feedstock. However, this would require the development of redundant capital plant, to produce hydrogen from a range of feedstocks, or flexible plants that could utilise a range of feedstocks. As for electricity generation, there is a trade-off between the cost of spare generation plant and the increased security that it brings. Unlike electricity, as a gas, hydrogen can be stored relatively cheaply in underground caverns, which reduces the value of spare capacity.

Hydrogen is not a primary fuel unlike oil, coal and natural gas. However, like electricity it is an energy carrier. Hydrogen is a secondary form of energy that is produced using primary energy sources. Advocates of the Hydrogen Economy recognise that hydrogen can be an environmentally friendlier source of energy for the consumer, especially in the transport sector whereby no harmful pollutants are released into the atmosphere.

The hydrogen economy is a system for delivering energy sourced from hydrogen through the establishment of a modified infrastructure. Moreover, hydrogen production, distribution, utilisation and storage are fundamental to the realisation of this system. Figure 3.*1* is the life cycle of hydrogen when sourced from renewable energies. The diagram also demonstrates that hydrogen is produced from water, which is used in conjunction with oxygen to generate useful energy such as electricity giving water as a product.
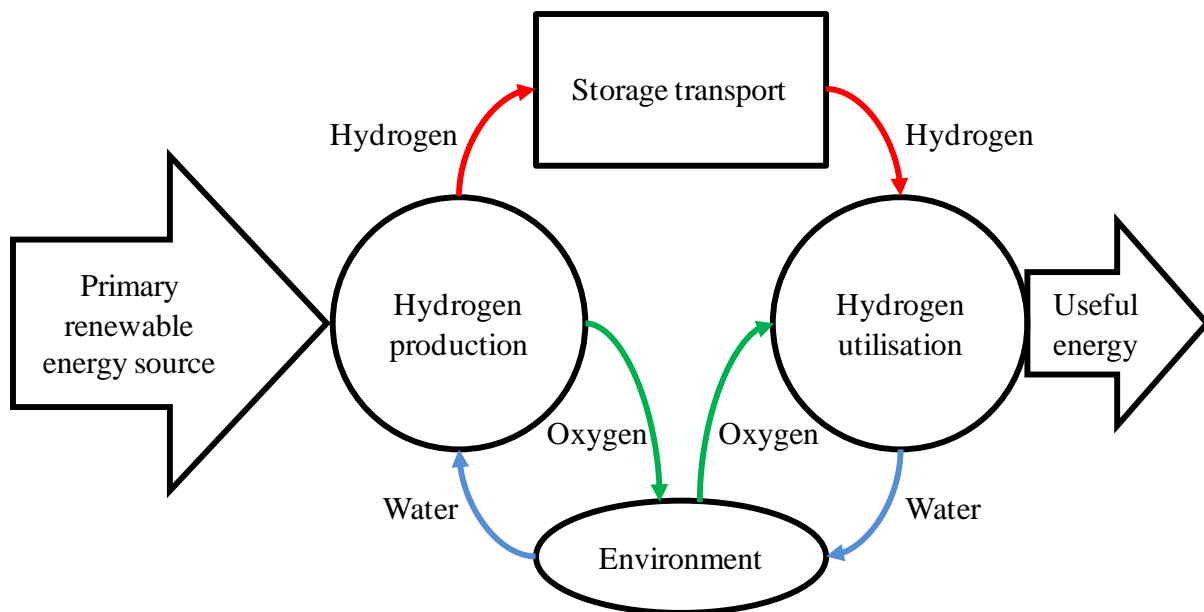
Figure 3.1. Hydrogen life cycle derived from a renewable energy source [1]

Hydrogen is mostly derived from fossil fuels at present, as these have the lowest costs [2]. Steam reforming of gases is explored in Section 3.2 and the gasification of carbonaceous solids and heavy liquids is examined in Section 3.3. Although both of these technologies currently have high CO_2 emissions, these emissions could be greatly reduced in the future using carbon capture and storage (CCS) technologies, with the potential of delivering carbon negative emissions when using biomethane and biomass feedstocks, respectively.

The other technology that is currently used to produce hydrogen is electrolysis. A number of different types of electrolysers have been developed commercially but all have high capital costs, which might be reduced in future, and high fuel costs for electricity, which can only be reduced through efficiency improvements. An important characteristic of electrolysers is the high purity of the hydrogen that they produce, which is much easier to prepare for use in fuel cell vehicles than hydrogen from other sources. Transport is potentially the principal market for hydrogen in the future [3-6]. Electrolysers are examined in Section 3.4.

Numerous hydrogen production technologies are at an early stage of development that use a range of renewable feedstocks. Novel water splitting and biological hydrogen production methods are discussed in Section 3.5, hydrogen storage in Section 7.

The chapter compares and contrasts these technologies from an energy security perspective in Section 3.6, before presenting the concluding remarks.

3.2 Steam reforming of gas, light oils and alcohols

Steam methane reforming (SMR) is the most widespread hydrogen production method at present, due to the high hydrogen yield and low capital cost. This method uses a catalyst, typically nickel, to facilitate the thermo-chemical reaction of natural gas and water at temperatures of around 850 °C and a pressure of up to 2.5 MPa [7]. The methane in natural gas reacts with steam to produce a syngas consisting of hydrogen and carbon monoxide. Saturating this gas with further steam (water-gas shift reaction) yields additional hydrogen as the CO is converted to CO_2. Including all energy inputs, SMR generates 9–13 kgCO2e/kg H_2 [8]. The conversion efficiency of hydrogen produced using SMR does not normally surpass 75% [7], but this is forecast to rise to 80% in the future.

A schematic diagram of a typical SMR plant is shown in Figure 3.*2*. First, the water and natural gas are pre-treated, with the natural gas desulphurised to avoid poisoning the catalyst in the reformation process. The natural gas is pre-reformed with steam at a lower temperature range (400-550°C) to convert all the hydrocarbons into methane and carbon oxides. The gases are heated then at a higher temperature in the reformer (450–1000 °C) yielding carbon monoxide (CO) and hydrogen molecules. In the following stage, a water-gas shift reaction run by a higher and a lower temperature catalytic reactor manages to extract an additional mol of hydrogen from each mol of CO from the previous stage and additional water. In the final stage, impurities are removed from the hydrogen-rich gas (e.g. unconverted CH_4 and CO) to meet the required purity. It is also possible to capture the CO_2 generated in the SMR. CO_2 could be removed from syngas, via adsorption/regeneration at the pressure swing adsorption (PSA) inlet, from the PSA tail gas, and from the SMR flue gas. Combining these different approaches, more than 99% of the CO_2 could be removed [9]. A CCS system requires additional energy inputs to scrub, compress and transport the CO_2, which could reduce the operating efficiency of the SMR plant by at least 5%[1] [10]. The facilities to scrub the CO_2 produced in the combustion and conversion processes, and to compress, transport and inject it into a suitable geological repository for permanent storage would only be economically viable for large plants or for a series of small plants in close proximity.

In the event of a failure of the CO_2 storage infrastructure, it would be possible to vent the CO_2 to the atmosphere, so the principal energy security concern for CCS is the increased feedstock requirement, caused by the reduction in the operating efficiency of the plant, a more complicated plant design that might decrease the overall reliability, and the cost premium for effectively handling a waste with no energy merits.

SMR currently has the lowest capital costs of the hydrogen production technologies in use today [2], although these would rise if CCS capabilities were deployed [10]. Small-scale reformers have been developed in some countries such as Japan where natural gas from the national grid is used in domestic fuel cell micro-CHP reformers for heat and electricity production; however, CCS is better suited for central hydrogen production plants.
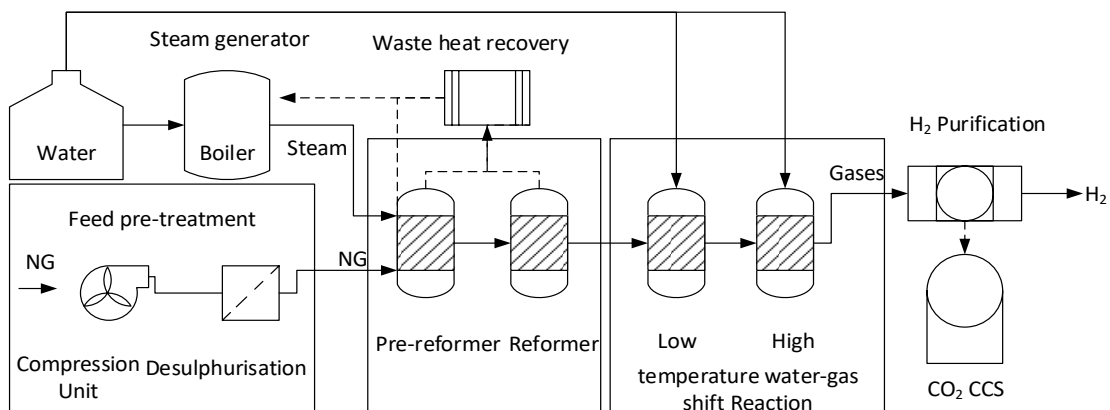

Figure 3.2. Flow diagram of a typical SMR plant.

Steam methane reformers can process natural gas and biomethane, LPG, naphtha or refinery off-gas as feedstock (Figure 3.*2*). Achieving fuel flexibility would be a desirable energy security goal; however, this does not happen in practice. One reason is that installing an additional feeding system is expensive. Also, enabling a plant to run with different feedstocks decreases its efficiency as the

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[1] Measured as % [kWh (H_2 out, HHV)/ kWh (natural gas in, HHV)]

catalyst choice and geometry are normally optimised for a particular feedstock. Fuel flexibility therefore reduces the hydrogen yield and hence the profitability of a plant [11]. This would not apply to switching between natural gas, biomethane, or synthetic natural gas (SNG), though.

Other potential feedstocks with higher oxygenated content, such as glycerine, glycerol, ethanol as well as other higher alcohols, have a high tendency to carbon formation and are not optimal feedstocks for steam reforming [12]. For these feedstocks, plants based on methanol cracking are a better solution. Since methanol and ethanol are more valuable products than natural gas, the number and capacity of such plants tend to be small. Figure 3.*3* shows that the design of steam methanol cracking (reforming) plants differs considerably from SMR designs such as Figure 3.*2*. Methanol reformation facilities are simpler and require a smaller footprint than steam methane reformers as they do not require a desulphurisation reactor, pre-reformers, steam generators or water-gas shift reactors. The hydrogen gas is purified with several adsorption processes via pressure swing adsorption obtaining pure hydrogen (99.999%).
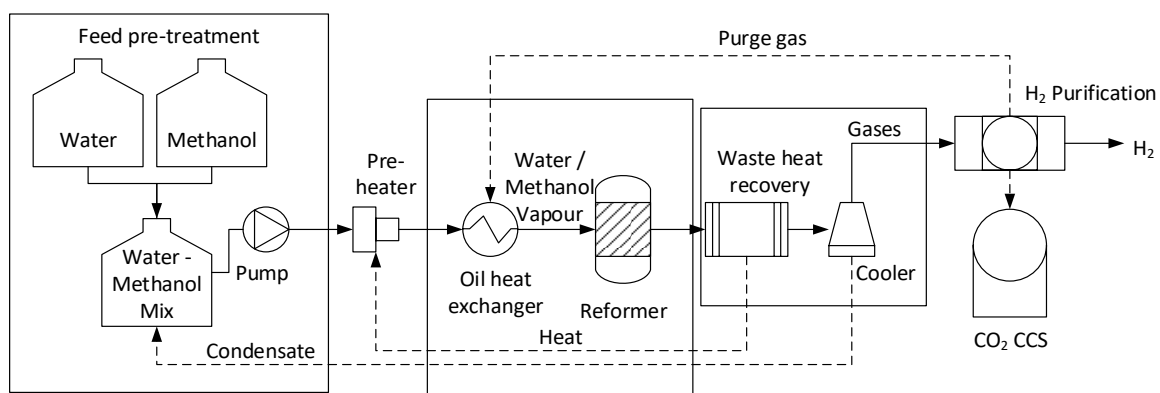

Figure 3.3. Flow diagram of a typical methanol cracking plant.

3.3   Gasification of coal, heavy oils and biomass

Gasification is a thermal process in which a feedstock with high carbonaceous content (e.g. biomass; coal; refuse-derived fuel) is heated with steam and/or oxygen at a temperature between 500 °C and 1,400 °C, and at a pressure that varies depending on the technology [13]. Processes using catalysts and fluidised-bed reactors are under development to decrease the operating temperature and improve their performance. Gasification produces a syngas, consisting of H_2 and CO, from which hydrogen can be extracted.

Coal gasification is a mature technology, but is an energy-intensive process with much higher carbon emissions than SMR. It is also more expensive, since lower feedstock costs are more than offset by higher capital costs and lower process energy efficiencies. NETL [14] reports overall hydrogen production efficiencies from coal gasification of 59–64% (% HHV). There are economies-of-scale for many components in gasification plants which mean that only large, centralised gasification plants are commercially-viable, generally in locations where natural gas is expensive or unavailable.

Several gasification technologies are currently used. Entrained-bed flow gasifiers produce the highest hydrogen yield from fossil fuel feedstocks (e.g. coal; petroleum coke). As shown in Figure 3.*4*, the coal needs to be pulverised (size <0.1 mm) and mixed with water to produce a slurry mix that is injected at the top of the gasifier. It is also possible to co-gasify small amounts of biomass with coal; however, it is good practice to pre-treat the biomass via torrefaction (mild pyrolysis at 200–300 °C) and then pulverise it before adding it to the mix. Alternatively, flash pyrolysis can convert solid biomass into a liquid bio-oil which can be fed into the gasifier or mixed with the char to

forma slurry [15]. Steam is introduced into the bottom of the gasifier. The coal reacts with oxygen at high temperature (1200–1300 °C) and pressure to form syngas and a layer of slag on the gasifier walls. This slag is removed at the bottom of the gasifier. At such high temperatures, the production of hydrocarbons (e.g. methane) and tar is minimal, obtaining syngas made basically of hydrogen and carbon monoxide. Since the feedstocks have a high carbon content and numerous impurities, gasification tends to produce a substantial amount of CO_2 and other air quality pollutants (e.g. particulate matter; SO_2). The CO_2 can be captured from the flue gas and stored, although Cormos [16] argues that bed flow gasifiers are the only ones suitable for CCS applications.
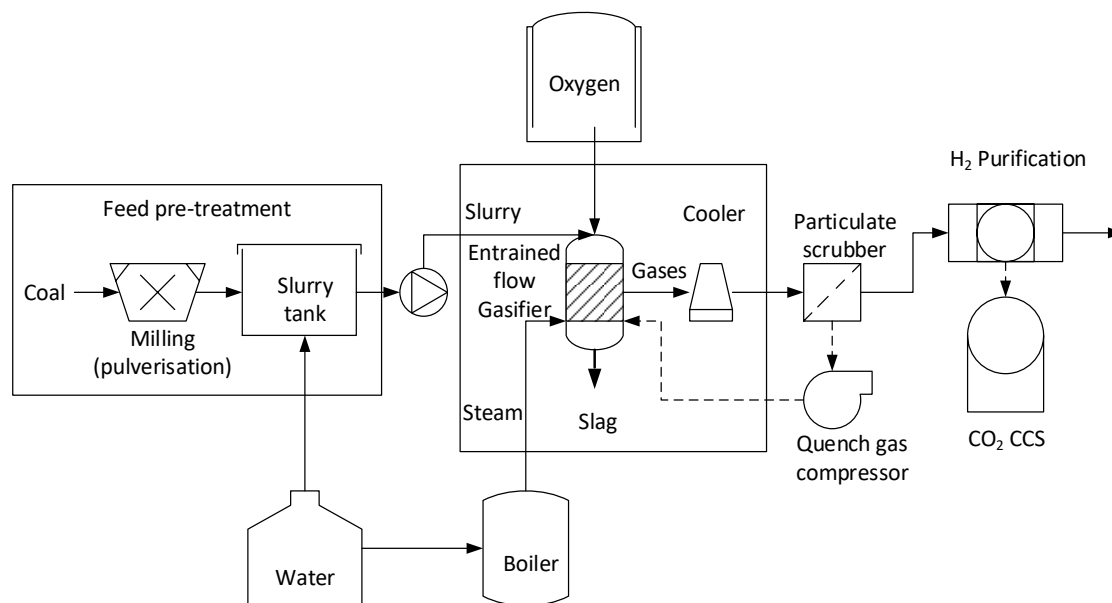
Figure 3.4. Flow diagram of a typical coal gasification plant.

Biomass normally refers to a renewable feedstock composed of solid organic matter, but can also refer to various waste products including animal waste, sludge, food processing arisings, and part of municipal solid waste (MSW). Biomass gasification with CCS offers the opportunity to sequester atmospheric CO_2, and such "negative emissions" are valuable in a low-carbon energy system if the effective price of emitting CO_2 is high enough.

Hydrogen can be produced from biomass by applying heat and steam, and/or oxygen, to lignocellulosic feedstock, with a conversion efficiency of around 35%–50%[2] [17]. The technology is mature and commercially available as wood gasifiers but no large commercial plants have been built. The main problem in large scale employment has been the lack of standardisation in biomass and waste derived feedstocks, an issue that will be difficult to solve, which prevents long-term stable automatic operation. Another problem is the high investment cost. Catalysts are under development to improve the conversion efficiency; for example, Kumar [18] found that using nickel catalysts on alumina reduced the formation of methane, which maximised hydrogen yield, while a sodium hydroxide catalyst promoted hydrogen gas formation during gasification and reduced carbon emissions. That study highlighted the high cost of alkali metal catalysts and their recycling as obstacles to using sodium hydroxide in biomass gasification. No catalysts are currently used in commercial biomass gasifiers [11].

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[2] Thermal efficiency based on higher heating values of biomass that has not been dried.

Table 3.1 shows that biomass and coal have quite different chemical compositions. While the carbon content of coal is very high (79%) and oxygen very low (15%), the carbon content of biomass is much lower (around 50%) and oxygen much higher (around 43%). This leads to the dry energy density of coal (32 MJ/kg) being almost double that of biomass (18 MJ/kg). Moreover, this difference is exacerbated by the moisture content of coal (9%) being much lower than that of biomass (10–28%, excluding torrified feedstock and sawdust). As a result of the higher moisture content of biomass and its lower energy density, biomass feedstock transportation costs are higher than coal. Biomass feed needs to be grinded, dried and pelletised to improve gasification conditions. If the biomass is torrified prior to gasification, there is a reduced risk of spontaneous combustion of the feed and a reduced need for precise temperature and humidity control. Bubbling fluidised bed (BFB) gasifiers are generally preferred to entrained flow gasifiers for biomass as they tolerate larger fuel particles. BFB gasifiers work well with particles of up to 80 mm in size, while entrained flow ones need pulverised feedstock smaller than 50 μm [15]. This means that as torrefaction and pulverisation of biomass is optional for BFB gasification, pre-treatment is cheaper than when preparing the same feedstock for combustion on entrained flow gasifiers. NETL [19] reports that BFB gasifiers are among the lowest capital cost options for biomass gasification and identify their suitability for fuels, chemicals, and hydrogen production.

In coal gasification the feed (slurry) is pumped into the gasifier, whilst solid biomass requires a screw conveyor to introduce the load into the gasifier as illustrated in Figure 3.5. Unless a single type of biomass is used, the different energy contents of each feedstock require careful management of the gasifier combustion parameters. Bubbling fluidised bed gasifiers run at lower temperatures (under 1000°C) than entrained bed flow ones and this allows the formation of tars that must be removed from the producer gas at the scrubbing stage to avoid the poisoning of hydrogen purification catalysts. Wet scrubbing produces a mixture with tar particles and water but scrubbing with biodiesel is also possible; however, this only works with small amounts of tar and requires 1 kg of biodiesel/kg tar [20], which increases the costs considerably.
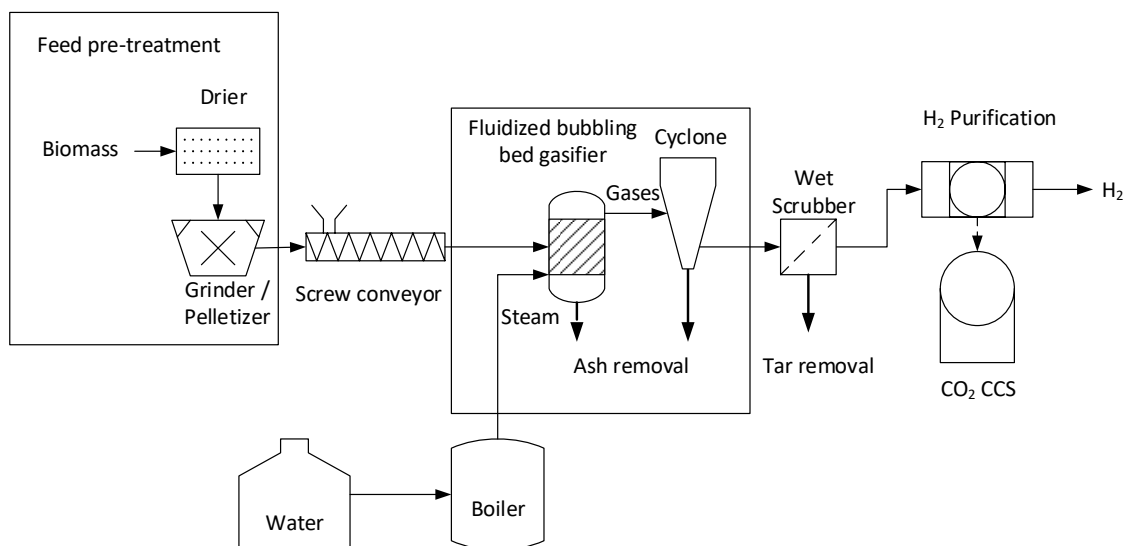

Figure 3.5. Flow diagram of a typical biomass fluidised bubbling bed gasification plant.

Particulates are removed at the lower end of the gasifier and also via a cyclone. Biomass gasification also produces a broad range of chemical compounds that present potential challenges to the system. Some of these issues and solutions are explained in Table 3.2.

The design of gasification plants is highly dependent on the feedstock that is used and the purpose of the plant (e.g. producing chemicals, green hydrogen, CHP or power). The differences include not only the pre-treatment of the feed, but also the selection of gasification and hydrogen purification technologies. Retrofitting or adapting a coal plant for fuel flexibility is technically and operatively challenging.

Analysis	Fossil Fuel		Biomass						Peat	Mixed waste	
Proximate	Coal	Plastic	Miscanthus	Bagasse	Hardwood Pellets	Sawdust	Wood Chips	Torrified Hardwood		RDF	MSW
Moisture content [a]	9	0.2	29	19	10	4	23	2	28	10	22
Ash content [b]	11	1	4	6	N/A	0.9	2	0.4	5	17	26
Volatile matter [c]	40	97	82	83	85	85	81	77	74	88	87
Fixed carbon [c]	60	3	18	17	15	15	19	23	26	12	13
Ultimate [c5]											
Carbon	79	74	49	49	51	52	52	54	56	55	49
Hydrogen	5	10	6	6	8	6	6	6	6	8	6
Nitrogen	2	0.1	0.5	0.6	0	0.1	0.4	0.2	2	1	2
Sulphur	1	0	0.1	0.1	0	0	0	0	0.4	0.4	0.6
Oxygen	14	4	44	44	42	42	42	41	36	34	31
Total (with halides)	97	100	98	73	5	50	100	100	88	99	70
Calorific Values (MJ/kg dry and ash free)											
Net calorific value (LHV)	31	35	19	18	20	17	19	21	22	23	19
Gross calorific value (HHV)	32	38	20	19	17	18	21	22	23	24	20
Other considerations											
Transportation cost	Low	Low	High	High	Medium	Medium	High	Low	High	Medium	High
Milling requirements	Standard	Special	Special	Special	Special	N/A	Special	Standard	Special	Special	Special

Table 3.1. Chemical composition of several feedstocks. a) Weight as received; b) Weight dry; c) Weight dry and ash free. Adapted from ECN [21], Kiel [22].

Box 3.1. Hydrogen production from waste
Hydrogen can be produced by gasifying municipal solid waste (MSW). MSW can contain a wide range of organic and inorganic materials (Table 3.1), which could lead to operational difficulties. An alternative is to use refuse-derived fuel (RDF), a higher-quality fuel that can be manufactured (at a cost) from MSW, commercial and industrial waste. It is a heterogeneous product that can contain plastics, organic and inorganic materials of homogenous particle size. However, despite RDF having a relatively high calorific value (24 MJ/kg), the energy yield of RDF gasification can barely cover the energy needed to produce the fuel [23]. Plasma gasification is a feasible technology used to obtain energy from MSW that can also generate hydrogen; however, it consumes a third of the power produced [20]. The primary purpose of these technologies are therefore waste disposal rather than hydrogen production.

Compound	Issue	Comment
Volatiles (particulates)	Carbon (coalite) is porous and reactive which increases risk of spontaneous ignition. Ash and soot are formed as well as aerosols that fouls pipe walls and equipment and causes abrasion.	Biomass has a high volatile content (~80% dry & ash free mass). Cyclone separators, filters and wet scrubbers are used to eliminate solid particles.
Tar	Tar creates deposits and fouls pipe and other equipment. It creates coke and charred materials reducing H2 yield.	Removal is necessary; however, it is challenging and costly. Removal methods include catalytic reactions inside and/or outside the gasifier and filtering systems or careful adjustment of operating conditions.
Alkali metals (e.g. K, Na)	Danger of agglomeration / melting in gasifier Downstream fouling by condensation of volatile salts Corrosion of metal materials Lowering of ash melting temperatures.	Additives are needed to mitigate risks. Lower temperature can help but reduce H_2 yield. Usually treated with web scrubbers.
Organic sulphur (H_2S, CS_2, COS, SO_x, mercaptans, etc.)	Desulphurisation requires precise temperature management to avoid poisoning of purification catalyst. It is also corrosive. Interaction with alkali metals.	Solutions include wet scrubbing using additives (expensive), sorbents and adsorption on metal catalysts.
Other aromatic hydrocarbons: BTX (benzene, toluene and xylene)	Coke forming tendency.	Can be reformed, but needs upstream S-removal to protect the catalyst, and upstream activated carbon does not make sense since it absorbs the BTX.
Nitrogen compounds	Most gas is as N_2; however, ammonia is also formed by the conversion of protein and other nitrogen rich biomass components and small amounts of cyanide (HCN). It may damage scrubbers.	Elimination is possible via catalytic reduction of NO_x or using catalysts before reaching the wet scrubbing stage.

Table 3.2. Challenges of biomass gasification in the post treatment of producer gas (cleaning). Adapted from: IEA Bioenergy [15], Bram van der [20], Balas et al. [24].

3.4 Electrolysis

Water electrolysis is a process in which water is split into hydrogen and oxygen atoms. In their most basic form, all electrolysers are composed of an anode, a cathode and an ion-conductive medium (electrolyte), as represented in Figure 3.6. In the proton conducting membrane electrolysers, the electrical current generates a flow of positive charged ions (protons) to the cathode (negative electrode) where these gain electrons and are reduced. In the oxygen and hydroxyle ion conducting types of electrolysers, negatively charged ions move to the anode (positive electrode) losing electrons and oxidising. In both processes, the constituents hydrogen and oxygen of the water are separated, resulting in hydrogen being released at the cathode and oxygen at the anode. Since electricity is an expensive feedstock, the electricity conversion efficiency is a key factor for electrolyser economics [2].

A key advantage of electrolysis over reforming and gasification technologies is the high purity of the produced hydrogen (>99.999%), which is suitable for powering fuel cells after only a drying stage. No CO_2 emissions are produced by electrolysers, although the lifecycle emissions will depend on the emissions embodied in the electricity feedstock. Electrolysers are the most suitable hydrogen production technology for distributed production and in combination with energy storage they can play a crucial role in supporting the generation of renewable power.
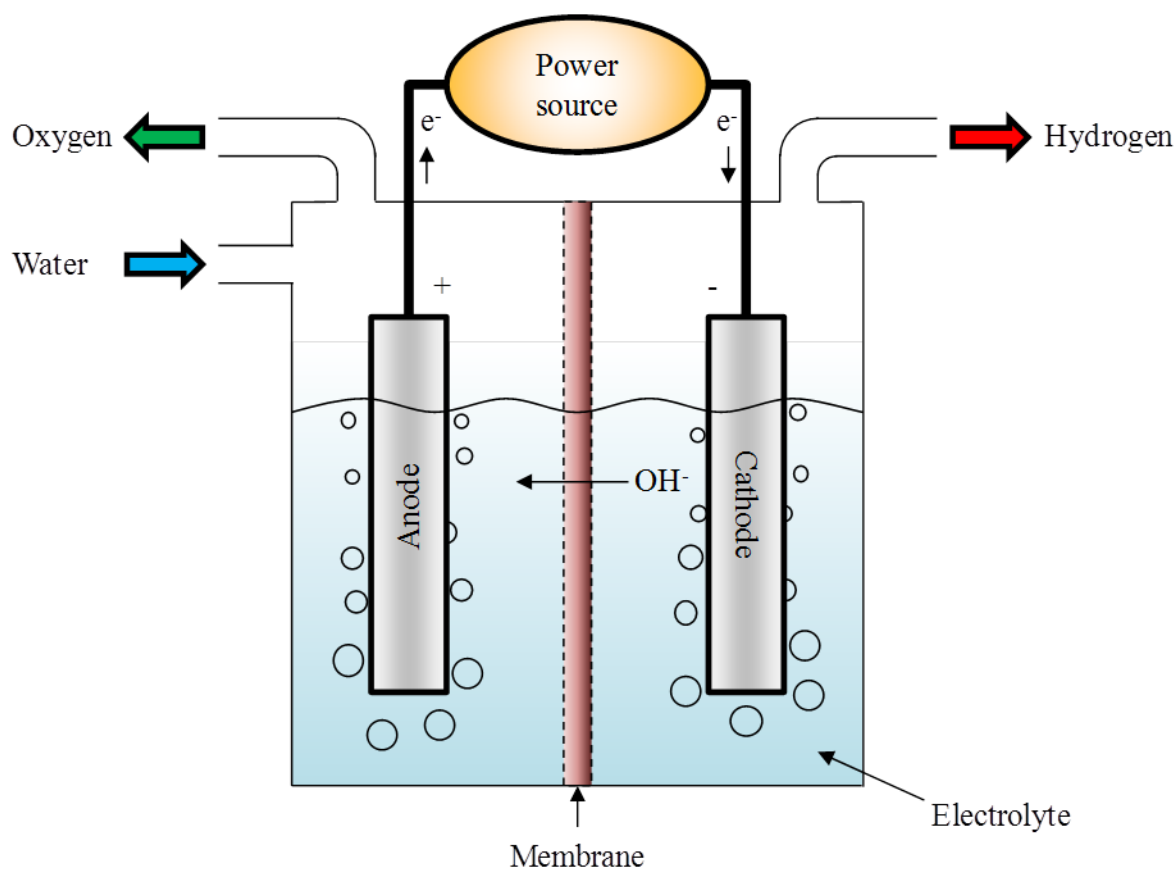

Figure 3.6. Basic water electrolyser with an alkaline electrolyte (hydroxyle ion transporting membrane).

3.4.1 Alkaline electrolysers

Alkaline electrolysers are the principal commercial technology used to produce hydrogen via electrolysis at present. A direct current is applied between an anode and a cathode submerged in an electrolyte (an alkaline solution such as potassium hydroxide), which causes hydrogen to form at the

cathode and oxygen at the anode. The hydrogen production rate is proportional to the current passing through the electrodes. The reaction is endothermic and reversible at ambient temperature.

Electrolysers can operate at atmospheric pressure, with the resulting gases being compressed afterwards, or can operate at higher pressures up to 20 MPa. They tend to operate at ambient temperature, with liquid water, but some high-temperature electrolysers have been proposed to reduce electricity consumption (Section **Error! Reference source not found.**). Commercial electrolysers have a hydrogen production efficiency of 68–80%, which depends on the cell voltage (typically 1.9–2.2 V), temperature (70–90 °C), electrolyte flow conditions and the operating pressure [25]. While alkaline capital costs tend to be lower than for other electrolysers technologies, plant output cannot be easily varied and overall costs are very sensitive to the price of electricity. Bertuccioli et al. [26] estimated that the system costs of alkaline electrolysers in the EU will decrease from 1,000–1,500 €/kW in 2014 to about 600 €/kW by 2020.

3.4.2   PEM electrolysers

Polymer electrolyte membrane (PEM) electrolysers are smaller than alkaline electrolysers as the electrolyte is a solid plastic material [27]. Oxygen from the water molecules and positively charged hydrogen ions (protons) are formed in the anode. The electrons flow through an external circuit and the hydrogen ions (H^+) move to the cathode through the membrane, where they combine with the electrons to form hydrogen gas (H_2). PEM electrolysers have a faster dynamic response and wider load ranges than alkaline electrolysers; however, they have higher capital costs as they require expensive catalysts. Much research and development effort is underway to improve the catalysts, membranes and bipolar plate materials and to reduce their costs.

The low-temperature operation and power cycling capability offers the opportunity to use PEM electrolysers to generate hydrogen at times of excess intermittent renewable generation, through power-to-gas. In 2013, the first systems were connected to electricity networks, with the resulting hydrogen being injected into a local gas [28]. Since power-to-gas electrolysers have low capacity factors, as they only operate when there is excess electricity generation, minimising the capital cost is important for making a business case. The costs might be reduced through the use of cheap or free electricity or by income from the provision of balancing services to the electricity system. Nevertheless, US DoE [29] estimated a real levelised cost of $5.2 kg^{-1} (by 2010) and a future cost of $4.2 kg^{-1} by 2025. The system costs of PEM electrolysers are currently twice the cost of alkaline ones and are expected to decrease to around 1,000 €/kW by 2020; however, for small systems (≤100 Kw), prices are already competitive with alkaline electrolysers [26].

3.4.3   Solid oxide electrolysers

Solid oxide electrolysers (SOE) use a solid ceramic material for the electrolyte and operate at very high temperatures (700–900 °C). Oxygen ions (O^{2-}) flow through the ceramic membrane to the anode and react to form oxygen gas. Free electrons then flow to the cathode, splitting water and forming hydrogen gas. SOEs have higher efficiencies than other electrolysers because part of the heat generated in the electrolyser is recycled to contribute to the high operating temperature [27]. However, costs are still expected to be relatively high in the long run, with estimations of $3.8 kg^{-1} by 2025 [30]. In the European Union, Bertuccioli et al. [26] interviewed several stakeholders and reported that by 2020 SOEs system costs could reach 1,000 €/kW if these would become commercially available.

The high temperature makes this process well suited for environments where there is a source of cheap heat, such as a Generation 4, high-temperature nuclear power plant, but more sensibly, any source of steam, even at lower temperatures. SOE are more efficient than conventional water

electrolysis as less energy is required for breaking the steam molecules than the liquid water molecules in conventional electrolysis [31], and also because some electricity can be replaced by waste heat, adding to the improved energy efficiencies and lower feedstock costs mentioned above [25]. Mougin [31] suggests potential electrical efficiencies of 89% (LHV), well above alkaline (58%) and PEM water electrolysis (63%), respectively. The US DoE [32] estimate that the costs for this method, at $2.9 kg^{-1} by 2030, would be substantially higher than for SMR, biomass gasification and alkaline electrolysis. Other disadvantages include degradation issues during operations and the risks associated with novel technologies at an early stage of development [31]. Nevertheless, SOE and SOFC (solid oxide fuel cells, see Chapter 4) are essentially identical as a device and research is currently ongoing as to run 'reversible' fuel cells, which would operate both for generating electricity from hydrogen and splitting water to hydrogen, depending on which way they are operated. Degradation issues seem to be much reduced in such appliances and they could revolutionise the provision of balancing power for electricity grids.

3.5   Production methods at an earlier stage of development

3.5.1   Solar thermo-chemical water splitting

Solar thermo-chemical water splitting uses solar energy to decompose water in order to produce hydrogen and oxygen molecules, generating hydrogen with a purity of 99% [33] with an efficiency of around 10% (Table 3.3). In most designs, solar radiation is concentrated with mirrors that point towards a tower where extreme temperatures (above 2200 °C) produce the disassociation of water atoms. This presents challenges in the selection of materials for the reactors and the membranes for the separation of the gases [33], as typical materials can sinter, melt and vaporise at this temperature, decreasing the efficiency of the process [34]. Despite not being at a commercial stage just yet, several publicly-funded projects have been promoted around the world where concentrated solar power facilities produce hydrogen; examples of these include Hydrosol 2 in Spain, CSP2 in France and Solzinc in Israel. The US DoE [35] estimate that the cost of hydrogen produced in this solar-thermo-chemical pathway would be $14.8 kg^{-1} in 2015; although it could decrease to $3.7 kg^{-1} by 2020. These estimates have a high level of uncertainty as there are no commercial plants at the moment. There are considerable research challenges in the area of new materials to resolve before solar thermo-chemical water splitting can become commercially-viable. Other considerations include the large land requirement and the need for high solar irradiance, which make this technology most suitable for desert areas.

Production Technology	Main Feedstocks	System Energy Efficiency[a] (%)		USA H$_2$ Cost[b] ($/kg)		Maturity Level[c]
		2015	2020	2015	2020	
Reforming: Steam Methane Reformation	Natural Gas + steam	74%	≥74%	2.1	≤2.1	Commercial
Gasification: Biomass	Biomass	46%	48%	2.1	2.0	Pilot Projects
Electrolysis: Alkaline	Water + electricity	73%[d]	75%[d]	3.0[d]	2.0[d]	Commercial
		72%[e]	75%[e]	3.9[e]	2.3[e]	
Water Splitting: Solar Thermo-chemical	Water + Sunlight	10%[f]	20%[f]	14.8	3.7	Pilot Projects

Biological: Photolysis (Photosynthesis)	Water + Sunlight	2%[f]	5%[f]	N/A	9.2	Pilot Projects
Biological: Dark fermentation	Biomass	4 mol H_2 / mol glucose	6 mol H_2 / mol glucose	N/A	N/A	Research Lab
Biological: Photo fermentation	Biomass + sunlight	0.1%	N/A	N/A	N/A	Research Lab

Table 3.3. Comparison of hydrogen production methods. Adapted from Holladay et al. [36] and US DoE [35]. a) LHV; b) Estimated hydrogen levelised cost in the USA. Source: US DoE [35]; c) As per November 2016; d) Central production; e) Distributed production; f) Solar-to-hydrogen ratio; defined as the energy of the net hydrogen produced divided by net full spectrum solar energy consumed (LHV).

3.5.2 Biological hydrogen production

Hydrogen can be produced via metabolic processes using micro-organisms such as microalgae, cyanobacteria (blue and green algae), purple non-sulphur and dark fermentative bacteria [37], operating under different environmental conditions (e.g. light, pH, temperature) and using various feedstocks. Bio-hydrogen production requires little energy, does not produce airborne pollutants, and uses renewable feedstocks that are relatively abundant and cheap (e.g. water, microorganisms, waste).

Certain micro-organisms can produce hydrogen via photosynthesis. To conduct the photolysis of water these micro-organisms need CO_2 and sunlight. Photobiological hydrogen can be produced by some micro-organisms directly by the activity of hydrogenase or indirectly when enzymes (e.g. hydrogenase, nitrogenase) decompose carbohydrates (e.g. glucose, cellulose) or glycogen into hydrogen [37]. Examples of the former include cyanobacteria (e.g. Synechocystis, nostoc sp) and green algae (Chlamydomonas sp.). Examples of the latter include microalgae and cyanobacteria that generate H_2 from intracellular energy reserves. These are typical of anaerobic digestion, where bacteria digest organic waste generating hydrogen, CO_2 and acetogens (e.g. lactic acid) before the methanogenesis (in the acetogenesis phase).

Other micro-organisms (e.g. anaerobic bacteria such as clostridium) can produce hydrogen from biomass in darkness via dark fermentation. Under this process, organic compounds (e.g. carbohydrates) are fermented delivering organic acids and a low hydrogen yield. Poudyal et al. [37] found that dark fermentation of hexose produces just around 2–4 mol H_2. Dark and photofermentation could be combined to improve the overall process productivity.

The principle drawbacks with biological production methods are low efficiencies, high capital costs of bioreactors and large land area requirements. If biological H_2 production is to succeed commercially, the energy yields of the micro-organisms and processes will need to be considerably improved. For this reason, genetic engineering of more resilient and productive micro-organisms is an active area of research [37].

3.6 Production of synthetic natural gas and other compounds

Hydrogen could be used as a feedstock to produce a range of organic chemicals. One route is to gasify biomass or waste, or to produce hydrogen from power-to-gas, and then to methanate the hydrogen to produce synthetic natural gas (SNG) as shown in Figure 3.7. The resulting SNG would be carbon-neutral if the feedstock were carbon-neutral, meaning that this is one of the few methods available to decarbonise heat provision from natural gas. The challenge is the high cost relative to the cost of natural gas, which means that it might only be viable for feedstocks such as waste for

which a disposal fee can also be collected. The figure shows a system of producing SNG for feed-in to the former natural gas grid. This would be using the existing infrastructure, avoiding any new investments. The primary energy source of the SNG would be biomass by anaerobic digestion and gasification as discussed in section 5, on one hand, and electrolytically produced syn-gas from renewable electricity, on the other hand. Feeding an SOE with a mixture of water and carbon dioxide (co-electrolysis) produces a similar syn-gas (CO and H_2 mixture) to the product from biomass gasification. The SNG is completely zero-carbon and substitutes natural gas, thus decarbonising the current gas supply system without a need to change technologies of gas use in the short term.

In the future, hydrogen could similarly be used as a base for more complex chemical reactions to synthesise a wide range of high-value, carbon-neutral chemical compounds in the chemical industry.
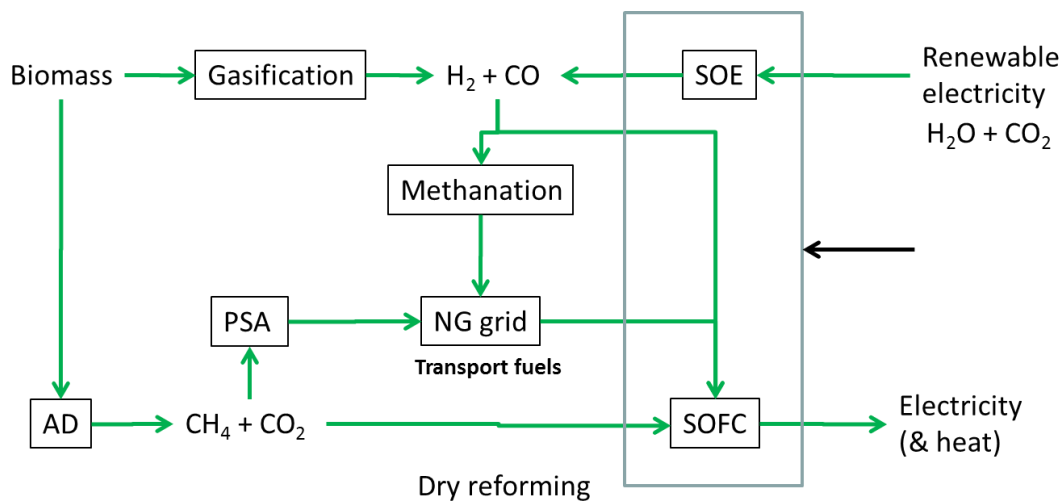

Figure 3.7. Production of synthetic national gas (SNG) via biomass conversion in gasification or anaerobic digestion, and from power-to-gas with subsequent methanation. SOFC is a solid oxide fuel cell. AD is anaerobic digestion.   NG is natural gas.

3.7   Water requirements for hydrogen production

Hydrogen production plants have high water requirements, both as a hydrogen feedstock and for process cooling. These are similar across production technologies with a range from 9–16 l/kgH_2, as shown in Table 3.*4*. Electricity generation has a similar water footprint but has a much wider range. The consequences are that hydrogen production plants need to be constructed near a substantial water source such as a river. Some electrolysis technologies require a salty electrolyte, and these would be most appropriately located on a shoreline. Given that water requirements are similar to electricity generation, they are unlikely to be significant factors affecting energy security in the UK.

Technology	Water for hydrogen production	Water for equivalent electricity production
Gas SMR	9 – 15	8 – 28
Biomass gasification	13 – 14	4 – 39
Electrolysis	11 – 16	
Nuclear power		16 – 28

Table 3.4. Water requirements for several hydrogen production technologies (litres/kgH_2) and equivalent water requirements to generate an equivalent amount of electricity by energy content. Hydrogen sources: [38-40]. Electricity source: [41].

3.8 Hydrogen Storage and Infrastructure

Hydrogen can be stored onsite at the point of production as compressed gas, liquid or chemically in a solid-state storage medium. Distribution of the hydrogen would be relatively simple since it can be delivered via pipeline to the point of use.

Currently, in most developed countries there exists a pipeline infrastructure for the delivery of natural gas to homes for the purpose of heating and cooking. Hydrogen could be transported from the point of production to the point of use in a similar manner. In order to tackle hydrogen embrittlement, these pipelines are typically fabricated with low carbon and manganese content, ≤ 1 and ≈ 0.2 wt%, respectively. These low concentrations reduce the yield strength of the steel to < 290 MPa and as a result limit the operating pressure to < 10 MPa, whereby 4 – 6 MPa are commonly used. Research has shown that polymeric coatings for steel pipes and fibre reinforced polymer pipelines are impermeable to hydrogen and can increase the operating pressures to a range of 7 to 25 MPa [42].

In the last two decades, billions of cubic metres of hydrogen were produced and kept in intermediate storage and transported via pipeline to serve the chemical and aerospace industry. For more than 50 years Germany has been using a 200 km pipeline to transport hydrogen for the chemical industry with virtually no problems. The United States, Japan and Italy also have an established pipeline network for the delivery of hydrogen for industrial applications [43].

Currently, there are only three liquefaction plants in Europe, one operated by Air Liquide in Waziers, France, another by Air Products in Rozenburg, Netherlands and one by Linde in Ingolstadt, Germany [42]. In the United Kingdom, the majority of hydrogen is transported in compressed gas cylinders to the point of use. In some countries, hydrogen is also transported by tanker in either a pressure vessel or in liquefied form. To help facilitate the transition over to a hydrogen economy, the existing pipeline infrastructure used by natural gas could be modified to enable the delivery of a hydrogen/natural gas mixture which could then be followed by the separation of hydrogen at the point of use [42, 44]

Hydrogen has a high gravimetric energy content, approximately three times more than petrol yet by volume has an energy content four times less than petrol [45]. This presents a problem when storing hydrogen for mobile applications especially since storage is limited to the space constraints of a road vehicle. In order to achieve the 300 mile range stipulated by the US DoE [44], utilising existing storage technologies such as compressed hydrogen tanks would require a space larger than most car boot. Not only does this provide a space issue but also the added problem of weight. A common method of storing hydrogen is in compressed gas form pressurised inside a tank at 35 or 70 MPa. Increasing the storage pressure would improve the energy density resulting in a smaller tank but a much heavier system. Hydrogen is a non-ideal gas meaning large amounts of energy are needed to compress hydrogen into smaller volumes. Compressed hydrogen tanks require 2.1% of the energy content to power the compressor [46].

Hydrogen can also be stored in the liquid state under cryogenic conditions. Typically, these conditions have hydrogen stored under 35 MPa at -253 °C. Storing hydrogen in a liquid state will improve its volumetric density facilitating containment in a smaller tank. The associated problems with storing hydrogen in this manner include boil-off, energy for hydrogen liquefaction, tank size and the attributed costs. Boil-off can present a significant safety issue in situations where a hydrogen powered vehicle is parked in confined and poorly ventilated spaces since hydrogen is susceptible to auto-ignition. According to the U.S. DoE, approximately 30% of the hydrogen lower heating value is

required for liquefaction indicating that this process is energy intensive therefore incurring large costs [44].

Currently, a hybrid system, named cryo compression, is being developed that provides a pressure vessel which is lighter and more compact than most storage media. BMW have launched a hydrogen powered car in 2015 utilising a cryo-compressed hydrogen storage tank. Furthermore, the operating temperature is not as low as cryogenic storage meaning there is less of a penalty for hydrogen liquefaction and reduced boil off [44].

Novel methods involve storing hydrogen either physically or chemically within select materials. Hydrogen can be stored on the surface of a material through adsorption, either in molecular or monatomic form. Hydrogen can also be dissociated into atoms, absorbed into a solid material and stored in the crystal lattice such as in metal hydrides or metal organic frameworks (MOFs). Other methods include the hydrogen atoms forming strong chemical bonds giving rise to chemical compounds such as complex hydrides and chemical hydrides [45].

For stationary storage in industrial applications, space is not as important as in mobile applications since the system is not limited to the volume constraints of a vehicle. As a result, the more traditional and established storage techniques such as compressed, liquid and slush hydrogen are utilised. Slush hydrogen is a combination of solid and liquid hydrogen coexisting together in thermodynamic equilibrium at the triple point which is at a lower temperature than liquid hydrogen and at a higher density.

Hydrogen can also be stored in large quantities underground in caverns, salt domes and depleted oil and gas fields. There are many storage sites across the globe such as the ICI salt cavern in Teesside, England storing 95% pure hydrogen and $3 - 4\%$ CO_2 [47-49]. Between 1956 and 1974 the French gas company Gaz stored syngas in an aquifer in Beynes, France citing no safety issues during this period. Russia has also stored hydrogen underground specifically for their aerospace industry under 9 MPa of pressure [48].

3.9   Conclusions

Hydrogen can be produced using a range of processes, from a range of feedstocks. Large amounts of hydrogen are already produced from natural gas, coal, oil and to a lesser extent electricity, for industrial uses around the world. The choice of production technology depends at the moment primarily on the feedstock availability and overall cost. Coal gasification plants have been in operation for the last two centuries, producing a syngas containing hydrogen and numerous other gases, while electrolysis and SMR have been used for the last century. These technologies are mature and the principal challenges going forward are to produce low-carbon hydrogen at an acceptably low cost. A further range of novel production methods are at an earlier stage of development but might become important over the coming decades.

All of these technologies cause high CO_2 emissions, including electrolysis when using electricity generated in fossil fuel plants. The key challenge for existing fossil-based technologies is to cost-effectively incorporate renewable feedstock and electricity sources into existing processes, or ultimately revert to costly waste treatment such as CCS facilities. For electrolysis, the challenges are to reduce capital costs, supply low-carbon electricity and perhaps improve the conversion efficiency. For the novel bio-hydrogen production methods, which are still in their infancy, there is a need to identify and invest in newer, more resilient and productive micro-organisms.

Hydrogen is more expensive to produce than existing fossil fuels, but this would change in the future if a substantial carbon tax were levied and/or externalities internalised. Hydrogen also offers lower

price volatility than fossil fuels. Since hydrogen can be produced from a range of feedstocks, energy security can be increased by diversifying the portfolio of production technologies in a similar way to electricity generation, or by constructing redundant back-up plant. The diversity of technologies and feedstocks, and maturity and resilience of hydrogen production systems, mean that hydrogen production could make a positive contribution to UK energy security.

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