

Introduction: the power-to-fuel concept

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Since the discovery of fire, man has learned to use fuels: by switching from wood to coal, to oil and finally to natural gas and increasing enormously, at the same time, the global fuel consumption. Fig. 1.1 shows as the resulting CO₂ emissions led the atmospheric concentration to more than 400 ppm and this could be the main cause of global warming and climate change. Today, efforts are being made from an increasing number of countries to reduce, and potentially eliminate, the use of fossil fuels through the use of biofuels and hydrogen. Hydrogen is an important feedstock gas in industrial applications (Bessarabov and Millet, 2018). It is generally produced through steam methane reforming (SMR), whereas electrolytic hydrogen production has been considered an option for small flows of hydrogen or for high purity hydrogen required by niche applications.

The renewable energy sources (RESs) with the highest potential are solar and wind, and luckily, the cost of energy generated from these RESs is constantly decreasing. However, they produce electric power which covers only around 20% of the final energy demand.

Electricity, although it was discovered by the Greek Thales of Miletus in the 4th century BCE, has entered into use only in recent times. In the second half of the 19th century, with the invention of the dynamo by the Italian Antonio Pacinotti and with its industrialisation carried out by the Frenchman Zénobe-Théophile Gramme, the conversion from fuel to electricity began. And ever since then the direction of the process has been this.

Today the reversal of the direction of the process, that is from electricity to fuel, is carefully considered. The reason lies on the one hand in the need to replace fossil fuels with renewable and carbon-neutral fuels and on the other hand with the difficulty of storing the electricity obtainable from most RESs.

1.1 Renewable energy sources and energy storage

Unlike fossil resources, RESs are well spread on the planet and this is undoubtedly a great advantage. Unfortunately, the time distribution slows down the spread of exploitation. Almost all RESs are in fact characterised by a random availability accompanied by the lack of intrinsic storage capacity. Actually, apart from large hydropower, only geothermal energy offers constant availability, whereas tidal energy is variable,

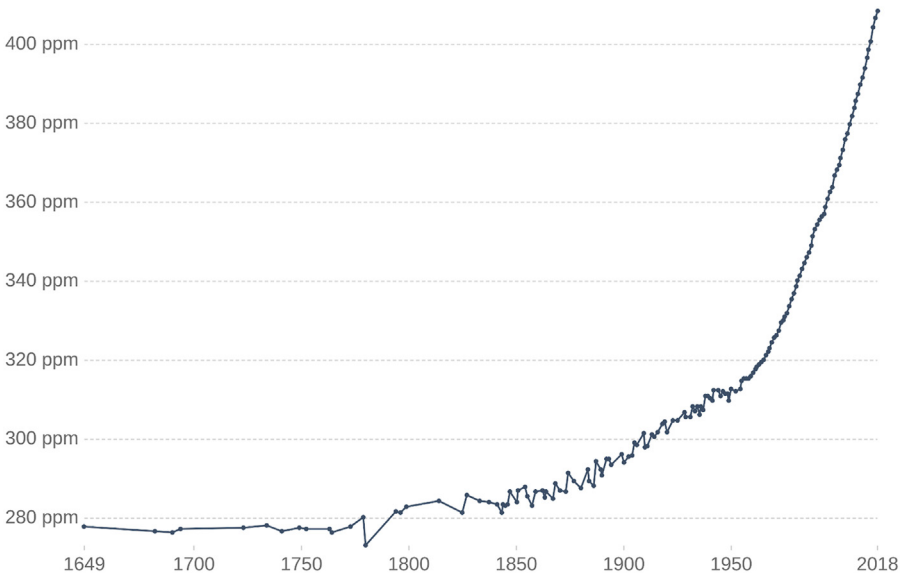


Figure 1.1 Global mean annual concentration of carbon dioxide in atmosphere (Our World in Data, 2020).

but its variability is foreseeable. Biomass can be stored; however, the sources whose exploitation shows the most favourable diffusion trend are solar and wind power, which generate electricity and are characterised by intermittency, with a consequent mismatch between production and demand. Moreover, a local surplus of electric power could not be completely transferred to another region due to probable grid instability problems. This will force to find an energy storage solution to allow the continuous replacing of fossil fuels with renewable and nonclimate-changing fuels.

Therefore electricity from solar and wind can be fed into the grid only if there is an effective demand and if the quality of the energy produced is such as not to jeopardise the stability of the grid itself. Otherwise, it is necessary to accumulate the surplus electricity.

In the event that the problem lies in the lack of electricity demand, it is still possible to transfer the surplus to centralised storage systems, such as pumping stations. If, on the other hand, the inability to transfer electricity to the grid is linked to the poor quality of the energy produced, then it is necessary to increase in some way its quality or to store energy on-site.

Unlike wind power, for solar energy, there is, at least in perspective, the possibility of direct conversion to fuel by means of thermochemical cycles for the production of hydrogen. Unfortunately, this is a prospect thought up about 60 years ago and not yet in view of a practical application. Over 100 different thermochemical cycles have been conceived, but only a few are still being studied, for example the sulphur-iodine cycle (Mathias and Brown, 2003). Initially designed to store the energy produced by nuclear reactors, these cycles are now also studied for solar energy storage, for example the zinc oxide cycle (Weidenkaff et al., 2000).

Electricity can be easily stored in rather small amount and for short periods, whereas the most promising system for storing large quantities of energy over long periods seems to be the conversion of the surplus of electricity into hydrogen by means of the electrolysis process. Hydrogen can also be used in all those applications or sectors where, for technical or economic reasons, electrification is difficult or not convenient, thus allowing to increase the penetration of RES in the market. Furthermore, hydrogen could play an important role to achieve a greater energy system integration, creating new links between different sectors, energy carriers and infrastructures, which today are separate from each other. This would result in a more interconnected, flexible, efficient and cleaner energy system (Fig. 1.2). Finally, electrolytic hydrogen produced from RES power can also be used as a basis to obtain a variety of chemicals and synthetic carbon-neutral fuels, such as those that will be presented in the following sections.

1.2 Power-to-fuel role in the energy transition

The hydrogen atom consists of a single proton and a single electron, which has a mass about 1800 times lower than that of the proton. The atomic weight is 1.00794 amu. The radius of the orbit of the electron is about 100,000 times higher than the radius of the proton and, therefore, the space occupied by the atom is practically empty.

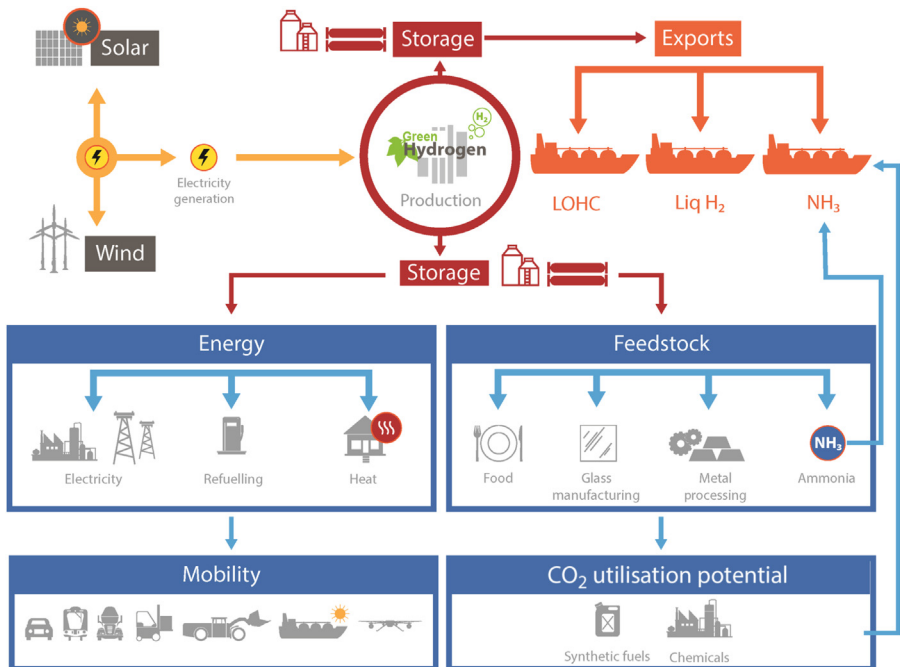


Figure 1.2 Hydrogen as an enabling chemical for sectoral integration: various examples.

Source: Courtesy D. Bessarabov, HySA.

Its molecule is diatomic with covalent bonding and the protons may have parallel (ortho-hydrogen) or antiparallels (para-hydrogen) spins. The molecular weight is 2.016 amu. At room temperature or above, hydrogen is a mixture (75% ortho-hydrogen + 25% para-hydrogen) and it is called normal-hydrogen. Hydrogen is colourless, odourless, tasteless, practically insoluble in water, highly flammable and nontoxic (simple asphyxiant). Several other characteristics of hydrogen are shown in [Table 1.1](#).

It is the main source of energy in the universe and constitutes 75% of the known matter. Hydrogen is an extremely versatile chemical element. Although on Earth it is present almost exclusively in combined form, it can be produced from any primary source by extracting it from water or other substances that contain it. [Table 1.2](#) shows the main hydrogen production options.

The main current processes for hydrogen production are by far based on reactions between fossil fuels and water: SMR and coal gasification. Neglecting the oxygen required for heat production, the reactions involved are respectively:



and



Table 1.1 Hydrogen main characteristics.

Critical temperature	33.25K
Critical pressure	13.2 bar
Density (@15°C, 1 atm)	0.0892 kg m ⁻³
Fusion point	14K
Boiling point	20.3K
Molar volume	11.42 · 10 ⁻³ m ³ mol ⁻¹
Gas constant	4.12 kJ kg ⁻¹ K ⁻¹
Specific heat at $p = \text{const}$	14.89 kJ kg ⁻¹ K ⁻¹
Speed of sound	1270 m s ⁻¹ at 298.15K
Lower heating value	119.93 MJ kg ⁻¹
Higher heating value	141.86 MJ kg ⁻¹
Energy density (gas, @15°C, 1 atm)	10.7 MJ Nm ⁻³
Energy density (liquid)	8491 MJ Nm ⁻³
CAS number	1333-74-0
Colour of the cylinder ogive	Red

Table 1.2 Main hydrogen production options.

Process	Energy source	Hydrogen donor
Coal gasification	Coal	Water/coal
Hydrocarbons partial oxidation	Hydrocarbons	Water/hydrocarbons
Hydrocarbons reforming		
Kvaerner process	Fossil/nuclear/renewable	Methane
Electrolysis		
Thermolysis	Nuclear/renewable	Water
Photoelectrolysis	Sun	
Photosynthesis		
Biomass gasification		Water/biomass
Biomass anaerobic digestion		
Reaction water/hydride	Chemical hydride	Water/hydride

plus the water gas shift reaction:



which regulates the chemical balance between carbon oxides.

The methane steam reforming process has the advantage to produce a syngas with a high hydrogen concentration since methane is characterised by the highest hydrogen to carbon ratio among the hydrocarbons. Moreover, the process is based on not expensive catalysts based on nickel. Heat is required both for steam production and for the advancement of reaction (1.1), which is endothermic. Heat recovery from syngas cooling allows to reduce the need for external combustion of methane, which is the usual heat source. A complete methane conversion can be obtained at about 900°C. If hydrogen is separated during the process, for example using a membrane, a lower temperature for a complete methane conversion is required and concentrated solar heat could replace the methane combustion reducing the carbon footprint of the process. A high pressure is unfavourable to the reaction advancement because of increasing mole number. However, pressures up to 30 bar are adopted both for reducing the reactor's volume and for reducing the power required for compression when compressed hydrogen is required.

Unless hydrogen is separated during the process, purification is required. Reaction (1.3) is favourable to hydrogen production when the temperature is low. Therefore a two-step water gas shift reaction is usually performed: a high-temperature reactor operates at about 400°C, allowing a good kinetics, whereas a low-temperature reactor works at about 200°C to reach a better chemical equilibrium. Finally, steam is condensed and carbon dioxide is separated, as well as residual carbon monoxide and other impurities.

Hydrogen can be produced also from heavier hydrocarbons by means of partial oxidation or autothermal reforming, both followed by water gas shift reaction.

Coal can be used to produce hydrogen by gasification. Ideally, the process would require only steam, but also reaction (1.2) is endothermic and oxygen is supplied to generate the required heat by internal combustion of coal. Different kinds of gasifiers (fixed bed, fluidised bed, and entrained bed), operating at different temperature and pressure, have been conceived. The product of coal gasification is a syngas mainly composed by hydrogen and carbon monoxide, and shift reactors to convert the latter into hydrogen are used, followed by final purification.

The last process based on fossil fuels is the Kvaerner process, which consists in methane dissociation using an electric arc:



Its main advantage is the complete removing of carbon oxide productions and emissions. The main drawback is the very low thermal efficiency because the energy content of carbon is lost. It is a process which can find application when carbon black has a market for not energy applications.

Hydrogen production from RES covers only a minimal share of the current hydrogen production.

Biomass gasification is in principle similar to coal gasification. There are three main differences:

- Biomass has a lower carbon content and, therefore, a lower heating value.
- Biomass is more reactive and, therefore, lower temperature is required.
- Biomass has to be collected from quite large land extension and, therefore, plant size is smaller.

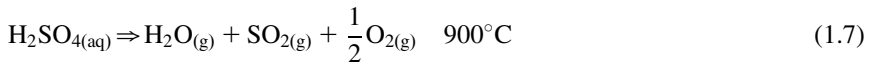
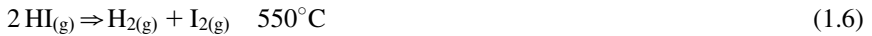
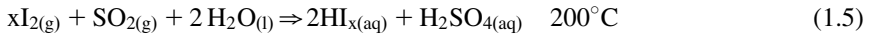
Whereas gasification is suitable for lignocellulosic biomass, anaerobic digestion can be used for the other types of biomass. In general, the final product is a biogas mainly composed by methane and carbon dioxide; however, it is possible to block the activity of methanogenic bacteria, in such a way to obtain a mix of hydrogen and carbon dioxide.

Remaining in the field of bioprocesses, photosynthetic hydrogen production is another option. Hydrogen is spontaneously produced by some microorganisms as a parasitic process to consume the energy surplus generated by an overexposure to sunlight. Responsible for the process are two different enzymes: hydrogenase and nitrogenase. The process can be aerobic (water dissociation) or anaerobic (organic substances dissociation) depending on the microorganism. Current efficiencies are very low, but genetic engineering could give good results in the future.

Another process based on sunlight is photoelectrolysis, in which both photochemical and electrochemical reactions are combined to dissociate water.

Water thermolysis could be a very interesting process, with good promising efficiency. Direct water thermolysis is not practicable due to very high temperature required. However, in the last 60 years, more than one hundreds of different thermochemical cycles involving from 2 to 5 reactions were developed. They consist in water dissociation using other substances which are recycled along the process. In general, the more reactions are used, the lower is the maximum temperature required. Some of the proposed cycles are 'hybrid' because they contain also one electrochemical reaction. Currently, only less than 10 of the proposed cycles are still under study since the others were not enough efficient or showed some drawbacks.

Just to make an example, S–I cycle carries out the water dissociation with three reactions:



A hydrogen production technology which is often listed among hydrogen storage system is the reaction between water and the so-called chemical hydrides. Actually, these are not technologies for hydrogen storage because for some cases hydrogen is totally supplied by water. They could be considered energy storage technologies since energy is required to produce these hydrides, possibly recycling the waste material generated.

Simple chemical hydrides are composed by hydrogen and one alkaline (e.g. sodium) or alkaline earth metal (e.g. calcium) and react spontaneously with water generating hydrogen and a metal hydroxide or oxide. For example:



Complex chemical hydrides contain also another element (e.g. boron) and require a catalyst to react with water generating hydrogen and an oxide. For example:



Also reaction between water and some metals (e.g. aluminium) can generate hydrogen.

All these technologies for hydrogen production have one or more of the following drawbacks:

- have a high carbon footprint;
- are still at laboratory level;
- are still too expensive to compete in the market; and
- generate a waste material.

Another technology to produce ‘green hydrogen’ is electrolysis, as long as energy from RES is used. In the past, electrolysis was used for the production of extremely pure hydrogen because of the high cost of electricity, but the need for energy storage from RES will change the scenario. Electrolysis will be extensively covered in the next two chapters because it is the basis for power to fuels, whereas the technologies briefly listed above can be explored for example in [Sørensen and Spazzafumo \(2018; section 2.1\)](#).

Hydrogen can also be easily converted into heat or electricity. In this second case, it is possible to use traditional internal combustion engines ([Yip et al., 2019](#)) and gas turbines ([ENEL, 2009](#)) but also fuel cells ([Grove, 1838](#)). Furthermore, it is possible, having pure oxygen available, to directly generate steam ([Sternfeld and Heinrich, 1989](#)) to use it as such or for high-performance thermodynamic cycles ([Sørensen and Spazzafumo, 2018; section 2.5.4](#)).

Hydrogen is therefore the key to significantly increase the exploitation of RES well beyond the absorption capacity of the electricity grid.

The bottleneck lies in the storage and distribution of hydrogen. Actually, hydrogen has the highest energy density per unit of mass but the lowest energy density per unit of volume (Table 1.3). This means that the storage as a gas, still the most used, is particularly bulky even when compressed at 70 MPa. The main alternatives are liquefied hydrogen, metal hydrides, organic liquids, carbon nanostructures, metal organic framework and chemical hydrides. Unfortunately, they are either not yet mature or have some disadvantages that limit their use.

Distribution is also problematic: although there are recently installed natural gas pipelines ready to accept 100% hydrogen (e.g. H21, 2018), many existing traditional natural gas pipelines are not suitable for the transport of hydrogen and however there is the need to replace pumping stations.

A first simple idea to use hydrogen avoiding storage and distribution problems is to mix it with natural gas. Several papers connected to the EU project NaturalHy are downloadable from the project website (NaturalHy, 2010). The end user could burn the mix of natural gas and hydrogen or could separate hydrogen for a specific application (e.g. low-temperature fuel cells). When burning the mix, it is necessary to take into account that

Table 1.3 Energy density of different fuels.

Fuel	LHV (MJ m ⁻³)	Status ^a	HHV (MJ kg ⁻¹)	LHV (MJ kg ⁻¹)
Hydrogen	10.78	Gas	141.86	119.93
	8491	Liquid		
Methane	32.56	Gas	55.53	50.02
	20,920	Liquid		
Propane	86.67	Gas	50.36	45.60
	23,489	Liquid		
Gasoline	31,150	Liquid	47.50	44.50
Diesel fuel	31,436	Liquid	44.80	42.50
Methanol	15,800	Liquid	22.88	19.96
Dimethyl ether	59.3	Gas	31.68	28.70
	19,230	Liquid		
Ammonia	14.34	Gas	22.50	18.65
	12,700	Liquid		
Urea	12,103	Solid	10.40	9.10
Formic acid	5606.18	Liquid	5.53	4.59

HHV, Higher heating value; LHV, lower heating value; STP, standard temperature and pressure.

^aFor volumetric energy density, gas density is considered at STP conditions, liquid density at boiling point temperature and ambient pressure.

some properties change depending on hydrogen content. Recently, SNAM, a leading Italian energy infrastructure operator, tested the distribution of natural gas added with 5% and 10% of hydrogen to a pasta factory and both distribution and utilisation were successful (SNAM, 2020a). Together with Baker Hughes, SNAM also tested a gas turbine fuelled by natural gas blended with 10% of hydrogen (SNAM, 2020b).

But hydrogen is not just a fuel, so much so that its almost exclusive use has always been linked to the chemical industry. Here, then, that its use to produce synthetic fuels can be decisive in accelerating the transition towards a system based mainly on electricity and hydrogen. In fact, among the synthetic fuels that can be produced, there are some that lend themselves very well to replace traditional liquid and gaseous fossil fuels, with the advantage of not requiring substantial changes to the existing distribution system.

In this way, it will be possible to increase the level of replacement of fossil fuels with carbon-neutral fuels and this will require an investment concentrated above all on a greater exploitation of renewable sources and on a greater production of hydrogen, leaving the investment in the pure hydrogen distribution infrastructure at a later date with also a view to hydrogen storage and distribution systems technically better and hopefully less expensive than the current ones.

1.3 Main synthetic fuels

The most interesting synthetic fuels which can be produced starting from hydrogen and a carbon source are methane, methanol, dimethyl ether (DME), urea and formic acid. In addition, also ammonia, which does not contain carbon, can be considered, since it can be produced starting from electrolytic hydrogen and a source of nitrogen. Next sections of this chapter report a brief summary of their characteristics.

The main potential carbon sources are fossil fuels, biomass and carbon dioxide. Obviously, 'green carbon' can be obtained only from biomass or directly captured from the air. Taking into consideration the low CO₂ concentration into the atmosphere, a very large volume of air should be treated to obtain even a single cubic metre of CO₂. However, researchers are working on carbon dioxide capture from air and new technologies are continuously developed (e.g. Monash University, 2020).

During the transition to a carbon-free energy system, we will continue to use fossil fuels, albeit in smaller and smaller quantities. So, there will be availability of carbon dioxide in great concentration at the smokestack of power plants and industrial plants that will make use of fossil fuels. This could be the main short- and medium-term carbon source. Oil industries are also working in this direction (e.g. Repsol, 2020). Obviously, a separation and purification process will be necessary.

The most used technology for carbon dioxide capture is chemical absorption with amines, either monoethanolamine or diethanolamine. Amines are liquid sorbents capable to separate carbon dioxide from a gas stream and regenerable by heating, generally using steam available inside the plant or generated by heat recovery. Other capture technologies are based on solid materials capable to adsorb carbon dioxide on their surface and releasing it by pressure or temperature changes. Also

porous or semiporous membranes can be used and the driving force is the difference in pressure between the two sides of the membrane.

As already stated, biomass also can be a source of carbon. When biomass is burned or converted into a syngas or biofuel which is burned in a stationary plant, carbon dioxide can be captured with the same technologies mentioned above. An interesting alternative is the direct treatment with hydrogen of biomass (hydrogasification) or biogas (methanation). These processes will be treated in a subsequent chapter.

Finally, it is interesting to consider the by-product of electrolysis: oxygen. Often electrolytic oxygen is released into the atmosphere if there is no possibility to sell. The use of oxygen for oxycombustion of fossil fuels, biomass or biofuels allows to obtain exhaust gases with a higher carbon dioxide concentration and consequent easier capture process.

1.3.1 Methane

Methane is the lightest hydrocarbon composed by a carbon and four hydrogen atoms located at the top of a regular tetrahedron, in the centre of which there is the carbon atom. It was discovered and isolated by the Italian scientist Alessandro Volta in the second half of the 18th century.

At room temperature and standard pressure, methane is a colourless and odourless gas. It is nontoxic, but it is an asphyxiant since its presence in the air reduces the oxygen concentration. It is extremely flammable and may form explosive mixtures with air in volume concentration between 5% and 15%.

It is by far the main constituent of natural gas, representing 85%–90% by volume, and pure methane can be used for all applications in place of natural gas, including direct use in high-temperature fuel cells. Moreover, large methane reservoirs in the form of clathrates ($4 \text{ CH}_4 \cdot 23 \text{ H}_2\text{O}$) are located on the ocean floor and in the arctic permafrost. These clathrates are not only a significant amount of fuel but also a potential risk for global warming since the global warming potential of methane is 28–36 times and 84–87 times that of carbon dioxide over a period of 100 and 20 years, respectively (Environmental Protection Agency, 2020; IPCC, 2013; section 8.7).

Most of the world's methane emissions are anthropogenic and derive mainly from waste landfills, coal mines, oil industry, agriculture and livestock, and for this reason, its concentration in the atmosphere has more than doubled in the last 250 years, from the preindustrial level of 722 ± 25 to 1803 ± 2 ppb in the year 2011 (IPCC, 2013; section 2.2).

Methane can also be produced starting from biomass and from the humid fraction of waste materials, and in this case, it is called bio-methane. The common process is anaerobic digestion that allows to obtain a raw gas which main components are methane and carbon dioxide. A subsequent purification step proceeds to remove carbon dioxide. In addition to being a renewable fuel, bio-methane contributes to reducing the emissions of climate-changing gases that would be emitted into the atmosphere due to the natural activity of microorganisms on the biomass left outdoors and on the wet waste sent to landfills.

Methane can also be obtained from methanation of carbon oxides with hydrogen (see Chapter 4: Power to Methane):



and this is a renewable fuel when hydrogen is produced from a RES and carbon comes from biomass or from captured CO_2 .

Reactions (1.10) and (1.11) are exothermic reactions favoured at low temperature. The reverse reactions, endothermic and occurring at high temperature, constitute the SMR process and together with the water shift reaction (1.3) allow to generate hydrogen from methane. Therefore methane can be considered also a hydrogen carrier.

1.3.2 Methanol

Methanol is the simplest alcohol and is composed by a methyl group and a hydroxyl group ($\text{CH}_3\text{-OH}$). It is a volatile, colourless, flammable liquid (flammability limits 6.7%–36%), toxic with an odour similar to that of ethanol. Methanol is miscible with water and biodegradable; therefore unlike gasoline, it cannot accumulate in water, air or soil. It is used also as a polar solvent.

Methanol is industrially produced by hydrogenation of carbon monoxide:



usually starting from a syngas obtained from partial oxidation of fossil fuels. A similar process can be accomplished also using lignocellulosic biomass as a feedstock and the final product is renewable and called bio-methanol. Obviously, the hydrogen required could come also from electrolysis using power from RES: this option will be discussed in Chapter 5, Power to Methanol.

Methanol can be also burned or used directly in low-temperature fuel cells (direct methanol fuel cells).

Hydrogen can be obtained from methanol steam reforming:



therefore, combining reaction (1.12) and (1.13), it can be also considered as a hydrogen carrier. The main advantage of synthetic methanol versus hydrogen and methane as a hydrogen carrier lies in its liquid form at ambient conditions, which makes it easier to store and transport, as it already happens with oil derivatives.

1.3.3 Dimethyl ether

DME is the simplest ether (CH_3OCH_3) and is a colourless, not toxic and highly flammable gas in the range 3.4%–27% by volume when mixed with air

(Mitsubishi Gas Chemical, 2020). It can be produced by dehydration of methanol:



but also from syngas or biogas (see Chapter 6: Power-to-DME: A Cornerstone Towards a Sustainable Energy System).

DME is interesting as an alternative fuel for diesel engines since it requires minor modifications of a diesel engine, is sulphur free and has a cetane number of 55, higher than that of oil-derived diesel fuel.

Also, DME direct fuel cells have been developed and tested. And also hydrogen can be produced from DME, so that also DME can be considered a hydrogen carrier.

1.3.4 Ammonia

Ammonia is the simplest nitrogen hydride, composed by a nitrogen atom and three hydrogen atoms (NH_3). It is a colourless gas, lighter than air, with a characteristic pungent smell. It was first isolated by the Scottish chemist Joseph Black. Its boiling point is -33.3°C , whereas freezing point is -77.7°C . Ammonia can act both as a base, forming salts containing ammonium ion (NH_4^+), and as an acid, forming compounds containing amide ion (NH_2^-). The ammonia molecule is polar and highly miscible with water.

The Haber–Bosch process, developed by Fritz Haber and Carl Bosch in the first decade of the 20th century, is the main process for ammonia production. Hydrogen and nitrogen react at high temperature (300°C – 550°C) under high pressure (15–30 MPa). A mixture of iron, potassium oxide and aluminium oxide is used as a catalyst. Ammonia produced is then liquefied at -33.3°C and separated from the residual gaseous mixture of hydrogen and nitrogen. The hydrogen used for the current industrial process is produced starting from fossil fuels, but it would be possible to use hydrogen generated starting from RES (see Chapter 7: Power to Ammonia and Urea) obtaining ‘green ammonia’ (Fúnez Guerra et al., 2020).

Although it is caustic and hazardous in its concentrated form, ammonia is widely used. It is a common nitrogenous waste, particularly among aquatic organisms, and it contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to food and fertilizers. Ammonia is also used for the synthesis of many pharmaceutical products and for many commercial cleaning products.

Ammonia is a fuel, although burns with difficulty in air and only when mixed at a concentration of 15%–27%:



However, it could also be used as a fuel in direct ammonia fuel cells.

Finally, ammonia decomposes in hydrogen and nitrogen when heated at high temperature (850°C – 950°C) in the presence of a suitable catalyst (e.g. nickel). Therefore ammonia can be considered also a hydrogen carrier.

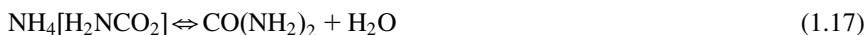
1.3.5 Urea

Urea was characterised in the 18th century by the Dutch chemist Herman Boerhaave and is an amide with formula $\text{CO}(\text{NH}_2)_2$, that is composed by two $-\text{NH}_2$ groups and a carbonyl functional group $\text{CO} =$. It is a colourless, odourless solid, highly soluble in water, and can irritate skin, eyes, and the respiratory tract.

The German chemist Friedrich Wöhler produced urea artificially in 1828, but the industrial process (Bosch–Meiser) was developed only one century later, in 1922. This process is based on the reaction between ammonia and carbon dioxide:



The ammonium carbamate is then decomposed in urea and water by supplying heat:



It is widely used in fertilizers because has a nitrogen content higher than that of other solid fertilizers and because many bacteria can produce ammonia from urea.

Urea can be used as a hydrogen carrier: electrolysis of urea aqueous solutions requires a voltage of 0.37 V (Boggs, King, and Botte, 2009) that is much lower than the voltage required for water electrolysis. Moreover, urea (and urine) can be directly used in alkaline fuel cells to produce electric power (Lan, Tao, and Irvine, 2010).

1.3.6 Formic acid

Formic (or methanoic) acid is the simplest carboxylic acid (HCOOH) and at room temperature is a colourless liquid having a penetrating odour, with flammability limits 12%–38%. It is slightly toxic, but it is urticant: in nature, it is found in some plants (e.g. nettle) and animals (especially ants), and actually its name comes from ‘formica’, the Latin word for ant. It was first isolated by the English naturalist John Ray and was first synthesised by the French chemist Joseph Gay-Lussac.

It is miscible in water, methanol, glycerol and ethyl acetate. It is a strong reducing agent.

Formic acid can be obtained from several chemical processes, for example by hydrolysis of methyl formate in presence of a large water excess:



in a two-step process which produces the methyl formate from methanol and carbon monoxide:



resulting in the global reaction:



Power to formic acid will be discussed in detail in Chapter 8, Power to Formic Acid.

Thermal decomposition of formic acid can produce carbon monoxide and water which can be converted in carbon dioxide and hydrogen (water gas shift reaction):



Direct decomposition to hydrogen and carbon dioxide can be also obtained in presence of catalysts like platinum and ruthenium. Therefore also formic acid can be considered a hydrogen carrier. The hydrogen content of formic acid is 53 g L^{-1} at room temperature and atmospheric pressure.

Also, formic acid fuel cells have been developed and tested.

Nomenclature

DME	dimethyl ether
HHV	higher heating value
LHV	lower heating value
RES	renewable energy source
SMR	steam methane reforming
STP	standard temperature and pressure

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