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## Hydrogen Production Processes

Hydrogen can be produced using a number of different processes. Thermochemical processes use heat and chemical reactions to release hydrogen from organic materials such as fossil fuels and biomass. Water ( $H_2O$ ) can be split into hydrogen ( $H_2$ ) and oxygen ( $O_2$ ) using electrolysis or solar energy. Microorganisms such as bacteria and algae can produce hydrogen through biological processes.

**Thermochemical Processes** Some thermal processes use the energy in various resources, such as natural gas, coal, or biomass, to release hydrogen from their molecular structure. In other processes, heat, in combination with closed-chemical cycles, produces hydrogen from feedstocks such as water. Learn more about the following thermochemical processes:

- [Natural gas reforming](#) (also called steam methane reforming or SMR)
- [Coal gasification](#)
- [Biomass gasification](#)
- [Biomass-derived liquid reforming](#)
- [Solar thermochemical hydrogen \(STCH\)](#).

**Electrolytic Processes** Electrolyzers use electricity to split water into hydrogen and oxygen. This technology is well developed and available commercially, and systems that can efficiently use intermittent renewable power are being developed. Learn more about [electrolysis](#).

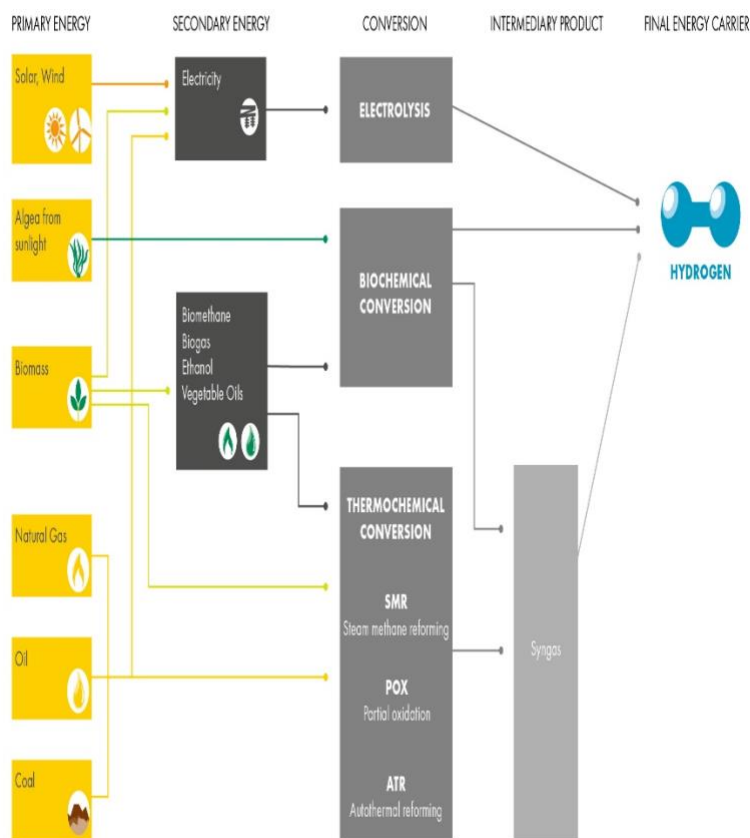
**Direct Solar Water Splitting Processes** Direct solar water splitting, or photolytic, processes use light energy to split water into hydrogen and oxygen. These processes are currently in the very early stages of research but offer long-term potential for sustainable hydrogen production with low environmental impact. Learn more about the following solar water splitting processes:

- [Photoelectrochemical \(PEC\)](#)
- [Photobiological](#).

**Biological Processes** Microbes such as bacteria and microalgae can produce hydrogen through biological reactions, using sunlight or organic matter. These technology pathways are at an early stage of research, but in the long term have the potential for sustainable, low-carbon hydrogen production. Learn more about the following biological processes:

- [Microbial biomass conversion](#)
- [Photobiological.](#)

### Hydrogen Production



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Hydrogen might be the most abundant element on earth but it can be found rarely in its pure form. Practically, this fact means that in order to produce hydrogen, it needs to be extracted from its compound.

Of course, this extraction process needs energy but hydrogen can be produced or extracted using virtually any primary source of energy, be it fossil or renewable. Characteristically, hydrogen can be produced using diverse resources including fossil fuels, such as natural gas and coal, biomass, non-food crops, nuclear energy and renewable energy sources, such as wind, solar, geothermal, and hydroelectric power to split water. This diversity of potential supply sources is THE most important reason why hydrogen is such a promising energy carrier.

Although most of the world's hydrogen production today is being produced through a more CO<sub>2</sub> intensive process called Steam Methane Reforming (SMR), hydrogen can also be produced through a process that makes use of renewable electricity, leading to the production of "green" or CO<sub>2</sub> neutral hydrogen.

### Steam Methane Reforming:

Method: Reforming - most notably Reforming of natural gas but also biogas  
In short: The primary ways in which natural gas, mostly methane, is converted to hydrogen involve reaction with either steam (steam reforming or steam methane reforming SMR when methane is used), oxygen (partial oxidation), or both in sequence (autothermal reforming)

In practice: Steam reforming: Pure water vapour is used as the oxidant. The reaction requires the introduction of heat ("endothermic").

- Partial oxidation: Oxygen or air is used in this method. The process releases heat ("exothermic").
- Autothermal reforming: This process is a combination of steam reforming and partial oxidation and operates with a mixture of air and water vapour. The ratio of the two oxidants is adjusted so that no heat needs to be introduced or discharged ("isothermal").

## Hydrogen as a By-Product or Industrial Residual Hydrogen

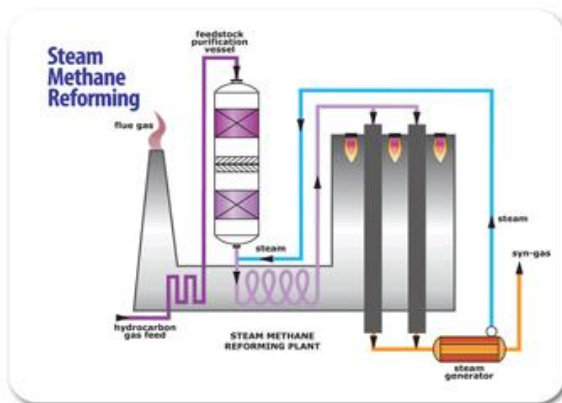
**Method:** Hydrogen from other industrial processes that create hydrogen as a by-product

**In Short:** Electrochemical processes, such as the industrial production of caustic soda and chlorine produce hydrogen as a waste product.

**In Practice:** Producing chlorine and caustic soda comes down to passing an electric current through brine (a solution of salt – sodium chloride – in water). The brine dissociates and recombines through exchange of electrons (delivered by the current) into gaseous chlorine, dissolved caustic soda<sup>1</sup> and hydrogen. By the nature of the chemical reaction, chlorine, caustic soda and hydrogen are always manufactured in a fixed ratio: 1.1 tonne of caustic and 0.03 tonne of hydrogen per tonne of chlorine.

## Reforming

Steam methane reforming (SMR):



As already described above, currently, most of the hydrogen produced today, is being produced through the CO<sub>2</sub> intensive process called Steam Methane Reforming.

High-temperature steam (700°C–1,000°C) is used to produce hydrogen from a methane source, such as natural gas. In steam-methane reforming, methane reacts with steam under 3–25 bar pressure (1 bar = 14.5 psi) in the presence of a catalyst to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. Steam reforming is **endothermic**—that is, heat must be supplied to the process for the reaction to proceed.

Subsequently, in what is called the "water-gas shift reaction," the carbon monoxide and steam are reacted using a catalyst to produce carbon dioxide and more hydrogen. In a final process step called "pressure-swing adsorption," carbon dioxide



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and other impurities are removed from the gas stream, leaving essentially pure hydrogen. Steam reforming can also be used to produce hydrogen from other fuels, such as ethanol, propane, or even gasoline.

*For chemists:*

Steam-methane reforming reaction  
 $\text{CH}_4 + \text{H}_2\text{O} (+ \text{heat}) \rightarrow \text{CO} + 3\text{H}_2$

Water-gas shift reaction  
 $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 (+ \text{small amount of heat})$

### Partial Oxidation

In partial oxidation, the methane and other hydrocarbons in natural gas react with a limited amount of oxygen (typically from air) that is not enough to completely oxidize the hydrocarbons to carbon dioxide and water. With less than the stoichiometric amount of oxygen available, the reaction products contain primarily hydrogen and carbon monoxide (and nitrogen, if the reaction is carried out with air rather than pure oxygen), and a relatively small amount of carbon dioxide and other compounds. Subsequently, in a water-gas shift reaction, the carbon monoxide reacts with water to form carbon dioxide and more hydrogen.

Partial oxidation is an **exothermic** process—it gives off heat. The process is, typically, much faster than steam reforming and requires a smaller reactor vessel. As can be seen in chemical reactions of partial oxidation, this process initially produces less hydrogen per unit of the input fuel than is obtained by steam reforming of the same fuel.

*For chemists:*

Partial oxidation of methane reaction  
 $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 (+ \text{heat})$

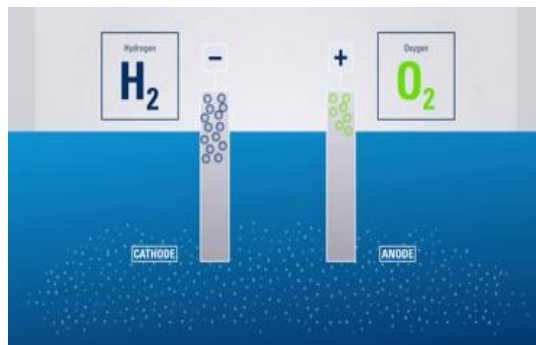
Water-gas shift reaction  
 $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 (+ \text{small amount of heat})$

### Steam methane reforming (SMR) for biogas

The process of SMR can also be utilized for the production of hydrogen from biogas.



## Electrolysis



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Despite the fact that hydrogen can be produced in numerous ways, the most interesting but also promising part is the production of hydrogen through electrolysis of water.

In this process, the electrolysis breaks down water into hydrogen and oxygen by using electricity. If the electricity used, springs from renewable energy sources like wind or solar and the hydrogen produced is used in a fuel cell, then the entire energy process would create no net emissions. In this case, we would be talking about “green hydrogen”.

The electrolyser consists of a DC source and two noble metal-coated electrodes, which are separated by an electrolyte. The electrolyte or ionic conductor can be a liquid, for example conductive caustic potash solution (potassium hydroxide, KOH) for alkaline electrolysis.

In an alkaline electrolyser the cathode (negative pole) loses electrons to the aqueous solution.

The water is dissociated, leading to the formation of hydrogen (H<sub>2</sub>) and hydroxide ions (OH<sup>-</sup>)

The charge carriers move in the electrolyte towards the anode. At the anode (positive pole) the electrons are absorbed by the negative OH<sup>-</sup> anions. The OH<sup>-</sup> anions are oxidised to form water and oxygen. Oxygen rises at the anode. A membrane prevents the product gases H<sub>2</sub> and O<sub>2</sub> from mixing but allows the passage of OH<sup>-</sup> ions. Electrolysers consist of individual cells and central system units (balance of plant). By combining electrolytic cells and stacks, hydrogen production can be adapted to individual needs.

Electrolysers are differentiated by the electrolyte materials and the temperature at which they are operated: low-temperature electrolysis (LTE), including **alkaline electrolysis (AE)**, **proton exchange membrane (PEM)** electrolysis and **anion exchange membrane (AEM)** electrolysis (also known as alkaline PEM), and high-temperature electrolysis (HTE). The latter group most notably includes **solid oxide electrolysis (SOE)**, but this is still at an advanced R&D stage and products are not yet commercially available. Once it reaches market maturity, its advantages are expected to include increased conversion efficiency and the possibility of producing



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a synthesis gas directly from steam and CO<sub>2</sub>, for use in various applications such as synthetic liquid fuels (E4tech 2014, IEA 2015b).

High temperature electrolysis is particularly interesting when there is a source of heat next to the electrolyser (as it is often the case in industrial plants or ) is more efficient economically than traditional room-temperature electrolysis. Indeed, some of the energy is supplied as heat, which is either free or cheaper than electricity, and also because the electrolysis reaction is more efficient at higher temperatures. The choice of a given electrolysis technology depends on the use needs and the local context.

Hydrogen is like electricity in the sense that its use does not generate any emission. Its carbon footprint is related to its production mode. In the case of hydrogen produced by electrolysis, its carbon footprint of hydrogen is directly related with the source of electricity. Hydrogen produced from carbon free renewable or nuclear electricity is therefore carbon free. Hydrogen produced with the grid mix has the same carbon intensity as the grid mix.

### Hydrogen as a by-product

As explained above hydrogen is produced by separating from its compound. `<a name="byproduct"></a>`

If the production of hydrogen can be the first objective of the separation process, it can also be that the separation process aims first at producing another molecule and produces hydrogen as a by-product.

Producing chlorine and caustic soda comes down to passing an electric current through brine (a solution of salt – sodium chloride – in water). The brine dissociates and recombines through exchange of electrons (delivered by the current) into gaseous chlorine, dissolved caustic soda and hydrogen. By the nature of the chemical reaction, chlorine, caustic soda and hydrogen are always manufactured in a fixed ratio: 1.1 ton of caustic and 0.03 ton of hydrogen per ton of chlorine. A number of studies have sought to quantify the amount of industrial residual hydrogen available. The EU project “Roads 2 HyCom” (Maisonnier et al. 2007) produced among other results a map showing hydrogen production sites in Europe. In this map the hydrogen sources were broken down into three categories: the “merchant” category supplies hydrogen to other industrial customers, while the “captive” category retains hydrogen on site for its own use. Only “by-product”



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hydrogen has no further use within the process or on site; only this category can be made available for other applications, such as fuel cell electric vehicles.

Hydrogen as a by-product is an interesting and cheap source of hydrogen to initiate the deployment of hydrogen applications in the area where it is produced. Not surprisingly regions with high quantities of hydrogen as a byproduct are among the most advanced in their hydrogen deployment strategy.