Hydrogen production

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Hydrogen production is the family of industrial methods for generating hydrogen. Currently the dominant technology for direct production is steam reforming from hydrocarbons. Many other methods are known including electrolysis and thermolysis.

In 2006, the United States was estimated to have a production capacity of 11 million tons of hydrogen. 5 million tons of hydrogen were consumed on-site in oil refining, and in the production of ammonia (Haber process) and methanol (reduction of carbon monoxide). 0.4 million tons were an incidental by-product of the chlor-alkali process.[1] Hydrogen production is an estimated $100 billion industry.[2]

Currently, the majority of hydrogen (~95%) is produced from fossil fuels by steam reforming or partial oxidation of methane and coal gasification with only a small quantity by other routes such as biomass gasification or electrolysis of water.[3]

Contents [hide]

Steam reforming [edit]

Main article: Steam reforming

Fossil fuels are the dominant source of industrial hydrogen.[4] Hydrogen can be generated from natural gas with approximately 80% efficiency,[citation needed] or from other hydrocarbons to a varying degree of efficiency. Specifically, bulk hydrogen is usually produced by the steam reforming of methane or natural gas.[5] At high temperatures (700–1100 °C), steam (H_2O) reacts with methane (CH_4) in an endothermic reaction to yield syngas.[6]

$$CH_4 + H_2O \rightarrow CO + 3\,H_2$$

Gasification

In a second stage, additional hydrogen is generated through the lower-temperature, exothermic, water gas shift reaction, performed at about 360 °C:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Essentially, the oxygen (O) atom is stripped from the additional water (steam) to oxidize CO to CO_2. This oxidation also provides energy to maintain the reaction. Additional heat required to drive the process is generally supplied by burning some portion of the methane.

CO_2 sequestration [edit]

Steam reforming generates carbon dioxide (CO_2). Since the production is concentrated in one facility, it is possible to separate the CO_2 and dispose of it without atmospheric release, for example by injecting it in an oil or gas reservoir (see carbon capture), although this is not currently done in most cases. A carbon dioxide injection project has been started by a Norwegian company StatoilHydro in the North Sea, at the Sleipner field.

Integrated steam reforming / co-generation - It is possible to combine steam reforming and co-generation of steam and power into a single plant. This can deliver benefits for an oil refinery because it is more efficient than separate hydrogen, steam and power plants. Air Products recently built an integrated steam reforming / co-generation plant in Port Arthur, Texas.[7]

Other production methods from fossil fuels [edit]

Partial oxidation [edit]

The partial oxidation reaction occurs when a substoichiometric fuel-air mixture is partially combusted in a reformer, creating a hydrogen-rich syngas. A distinction is made between *thermal partial oxidation* (TPOX) and *catalytic partial oxidation* (CPOX). The chemical reaction takes the general form:

$$C_nH_m + {}^{n}/_{2}\, O_2 \rightarrow n\, CO + {}^{m}/_{2}\, H_2$$

Idealized examples for heating oil and coal, assuming compositions $C_{12}H_{24}$ and $C_{24}H_{12}$ respectively, are as follows:

$$C_{12}H_{24} + 6\, O_2 \rightarrow 12\, CO + 12\, H_2$$
$$C_{24}H_{12} + 12\, O_2 \rightarrow 24\, CO + 6\, H_2$$

Plasma reforming [edit]

The Kværner-process or Kvaerner carbon black & hydrogen process (CB&H)[8] is a plasma reforming method, developed in the 1980s by a Norwegian company of the same name, for the production of hydrogen and carbon black from liquid hydrocarbons (C_nH_m). Of the available energy of the feed, approximately 48% is contained in the hydrogen, 40% is contained in activated carbon and 10% in superheated steam.[9] CO_2 is not produced in the process.

A variation of this process is presented in 2009 using plasma arc waste disposal technology for the production of hydrogen, heat and carbon from methane and natural gas in a plasma converter[10]

Coal [edit]

Coal can be converted into syngas and methane, also known as town gas, via coal gasification. Syngas consists of hydrogen and carbon monoxide.[11] Another method for conversion is low temperature and high temperature coal carbonization.[12]

Petroleum coke [edit]

Similarly to coal, petroleum coke can also be converted in hydrogen rich syngas, via coal gasification. The syngas in this case consists mainly of hydrogen, carbon monoxide and H2S, depending on the sulfur content of the coke feed. Gasification is an attractive option for producing hydrogen from almost any carbon source, while providing attractive hydrogen utilization alternatives through process integration. [13]

From water [edit]

Main article: Water splitting

Many technologies have been explored but it should be noted that as of 2007 "Thermal, thermochemical, biochemical and photochemical processes have so far not found industrial applications."[4] High temperature electrolysis of alkaline solutions has been used for the industrial scale production of hydrogen (see Sable Chemicals) and there are now a number of small scale polymer electrolyte membrane (PEM) electrolysis units available commercially.[14][15][16]

Electrolysis [edit]

There are three main types of cells, solid oxide electrolysis cells (SOECs), polymer electrolyte membrane cells (PEM) and alkaline electrolysis cells (AECs).[17] SOECs operate at high temperatures, typically around 800 °C. At these high temperatures a significant amount of the energy required can be provided as thermal energy (heat), and as such is termed High temperature electrolysis. The heat energy can be provided from a number of different sources, including waste industrial heat, nuclear power stations or concentrated solar thermal plants. This has the potential to reduce the overall cost of the hydrogen produced by reducing the amount of electrical energy required for electrolysis.[3][18][19][20] PEM electrolysis cells typically operate below 100 °C and are becoming increasingly available commercially.[3] These cells have the advantage of being comparatively simple and can be designed to accept widely varying voltage inputs which makes them ideal for use with renewable sources of energy such as solar PV.[21] AECs optimally operate at high concentrations electrolyte (KOH or potassium carbonate) and at high temperatures, often near 200 °C.

Chemically assisted electrolysis [edit]

In addition to reducing the voltage required for electrolysis via the increasing of the temperature of the electrolysis cell it is also possible to electrochemically consume the oxygen produced in an electrolyser via introducing a fuel (such as carbon) oxygen side of the reactor. This reduces the required electrical energy and has the potential to reduce the cost of hydrogen produced in this manner.[22]

Radiolysis [edit]

Nuclear radiation routinely breaks water bonds, in the Mponeng gold mine, South Africa, researchers found in a naturally high radiation zone a community dominated by a new phylotype of *Desulfotomaculum*, feeding on primarily radiolytically produced H_2.[23] Spent nuclear fuel/"nuclear waste" is also being looked at as a potential source of hydrogen.

Thermolysis [edit]

Water spontaneously dissociates at around 2500 °C, but this thermolysis occurs at temperatures too high for usual process piping and equipment. Catalysts are required to reduce the dissociation temperature.

Thermochemical cycle [edit]

Main article: thermochemical cycle

Thermochemical cycles combine solely heat sources (*thermo*) with *chemical* reactions to split water into its hydrogen and oxygen components.[24] The term *cycle* is used because aside of water, hydrogen and oxygen, the chemical compounds used in these processes are continuously recycled. If electricity is partially used as an input, the resulting thermochemical cycle is defined as a hybrid one.

The sulfur-iodine cycle (S-I cycle) is a thermochemical cycle processes which generates hydrogen from water with an efficiency of approximately 50%. The sulfur and iodine used in the process are recovered and reused, and not consumed by the process. The cycle can be performed with any source of very high temperatures, approximately 950 °C, such as by Concentrating solar power systems (CSP) and is regarded as being well suited to the production of hydrogen by high-temperature nuclear reactors,[25] and as such, is being studied in the High Temperature Test Reactor in Japan.[26][27][28][29] There are other hybrid cycles that use both high temperatures and some electricity, such as the Copper–chlorine cycle, it is classified as a hybrid thermochemical cycle because it uses an electrochemical reaction in one of the reaction steps, it operates at 530 °C and has an efficiency of 43 percent.[30]

Ferrosilicon method [edit]

Ferrosilicon is used by the military to quickly produce hydrogen for balloons. The chemical reaction uses sodium hydroxide, ferrosilicon, and water. The generator is small enough to fit a truck and requires only a small amount of electric power, the materials are stable and not combustible, and they do not generate hydrogen until mixed.[31] The method has been in use since World War I. A heavy steel pressure vessel is filled with sodium hydroxide and ferrosilicon, closed, and a controlled amount of water is added; the dissolving of the hydroxide heats the mixture to about 200 °F and starts the reaction; sodium silicate, hydrogen and steam are produced.[32]

Photobiological water splitting [edit]

Main article: Biological hydrogen production (Algae)

An algae bioreactor for hydrogen production.

Biological hydrogen can be produced in an algae bioreactor.[33] In the late 1990s it was discovered that if the algae are deprived of sulfur it will switch from the production of oxygen, i.e. normal photosynthesis, to the production of hydrogen. It seems that the production is now economically feasible by surpassing the 7–10 percent energy efficiency (the conversion of sunlight into hydrogen) barrier.[34] with a hydrogen production rate of 10-12 ml per liter culture per hour.[35]

Photocatalytic water splitting [edit]

Main article: Photocatalytic water splitting

The conversion of solar energy to hydrogen by means of water splitting process is one of the most interesting ways to achieve clean and renewable energy systems. However if this process is assisted by photocatalysts suspended directly in water instead of using photovoltaic and an electrolytic system the reaction is in just one step, it can be made more efficient.[36][37]

Biohydrogen routes [edit]

Biomass and waste streams can in principle be converted into biohydrogen with biomass gasification, steam reforming, or biological conversion like biocatalysed electrolysis[22] or fermentative hydrogen production.[4]

Fermentative hydrogen production [edit]

Main articles: fermentative hydrogen production and dark fermentation

Fermentative hydrogen production is the fermentative conversion of organic substrate to biohydrogen manifested by a diverse group of bacteria using multi enzyme systems involving three steps similar to anaerobic conversion. Dark fermentation reactions do not require light energy, so they are capable of constantly producing hydrogen from organic compounds throughout the day and night. Photofermentation differs from dark fermentation because it only proceeds in the presence of light. For example photo-fermentation with Rhodobacter sphaeroides SH2C can be employed to convert small molecular fatty acids into hydrogen.[38]

Fermentative hydrogen production can be done using direct biophotolysis by green algae, indirect biophotolysis by cyanobacteria, photo-fermentation by anaerobic photosynthetic bacteria and dark fermentation by anaerobic fermentative bacteria. For example studies on hydrogen production using *H. salinarium*, an anaerobic photosynthetic bacteria, coupled to a hydrogenase donor like *E. coli*, are reported in literature.[39]

Biohydrogen can be produced in bioreactors that utilize feedstocks, the most common feedstock being waste streams. The process involves bacteria feeding on hydrocarbons and exhaling hydrogen and CO_2. The CO_2 can be sequestered successfully by several methods, leaving hydrogen gas. A prototype hydrogen bioreactor using waste as a feedstock is in operation at Welch's grape juice factory in North East, Pennsylvania (U.S.).[citation needed]

Enzymatic hydrogen generation [edit]

Due to the Thauer limit (four H_2/glucose) for dark fermentation, a non-natural enzymatic pathway was designed that can generate 12 moles of hydrogen per mole of glucose units of polysaccharides and water in 2007.[40] The stoichiometric reaction is:

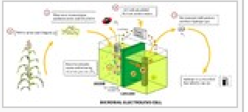
$$C_6H_{10}O_5 + 7\ H_2O \rightarrow 12\ H_2 + 6\ CO_2$$

The key technology is cell-free synthetic enzymatic pathway biotransformation (SyPaB).[41][42] A biochemist can understand it as "glucose oxidation by using water as oxidant". A chemist can describe it as "water splitting by energy in carbohydrate". A thermodynamics scientist can describe it as the first entropy-driving chemical reaction that can produce hydrogen by absorbing waste heat. In 2009, cellulosic materials were first used to generate high-yield hydrogen.[43] Furthermore, the use of carbohydrate as a high-density hydrogen carrier was proposed so to solve the largest obstacle to the hydrogen economy and propose the concept of sugar fuel cell vehicles.[44]

Synthetic biology[45][46][47]

Biocatalysed electrolysis [edit]

Main articles: electrohydrogenesis and microbial fuel cell



A microbial electrolysis cell

Besides dark fermentation, electrohydrogenesis (electrolysis using microbes) is another possibility. Using microbial fuel cells, wastewater or plants can be used to generate power. Biocatalysed electrolysis should not be confused with biological hydrogen production, as the latter only uses algae and with the latter, the algae itself generates the hydrogen instantly, where with biocatalysed electrolysis, this happens after running through the microbial fuel cell and a variety of aquatic plants[48] can be used. These include reed sweetgrass, cordgrass, rice, tomatoes, lupines and algae.[49]

Xylose [edit]

In 2014 a low-temperature 50 °C (122 °F), atmospheric-pressure enzyme-driven process to convert xylose into hydrogen with nearly 100% of the theoretical yield was announced. The process employs 13 enzymes, including a novel polyphosphatexylulokinase (XK).[50][51]

Carbon neutral hydrogen [edit]

Currently there are two practical ways of producing hydrogen in a renewable industrial process. One is to use power to gas where electric power is used to produce hydrogen from electrolysis and the other is landfill gas to produce hydrogen in a steam reformer. Hydrogen fuel, when produced by renewable sources of energy like wind or solar power, is a renewable fuel.[52]

In 2014, it was demonstrated that it is possible to synthesize synthetic fuel that is also a carbon-neutral fuel from elemental carbon and hydrogen, with both the carbon and hydrogen being derived from seawater, which contains a much more economical source of Carbon dioxide than the air.[53][54] With researchers estimating that carbon extraction from seawater would cost about $50 per ton.[55] The U.S. Navy estimates that their typical naval nuclear reactor generating 100 megawatts of electricity could, in theory, produce 41,000 US gallons of jet fuel per day and shipboard production from nuclear power would cost about $6 per gallon. While that was about twice the petroleum fuel cost in 2010, it is expected to be much less than the market price in less than five years if recent trends continue. Moreover, since the delivery of normal jet fuel to the aircraft carrier battle group costs about $8 per gallon, shipboard production would be much less expensive.[56] This method of synthesizing jet fuel is currently only experimental.

Use of hydrogen [edit]

Hydrogen is mainly used for the conversion of heavy petroleum fractions into lighter ones via the process of hydrocracking and other petroleum fractions (dehydrocyclization and the aromatization process). It is also required for cleaning fossil fuels via hydrodesulfurization.

Hydrogen is mainly used for the production of ammonia via Haber process. In this case, the hydrogen is produced in situ. Ammonia is the major component of most fertilizers.

Earlier it was common to vent the surplus hydrogen off, nowadays the process systems are balanced with hydrogen pinch to collect hydrogen for further use.

Hydrogen may be used in fuel cells for local electricity generation, making it possible for hydrogen to be used as a transportation fuel for an electric vehicle.

Hydrogen is also produced as a by-product of industrial chlorine production by electrolysis. Although requiring expensive technologies, hydrogen can be cooled, compressed and purified for use in other processes on site or sold to a customer via pipeline, cylinders or trucks. The discovery and development of less expensive methods of production of bulk hydrogen is relevant to the establishment of a hydrogen economy.[4]

See also [edit]

Sustainable development portal

- Ammonia production
- Biological hydrogen production (Algae)
- Hydrogen
- Hydrogen analyzer
- Hydrogen compressor
- Hydrogen economy
- Hydrogen embrittlement
- Hydrogen leak testing
- Hydrogen pipeline transport
- Hydrogen piping
- Hydrogen purifier
- Hydrogen purity
- Hydrogen safety
- Hydrogen sensor
- Hydrogen storage
- Hydrogen station
- Hydrogen tank
- Hydrogen tanker
- Hydrogen technologies
- Hydrogen valve
- Industrial gas
- Liquid Hydrogen
- Next Generation Nuclear Plant (partly for hydrogen production)
- *The Phoenix Project: Shifting from Oil To Hydrogen* (book)
- Renewable energy
- The Hype about Hydrogen
- Lane hydrogen producer
- Linde-Frank-Caro process
- Liquid nitrogen production
- Underground hydrogen storage

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