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HYDROGEN GENERATION USING LOW CARBON TECHNOLOGIES

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Abstract: *Hydrogen is the cleanest fuel as it only emits water when combusted. Furthermore, it has the highest combustion energy as compared to fossil fuels. Steam-methane reforming is the dominant process for hydrogen production, but it is energy intensive and suffers from chemical equilibrium limitation. In this paper, alternative technologies for hydrogen production are discussed. This includes gasification of fossil fuels, electrolysis and biological techniques. Carbon dioxide emissions from these processes are discussed as well. The paper also compares the technologies in terms of technical and economic points of view.*

Keywords*: steam-methane reforming, gasification, electrolysis, biophotolysis, water splitting.*
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1. Introduction

Hydrogen is the lightest and most abundant element in the universe and is the fuel of the future. It is viewed as a future energy carrier as it is renewable [1], does not produce the ‘greenhouse’ gas (CO_2), reacts with oxygen to give a totally environmentally friendly product (viz. water) and at the same time provides 286MJ of energy per kmol of hydrogen consumed [2]. Moreover, the reaction of oxygen with hydrogen produces more energy per unit mass (143 MJ/kg) than with natural gas (42-55 MJ/kg for methane) or gasoline (48 MJ/kg for octane)[3]. However, on earth it only exists in forms combined with other elements – particularly oxygen and carbon [4]. Thus, separation processes are necessary, which are primarily from carbon and produce large quantities of greenhouse gases. The world production of hydrogen is estimated at around 50 million tons [5].

Hydrogen is of increasing importance. It is employed extensively as an industrial gas being a feedstock for the production of ammonia, which, in turn, is used to produce highly important fertilisers [6]. It is also the basic raw material for the manufacture of methanol and for catalytic reforming of petroleum products. Ways of using hydrogen for the production of electricity or for the storage of energy are expanding rapidly. Fuel cell technology has made considerable advances and is an increasing area for the use of hydrogen. The number of fuel cells in use and proposed is expanding exponentially [7]. A typical breakdown of the industrial uses of hydrogen in the USA is given in Table 1.

The majority of the hydrogen market is currently used in the oil refining, metals treatment, fertiliser manufacturing and food production industries. Although hydrogen holds considerable possibilities in its use for direct power production, transport and electrical grid stabilisation the quantity utilised in 2009 in fuel cell systems only amounted to about 60000 tons [8]. However, this is increasing rapidly showing a 50% increase since 2007 and a parallel decrease by a factor of six in the cost of hydrogen fuel cells. The possibility of storing energy through the storage of hydrogen is of increasing national interest in order to reduce dependence on imported energy. In this respect, projected storage densities for hydrogen-based systems will soon be much greater than energy storage by more conventional means (e.g., lithium-ion batteries).

The production of hydrogen globally is about 50 million tons and there are four main sources of production: natural gas (about 48% of the total production), oil (30%), Coal (18%), and the remaining 4% is for electrolysis, biological and other techniques [9].

Table 1. USA Hydrogen Production Capacity [10]

Application	Production Capacity (MT/yr.)
Oil Refinery	2723
Ammonia	2271
Methanol	189
Off-site refinery	1264
Compressed gas	313
Liquid hydrogen	58
Catalytic reforming	2977
Other off-gas recovery	478
Chlor-alkali processes	389
Total	10662

The majority of hydrogen production technologies use fossil fuels as a source [11]. To describe the types of process involved, the division is often made between what are termed ‘captive’ hydrogen production (where hydrogen is produced and used on-site) and ‘merchant’ hydrogen where hydrogen is produced as an industrial gas for use on other sites. Most of the hydrogen in these categories is manufactured by reforming processes or gasification of oil or coal. A further distinction can be made with ‘by-product’ hydrogen where hydrogen is produced as a by-product from another process such as in the manufacture of caustic soda and chlorine by the chlore-alkali process and from catalytic reforming. Figure 1 outlines the more common hydrogen production pathways at present in existence.

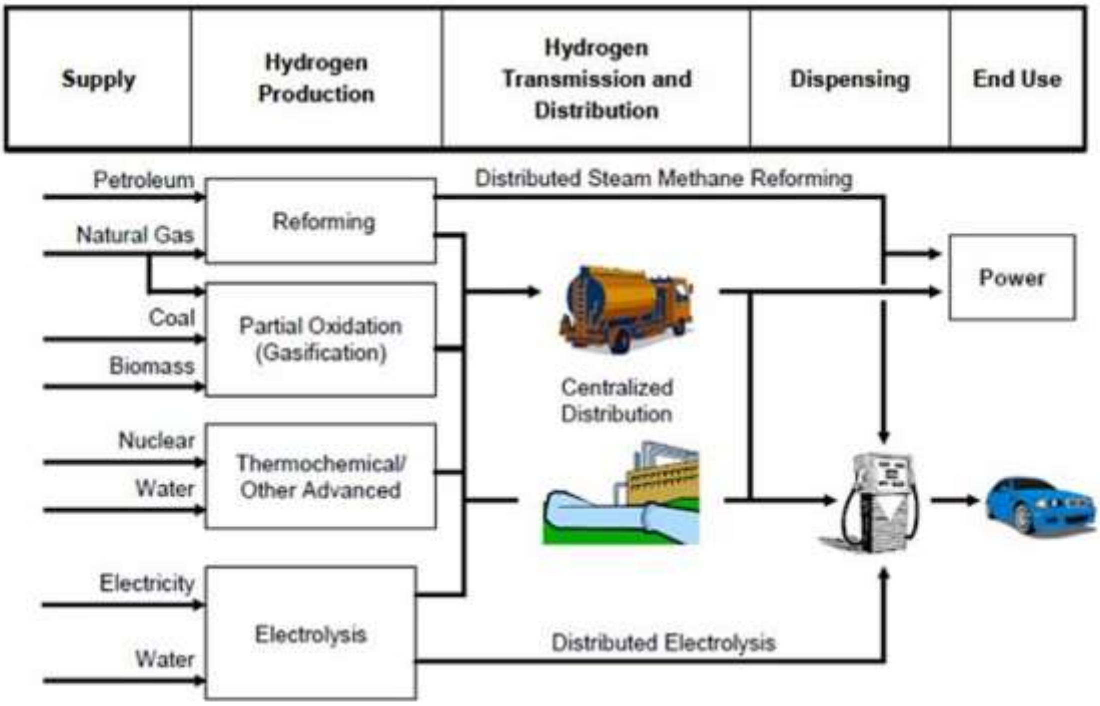

Fig. 1. Hydrogen Production Pathways [10].

2. Hydrogen Production

2.1 Fossil Fuels

2.1.1 Steam Reforming

This is the process by which the majority of bulk hydrogen is currently produced. The feedstock can either be methane or natural gas, which is mixed with steam and heated to 727 – 1127°C in the presence of a nickel catalyst [12]. The resulting endothermic reaction produces ‘syngas’ as follows:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (1)$$

This is followed by the exothermic water-gas shift reaction at ~357°C:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

Steam reforming produces a gas which is ~70 wt.% hydrogen on a dry basis with the cost of production ranging between \$3-\$6 per kg produced [13]. The rise in global warming has resulted in pressures on industry to capture (sequester) the produced carbon dioxide and store it in deep rock formations [14]. However, the cost of sequestration is ever-growing problem.

2.1.2 Gasification of Coal and Heavy Oils

Hydrogen can be produced from a number of heavy hydrocarbon fuels by partial oxidation. Coal gasification is the process of heating finely divided coal with steam and a less than stoichiometric volume of oxygen [15]. Syngas is produced through the reaction, which is typically:

$$3C(Coal) + O_2 + H_2O \rightarrow 3CO + 3H_2 \qquad (3)$$

Underground coal gasification is increasingly being developed and any produced is generally sequestered. Similarly, syngas is produced from heavy oil fractions and residues. This is typically:

$$C_{12}H_{24} + 6O_2 \rightarrow 2CO + 12H_2 \qquad (4)$$

The syngas is washed to remove impurities (hydrogen sulphide, phenols). Additional hydrogen is produced via reaction (2). The hydrogen thus produced is increasingly used to power turbines directly to produce electricity in an Integrated Gasification Combined Cycle [16].

2.2 Electrolysis

Electrolysis is a mature science having been first demonstrated by Williamson and Carlisle in 1800. There is an abundance of water on the Earth and there has been considerable interest in the electrolysis of water to produce hydrogen. Water naturally dissociates into hydronium ions (H_3O^+) and hydroxyl ions (OH^-). When a DC source is connected to electrodes (typically of stainless steel) placed in water the H_3O^+ ions move towards the negative electrode (cathode) and the OH^- ions towards the positive electrode (anode) [17]. If a sufficient potential difference is applied between the two electrodes, then electrolysis of the water occurs with hydrogen being produced at the anode and oxygen at the cathode (Figure 2).

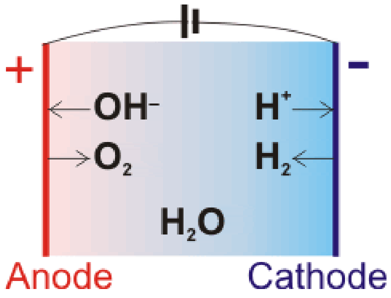

Fig. 2. Simple electrolytic cell [18]

The water in the vicinity of the electrodes will change pH due the ions being produced. The electrode potential of the cell can be raised by placing a porous membrane between the electrodes.

This causes the concentrations of OH^- and H_3O^+ ions to increase in the sections containing the cathode and the anode respectively with a resulting increase in the electrode potentials. The electrode potentials for the limiting cases of pH 14 and pH 0 are given in Table 2. The cell potential can be determined from the Nernst equation:

$$E = E^0 + \frac{RT}{nF} ln\left(\frac{\prod(concentrationoxdisedcomponets)}{\prod(concentrationreducedcomponets)}\right) \quad (5)$$

where E^0 is the standard cell potential, n is the number of electron moles transferred, F is the Faraday constant (96485 C.mol^{-1}), T (K) is the temperature, and R is the gas constant.

Pure water is a poor conductor of electricity having a very small ionisation constant ($K_w = 10^{-14}$) and thus the production of hydrogen is very slow. To increase the rate of electrolysis a water-soluble electrolyte is added such as NaCl [19]. If the requirement is to generate hydrogen gas, then the electrolyte should be chosen such that it has a cation with an electrode potential lower than that of H^+ otherwise the H^+ ion will be reduced instead of the cation and no hydrogen will be produced. The potential at any point within the cell is a function of the concentration of the various species present, gas partial pressure, and effective electrode surface area at that location. (The surface area is lost due to the formation of bubbles on the surface).

Table 2. Electrode Potentials at different pH's

	Electrode	pH	Reaction	Electrode potential (E^0volts)
1	Anode	0	$2H_2O \rightarrow O_2 + 4H^{++4e^-}$	+1.229
2	Anode	14	$4OH^{-\rightarrow O_2+H_2O+4e^-}$	+0.401
3	Cathode	0	$4H^{++4e^{-\rightarrow 2H_2}}$	0.0
4	Cathode	14	$4H_2O + 4e^{-\rightarrow 2H_2+4OH^-}$	-0.828

Also, in order to overcome the activation energy barriers in producing a sufficient reaction rate an extra potential difference (~ 0.5V) is required. Moreover, a further p.d. (~1V) is necessary to overcome the electrical resistance of the cell. The latter leads to a power loss of about 20%. Hence, the minimum voltage required for the electrolysis of water is 1.229V and the potential required to commence the electrolysis of water is $\frac{\Delta H^0}{nF}$=-1.481V, which results in a loss of efficiency of ~21% as well as further losses from the heat produced from the overpotentials applied. Thus, generating water using the simple electrolytic cell is only about 60% efficient and is of little use in the large-scale generation of hydrogen. Modifications of the process however are more encouraging. New advances which have been made recently are the development of polymer electrolyte membrane (PEM) electrolysis, high-temperature electrolysis (HTE) and modifications to the process of alkaline water electrolysis (AWE) [20].

2.2.1 Polymer Electrolyte Membrane (PEM) Electrolysis

Fig. 3 shows the construction of a PEM cell in which the electrolyte consists of a semi-permeable membrane designed to conduct protons while acting as an electronic insulator and reactant barrier. (e.g., to O_2 (*g*) and H_2 (*g*)) [21]. The PEM cell was developed to overcome the problems of low current density, partial load, and low-pressure operation that occur with traditional AWE systems.

The operation and performance of the PEM electrolyser depends on the operating conditions like temperature, voltage, current density, and power [22, 23]. During water electrolysis, the cathode is the site for Hydrogen Evolution Reaction (HER) while the anode is the site for the Oxygen Evolution Reaction (OER) [24]. The operation requires a theoretical voltage of 1.23 V to produce hydrogen, however, a voltage range of between 1.8 to 2.0 V may be required in practical applications due to over potentials on the electrodes.

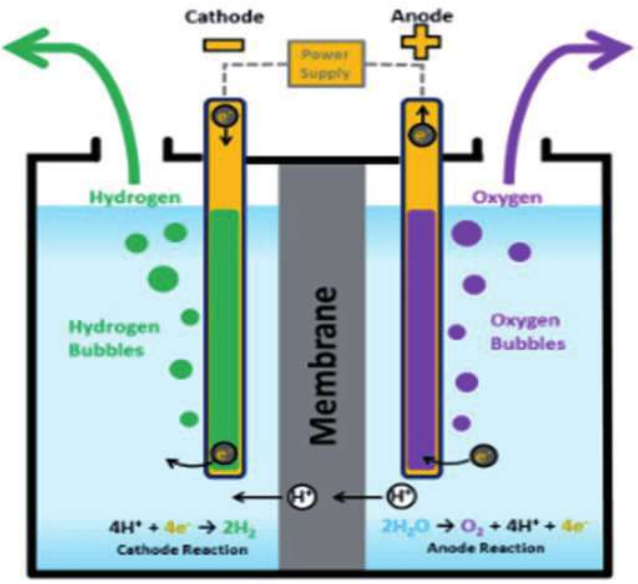

Fig. 3. PEM Cell [21]

However, low energy-cost PEM systems are designed, with reduced electrolyser voltage from 1.8 V to 0.5-0.6 V to enhance the economic viability of the hydrogen production projects [25]. Various types of electrocatalysts are produced and proposed or used to reduce the problem of overpotentials for OER and HER, including Phosphated IrMo bimetal clusters [26] and Carbon-supported single atom catalysts [27] and other variations of the anode electrocatalysts [28]. Further research evidence suggests that the efficiency and input power of the electrolyser lies in the range of 72% to 88% and is inversely correlated to the input power. Experimental simulations of offshore hydrogen production using PEM showed that the yield of hydrogen produced, and the cost varies; the highest yield of H_2 was 17242 k produced using 1.852 MW electrolyser and the minimum cost of 4.53 \$/kg H_2[29].

2.2.2 High-Temperature Electrolysis (HTE)

If steam can be produced by employing heat from some other process, then this can act as feed for an HTE unit which will then convert the steam into hydrogen and oxygen [30].

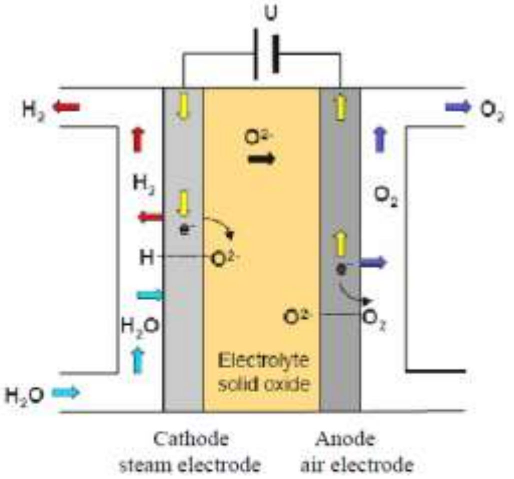

Fig. 4. HTE Cell [33]

The higher the temperature at which the electrolysis takes place, the more favourable are the thermodynamic and electrochemical conditions.

Thus, less electrical energy is required to produce 1 m^3 of hydrogen than with other electrolysing processes [31]. The HTE unit (Figure 4) is so far largely experimental and takes the form of a solid oxide electrolyser cell (SOEC). This is a solid oxide fuel cell using a solid oxide or ceramic electrolyte in regenerative mode to produce hydrogen and oxygen [32] from steam at temperatures in the range 727-1027°C. Sources of heat energy under investigation are nuclear fission (nuclear power stations), solar thermal collectors, and geothermal sources. The proposed HTE Plant arrangement is given in Fig.5.

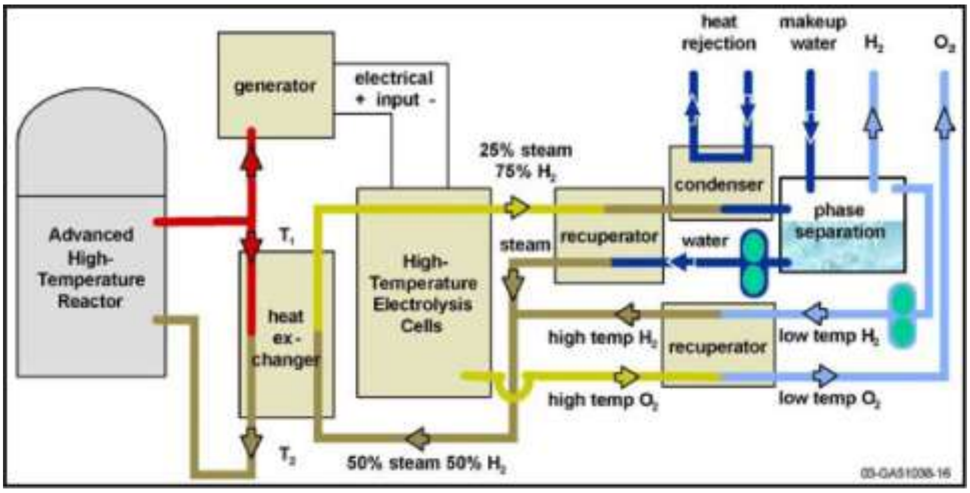

Fig. 5. Proposed HTE Plant arrangement [30]

2.2.3 Alkaline Water Electrolysis (AWE)

The AWE unit consists of two electrodes with an alkaline electrolyte solution such as sodium hydroxide. Unlike, PEM and HTE, the electrodes transport hydroxide ions (OH-) from one electrode to the other [34]. The design was improved by operating at a higher pressure with the use of nickel-coated electrodes. The AWE unit is reported to have a longer operating life and the process is given in Fig.6.

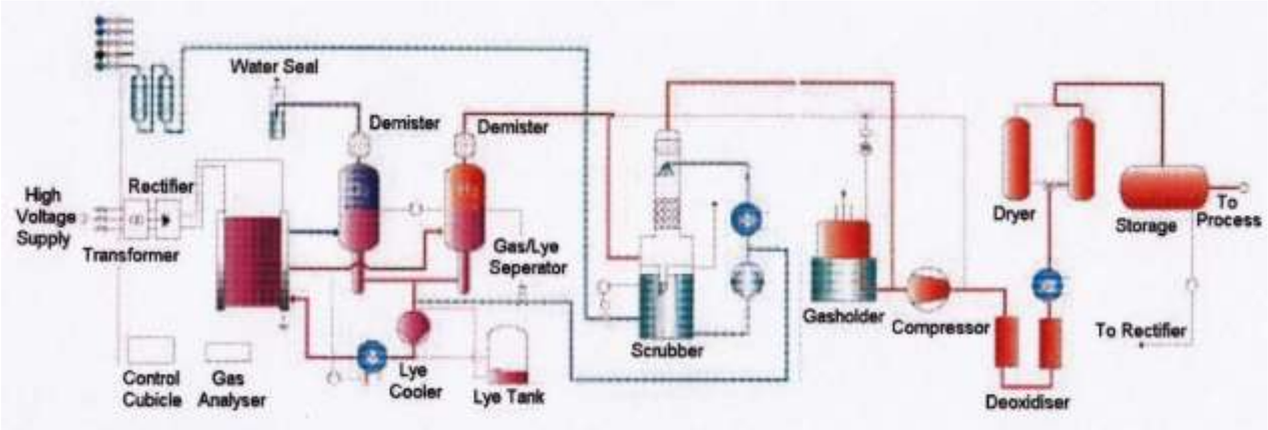

Fig. 6. Alkaline water electrolysis (AWE) plant arrangement [30]

A conventional commercial-scale AWE can use low-cost electrode materials, such as Ni. The rates of electrolysis and the energy consumption required to produce H_2 using AWE are dependent on the cell voltage of the electrolyser. The common approach to enhance the efficiency of the H_2 production results in reducing cell voltage [35]. However, the formation of bubble at the electrode, which causes polarization loss. The accumulation of bubbles induces overpotential. Using superaerophobic electrodes (catalysts) has been shown to circumvent the problem, with superior performance at lower reaction rates. Moreover, research shows that electrolytic voltage and current depends on the electrolyte temperature and pressure of the water electrolyzer. Tables 3 and 4 compare AWE, PEM, and HTE in terms of evolution reactions, benefits, and limitations.

Table 3. Anode and Cathode Reactions for Different Types of Water Electrolysis

Technology	Alkaline Electrolysis (AWE)	Polymer Membrane Electrolysis (PEM)	High-Temperature Electrolysis (HTE)
Oxygen Evolution Reaction (OER) (Anode)	$2OH^{-\to\frac{1}{2}O_2+H_2O+2e^-}$	$H_2O \to \frac{1}{2}O_2 + 2H^{++2e^-}$	$O^{2-\to\frac{1}{2}O_2+2e^-}$
Hydrogen Evolution Reaction (HER) (Cathode)	$H_2O + 2e^{-\to H_2+2OH^-}$	$2H^{++2e^-\to H_2}$	$H_2O + 2e^{-\to H_2+O^{2-}}$
Charge Carrier	OH^-	H^+	O^{2-}
Operating Temperature Range	37-87°C	17-97°C	727-1027°C

Table 4. Comparison of Methods of Electrolysis of Water [31]

Technology	**Advantages**	**Disadvantages**
Alkane Water Electrolysis (AWE)	• Well-established. • Equipment has a long life. • Efficiency ~70%.	• Low current density. • Low-purity products. • Corrosive electrolyte. • Poor dynamic operation. • Low partial loads range. • Low-pressure operation.
Polymer Electrolyte Membrane (PEM)	• High current density. • High voltage efficiency. • Good partial load range. • Compact design. • higher purity products. • Rapid system response.	• New technology. • Expensive components. • Noble metal catalyst. • Corrosive acidic environment. • Expensive membrane.
High Temperature Electrolysis (HTE)	• 100% efficiency. • Low-cost catalyst. • High-pressure operation.	• Not commercialised. • Require high temperature. • Limited operating life.

2.3 Biological Methods

In spite of the fact that biological systems have low conversion efficiencies, biological hydrogen production has a number of advantages over thermo-chemical or photo-electrochemical processes [36,37]. An increase in environmental problems throughout the world leads to the formation of a number of national bodies concerned with biological hydrogen production [38]. Major biological processes used to produce hydrogen are the bio-photolysis of water by algae and photo-fermentation of organic materials by bacteria. Typical source materials for the latter are wood, waste from industrial biodiesel, domestic waste, and waste from the starch industry.

Although it is theoretically possible to produce hydrogen and oxygen by direct photosynthesis, there are many difficulties to be addressed. The reducing power of the process of photosynthesis must be as close as possible to the maximum possible solar conversion efficiency, which is ~10%, and then efficiently transferred to an enzyme (hydrogenase) that catalyses the reversible oxidation of molecular hydrogen. Plants and other organisms which provide photosynthesis use only 3-4% of the sun's available energy [39]. The development of low-cost photo-bioreactors that provide efficient microbial production of hydrogen from water and light is difficult. More practical approach is the conversion of organic substrates and wastes to hydrogen using anaerobic hydrogen-fermenting bacteria. However, such bacteria produce only small amounts of hydrogen [40]. Table 7 lists organisms that produce hydrogen by different processes.

'Indirect biophotolysis' is more promising and a two-stage, indirect biophotolysis system has been constructed in which the CO_2 fixation stage (occupying ~90% of the total area for the process) consists of open ponds. These are much less expensive for producing hydrogen than the closed photo-bioreactors [41].

2.3.1 Biophotolysis

Biophotolysis is a process in which light energy is absorbed by microalgae that provide the initial photochemical changes involved in photosynthesis. The energy produced reduces ferredoxin and gives electrons to the hydrogenase enzyme. There are two types of biophotolysis: direct and indirect.

Direct biophotolysis: biophotolysis produces hydrogen directly from water by means of photosynthesis using microalgae according to:

$$2H_2O + SolarEnergy \rightarrow 2H_2 + O_2 \qquad (6)$$

This is a two-stage process in which the first step is the splitting of the water molecule to produce oxygen. This is followed by the production of hydrogen by the protons being reduced by the addition of electrons. The problem is that oxygen is a strong inhibitor of hydrogenase activity. This creates a feedback problem. One way of solving this is to put the two reactions into separate compartments with two separate reactions and use CO_2 as an intermediate to go between the two. Some success has been achieved with 22% of the light energy converted into hydrogen energy [42]. Difficulties with this process are due to the fact that the oxygen produced by photosynthesis during this reaction inhibits the hydrogenase enzyme which is necessary for the production of hydrogen and the whole of the solar energy capture area needs to be enclosed in a photobioreactor.

Indirect Biophotolysis: photosynthesis is used to produce biomass, followed by concentration of the biomass, after which dark aerobic fermentation is used to produce the hydrogen. This also gives two moles of acetate, which are also converted into hydrogen. The reactions are:

$$6H_2O + 6CO_2 + Solarenergy \rightarrow 2C_6H_6O_6 + 6O_2 \qquad (7)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2 \qquad (8)$$

$$2CH_3COOH + 4H_2O + SolarEnergy \rightarrow 8H_2 + 4CO_2 \qquad (9)$$

Where equations (7) and (9) are light-dependent and equation (8) is light-independent.

An alternative approach is to employ nitrogen-fixing cyanobacteria to separate the evolution of the hydrogen and oxygen in terms of time (e.g., by using a day-night cycle) or spatially by using two separate bioreactors. Table 5 shows various microorganisms and their production rate of hydrogen.

Table 5. Different biological hydrogen production processes [40]

Microorganism	**Raw Material**	**Maximum Production of Hydrogen (mmol H_2/hr)**	**Major Products**
Oscillatoria	Special media	0.4	H_2, CO_2, O_2
Anabaena	Various	1.2	H_2, O_2
Rhodopseudomonas	Various	2.0	H_2, CO_2, O_2, VFA
Rhodobacter	Various	5.9	H_2, CO_2, O_2, VFA
C. butyricum	Glucose	7.3	H_2, CO_2, VFA
Citrobacter	Cellulose	11	H_2, CO_2, VFA
E. aerogenes	Sugar cane	11.36	H_2, CO_2, VFA
E. cloacae	Sucrose	37.03	H_2, CO_2, VFA
C. sacchareolyticus	Sucrose	8.4	H_2, CO_2, VFA
T. elfi	Glucose	4.5	H_2, CO_2, VFA

VFA: volatile fatty acid

2.3.2 Dark Fermentation

Dark fermentation produces hydrogen by anaerobic fermentation in the absence of light from biomass and other organic substrates. It is a complex process using groups of anaerobic microorganisms that produce a series of biochemical reactions [43]. In order to increase the yield of hydrogen, it is necessary to control several parameters – namely pH, the organic food; the nutrition feed rate, temperature, solids retention time, and the partial pressure of the hydrogen.

Dark fermentation has several advantages as compared with other biological methods of hydrogen production because of its ability to produce hydrogen continuously without the presence of light, a higher hydrogen production rate, process simplicity, lower net energy input, and use of low-value waste as a raw material [44]. The process takes place in several stages where different bacteria produce hydrogen by a series of complex biochemical reactions. First, enzymes are used to hydrolyze high molecular weight organic compounds to water-soluble organics. Second, the organics are converted into volatile fatty acids, hydrogen, and carbon dioxide (See Table 6). One improvement is to employ photosynthetic bacteria which, in the light, can convert organic substrates (including many wastes) quantitatively into hydrogen and carbon dioxide. In principle, relatively little light energy is required meaning that only small photo-bioreactors are necessary for the reaction, as most of the hydrogen energy is derived from the organic substrates. So far, however, measured photosynthetic efficiencies are not much higher than those obtained in biophotolysis reactions. Another new development, with potential for near-term practical application for photosynthetic bacteria, is their use as catalysts for the conversion of carbon monoxide to hydrogen in the absence of light, i.e., dark conversion. Table 6 shows the rate of fermented hydrogen by different sources.

Another possible economic method of hydrogen production by dark fermentation is to convert lower-cost substrates at high yields, such as deriving hydrogen from organic wastes using dark fermentative processes. As model for such a process is the fermentation to methane of waste sludges, animal manures, and food-processing wastes. Hydrogen fermentations could employ hardware similar to that used currently in industrial methane fermentations. The economics of hydrogen fermentations could be favourable at even less than stoichiometric yields.

Table 6. Fermentative hydrogen yields from various sources [39, 41]

Source	**Origin**	**Microorganism**	**Method**	**Maximum H_2 Production (Mol H_2/mol glucose)**
Wheat straw	Lignocellulose	C. saccharolyticus	Batch	3.8

Maize leaves	Lignocellulose	C. saccharolyticus	Batch	3.6
Elephant grass	Energy crops	C. saccharolyticus	Batch	3.4
Corn stover	Lignocellulose	Mix. mesophilic cultures	Continuous	3.0
Sugar factory	Wastewater	Mix. mesophilic cultures	Continuous	2.6
Sorghum residue	Lignocellulose	Rumicoccus albus	Batch	2.59
Wastepaper	Waste	Ruminococcus albus	Batch	2.29
Rice winery	Wastewater	Mixed culture	Continuous	2.14
Sugarbeet	Energy crops	Mix. mesophilic cultures	Continuous	1.9
Food waste	Waste	Mix. mesophilic cultures	Batch	1.8
Sweet sorghum	Energy crops	C. saccharolyticus	Batch	1.75
Sugarcane bagasse	Lignocellulose	Clostridium butyricum	Batch	1.73
Wood fibres	Lignocellulose	Clostridium thermocellum	Batch	1.47
Wheat starch	Energy crops	Mix. mesophilic cultures	Continuous	1.26
Cheese whey	Waste	Mix. mesophilic cultures	Continuous	0.9
Corn starch	Energy crops	Mix. mesophilic cultures	Continuous	0.51

Production costs of methane fermentations range from about \$3–\$8 per MMBTU, whereas hydrogen produced in similar equipment could be sold for as much as \$15 per MMBTU. Another method is the production of a mixture of hydrogen and methane in a two-stage process. This could be used as a fuel for cars as hydrogen-methane mixtures significantly reduce air pollutants in internal combustion engines, compared with using pure methane as a fuel.

2.4 Biomass Liquid Reforming

Liquids produced from biomass such as ethanol and bio-oils can be reformed to produce hydrogen. The process is similar to that used for the reforming of natural gas, i.e., by reforming the bio-liquid with steam at high temperatures [45]. For example, for ethanol:

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2 \tag{10}$$

This is followed by the exothermic water-gas shift reaction (Equation 2), which produces more hydrogen. Liquids produced from biomass can be produced at large centralised units near to large sources of biomass. These can be lignocellulose from forests or plant biomass from crops [46].

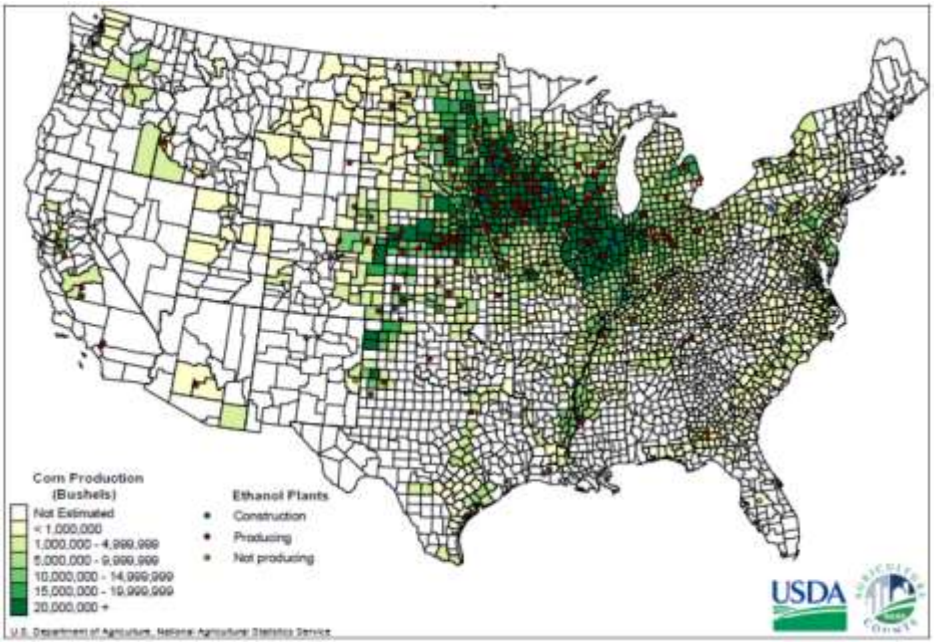

Fig. 7. Location of bioethanol plants in the USA and sources of corn [45]

Fig. 7 shows the concentration of bioethanol plants close to annual crops such as corn. Bioliquids have the advantage of having a high-energy density and can be transported economically to sites where they can be reformed and where the hydrogen produced can be immediately converted into electrical power.

2.5 Thermochemical Water Splitting

Processes of thermo-chemical water splitting employ high temperatures (527–2027°C) obtained using solar cells or waste heat from nuclear power stations. The method is similar to that of the HTE cell described in Section 3.2. A number of different water-splitting cycles are under investigation [47]. Two of these are illustrated in Fig. 9. Developments show that solar fuel cell technologies are capable of operating at efficiencies over 10%. Other directions involve the development and use of self-supported photo-catalysts made of particulate or colloidal semiconductors. These do not require the use of the high-cost transparent electrodes or the carefully directed illumination required by the cycles shown in Fig.8. On the other hand, they do produce the simultaneous release of water and oxygen which forms a potentially explosive mixture.

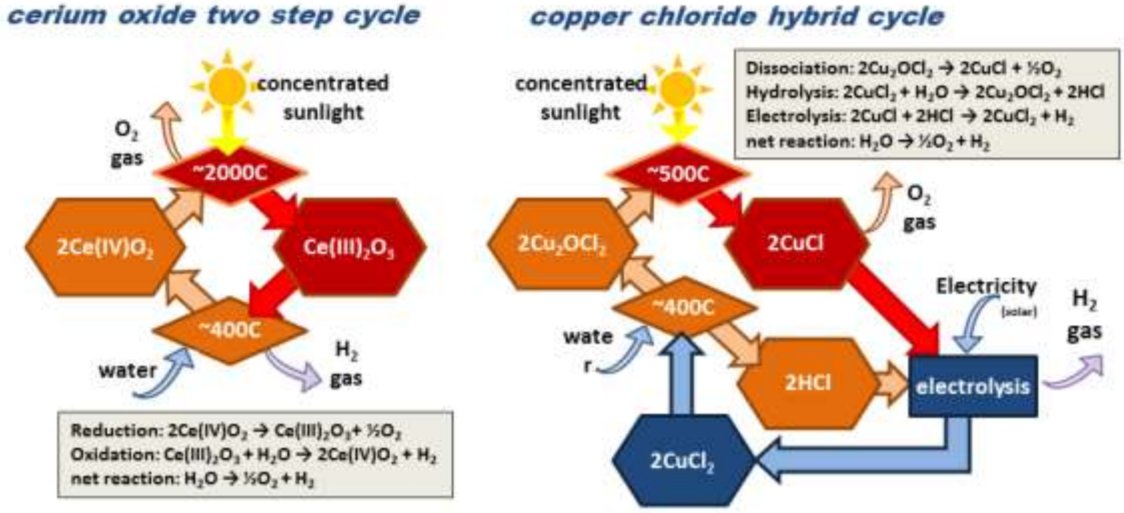

Fig. 8. Thermo-chemical water-splitting cycles [48]

3. Economic Assessment

Steam methane reforming is still the dominant process for hydrogen production. Not all the technologies mentioned before are commercialised. The available technologies are fossil fuel gasification and alkaline electrolysis [49]. Processes such PEM electrolysis, electrolysis, biophotolysis, and dark fermentation are still under development.

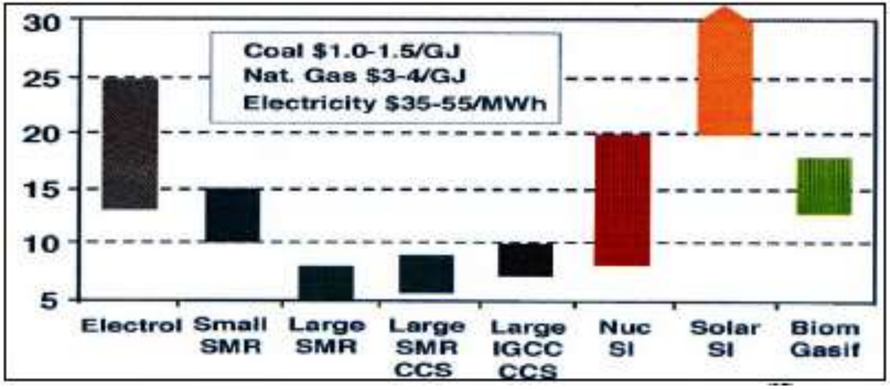

Fig. 9. Estimated costs of hydrogen production with different technologies [50]. (SMR: steam methane reforming, CCR: with carbon capture, SI: sulphur-iodine cycle)

Fig.9 shows that steam methane reforming is still the best option for hydrogen generation in terms of production cost (~7.5$ per GJ). Other processes such as electrolysis and gasification cost about 20 $ per GJ and 15$ per GJ, respectively.

Another important economic factor involved in the development of the hydrogen economy is the methodology of distribution. Although hydrogen has higher energy content per unit mass than other sources of energy, the converse is true for energy content per unit volume due to its very low density. If hydrogen is to be developed as the fuel of the future to be readily available for vehicles driven by fuel cells, and as a universal means of storing energy then economic methods of distribution must be found. Comparisons of current hydrogen distribution are given in Table 7.

Table 7. Comparison of transport methods for hydrogen [51,52]

Method	Distance	Cost	Notes
Pipeline	~700 miles	• Least expensive/	• Located close to refineries. • Compressor requires higher energy compared to natural gas.
High-Pressure Trailer	< 200 miles	• Expensive.	• Transport of compressed hydrogen by road and rail (adds \$1–\$2/GJ to the production cost).
Liquefied-Hydrogen Tanker	Long distances	• Expensive but more viable.	• Require cryogenic liquefaction of hydrogen (adds \$7–\$9/GJ).

4. Conclusions

Hydrogen will be a fuel of major importance. It is clean and does not produce gases that harm the environment and has a terrestrially unlimited feedstock, viz. water [53]. There is a wide range of processes that can produce hydrogen. At present, the only economic and commercialised method is the steam reforming of hydrocarbons. This process, however, produces considerable quantities of carbon dioxide which, unless sequestered in some way, will find its way into the atmosphere and increase global warming. Global warming related risks are well-known and a large number of international programmes have been set up to investigate environmental techniques to produce hydrogen [54]. Studies on hydrogen production by fuel cells, solar power and biological methods are increasing rapidly. Further developments are required to overcome technical problems and safety issues associated with these processes. A comparison of the efficiencies of the various commercial or pre-commercial methods of hydrogen generation are summarised in Table 8.

Table 8. Efficiencies of methods of hydrogen generation [50]

<table>
<tr><th colspan="6">Hydrogen Production from Electrolysis</th></tr>
<tr><th>Technology</th><th>Large-Scale Alkaline</th><th>High Pressure Alkaline</th><th>Advanced Alkaline</th><th>PEM</th><th>HTE</th></tr>
<tr><td>Status</td><td>Commercial</td><td>Commercial</td><td>Pre-Commercial</td><td>Pre-Commercial</td><td>Prototype</td></tr>
<tr><td>Temperature (°C)</td><td>37–87</td><td>37–87</td><td>37–47</td><td>17–97</td><td>727–1027</td></tr>
<tr><td>Pressure (bar)</td><td>Up to 25</td><td>Up to 690</td><td>Up to 120</td><td>Up to 400</td><td>Up to 30</td></tr>
<tr><td>Output (kWh/kgH_2)</td><td>48–60</td><td>56–60</td><td>42–48</td><td>40–60</td><td>28–39</td></tr>
<tr><th colspan="6">Hydrogen Production from Natural Gas Reforming</th></tr>
<tr><th>Technology</th><th>Large Scale Steam Reforming</th><th>Small Scale Steam Reforming</th><th>Partial Oxidation</th><th colspan="2">Auto Thermal Reforming</th></tr>
</table>

Status	Commercial	Future	Commercial	Future	Commercial	Pre-commercial
CO_2 Capture	Without	With	Without	Without	Without	Without
Efficiency %	72–77	61–70	72–77	61–70	66–76	66–73

Hydrogen Production from Coal Gasification

Technology	Current Gasification		Oxygen-Blown Gasification		Advanced CO_2 membrane	With cogeneration		Cogeneration membrane
CO_2 Capture	Without	With	Without	With	With	Without	With	With
LH Value*	57	51	67	62	64	83	70	77

*LH: Lower heating value is a measure of the quantity of heat released by a fuel.

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ПРОИЗВОДСТВО ВОДОРОДА С ИСПОЛЬЗОВАНИЕМ НИЗКОУГЛЕРОДНЫХ ТЕХНОЛОГИЙ

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Аннотация: Водород является самым чистым топливом, поскольку при сгорании он выделяет только воду. Кроме того, он имеет самую высокую энергию сгорания по сравнению с ископаемым топливом. Парометановый риформинг является доминирующим процессом производства водорода, но он энергоемок и страдает от ограничений химического равновесия. В данной статье обсуждаются альтернативные технологии производства водорода. Это включает газификацию ископаемого топлива, электролиз и биологические методы. Обсуждаются также выбросы углекислого газа в результате этих процессов. В статье также сравниваются технологии с технической и экономической точек зрения.

Ключевые слова: парометановая конверсия, газификация, электролиз, биофотолиз, расщепление воды.

AŞAĞIKARBON TEXNOLOGİYALARINDAN İSTİFADƏ ETMƏKLƏ HİDROGENİN İSTEHSALI

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Xülasə: Hidrogen ən təmiz yanacaqdır, çünki yandıqda yalnız su ayrılır. Bundan əlavə, təbii yanacaqlarla müqayisədə ən yüksək yanma enerjisinə malikdir. Metanın buxar riforminqi hidrogen istehsalının dominant prosesidir, lakin o, enerji tələb edir və kimyəvi tarazlıq məhdudiyyətləri vardır. Bu məqalə alternativ hidrogen istehsalı texnologiyalarından bəhs edir. Buraya təbii qazlaşdırılması, elektroliz və bioloji üsullar daxildir. Burada həmçinin karbon qazı emissiyaları da müzakirə olunur. Məqalədə həmçinin təklif olunan texnologiyalar texniki və iqtisadi baxımdan müqayisə edilir.

Açar sözlər: metanın buxar çevrilməsi, qazlaşdırma, elektroliz, biofotoliz, suyun parçalanması.