Hydrogen Production: State of Technology

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Abstract. Presently, hydrogen is for ~50% produced by steam reforming of natural gas – a process leading to significant emissions of greenhouse gas (GHG). About 30% is produced from oil/naphtha reforming and from refinery/chemical industry off-gases. The remaining capacity is covered for 18% from coal gasification, 3.9% from water electrolysis and 0.1% from other sources. In the foreseen future hydrogen economy, green hydrogen production methods will need to supply hydrogen to be used directly as fuel or to generate synthetic fuels, to produce ammonia and other fertilizers (viz. urea), to upgrade heavy oils (like oil sands), and to produce other chemicals. There are several ways to produce H₂, each with limitations and potential, such as steam reforming, electrolysis, thermal and thermo-chemical water splitting, dark and photonic fermentation, gasification, and catalytic decomposition of methanol. The paper reviews the fundamentals and potential of these alternative process routes. Both thermo-chemical water splitting and fermentation are marked as having a long term but high "green" potential.

1. Introduction
At present, hydrogen, representing a market of roughly fifty billion US$ for 40 Mt annual production, is mainly used as a chemical substance rather than a fuel [1]. Most of its current uses are found as processing agent in oil refineries (e.g. for desulphurization and upgrading conventional petroleum) and in chemicals' production processes (e.g. methanol, hydrogenation of fats/oils, ammonia and pharmaceuticals). Prospects of future population growth with consequently increased requirement of food and of various commodities, enhances the demand of hydrogen, at least to satisfy the needs of conventional chemical processes, and notwithstanding the high potential for using H₂ as transportation fuel.
Presently, hydrogen is mainly produced by steam reforming of natural gas, which covers close to 50% of the global demand for hydrogen. About 30% is produced from oil/naphtha reforming and from refinery/chemical industry off-gases, 18% from coal gasification, 3.9% from water electrolysis and 0.1% from other sources. In the foreseen future hydrogen economy, "green" hydrogen production methods will need to be applied to supply hydrogen to be used in the traditional and in new applications [2, 3]. There are several ways to produce H₂, each with limitations and potential:

- Thermal splitting of natural gas, either by steam reforming of methane or by its thermal splitting, reforming of oil/naphtha;
Electrolysis of water, purely electrical, or with high pressure steam and electricity by alkaline, Proton Exchange Membrane, or solid oxide electrolysers;
- Thermal water splitting, at temperatures in excess of 1500 °C;
- Thermo-chemical water splitting, where redox chemicals and heat induce a combined chemical reduction/oxidation cycle, using H$_2$O in the re-oxidation cycle to provide O;
- Photonic water splitting by photon electrolyser;
- Dark and photonic fermentation of carbohydrates, using appropriate bacterial strains;
- Gasification, to decompose coal or biomass with heat, pressure, and possibly steam;
- Catalytic decomposition of CH$_3$OH or HCOOH;

The most relevant technologies will be summarized below.

2. Hydrocarbon reforming technology
The hydrogen production technology using the hydrocarbon fuels can be divided into a steam reforming process, the partial oxidation process, and the auto-thermal reforming process (ATR).
In the steam reforming process, hydrogen, carbon monoxide and carbon dioxide are primarily present in the gas flow stream. It has been demonstrated that improving the operating conditions such as temperature, pressure, etc. in the fuel processing reactors, will maximize the hydrogen production and minimize the carbon formation [4]. Table 1 compares the reforming processes [5, 6].

| Technology                  | Advantages                                                                 | Disadvantages                                      |
|-----------------------------|-----------------------------------------------------------------------------|----------------------------------------------------|
| Steam reforming             | Most industrially applied process; no oxygen required; lowest process temperature, and optimum H$_2$/CO ratio for H$_2$ production. | High production of GHG.                            |
| Auto-thermal reforming      | Low process temperature and low methane slip.                                | Still limited experience, requires air or oxygen.  |
| Partial oxidation           | Decreased desulfurization requirement, no catalyst required, and low methane slip. | Low H$_2$/CO ratio, very high processing temperatures, soot formation/handling makes process more complex. |

3. Electrolysis
Electrolysis is responsible for only ~4% of the current H$_2$ production. Steam electrolysis will split water with heat, pressure and electricity. It could be attached to a nuclear power plant, to photovoltaic or wind turbine power generators, or to a concentrated solar power plant. Major research deals with the development of the process electrodes. Water must be desalinated and demineralized before electrolysis.

- Electrolysis as such will split water with electricity;
  \[ 2 \text{H}_2\text{O} (l) \rightarrow 2 \text{H}_2 (g) + \text{O}_2 (g), \ E_0 = -1.229 \text{ V}, \] needs catalysts (e.g. Platinum)

The cost of H$_2$ production through electrolysis varies from 2.5 to 3.5 $/kg, significantly in excess of the reforming production methods (+ 20 % to 50 %). Electrolysis is hence not a priority, except if coupled to a cheap electricity source [9]. Table 2 illustrates typical data for water electrolysis.

| Specification | Alkaline | PEM | SOE |
|---------------|----------|-----|-----|
| Technology maturity | State of the art | Demonstration | R&D |
hotocatalytic water splitting process produces hydrogen from water using solar light. The reaction of photolysis is illustrated as follows:

\[
\text{H}_2\text{O}(l) \xrightarrow{\text{heat}} \text{H}_2(g) + 0.5 \text{O}_2(g)
\]

The reaction requires a high-temperature heat source at above 2500 K to have a reasonable degree of dissociation [13] (even up to 3000 K for 64% dissociation at 1 bar). An additional drawback of this process comes from the need of an effective technique to separate H\(_2\) and O\(_2\) to avoid ending up with an explosive mixture. Semi-permeable membranes based on ZrO\(_2\) and other high-temperature materials can be used for this purpose at up to 2500 K. Separation can also be achieved after the product gas mixture is quenched to a lower temperature: recombination of hydrogen and oxygen can indeed be avoided if the product gas is rapidly cooled by quenching through a sharp temperature decrease of 1500 – 2000 K within a few milliseconds. Palladium membranes can then be used for effective hydrogen separation. The heat can be supplied by nuclear reactors or concentrated solar power plants. The major drawback remains however the selectivity of materials that can withstand the very high temperature needed [13, 14].

5. Photonics
The H\(_2\) production by the photocatalytic water splitting process produces hydrogen from water using ordinary light, albeit at low efficiency. The main reactions of this process are as follows:

- Photo-reduction: \(2\text{H}_2\text{O} + 2e^{\text{hv}} \rightarrow \text{H}_2 + 2\text{OH}^-\)
- Photo-oxidation: \(2\text{H}_2\text{O}^{\text{hv}} \rightarrow 4\text{H}^+ + 4e^- + \text{O}_2(g)\)

Titanium oxide (TiO\(_2\)) is used in the photolysis reactions [15-19].

Photoelectrolysis is similar to photovoltaic systems, both technologies use semiconductor materials. In photovoltaics, p-type and n-type semiconductor materials are used. In photoelectrolysis, instead of generating an electric current, water is decomposed into hydrogen and oxygen. The reaction of photoelectrolysis is illustrated as follows:

\[
\text{H}_2\text{O}^{\text{hv}} \rightarrow \text{H}_2(g) + 0.5 \text{O}_2(g)
\]

Different photoelectrode materials such as WO\(_3\), Fe\(_2\)O\(_3\), and TiO\(_2\) have been investigated to use in photoelectrolysis method as a thin film [18, 19]. The hydrogen production achieves an efficiency of of 18.3% for a single band gap, whereas dual-band gap systems achieve >30% conversions.

6. Biomass thermo-chemical production routes
Biomass can be used as primary "green" resource to produce hydrogen [20-24]. If the moisture content is too high, either the biomass must be dried before gasification or supercritical steam gasification can be applied. Wood sawdust, sugar cane bagasse, short rotation forestry products, etc. are some general forms of biomass that can be used to produce hydrogen. The global reaction of biomass gasification process to produce hydrogen reads as:

\[a\text{C}_1\text{H}_m\text{O}_n + \gamma\text{H}_2\text{O} \xrightarrow{\text{heat}} a\text{H}_2 + b\text{CO} + c\text{CO}_2 + d\text{CH}_4 + e\text{C} + f\text{Tar}\]

With \(a\text{C}_1\text{H}_m\text{O}_n\) as the general chemical representation of the biomass. The formation of tars is undesirable because of their negative effect on ducts and equipment by clogging and fouling. Tar
formation can be diminished by proper control and using various catalysts. Table 3 indicates the \( \text{H}_2 \) yield and operating parameters of typical gasifiers. It is found that the hydrogen yield reaches 80-130 g\( \text{H}_2 \)/kg biomass with 50 % molar concentration in the product gas, which reaches a heating value of 15 – 20 MJ/m\(^3\). The biomass is introduced into a gasifier at an operating temperature of 1000 – 1500 K.

| Biomass     | T (°C) | Steam-biomass ratio | \( \text{H}_2 \) yield (%) |
|-------------|--------|----------------------|----------------------------|
| Pine & eucalyptus | 880     | 0.8                  | 41                         |
| Pine sawdust  | 750     | 0.5                  | 40                         |
| Mixed sawdust | 750     | 0.51                 | 62.5                       |
| Mixed sawdust | 800     | 4.7                  | 57.4                       |
| Mixed sawdust | 800     | 1.4                  | 48.8                       |
| Mixed sawdust | 800     | 1.1                  | 46                         |
| General biomass | 777     | 1.5                  | 59                         |

7. Thermo-chemical water splitting by redox processes

Nearly all (pure) thermo-chemical water-splitting cycles (i.e. closed loop reaction sequences operated predominantly with thermal energy inputs) published to date can be grouped into one of the five generic classes shown in Table 4 [25-27].

| Classes | Production cycles* |
|---------|---------------------|
| Class 1: Metal-metal oxide cycles | \( \text{M} + \text{H}_2\text{O} \rightarrow \text{MO} + \text{H}_2 \) \( \text{MO} \rightarrow \text{M} + 0.5 \text{O}_2 \) |
| Class 2: Metal oxide-metal hydroxide cycles | \( \text{M} + 2\text{H}_2\text{O} \rightarrow \text{M(OH)}_2 + \text{H}_2 \) \( \text{M(OH)}_2 \rightarrow \text{MO} + \text{H}_2\text{O} \) \( \text{MO} \rightarrow \text{M} + 0.5 \text{O}_2 \) |
| Class 3: Metal oxide – metal sulfate cycles | \( \text{MO} + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{MSO}_4 + \text{H}_2 \) \( \text{MSO}_4 \rightarrow \text{MO} + \text{SO}_3 \) \( \text{SO}_3 \rightarrow \text{SO}_2 + 0.5 \text{O}_2 \) |
| Class 4: Metal – metal halide cycles | \( \text{M} + 2\text{HX} \rightarrow \text{HX}_2 + \text{H}_2 \) \( \text{HX}_2 \rightarrow \text{M} + \text{X}_2 \) \( \text{X}_2 + \text{H}_2\text{O} \rightarrow 2\text{HX} + 0.5 \text{O}_2 \) |
| Class 5: Metal oxide – metal halide cycles | \( \text{M} + \text{H}_2\text{O} \rightarrow \text{MO} + \text{H}_2 \) \( \text{MO} + 2\text{HX} \rightarrow \text{HX}_2 + \text{H}_2\text{O} \) \( \text{HX}_2 \rightarrow \text{M} + \text{X}_2 \) \( \text{X}_2 + \text{H}_2\text{O} \rightarrow 2\text{HX} + 0.5 \text{O}_2 \) |

*\( \text{M} \) can be interpreted as either a zero-valent metal or the lower valency state of an oxide pair or halide pair.

Of course, other types of cycles are possible for hybrid electro-thermochemical cycles that include one or more electrolytic steps with work energy (electricity) input. Other types of cycles can also be derived for other forms of work energy input, such as photolysis. Myriad combinations of these five classes can be made. In general, however, the simpler schemes are expected to be more desirable in terms of both efficiency and capital cost.
No two-step thermochemical cycles, the metal – metal oxide cycles (Class 1 in Table 2) are known to be operable within the temperature range of interest below 1500 K. Two-step cycles theoretically might be constructed from metal – metal hydride pairs, but none have been reported. Many compounds theoretically form three-step cycles of the metal oxide – metal hydroxide Class 2 or the metal oxide Class 1. The Los Alamos Scientific Laboratory and Westinghouse Electric Corp. research can be considered a member of both Class 2 with $M = \text{sulfur dioxide}$ and of Class 3 with $\text{MO} = \text{water}$.

Both operating temperature of the carrier redox-cycles are very high ($\geq 1000 \, \text{K}$), hence limiting the application again to situations where cheap thermal energy is available. However, these redox cycles are not entirely reversible, reducing the process efficiency with the number of cycles [25-27].

Possible developments could evaluate:

- The development of mixed metal oxides, to achieve a near complete reversibility (but still operating at $> 1100 \, \text{K}$);
- The selection of redox pairs operating at lower temperatures, e.g. $\text{Cr}_2\text{O}_3$ and $\text{SrO}$, where temperatures are reduced to $< 1000 \, \text{K}$;
- The use of $\text{H}_2\text{O}$, $\text{NH}_3$ and $\text{CO}_2$ mixes, together with $\text{KI}$, where the maximum temperature of the 4-step reaction is 900 K.

8. Biological hydrogen production processes

Bio-hydrogen research has increased [20, 28-30]. It has been demonstrated that it can utilize anaerobic bacteria in dark fermentation bioreactors, or can use algae in the photo-fermentative process [28, 31-32]. The main processes include the photolytic process to produce hydrogen from water using the green algae, the hydrogen production using the dark-fermentative process of anaerobic digestion, the two-stage dark/fermentative process of anaerobic digestion, the two-stage dark/fermentative process, the photo-fermentative processes. The biological methods have a low environmental impact and fair hydrogen production efficiency. By using the anaerobic microorganisms the dark fermentation reaction is carried out to convert carbohydrates to hydrogen and other final products [20], according to:

$$\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{COOH} + 2\text{CO}_2 + 4\text{H}_2$$

The low hydrogen production capacity compared with high unit capital investment has been investigated and remains the major challenge of the dark fermentation method.

9. Conversion of methane (or hydrocarbons)

$\text{H}_2$ produced from methane or hydrocarbons, is the most common method of producing commercial bulk hydrogen. Very little research is required, since processes have been known for over 50 years. Only the direct thermal splitting of $\text{CH}_4$ is a novelty, but temperatures in excess of 1500 K are required.

The principles are illustrated below, for the sake of completeness.

Steam reforming converts methane in a natural gas using steam, sometimes referred to as steam methane reforming (SMR) and is the most common method of producing commercial bulk hydrogen. At high temperatures (700 – 1100 °C) and in the presence of a metal-based catalyst (nickel), steam can react with methane to yield carbon monoxide and hydrogen. These two reactions are reversible in nature [33].

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$$

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$$

The efficiency of the process is approximately 65 % to 75 %. $\text{CO}_2$ must be sequestered.

10. Methanol to hydrogen

Since $\text{H}_2$ is difficult in transport and handling, methanol is now considered as a cheap and abundant source of $\text{H}_2$, since it contains 12.6 wt% of $\text{H}_2$. Methanol is now widely produced from the gas phase associated with crude oil extraction, from biochemical production, or even as fermentation by-product. Whereas initial technologies were conducted at high temperature and pressure ($> 200 \, \text{°C}, 20 - 50 \, \text{bar}$), the current development looks at a catalytic low-temperature dehydrogenation processes, preferably in aqueous medium, at ambient pressure and temperature (≥ 100 °C). This has been the focus of research of Oxford University (copper nanoparticles in zinc gallium oxide) [33, 34] or using $\text{CuZnGaO}_x$, $\text{CuZnAlO}_x$ as examined by East China University (Shanghai) [33, 34].
Clearly, there is scope for further development to provide a decentralized H₂ production from a transportable and cheap CH₃OH, a low T, P process, a further nanoparticle-based catalysis, and the demonstration of catalyst durability and maintained selectivity (low to no CO produced).

11. The H₂ technology efficiencies
The H₂ technology efficiencies are summarized below in Table 5.

| Technology                        | Feed stock          | Efficiency | Maturity  |
|-----------------------------------|---------------------|------------|-----------|
| Alkaline electrolyser             | H₂O + Electricity   | 50% - 60%  | Commercial|
| PEM electrolyser                  | H₂O + Electricity   | 55% - 70%  | Near term |
| Solid oxide electrolysis cells    | H₂O + Electricity + Heat | 40% - 60%  | Med term  |
| Steam reforming                   | Hydrocarbons        | 70% - 85%  | Commercial|
| Partial Oxidation                 | Hydrocarbons        | 60% - 75%  | Commercial|
| Auto-thermal reforming            | Hydrocarbons        | 60% - 75%  | Near term |
| Ammonia decomposition             | Ammonia             | 28.3%      | Near term |
| Biomass gasification              | Biomass             | 35% - 50%  | Commercial|
| Photolysis                        | Sunlight + Water    | 0.5%       | Long term |
| Dark fermentation                 | Biomass             | 60% - 80%  | Long term |
| Photo fermentation                | Biomass + Sunlight  | 0.1%       | Long term |
| Thermochemical water splitting    | H₂O + Heat          | NA         | Long term |

12. Possibilities for additional research
From the extensive and up-to-date review, there are clear indications on what can or needs to be done.
(i) There is only a limited scope for research in:
- Electrolysis (catalyst + electrode development, only);
- Thermal water splitting (no cheap energy source);
- Conversion of methane.

(ii) There is scope for development of:
- Thermo-catalytic conversion routes from biomass (ER ratio, tar reduction, H₂/CO₂ separation, etc.);
- Thermo-chemical redox systems, especially to improve the long duration reversibility of the MOx carriers, and/or the developments of novel redox pairs operating at lower temperature;
- Methanol-to-hydrogen processes, especially towards catalyst viability and durability, and investigating different compound catalysts to operate at low temperature.

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