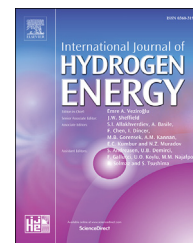


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# Hydrogen: A brief overview on its sources, production and environmental impact

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## ABSTRACT

A brief overview is presented involving the terms of availability of hydrogen, its properties and possible sources and its production methods, and finally, its relationship with renewable energy utilisation, environment and climate.

Solar hydrogen, preferably obtained from water, is confirmed once more to be the most environment and climate compatible (causing the least damage), energy source; though not necessarily the most economic one. Production cost of hydrogen obtained from terrestrial biomass, is not the lowest either, however carbon-neutral feature of terrestrial biomass renders it highly desirable in view of steep rise in global temperature.

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## Introduction

Growth in population and economy in the world are directly proportional to fossil fuel utilisation and environment deterioration [1–3]. The present situation in this relationship is shown in Table 1 [4–8]. Presently, 81% of total primary energy supply, and 66% of electricity generation are based on fossil fuels (coal, natural gas and oil), leading to almost 100% of CO<sub>2</sub> emissions in the world [9]. At current consumption rates, world's proven coal, oil and natural gas reserves are expected to last for approximately 200, 40 and 60 years. Peak production rates of liquid fuels, and natural gas seem likely to occur in 2005–2015 and in 2030 [10]. Afterwards, the overall resources will be in decline.

Sustainability of conventional fuels has been a major concern because of their depletable nature. Presently, the concern is rather focused on the rise in global temperature

mainly due to GHG (greenhouse gas) emissions resulting from their processing and combustion [11].

Owing to efforts in the direction of transition to low carbon energy technology, experts hope to “bend down” the GHG emission curve by 2020 [12]. Cutting down the rate of global warming to 1.5 °C is another goal on which IPCC and COP are jointly working [13,14]. Using hydrogen as a fuel will definitely contribute to that effect.

A “sustainable energy source” would be one that is not substantially depleted by continued use, does not involve significant pollutant emissions or other environmental problems, health hazards or social injustices [15]. Renewable energy forms, especially hydrogen produced from water using solar energy comes very close to this definition.

Various studies are available involving all aspects of hydrogen technology and the rationale for the hydrogen energy system [16–21] including the present energy system, its depletable fossil fuels and their adverse effects on the

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**Table 1 – Worldwide fossil fuel consumption and environmental damage 2015–2016 [4–8].**

<b>Fossil fuel used [4]</b>	(in $10^{18}$ J per year)
Coal	112.5
Petroleum	208.6
Natural gas	126.6
Total	447.8
<b>Damage on Environment [5,6]</b>	(in $10^9$ \$)
Coal	522.0
Petroleum	442.8
Natural gas	252.0
Total	1216.8
<b>Effect on Economy and Society</b>	
Population (total) [7]	$7.4 \times 10^9$
Distribution of damage	\$ 164.4 per capita
Gross world product (WP) [8]	\$ $74,152.5 \times 10^9$
Distribution of WP	\$ 10,020.6 per capita
Total damage/WP	0.0164

environment and climate change [22], the critical role of hydrogen as an energy currency [23], and issues related to climate change and hydrogen energy [1–3].

In the present study, a brief overview on hydrogen is presented including its sources, main production methods, and positive impact on the environment and global warming, with emphasis on rapidly informing the readers especially who are new to or outside of the field regarding the urgency of acceptance of hydrogen as an alternative. Possibility of wider information on the subjects covered is offered through cited references most of which are review papers.

## Hydrogen

Hydrogen is not readily available on Earth in elemental form. However, it can be produced from its compounds found in natural or industrial sources. Hydrogen is the most abundant element in the universe, making up approximately 75% of all matter [24]. In Earth's crust, it is the tenth most abundant element, and it is found in combination with other elements. Hydrogen is not found in Earth's atmosphere since the Earth's gravitational pull is not strong enough (unlike Jupiter and Saturn) to retain the light weight  $H_2$  molecules. Scientist believe that helium and hydrogen, were the first elements formed in the early stages of cosmic evolution.

Three isotopes of hydrogen are available: protium, deuterium and tritium. Consisting of one proton and one electron, protium is the main component of hydrogen, the simplest element. Although it is the lightest element, hydrogen has the highest energy content per unit mass among all fuels. Some of its properties are given in Table 2 [16].

Hydrogen is scarce on Earth's surface (0.14%), and it is found only in trace amounts (0.07%) in the atmosphere. Though quite uncommon, presence of hydrogen has been encountered in larger amounts in some wells containing nitrogen [25]. Small amounts of hydrogen may exist in mixtures with natural gas in crustal reservoirs.

Although a variety of technology at different scales have been developed for hydrogen as an energy carrier, it is widely used as chemical feedstocks in the industry.

**Table 2 – Properties of hydrogen [16].**

Molecular weight	2.016	Amu
$\rho$ (gas)	0.0838	kg/m <sup>3</sup>
HHV	141.90	MJ/kg
	11.89	MJ/m <sup>3</sup>
LHV	119.90	MJ/kg
	10.05	MJ/m <sup>3</sup>
T (boiling)	20.3	K
$\rho$ (liquid)	70.8	kg/m <sup>3</sup>
Critical point		
temperature	32.94	K
pressure	1284	kN/m <sup>2</sup>
density	31.40	kg/m <sup>3</sup>
T (self-ignition)	858	K
Ignition limits in air	4–75	(vol%)
Stoichiometric mixture in air	29.53	(vol%)
T (flame)	2318	K
D	0.61	cm <sup>2</sup> /s
C <sub>p</sub>	14.89	kJ (kg.K)

Wide-scale use of hydrogen as a fuel would lead to escalation in production capacity by several folds. The energy input for hydrogen production is always greater than the energy output from hydrogen. Consequently, energy, as well as feed stocks, will be required to obtain hydrogen. Considering the levels of energy consumption in the world and the adverse effects of the present fossil based energy sources on the environment, renewable energy sources are ideal for sustainable hydrogen production [26,27].

## Hydrogen production methods

Hydrogen gas has an important role in industrial processes, mostly as feedstocks. Presently, fossil fuels constitute the main sources for hydrogen production. Chemical grade hydrogen is possible by water electrolysis. Approximately 95% of the hydrogen produced is used captively [24]. As utilisation of hydrogen as a fuel grows and as global temperature keeps rising, it will be necessary to produce it at larger scale using diminishing amounts of fossil resources. Several detailed reviews on overall evaluation of hydrogen production methods are available [18,28–41].

Methods are available for hydrogen production from fossil fuels [16,42–63], especially from methane, the main constituent of natural gas [16,47–53,55–59] and coal [16,42,58,61–63], from biomass [16,60,63–80], water [16,81–137]; compounds like metal hydrides [16,138–142] and  $H_2S$  [143–152] and biological sources [16,153–165].

Various studies on hydrogen production costs are also available [11,21,28,34–37,40,41,71], allowing comparison of methods [18,28,107]. The results for solar hydrogen from water are presented in Table 3 [107] as an example.

Fossil based hydrogen production methods have commercialized mature technologies established at higher efficiency and lower product cost ranges. Natural gas is mostly methane, and the SMR (steam reforming of methane) process is widely used for hydrogen production from natural gas, at an efficiency range of 65–75%. Another process is partial oxidation of natural gas which has lower efficiency 50% [16]. For

**Table 3 – Production cost of solar hydrogen relative to commercial hydrogen [107].**

Solar process	Detail	Cost/(cost) <sub>j</sub>	Coast/(cost) <sub>k</sub>	Cost/(cost) <sub>l</sub>
Water:				
a) Electrolysis	PVE (solar cell panels)	3.9	15.2	22.8
b) Electrolysis	STE (parabolic dish + steam turbine)	1.1	4.4	6.6
c) Electrolysis	STE (solar tower + steam turbine)	2.6	10.1	15.15
d) Thermolysis	SPH (parabolic dish)	3.3	12.5	18.75
e) Hybrid thermolysis	(b + d)	2.2	8.6	12.9
Coal:				
f) Solar gasification	SPH (solar tower) + KT type gasifier	0.8	2.9	4.35
g) Hybrid solar coal gasification	(f + commercial KT Process)	0.7	2.6	3.9
Thermochemical:				
h) Solar cycle	SPH (solar tower) + GA TC	1.9	7.3	10.95
i) Hybrid cycle	Mark 11 TC	1.6	6.2	9.3
Commercial Process:				
j) Electrolysis (water)	\$ 0.10/kWh	1.0	3.8	5.0
k) Gasification (coal)	\$ 10/ton coal, 15% FCR	0.3	1.0	1.5
l) SMR (Natural Gas)	[150]	0.2	0.67	1.0

GA: General Atomic.  
KT: Koppers Totzek.  
PVE: PV electricity.  
SPH: Solar process heat.  
STE: Solar thermal electricity.  
TC: Thermochemical cycle.

coal gasification, Koppers-Totzek process is the leading technology, capable of producing up to 97% pure hydrogen. It may be possible to keep fossil-based hydrogen production in practice in the near term and mid term through application of carbon sequestration [54–58] and solar thermal processes [53,62,63,102,110].

Hydrogen can also be produced from **biomass** via pyrolysis/gasification [64–80] using a process similar to gasification of coal. However, since biomass has lower calorific value than coal larger size plants are required. Thermal methods are quite suitable for hydrogen production from bio-oil [77] and biogas [78], derivatives of biomass. Photochemical [79] and photoelectrochemical [80] processes based on photocatalytic degradation of organic matter, are being developed with the purpose of producing electricity and hydrogen from organic waste.

Various methods of hydrogen production from **water** are available including electrolysis [81–104], direct thermal decomposition or thermolysis [105–107], thermochemical processes [108–121] and photolysis [122–135].

The efficiency levels for water electrolysis may vary from 70 to 90% [81,92]. Various plants for PV electrolysis are operational world over [95–99]. Electrolysis by electricity from concentrated solar power (CSP) [100] or wind [103,104] is also possible. Based on life cycle analysis (LCA) studies [88], it has been shown that electrolysis processes powered by electricity from renewable energy sources have low global warming potential (GWP), less than 5 kg CO<sub>2</sub> eq/kgH<sub>2</sub>, wind electrolysis having the lowest. Whereas for electrolysis using electricity from the grid, GWP can be as high as 30 kg CO<sub>2</sub> eq/kg H<sub>2</sub>.

**Thermochemical** hydrogen production from water is possible through single step or multi step processes. Above 2000 K direct thermal decomposition of water is possible [105–107]. The extent of single-step water dissociation varies directly with temperature (from 1% at 2000 K to 34% at 3000 K).

Lowering pressure has a favourable effect on the process. Hydrogen can be produced at relatively lower temperatures, through thermochemical cycles [16,108–121], where dissociation of water into hydrogen and oxygen is possible through two or more successive reaction steps involving redox materials such as sulfur and some metal oxides. Sulfur-based cycles can be operated at lower temperatures ( $T < 1200$  K) relative to metal oxide cycles [114]. Nearly 2000–3000 thermochemical cycles have been studied, 20–30 of which may be suitable for large-scale hydrogen production. Efficiencies up to 40–50% can be reached with thermochemical cycles. Some examples are H<sub>2</sub>SO<sub>4</sub>–I<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>–HBr, CaBr<sub>2</sub>–Fe<sub>2</sub>O<sub>3</sub> (UT-3) and FeCl<sub>2</sub> (Mark 9) cycles [83,108,119]. Thermochemical methods are suitable for high temperature solar energy utilization through CSP systems [105–107,110–114] and nuclear heat [110,119–121].

Hydrogen can be released from water via light-driven methods involving photobiological [123–126], photochemical [123,129–134] and photoelectrochemical systems [123,135–137]. These methods are at early stages of development and have considerably low efficiency levels presently. However anticipation for new break through via discovery of new catalytic materials continue.

Hydrogen production is possible through pyrolysis and hydrolysis of **metal hydrides**. Lithium and magnesium hydride (LiH, MgH<sub>2</sub>), lithium and sodium borohydride (LiBH<sub>4</sub>, NaBH<sub>4</sub>), lithium and sodium aluminium hydride (LiAlH<sub>4</sub>, NaAlH<sub>4</sub>) are often considered [16,138–142].

**Hydrogen sulfide** is a potential source for hydrogen production and technology is being developed involving thermal, thermochemical, electrochemical, photochemical and plasmochemical methods that are at different levels of maturity [143–152].

**Biohydrogen** production with (micro)organisms [153–165] is a relatively new area involving direct and indirect

biophotolysis of water; photo and dark fermentation, and microbial electrolysis of organic matter by bacteria. In biophotolysis, special microorganisms such as green algae and cyanobacteria produce hydrogen by consuming and splitting water through their natural metabolic processes using sunlight [124–126,153–158]. Photodecomposition of organic compounds by photosynthetic bacteria [157–161] when exposed to near IR light, purple bacteria (non-sulfur) can produce hydrogen (with a special enzyme) by breaking down organic material. In dark fermentative hydrogen production from organic compounds [162–165] anaerobic bacteria can decompose organic material (without the aid of sunlight) into hydrogen and other products. In microbial electrolysis [155,156,165] a low voltage is produced at the anode of the cell as the bacteria decompose organic material. Hydrogen is produced at the cathode. Generally, additional energy is required. Hybrid biohydrogen systems are integrated systems where byproducts of one approach serve as inputs to another [124,154] and hydrogen is produced as a result.

Light-driven biohydrogen methods such as biophotolysis and photofermentation are mostly limited by low light conversion efficiencies. In dark fermentative processes, yields are limited by metabolic routes [155]. Microbial electrolysis cannot be self-sustaining since for improved yields, supply of excess voltage is required. Hybrid systems are considered for improving the performance of biohydrogen processes.

#### Evaluation and future possibilities for methods

Fossil based centralized hydrogen production methods have commercial, mature technology and established feedstock infrastructure. Although carbon sequestration helps extend utilization of fossil-based technology, large scale land damage caused due to extraction of fossil fuels and risk of oil spills in oceans during transportation of petroleum by tankers still remain to be dealt with.

Water electrolysis has well developed technology and uses electricity from the grid and the existing infrastructure. These present technologies are expected to supply the near-term hydrogen market as well.

Steam reforming of natural gas and coal gasification with carbon capture may continue during the midterm hydrogen market along with gasification of biomass and reforming of liquid fuels derived from biological sources, some of which already have infrastructure present.

The long term, hydrogen market may be supplied by water electrolysis using renewable electricity, thermochemical cycles; even by biological and photoelectrochemical methods; all with clean and sustainable technologies.

#### Economic aspects

Relatively new hydrogen production technologies, including the ones using renewable energy are not as costwise competitive presently, although they are highly pollution-free.

In the case of fossil-based (natural gas, oil and coal) hydrogen production, cost of manufacturing is lower than the “environmental cost” of using the fuel itself. Since that cost is negligible for hydrogen, it would be only logical to produce hydrogen from these fuels instead of directly using them.

Various studies evaluating hydrogen production methods in terms of efficiency, cost and environmental impact are available [18,21,28,88]. In view of these studies, hydrogen from water by thermochemical methods and by electrolysis using solar energy; hydrogen from biomass and fossil fuels using carbon sequestration may become mainstream hydrogen production technologies with large-scale plant capacities. However, small-scale distributed hydrogen production may also be possible via reforming of natural gas and water electrolysis using renewable electricity from the grid.

#### Hydrogen, environment and climate change

Main alternatives to the presently established fossil fuel energy system are the coal/synthetic fossil fuel system and the solar hydrogen system [16], although they are not equivalent in terms of environmental impact. Synthetic fossil fuels may offer convenient production routes, but they may involve equally or even more polluting processes compared to regular fossil fuels. On the other hand, solar hydrogen offers a clean and permanent energy system since renewable solar energy and/or its derivatives (i.e. hydro, wind, wave) are used as primary energy inputs for production of hydrogen, a secondary energy source, also environmentally compatible [16].

In view of the three energy systems, environmental factors like pollution, vapor generation and environmental damage are at significantly low levels for the solar hydrogen energy system compared to the other energy systems (Table 4).

**Table 4 – Environment related properties of the main energy systems [23].**

Energy system	Pollutants (kg/GJ)						Vapor generation (10 <sup>12</sup> kg/y)			Environ-mental damage ratio <sup>c</sup>	Environ-mental compatibility factor
	CO <sub>2</sub>	CO	SO <sub>2</sub>	NO <sub>x</sub>	HC	PM <sup>a</sup>	Energy system	Global warming	(%) <sup>b</sup>		
Fossil fuel	72.40	0.80	0.38	0.34	0.20	0.09	8.9	3900	0.782	18.24	0.055
Coal/Synthetic fossil fuel	100.00	0.65	0.50	0.32	0.12	0.14	9.3	3900	0.782	22.62	0.044
Solar-hydrogen energy	0.00	0.00	0.00	0.10	0.00	0.00	6.0	0.0	0.001	1.0	1.00

<sup>a</sup> Particulate matter.

<sup>b</sup> With respect to annual vapour generation due to solar heating ( $5 \times 10^{17}$  kg/y).

<sup>c</sup> (Damage due to fuel)/(Damage due to solar hydrogen).



The disadvantages of the coal/synthetic fuel system and the advantages of the solar hydrogen system can be seen in Table 4 [16,23]. Emissions of CO<sub>2</sub>, CO, SO<sub>x</sub>, hydrocarbons and particulates are eliminated in the solar hydrogen system; NO<sub>x</sub> will not form if flame combustion in air is avoided [16].

In Table 4 [16,23] In addition to depletion of natural resources, the adverse consequences of fossil and nuclear fuel utilisation at current rates include global warming, leading to climate change, acid rain, and risk of nuclear radiation. Following industrial revolution, greenhouse gases (mainly CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O) emitted during combustion of fossil fuels have been contributing to the accelerating increase in the Earth's surface temperature. Whereas, originally, same gases (produced naturally in right proportion) have been instrumental in maintaining the global temperature around 15 °C [15] keeping incoming solar radiation at equilibrium with outgoing infrared energy.

Based on carbon dioxide data from 1958 (measured at Mauna Loa, Hawaii) and pre-1958 data (estimated from ice cores), scientists estimate that during the twentieth century these 'anthropogenic' emissions caused a rise in the earth's global mean surface temperature of 0.6 °C [166].

For half a million years before the twentieth-century, atmospheric concentrations of CO<sub>2</sub> have varied between about 200 and 300 parts per million by volume (ppmv). But during the twentieth century they rose beyond this range, increasing to 370 ppm by 2001. Projections by the Intergovernmental Panel on Climate Change (IPCC) suggest they could rise to around 700 ppmv by the end of the twenty-first century if no action is taken to limit emissions. The projection shown for 2100 is near the middle of the IPCC range [15]. If emissions are not reduced, the surface temperature is predicted to rise by 1.4–5.8 °C by the end of the twenty-first century, leading to frequent extremes in climate and about 0.5 m rise in sea levels resulting in inundation of low lands. Reduction in emissions in the range of 60–80% may be necessary for slowing down the process, which may be possible by switching to carbon-free energy.

Activities directed towards reversing the process of climate change have been accelerated since the eighties, and they are becoming more focused on commitment acts from states [167,168]. Perceived as a scientific and political issue, climate change has been under investigation by scientists for the past hundred years [167–177]. The possibility of changes in climate due to increase in accumulation rate of CO<sub>2</sub> in the atmosphere was first brought up by the Nobel laureate S. Arrhenius in 1879 [169].

In the 1st World Climate Conference which was held in 1979 under the auspices of World Meteorological Organisation (WMO), the subject of climate change was brought to public attention, and it was concluded that, long term dependence on fossil fuels and deforestation would result in CO<sub>2</sub> accumulation in the atmosphere which in turn would lead to variations in climate. Through a joint initiative of WMO and United Nations Environmental Program (UNEP), The Intergovernmental Panel on Climate Change (IPCC) was formed and held its 1st meeting in November 1988. First Evaluation Report of IPCC [170] was issued in August 1990. A supplement followed in 1992 [171].

One of the significant initiatives for keeping or reducing the greenhouse gas emissions at a certain level was the UN

Framework Convention on Climate Change in June 1992, which was signed by 166 countries and the European Union (EU) within a year and which came into effect on March 21, 1994. Thus, the concept of sustainable growth started maturing.

The Kyoto Protocol involving an agreement for 5% reduction in GHG emissions was concluded in 1997. The protocol came into effect on February 16, 2005.

Various national initiatives against environmental damage and air pollution were also taken. The Clean Air Act in 1963 and the Clean Air Act Amendments (CAAA) in 1990 of the United States, the Canadian Environmental Protection Act (CEPA) in 1988 [173], and emission control regulations in European Union [174] in 1998 can be mentioned as fundamental examples. Regulations for emission control limit the extent to which plants and vehicles impact air quality. The emission characteristics can be influenced by the level of emission standards, required emission durability, fuel composition and in-use inspection and maintenance [175,176].

The Kyoto Protocol in 1997 [177] did not impose binding targets for the biggest polluters such as US, China and India.

The Paris accord in November 2015 invited more than 190 countries to cut down emissions within a United Nations sponsored plan allowing 2°C increase in temperature in terms of voluntary commitments for targets that involve measurement and report of progress, but that are not legally binding. For example, China's emissions may subside after 2030, and 28–30% decrease in GHGs may be considered in US by 2025. However, despite all pledges, 3.4 °C rise in global temperature seems inevitable in 21st century. The countries that are under risk of inundation by rising seas are naturally alarmed [178].

In COP23 held in Bonn (06–17 Nov. 2017) the tolerable increase in temperature has been targeted as 1.5 °C [14]

## Hydrogen and terrestrial biomass

Terrestrial biomass is a renewable, widespread and abundant energy source which captures carbon dioxide (CO<sub>2</sub>) that leads to the green-house effect in the atmosphere, through photosynthesis and keeps it within the carbon cycle [15,179]. Application of biochar, obtained from terrestrial biomass via pyrolysis, to soil [180] can provide a sink for CO<sub>2</sub> from the atmosphere. Solid biomass resources, a great majority of which are lignocellulosic, can be converted into gaseous fuels through thermochemical gasification involving successive drying, pyrolysis and gasification in the reactor stage. Mainly, hydrogen (H<sub>2</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrogen (N<sub>2</sub>), particulates, tar, ammonia (NH<sub>3</sub>) and sulfur compounds are generally found in the resulting 'product gas'. Hydrogen is separated from synthesis gas (H<sub>2</sub> + CO) which is obtained from 'product gas' following cleaning, reforming and shift processes. Before separation of hydrogen, the mass lower heating value (LHV<sub>mass</sub>) of the product gas may be around 4.65 MJ/kg [181,182], and the overall efficiency of the process is estimated as over 80% [181,183,184]. Electricity production with high efficiency (>70%) [185] is possible as well, via combining catalytic biomass gasification with solid oxide fuel cells (SOFC), in decoupled (external gasification) or direct (internal gasification) mode [186–189].

With this technology, 50% reduction in GHGs is anticipated using low cost/readily available feed stocks (biomass, tar, plastics, etc ...). Since less CO<sub>2</sub> production in pure form is expected, less carbon sequestration and less gas separation loads can be considered as additional gains [186].

## Conclusion

Economic development, energy utilization, environment and climate are interrelated but “securing energy and environment at lowest cost” is becoming increasingly difficult. Although climate change has both natural and anthropogenic components, global warming due to greenhouse gases, especially CO<sub>2</sub>, is the main contributor to anthropogenic climate change. According to current estimates, CO<sub>2</sub> content of the atmosphere will approach 400 ppm by 2010, and 600 ppm during the second half of the 21st century.

Even if all the pledges of the Paris agreement in November 2015 are met, the global temperature is expected to increase by 3.4 °C within the present century. Consequently, in COP23 (Bonn, 2017) a tolerable limit of 1.5 °C rise has been agreed on.

The best alternative would be to sustain the economic growth level by switching to hydrogen economy and using renewable energy sources. Hydrogen produced from water and terrestrial biomass using solar energy will be the most sustainable energy currency in the long term. Timely implementation of educational, financial, legislative, social and technological initiatives are necessary to make this happen.

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