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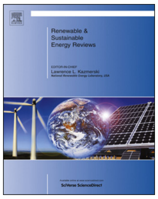

Hydrogen: A sustainable fuel for future of the transport sector

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ABSTRACT

Mobility (transport of people and goods) is a socio-economic reality and need for which is bound to grow in the coming years. Modes of transport should be safe, economic and reasonably environmental friendly. Hydrogen could be ideal as a synthetic energy carrier for transport sector as its gravimetric energy density is very high, abundantly available in combined form on the earth and its oxidation product (water) does not contribute to greenhouse gas emissions. However, its sustainable production from renewable resources economically, on-board storage to provide desirable driving range, usage in durable energy conversion devices and development of infrastructure for its delivery remain significant challenges. In this article, recent developments in the field of production, storage, transport and delivery of hydrogen along with environmental and safety aspects of its use as an energy carrier are presented. Almost any energy source can be used to produce hydrogen. Presently, non-renewable sources dominate hydrogen production processes but the need of the hour is to develop and promote the share of renewable sources for hydrogen production to make it completely sustainable. Hydrogen may be used as fuel for almost any application, where fossil fuels are used presently and would offer immediate benefits over the conventional fuels, if produced from renewable sources. For achieving a successful "hydrogen economy" in the near future, the technical and economic challenges associated with hydrogen must be addressed quickly. Finding feasible solutions to different challenges may take some time but technological breakthrough by way of on-going efforts do promise hydrogen as the ultimate solution for meeting our future energy needs for the transport sector.

Contents

Abbreviations: GHG, greenhouse gas; CNG, compressed natural gas; DME, dimethyl ether; Bcm, billion cubic metres; btoe, billion tonnes of oil equivalent; SMR, steam methane reforming; POX, Partial Oxidation; CPOX, Catalytic Partial Oxidation; PEC, photoelectrochemical; PV, photovoltaic; CG, coal gasification; BG, biomass gasification; FCNF's, functionalised carbon nanofibres; TW, terawatt

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1. Introduction

Energy production for growing needs and associated environmental challenges are twin issues of paramount interest that require our serious attention in the 21st century [1]. The global primary energy demand was estimated to be 13.371 billion tonnes of oil equivalent (btoe) in 2012 by International Energy Agency and is projected to reach 18.30 btoe in 2035 in current policies scenario, representing a growth rate of 1.37% [2]. To satisfy the world's growing appetite for energy and keep our planet healthy, at least 10 TW (terawatt) of carbon-free power generating capacity has to be created by 2050 [3]. The dramatic increase in the international prices of petroleum in the recent years, the finite nature of fossil fuels, growing concerns relating to adverse environmental impact associated with increasing use of fossil fuels on greenhouse gas emissions, and health and safety considerations are forcing the international community to search for new energy sources and develop alternative ways of powering the world's growing population of motor vehicles [4]. Energy related global CO_2 emissions were estimated to be 30.4 gigatonnes (Gt) in 2010 [5].

At present, a large portion (about 65%) of the world energy demand is met by the liquid and gaseous fossil fuels (i.e., petroleum and natural gas), because of their widespread availability and convenience of use, with petroleum oil being the largest primary fuel contributing a share of more than one third of the global primary energy mix and more than 92% of transport energy demand and balance being provided by natural gas (5%) and electricity 3% [6,7]. However, world's fossil fuel production is expected to peak soon, and thereafter begin to decline. While some energy experts estimate that about half the world's oil production is consumed by road vehicles, the International Energy Agency (IEA) estimates that about 77% of global transport oil demand in 2010 was on account of road transport and the respective shares of biofuel, gas and electricity in transport sector was estimated to be 39%, 3%, and 1% respectively in 2010 [6,8]. By 2050, the global energy demand is projected to double or triple and oil and gas supply is unlikely to meet the demand.

The constantly increasing number of automobiles raises environmental concerns, such as exhaust emissions and global warming, and account for some 18% of primary energy use and some 17% of global CO_2 emissions [9]. Local air pollution (particulate matter, ozone), climate change, congestion, land use, accidents, and noise are particular concerns in this respect. Local air pollution, especially from road transport, is quickly becoming a major issue for urban air quality, particularly in the world's growing megacities. The consumption of fossil fuels is responsible for the increase in the CO_2 in the atmosphere of approximately 3×10^{12} kg/year, a major contributor of global warming [10,11].

The major problem is the fact, that a large amount (approximately 98%) of the CO_2 on earth is dissolved in the water of the oceans (7.5×10^{14} kg C in the atmosphere, 4.1×10^{16} kg C in the oceans). About 2×10^{12} kg C per year dissolves in the water of the ocean. The solubility of carbon dioxide decreases with the increasing temperature of water by approximately 3%/K. If the average temperature of the oceans increases, the carbon dioxide solubility equilibrium between atmosphere and ocean shifts towards the atmosphere and leads to a reduction in the CO_2 flux into the ocean and therefore, to an additional increase of the greenhouse gas in the atmosphere [12].

To resolve the problems of increasing fuel requirement and containing emissions associated with road transport, there is an urgent need to find out solutions for use of energy in vehicles. The principal options are demand-side measures, development and use of more efficient vehicles and use of cleaner alternative fuels that are sustainable like bio-ethanol, bio-diesel, CNG and hydrogen [11]. Bio-diesel, a substitute to petroleum-diesel is derived from vegetable oils, animal fats, and used waste cooking oil including triglycerides. Significant efforts are being made globally for liquid biofuel production from vegetable oils and *Jatropha curcas* L (JCL), which has attracted a lot of attention of investors, policy makers and clean development mechanism project developers. The oil produced by this crop can be easily converted to liquid bio-fuel [13]. Additionally, the press cake can be used as a fertilizer and the organic waste products can be digested to produce biogas. But biofuels alone cannot solve the dual problem of meeting a growing fuel demand for transport sector and reducing emissions.

CNG is another alternative automotive fuel that is being used in many countries. Of all the alternatives, CNG achieves the greatest reduction of 20–25% in CO_2 emissions from vehicles excluding hydrogen and electricity [11]. To further reduce the emissions from CNG, hydrogen can be blended with CNG. The alternatives to petrol and diesel exhibit some kind of constraints and drawbacks. No other fuel is expected to be as easy and cheap to produce and handle as petrol and diesel. While petrol and diesel can be produced from crude oil with high conversion efficiencies, the production of any alternative fuel will generally involve higher conversion losses. Moreover, the gaseous fuels are relatively difficult to handle and require a new distribution and refuelling infrastructure. Energy carriers like hydrogen and electricity even require new elements of drive-train like fuel cells, motors and batteries.

Among the possible alternatives, hydrogen looks promising for transport applications on three counts: GHG emissions reduction, energy security and reduction of local air pollution. The breakthroughs in fuel cell technology in the late 1990s and use of hydrogen in the internal combustion engines without incurring major investments are the main reasons behind the growing interest in hydrogen especially for transport application. Hydrogen is emission-free at the point of final use and thus avoids the transport-induced emissions of both CO_2 and air pollutants. This is also where fuel cells can make the significant impact by way of their high conversion efficiencies compared to the internal combustion engine [7].

According to the report put forward by the European Commission in 2003 and the US Department of Energy in 2004 [4], in many countries hydrogen is considered as an important alternative energy vector and fuel cell as a key technology for meeting energy needs in the stationary power, transportation, industrial and residential sectors on sustainable basis. In the present review, applications of hydrogen, its production methods, properties as a transportation fuel with environmental and safety aspects, its storage and delivery are discussed in the following sections.

2. Applications of hydrogen

Recent literature [14–19] focuses on the applications of hydrogen, covering every sphere of human being's activity – be it industrial, transport, domestic or space. Hydrogen is mainly used in petroleum refineries [20,21], ammonia/fertiliser production [22,23] and, to a lesser extent for metal refining such as nickel, tungsten, molybdenum, copper, zinc, uranium and lead and amounts to consumption of more than 60 million metric tonnes worldwide [24,25]. Hydrogen may be used as fuel in almost any application, where fossil fuels are used presently – particularly for motorising the vehicles, which would offer immediate benefits in terms of reduced pollution and cleaner environment [14,26,27]. Currently hydrogen is being used for synthesis of ammonia and other nitrogenized fertilizers, refining and desulphurisation (hydrogenation reactions, hydrodesulphurization); hydrogenation of hazardous wastes (dioxins, PCBs); chemical plants, food preparation; synthesis of methanol, ethanol, dimethyl ether (DME); alternative fuels synthesis by Fischer–Tropsch (FT) process; gas to liquid (GTL) synthesis technology; rocket fuel; IC engine fuel; high temperature industrial furnaces fuel [28]. Balat et al. have put forward a small report on the world hydrogen consumption, for the production of ammonia, chemical and its use in photochemistry. Out of the total 500 billion cubic metres (Bcm) of hydrogen, ammonia production consumes 250 Bcm followed by production of other chemical products, which consume 65 Bcm, and petro chemistry consume 185 Bcm of hydrogen, accounting for shares of 50%, 13% and 37% respectively [15,28].

Jain reports various application of hydrogen for future such as for electricity generation, as cooking fuel, fuel for automobiles and jet planes, industrial applications, fuel for hydrogen village and for meeting all our domestic energy requirements [16].

Hydrogen finds various prospective energy uses from powering vehicles in a non-polluting manner, heating homes & offices to fuelling aircrafts. On one hand, the use of hydrogen in running city buses, powering mining equipment are few examples of mobile applications that have advanced to demonstration levels and on the other its use in home generators and large electrical generating systems signifies promising utilisation in stationary applications. Hydrogen is a potential fuel having many advantages over its conventional counterparts. However, a widespread and practical use will definitely call for measures for sustainable distribution from the producer to the end-users, more support facilities, fuelling stations and many other new concepts and technologies.

3. Hydrogen production

To many countries in the world, hydrogen is the second most important form of energy carrier next to electricity. Hydrogen can be produced from a variety of feedstock. These include reformation of fossil resources, such as natural gas, oil and coal, as well as renewable resources, such as biomass and also by water splitting either through electrolysis using electricity generated by renewable energy sources (e.g. sunlight, wind, wave or hydro-power) or directly by photo-catalysis. A variety of processes can be used, including chemical, biological, electrolytic, photolytic and thermochemical for its production [29–32]. A detailed overview of various hydrogen production technologies has been reported by Holladay et al. [17]. The common hydrogen production methods include the following.

3.1. *Steam methane reforming*

Steam methane reforming (SMR) is a process by which natural gas or methane containing streams, such as biogas or landfill gas, is reacted with steam in the presence of a catalyst to produce hydrogen and carbon dioxide. According to US DOE report of 2010, when starting with natural gas, SMR is approximately 72% efficient in producing hydrogen on a lower heating value basis [33]. SMR produces a hydrogen rich gas that is typically of the order of 70–75% hydrogen on a dry mass basis, along with smaller amounts of methane (2–6%), carbon monoxide (7–10%), and carbon dioxide (6–14%). About half of the global supply of hydrogen is produced by reforming natural gas [34,35]. Presently, this is the most commonly used method for hydrogen production in view of its favourable economics [14,18]. The reforming of natural gas, however, is not an attractive production route for a sustainable and mature hydrogen economy, because the order-of magnitude increase in demand would deplete the finite natural gas reserves and coupled to it the concentration of gas reserves in a relatively few regions of the world could lead to geopolitical tension and unstable supplies. Consequently, the purpose of achieving energy security, one of the objectives of hydrogen economy would get defeated. Environmental impact is also a major concern, as reforming natural gas to hydrogen produces as much pollution and CO_2 as burning the natural gas directly [36]. On the other hand, hydrogen can be produced from reformation of biogas in decentralised manner in large countries like India and will be carbon neutral. This not only will utlise locally available bio-wastes but also reduce dependence on imported fossil fuels.

3.2. *Auto-thermal reforming of oil*

Partial Oxidation (POX) is an alternative to SMR and is generally preferred with higher hydrocarbons or if pure oxygen is available. With lower product concentration of hydrogen, this process offers lower efficiency in comparison to SMR but offers rapid dynamic response and compactness [37]. POX can be performed with or without catalyst. Catalytic Partial Oxidation (CPOX) can be carried out at relatively lower temperature than 1300–1500 °C used in POX [38,39]. Auto-thermal Reforming (ATR) adds steam to CPOX. It consists of a thermal zone where POX or CPOX is used to generate the heat needed to drive the downstream steam reformation reactions in a catalytic zone. The heat from the POX negates the need for an external heat source, simplifying the system and decreasing the start-up time. A significant advantage of this process over SMR is that it can be stopped and started very rapidly while producing a larger amount of hydrogen than POX alone. For ATR to operate properly both the oxygen to fuel ratio and the steam to carbon ratio must be properly controlled at all times in order to control the reaction temperature and product gas composition while preventing coke formation [17].

3.3. *Gasification of coal and other hydrocarbons*

In the POX process, also known more generally as “gasification,” hydrogen can be produced from a range of hydrocarbon fuels, including coal, heavy residual oils, and other low-value refinery products. The hydrocarbon fuel is reacted with oxygen in a less than stoichiometric ratio, yielding a mixture of carbon monoxide and hydrogen at 1200–1350 °C [40]. Gasification (coal, petroleum coke, and gasification and reforming of heavy oil) also dominates hydrogen production along with steam methane reforming [18,33].

3.4. Electrolysis of water

Electrolysis is the process by which water molecules are split directly into hydrogen and oxygen molecules using electricity in an electrolyser device. The two most common types of electrolysers are alkaline (uses a potassium hydroxide electrolyte) and PEM (uses a solid polymer membrane electrolyte). Hydrogen can be produced via electrolysis of water from any electrical source, including utility grid power, solar photovoltaic (PV), wind power, hydropower, or nuclear power. Electrolysis is currently done at a wide range of scales, from a few kW to up to several MW. The electrolysis reaction produces pure oxygen as a by-product along with pure hydrogen [41]. In contrast, a photoelectrochemical (PEC) water-splitting process is a zero emission process and uses free solar energy to split water in a single step without converting solar energy into electricity firstly and then use it in an electrolyser to split water [42]. However, PEC systems are currently under development and are not commercially available.

Although water electrolysis has been known for around 200 years [43,44] and has the advantage of producing extremely pure hydrogen, its applications are often limited to small scale and unique situations, where access to large scale hydrogen production plants is not possible or economical, such as marine, rockets, spacecrafts, electronic industry and food industry as well as medical applications [18,45,46]. Mustafa Balat reported natural gas to be the major source of hydrogen production accounting 48% of the total share, oil being the second with 30% followed by coal with 18% and electrolysis contributing 4% of the total share [15]. Hydrogen production form electrolysis of water is considered as an energy intensive method and efforts are underway to improve the efficiency of electroysers.

3.5. Hydrogen from biomass

Biomass conversion technologies can be divided into thermochemical and biochemical processes. Thermo-chemical processes obtain higher reaction rates as they can be operated at higher temperatures and, therefore, tend to be less expensive. They involve either gasification or pyrolysis (heating biomass in the absence of oxygen) to produce a hydrogen-rich stream of gas known as “syngas” (a blend of hydrogen and carbon monoxide). They can utilise a broad range of biomass types. Gasification of biomass has been identified as a possible method for producing large quantities of renewable hydrogen in efficient manner, wherever it is beneficial to exploit biomass resources and thereby reducing dependence on insecure fossil energy sources [4,33]. Several processes available to make hydrogen from biomass can yield other useful products/by-products such as adhesives, carbon black, activated carbon, polymers, fertilizers, ethanol, various acids, Fischer–Tropsch diesel fuel, waxes, and methanol.

3.6. Nuclear energy

Various nuclear energy based hydrogen production methods employing either thermal energy or electricity are possible, which include splitting of water using various thermo-chemical processes such as the sulphur–iodine cycle, electrolysis of water using nuclear power, and high-temperature steam electrolysis that would use nuclear system waste heat to lower the electricity required for electrolysis [47].

While the use of nuclear energy for hydrogen production is attractive from a carbon-limiting perspective, it raises other serious environmental and health concerns related to the mining and processing of uranium, the potential for accidents, and the management and disposal of radioactive wastes [41].

3.7. Biological processes

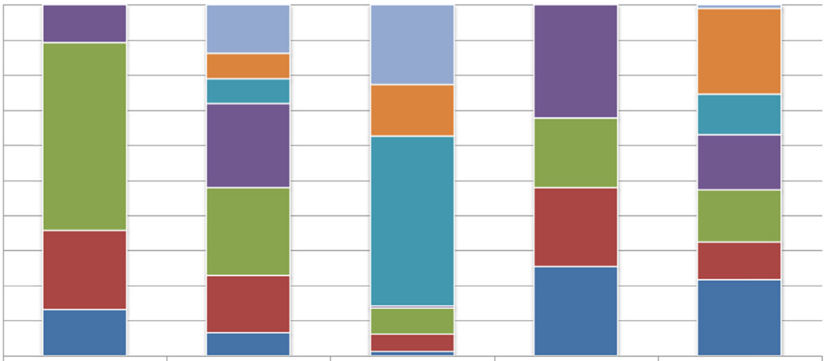
Due to increased attention to sustainable development and waste minimisation, research in bio-hydrogen has substantially increased over the last several years. The main bioprocess technologies used for bio-hydrogen production include: photolytic hydrogen production from water by green algae or cyanobacteria (also known as direct photolysis), dark-fermentative hydrogen production during the acidogenic phase of anaerobic digestion of organic material, photo-fermentative processes, two stage dark/fermentative, and hydrogen production by water–gas shift [17,48–59].

Nitrogenase and hydrogenase play very important role in biological hydrogen production. Sucrose, when used as a substrate, can yield up to 28% of energy in the form of hydrogen. Biological hydrogen production offers advantage over other processes such as electrochemical and thermochemical routes in terms of low energy requirements and lower initial investment cost but suffers comparatively from low conversion efficiencies. Biological experimentation should continue in order to drive up the hydrogen production rate and efficiencies.

A study carried out by Pilavachi et al. compares seven hydrogen production methods namely SMR, POX, coal gasification (CG), biomass gasification (BG), the photovoltaic–electrolysis system (PV–EL), the wind turbine–electrolysis system (W–EL), the hydropower–electrolysis system (H–EL). The comparison has been made based on five criteria's viz. CO_2 emissions, operation and maintenance (O&M) costs, capital cost, feedstock cost and hydrogen production cost using the Analytical Hierarchy Process (AHP) [60]. In the majority of cases, the processes that combine renewable energy sources with electrolysis (PV–EL, W–EL and H–EL) are considered to be better than the conventional processes (SMR, POX, CG and BG) and are higher in ranking. On the contrary, the conventional hydrogen production processes (SMR, POX, CG and BG) rank last in most of the cases. More specifically, in most of the cases the first in ranking hydrogen production process is considered to be the hydropower–electrolysis system (H–EL) and the worst is CG [60] as shown above in Fig. 1.

Presently, SMR, CG and water electrolysis are proven technologies for hydrogen production that are employed on an industrial scale throughout the world. SMR of natural gas is the most widely used process in the chemical and petro-chemical industries and currently is the cheapest method for hydrogen production; and has the lowest CO_2 emission among all fossil production routes for hydrogen production. Electrolysis is preferred if high-purity hydrogen is required but it is more expensive. With an assumed increase in natural gas prices, CG is expected to become the most economical option from around 2030 onwards. BG, though at an early stage of development currently, is expected to become the cheapest renewable hydrogen supply option in the coming decades, although biomass has restricted potential and competes with other biofuels as well as heat and power generation. BG can be applied in small decentralised plants during the early phases of infrastructure rollout and in centralised plants in later periods for hydrogen production. Steam reformers and electrolysers can also be scaled down and implemented for on-site applications at fuelling stations (although still more expensive), while CG or nuclear energy based routes are suitable for large-scale, and central production only, and therefore, suited to later phases with high hydrogen demand [11].

Full benefits of hydrogen as a clean, versatile, and efficient fuel may be realized only if hydrogen is produced from renewable energy sources (solar, wind, biomass) via variety of pathways and methods, but only a few of them are commercially viable currently and these sources may provide local facilities for hydrogen production but certainly will not be able to match the demand



H_2 production process	CO_2 emissions (kg CO_2/kg/H2) (2006)	O & M costs (US\$/(kgH_2/day)) (1993)	Capital Cost (US\$/(kgH_2/day)) (2005)	Feedstock cost (US\$/(kgH_2/day)) (1989)	H_2 production cost (US\$/kgH_2) (2007)
🟦 H-EL	0	30.51	4927.05	0	1.4
🟧 W-EL	0	15.71	3170.86	0	36.75
🟦 PV-EL	0	15.71	10448.56	0	17.36
🟪 BG	5.89	52.56	104.82	194.88	23.78
🟩 CG	29.33	54.9	1637.19	120.15	22.37
🟥 POX	12.35	35.84	1058.17	136.61	16.07
🟦 SMR	7.33	14.51	284.77	154.32	32.75

Fig. 1. Aggregated data for criteria-alternative options [60].

of hydrogen required globally as the new energy source [14,61]. Renewable pathways for producing hydrogen avoid generating global warming pollutants in the first place and, depending on the viability of carbon capture and storage may therefore prove more attractive in the long run. At present, however, these options are generally more expensive. Yet even with CO_2 recovery and sequestration costs included, hydrogen production from fossil fuels is estimated to be much less costly than electrolytically produced hydrogen for large-scale markets [62]. A recent US Energy Information Association report suggests that solar is most likely the only source of energy capable of producing enough hydrogen required by a hydrogen economy [2].

Currently the cost of hydrogen is more than twice as much as that of diesel and petrol on per unit energy basis and substantial progress is needed to make environmentally sustainable hydrogen production pathways cost-competitive vis-a-vis petroleum fuels, even assuming that hydrogen powered vehicles will be significantly more efficient than their conventional gasoline-powered counterparts [28,41].

4. Hydrogen: an efficient transportation fuel

Hydrogen has in the recent years has been attracting a lot of attention as a preferred energy carrier especially for transportation applications due to a number of reasons: (a) it is believed to be a clean fuel, which emits almost nothing other than water at the point of use; (b) it can be produced using any energy sources, with locally available renewable energy being most attractive; and (c) it works with fuel cells and together, they may serve to contribute towards sustainable energy supply [18,63].

Hydrogen is a lightest, colourless, odourless and non-toxic gas [64,65]. Hydrogen has the highest specific energy content of all conventional fuels and is the most abundant element in the universe [4,15]. Hydrogen has a high energy yield of 120 MJ/kg, which is about 2.75 times greater than hydrocarbon fuels but density of liquid hydrogen is much less than gasoline [62]. These properties give hydrogen advantages that it stores approximately 2.6 times more energy per unit mass than gasoline, meaning that hydrogen has higher heating or calorific value than gasoline. But due to its lower volumetric energy density it needs an approximately 4 times more volume than gasoline to store the same energy. Hydrogen can be used as a fuel in an IC engine as it may ensure that the vehicle manufacturers can make use of the existing infrastructure for engine manufacturing and is not vastly different from other gaseous fuels used in the IC the engines [66]. In fact, the blending of hydrogen and ethanol has been used as an alternative to renewable fuel in a carbureted spark ignition engine [67,68].

Balat reported the physical and chemical properties of hydrogen in comparison to gasoline and methane (Table 1). It indicates that hydrogen has a wide range of flammability in comparison with other fuels. Hydrogen engines, therefore, can be operated more effectively on excessively lean mixtures than gasoline engines. 4% Hydrogen by volume along with air produces a combustible mixture. Hydrogen has very low ignition energy (0.02 MJ). Compared to the other fuels, hydrogen has a higher ignition temperature. The hydrogen flame speed is nearly an order of magnitude higher (faster) than that of gasoline. Hydrogen has very high diffusivity.

This ability to disperse in air is considerably greater than gasoline and is advantageous for two main reasons: (1) it facilitates the formation of a uniform mixture of fuel and air, and (2) if a hydrogen leak develops, the hydrogen disperses rapidly. Thus, unsafe conditions can either be avoided or minimised. The very low density of hydrogen results in two problems, when used in an internal combustion engine: (a) a very large volume is necessary to store enough hydrogen to give a vehicle an adequate driving range, and (b) the energy density of a hydrogen–air mixture, and hence the power output, is reduced [15].

Due to its versatile nature, hydrogen, can be converted to other forms of energy in five different ways; i.e., in addition to flame combustion, it can be converted directly to steam, converted to heat through catalytic combustion, act as a heat source and/or heat sink through chemical reactions, and converted directly to electricity through electrochemical processes, whereas the other fuels

Table 1
Physical and chemical properties of three fuel options (hydrogen, methane, and gasoline) [15].

Property	Hydrogen	Methane	Gasoline
Molecular weight (g/mol)	2.016	16.04	~110
Mass density (kg/N m^3) at P =1 atm=0.101 MPa, T=0 °C	0.09	0.72	720–780 (liquid)
Mass density of liquid H_2 at 20 K (kg/Nm^3)	70.9	–	–
Boiling point (K)	20.2	111.6	310–478
Higher heating value (MJ/kg) (assumes water is produced)	142.0	55.5	47.3
Lower heating value (MJ/kg) (assumes steam is produced)	120.0	50.0	44.0
Flammability limits (volume%)	4.0–75.0	5.3–15.0	1.0–7.6
Detonability limits (vol%)	18.3–59.0	6.3–13.5	1.1–3.3
Diffusion velocity in air (m/s)	2.0	0.51	0.17
Ignition energy (mJ)		0.29	
– At stoichiometric mixture	0.02	20	0.24
– At lower flammability limit	10		n/a
Flame velocity in air (cm/s)	265–325	37–45	37–43
Toxicity	Non-toxic	Non-toxic	Toxic above 50 ppm

can be transformed into other forms of energy only through combustion. In other words, hydrogen is a versatile fuel [69].

4.1. *Environmental and health aspects of using hydrogen as a transportation fuel*

Transport sector is a major contributor of the global fossil fuel combustion-related CO_2 emissions. Total fossil fuel-related CO_2 emissions increased to 28.8 Gt in 2007 from 20.9 Gt in 1990 and transport sector accounted for 4.58 (1990) and 6.63 (2007) Gt, representing an increase of approximately 45% [70]. According to the World Energy Outlook 2009, global energy-related CO_2 emissions could increase to over 40 Gt by 2030 and transport emissions would make up over 9 Gt of it [71]. These emitted pollutants have a serious negative impact on the health and environment. The health impacts include various respiratory health problems, eye irritation, allergies, myocardial ischaemia and angina [72]. The various environmental impacts include global warming, air pollution, smog, acid rain etc.

Technologies for fossil fuel extraction, transportation, processing and particularly their end use (combustion), have harmful impacts on the environment, which cause direct and indirect negative effects on the economy [8]. The CO_2 emission per unit of fossil fuel energy (in GJ) depends on fossil fuel type, and is around 85.5 kg CO_2 for coal, 69.4 kg CO_2 for petroleum and 52 kg CO_2 for natural gas. It is expected that emissions of CO_2 will reach 8.2–10.0 Gt in around 2020. Global climate change due to CO_2 emissions is possibly the most important environmental problem that human beings face [19]. Hydrogen powered vehicles are zero emission devices at the point of use, with consequential local air quality benefits. Hydrogen powered fuel cells could contribute to reducing or eliminating emissions of CO_2 and other greenhouse gases from road transportation vehicles [4,11]. Hence, hydrogen powered energy systems appear to be an attractive alternative to current fossil fuel-based energy systems in the future [4].

4.2. *Hazard and safety considerations of using hydrogen as a fuel*

The fuels having low density and high diffusion coefficient are considered to be safer. Higher specific heat causes a fuel to be safer, since it slows down the temperature increases for a given heat input. Wider ignition limits, lower ignition energies, and lower ignition temperatures make the fuels less safe, as they increase the limits in which a fire could commence. Higher flame temperature, higher explosion energy, and higher flame emissivity make a fuel less safe, since its fire would be more damaging [8]. The characteristics related to fire hazard of fuels are summarised in Table 2.

Table 2
Characteristics related to fire hazard of fuels [8].

Property	Gasoline	Methane	Hydrogen
Density[a] (kg/m^3)	4.40	0.65	0.084
Diffusion coefficient in air[a] (cm^2/s)	0.05	0.16	0.610
Specific heat at constant pressure[a] (J/g K)	1.20	2.22	14.89
Ignition limits in air (vol%)	1.0–7.6	5.3–15.0	4.0–75.0
Ignition energy in air (mJ)	0.24	0.29	0.02
Ignition Temperature (°C)	228–471	540	585
Flame Temperature in air (°C)	2197	1875	2045
Explosion energy[b] (g TNT/kJ)	0.25	0.19	0.17
Flame emissivity (%)	34–43	25–33	17–25

[a] At normal temperature and pressure.
[b] Theoretical maximum; actual 10% of theoretical.

Hydrogen is four times as diffusive as natural gas, and 12 times as diffusive as gasoline as it is very light and its density is 6.9% that of air. Therefore the risk of fire or explosion is very less as a hydrogen leak rapidly dissipates as it rises from its source. Due to its non-toxicity, a hydrogen leak would not cause environmental damage. In a confined space, hydrogen could lead to fire or explosion, if mixed with air. Any fire started would burn out quickly as the hydrogen is dissipated. It is difficult to make a hydrogen–air mix explode – a transient spark can set it off – but it will burn rather than explode, in open air [73]. Some studies have suggested that hydrogen vehicles would have lower risks than petrol vehicles in confined spaces as petrol leaks would create a larger cloud of flammable gas. Hydrogen blazes with little radiation of heat, so nothing would burn unless it is immediately next to the flame [73]. Another safety advantage is that it is clear flame cannot sear skin at a distance because of the little thermal radiation emitted by the flame due its lack of soot content. Hydrogen can burn in lower concentrations and this can cause safety concerns [19,23].

Nejat et al. compared three fuels for safety aspects as given in Table 3. For each of the toxic elements and fire hazard characteristics, it ranks the fuels from 1 to 3, 1 being the safest and 3 the least safe. It was reported that hydrogen was the safest fuel with a safety factor of 1.00. Next to hydrogen was methane with a safety factor of 0.80 and gasoline was reported to be the least safe fuel among the three with a safety factor of 0.53 [8]. In view of the above discussion, it can be safely concluded that hydrogen is safe fuel to handle.

5. Hydrogen storage

Storage of hydrogen may be needed at different scales: on-board vehicles, at filling stations, at production centres, and nationally as a

Table 3
Safety ranking of fuels [11].

Characteristic	**Fuel ranking**[a]		
	Gasoline	**Methane**	**Hydrogen**
Toxicity of fuel	3	2	1
Toxicity of combustion (CO, SOx, NOx, HC, PM)	3	2	1
Density	3	2	1
Diffusion coefficient	3	2	1
Specific heat	3	2	1
Ignition limit	1	2	3
Ignition energy	2	1	3
Ignition temperature	3	2	1
Flame temperature	3	1	2
Explosion energy	3	2	1
Flame emissivity	3	2	1
Totals	30	20	16
Safety factor	0.53	0.80	1.00

[a] 1, safest; 2, less safe; 3, least safe.

strategic reserve [74]. Hydrogen storage is regarded as one of the most critical challenges associated with hydrogen economy, which must be solved before a technically and economically viable hydrogen fuel system can be established [11,75,76]. The main drawback of using hydrogen as a transportation fuel is huge on-board storage tanks, which are required because of extremely low density of hydrogen. For on-board energy storage, vehicles need compact, light, safe and affordable containment. Therefore, when the first report on hydrogen storage in carbon nano-tubes was published, it triggered a world-wide tide of research on carbon nanotubes as it promised to provide solution to the problem of on-board hydrogen storage [12,77]. Nanostructures have been reported to have very high hydrogen storage capacities (wt%) and energy consumed for storage is also very low. However, the initial euphoria associated with carbon nanomaterials vanished, when the initial results could not be repeated. A modern, commercially available car optimised for mobility and not prestige with a range of 400 km burns about 24 kg of petrol in a combustion engine. To cover the same range, about 8 kg hydrogen would be needed for the combustion engine version or about 4 kg hydrogen for an electric car with a fuel cell. Hydrogen can be stored physically by changing its state conditions (temperature, pressure, phase), and chemically or physio-chemically in various solid and liquid compounds (metal hydrides, carbon nanostructures, alanates, borohydrides, methane, methanol, ammonia, light hydrocarbons) [78,79]. There are several studies which report the development of hydrogen storage materials like metal hydrides [80–82], Mg-based alloys [83–85], carbon-based materials [86–88], chemical hydrides [89], boron compounds [90], etc.

The crucial challenge is to find a storage material that can satisfy three competing requirements: high hydrogen storage capacity, reversibility of the discharging/charging cycle at moderate temperatures in the range of 70–100 °C to be compatible with the present generation of fuel cells, and fast discharging/charging kinetics with minimum energy barriers to hydrogen release and charge. The first requires strong chemical bonds and close atomic packing; the second requires weak bonds that are breakable at moderate temperature; and the third requires loose atomic packing to facilitate fast diffusion of hydrogen between the bulk and the surface, as well as adequate thermal conductivity to prevent decomposition by the heat released upon hydriding. Although several materials have been found to satisfy one or more of the requirements, none has proven to satisfy all the three. In addition to these basic technical criteria, viable storage media must satisfy cost, weight, lifetime, and safety requirements as well [36,91]. Charging of hydrogen in the storage material of an automobile is also linked to the waiting time at the dispensing station. Fast charging kinetics would result in lower waiting time.

For mobile and stationary applications the volumetric and gravimetric density of hydrogen in a storage material is crucial. Hydrogen can be stored using six different methods and phenomena: (a) high-pressure gas cylinders (up to 700 bar), (b) liquid hydrogen in cryogenic tanks (at 21 K), (c) adsorbed hydrogen on materials with a large specific surface area (at $T < 100$ K), (d) absorbed on interstitial sites in a host metal (at ambient pressure and temperature), (f) chemically bonded in covalent and ionic compounds (at ambient pressure), or (g) through oxidation of reactive metals, e.g. Li, Na, Mg, Al, Zn with water [12].

Schlapbach and Züttel have reviewed various hydrogen storage ways for mobile applications. These are conventional hydrogen storage, hydrogen adsorption on solids of large surface area, hydrogen storage by metal hydrides, alanates and other light hydrides [92]. Curved microporous structures have more potential for attraction of hydrogen molecules than open flat surface. Therefore, nanotubes hold great promise in realizing the storage application. Certain light hydrides such as sodium, boron and lithium show high hydrogen absorption but the reversibility of the process still remains a technical challenge as hydrogen is needed to be desorbed in a wide temperature range from 80 °C to 600 °C. Jain reported various hydrogen storage devices: metal hydrides, complex hydrides, carbon nanotubes, glass spheres, zeolites and chemical storage [16]. The traditional hydrogen storage facilities, both for stationary and mobile applications, are complicated because of its very low boiling point (20.2 K) and very low density both as a gas (0.09 kg/N m^3) and a liquid (70.9 kg/N m^3) [15]. Hydrogen is currently stored in vehicles as a gas in high-pressure cylinders (up to 700 bar) or as a liquid at 20 K in cryogenic reservoirs [36,93]. One downside of the current methods is a significant energy penalty – up to 20% of the energy content of hydrogen is required to compress the gas and up to 40% to liquefy it. Another critical issue that confronts the use of high-pressure and cryogenic storage centres concerns public perception and acceptability associated with the use of pressurised gas and liquid hydrogen containment [61].

Broadly, hydrogen can be stored in (a) gaseous form (b) liquid form, and (c) in solid state materials or in liquid organic hydrides. Hydrogen storage requires a major technological breakthrough and this is likely to occur in the most viable alternative to compressed and liquid hydrogen, namely the storage of hydrogen in solids or liquids. Storage of hydrogen in liquid form is difficult, as very low temperatures are required to liquefy hydrogen [19]. Several classes of solid-state hydrogen storage materials demonstrate higher energy density than that of liquid hydrogen like $LiBH_4$ [94]. However, much more work is required to improve their hydrogen absorption/desorption characteristics. For instance, functionalised carbon nano fibres (FCNF's) have proved to show an increased hydrogen uptake of above 200% with respect to unfunctionalized carbon, depending on degree of functionalization [95]. The most promising hydrogen storage routes are in solid materials that chemically bind or physically adsorb hydrogen at volume densities greater than that of liquid hydrogen [96]. Solid state storage systems would be viable for transport applications if they have around 6–9 wt% of hydrogen and a cycle life of > 1500. Hydrogen storage for transportation presents a major materials research challenge, namely, to find a storage medium that combines a hydrogen density greater than that of the liquid with fast kinetics allowing rapid charging and discharging. Advanced storage methods like high compression storage in cylinders/tanks, hydrides, carbon nanostructures need to be developed to achieve system storage efficiency of > 9 wt%, reduce overall size, improve recycle life and ensure safe transportation and refuelling [97]. With exceptionally high surface areas and chemically-tuneable

Table 4
Various aspects of different hydrogen delivery methods [74].

	Pipeline	Liquid (road)	Liquid (ship)	Tube trailer
Advantages	– Large volumes – High efficiency – Also provides storage and buffering – Low variable cost	– Higher volumes than compressed gas – High efficiency	– Could allow international transport – Very high volumes	– Can be deployed at small scales
Disadvantages	– Capital intensive – Needs large volumes of hydrogen to justify pipeline costs – Required volume increases with distance	– Expense and inefficiency of the liquefaction process – Boil-off losses – Increases road traffic	– No experience of LH_2 shipment – Not feasible until large supply and demand exists – Boil-off losses are more significant than road	– Small deliveries per truck – Energy inefficient – Cannot handle large capacities – Increases traffic
Suitable for	– Large and very large quantities of gas – Where pipeline storage is used	– Large quantities of gas – Where liquid storage is used	– Very large quantities of gas – International transport	– Small quantities of gas – Small distances
Capacity	– Up to 100,000 kg/h (3.9 GW)	– Up to 4000 kg per truck	– Potentially 10 million kg per shipment	– Up to 400 kg (delivered) per truck
Capital costs	– $200,000–1,000,000 per km – $0.1–2.0/kg H_2 or more depending on distance and capacity	– $300,000–400,000 per truck – $0.3/kg H_2 (excluding liquefaction plant)	– $155 million for – LNG barge could be 3–4 times higher for LH_2 barge	– w$300,000 per truck – $0.10–0.40/kg
O&M costs	– Energy costs of pipeline compressors – w$0.03/kg	– Driver labour at w$18/h – $0.02–0.20/kg	– Crew labour and fuel – Uncertain	– Driver labour – $0.5–2.0/kg
Total cost $/kg/100 km	$0.10–1.00	$0.3–0.5	$1.8–2.0	$0.5–2.0/kg
Energy required	Pipeline compressors	Transport fuel	Transport fuel	Transport fuel
Efficiency	– 99.2% per 100 km	– 99% per 100 km for transport – 75% efficiency of liquefaction	– fuel use unknown – boil-off 0.3% per day	– 94% per 100 km

structures, mesoporous metal-organic frameworks have recently emerged as some of the most promising candidate materials [98–100]. Many conventional bulk materials have been explored and rejected as storage media because they do not meet these criteria. However, nanomaterials open new opportunities for addressing this challenge, with the potential for high surface areas and hybrid structures that enable multifunctional performance, such as low-energy dissociation of hydrogen molecules on the surface and rapid diffusion of atomic hydrogen to the interior.

6. Hydrogen transport and delivery

Hydrogen delivery is an important consideration for a viable hydrogen economy. It needs an infrastructure to deliver hydrogen from where it is produced to the dispenser at a refuelling station or stationary power generating facility. There are three potential hydrogen-delivery pathways: (a) compressed tube trailers, (b) cryogenic liquid trucks, and (c) compressed gas pipelines. A combination of these three options could be used during various stages of hydrogen fuel market development: (i) for the initial introductory period, tube trailers could be used because the demand probably will be relatively small and it would avoid the boil-off incurred with liquid hydrogen storage; (ii) cryogenic tanker trucks are suitable for meeting demands of growing markets as they can haul larger quantities than tube trailers; and (iii) pipelines could be strategically laid to transport hydrogen to high demand areas as demand for hydrogen increases, which calls for establishment of more on-line hydrogen production capacities [101,102]. Table 4 summarises the various aspects of different hydrogen delivery methods.

The important factors affecting the delivery cost are: scale (hydrogen flow rate into the city), number of stations and delivery distance [103]. Although pipeline transport is preferred for gases, hydrogen transport by trucks will play a role in a hydrogen economy for carrying relatively small quantities of hydrogen over shorter distances. However, the low density of the gaseous hydrogen, makes transport of pressurised or liquid hydrogen extremely inefficient [73,104]. Even though cost effective, pipeline transportation suffers limitations of delivery range and corrosion. Since hydrogen can easily migrate into the crystal structure of most metals, hydrogen pipes are expected to avoid problems like hydrogen embrittlement and corrosion. For metal piping at pressures up to 7000 psi (48MPa), high-purity stainless steel piping with a maximum hardness of 80 HRB is preferred [105]. Hydrogen delivery is a critical contributor to the cost, energy use and emissions associated with hydrogen pathways involving central plant production. The choice of the lowest cost delivery mode (compressed gas trucks, cryogenic liquid trucks or gas pipelines) will depend upon specific geographic and market characteristics (e.g. city population and radius, population density, size and number of refuelling stations and market penetration of fuel cell vehicles) [106].

Pipelines have been used to transport hydrogen for more than 50 years, and today, there are about 16,000 km of hydrogen pipelines around the world that supply hydrogen to refineries and chemical plants; dense networks exist for example between Belgium, France and the Netherlands, in the Ruhr area in Germany or along the Gulf coast in the United States. Pipelines are characterised by a very low operating cost, mainly for compressor power, but high capital costs. The liquid form of hydrogen could be transported via many forms such as trucks, railcars or ships. Liquid hydrogen has a high operating cost due to the electricity needed for liquefaction (which accounts for 30–60% of the total liquefaction costs and may also represent a significant CO_2 footprint). To achieve the desired cooling in liquefaction processes a combination of compressors, heat exchangers, expansion engines, and throttle valves are used [107]. The capital cost of this type of system depends on the quantity of hydrogen to be handled and the delivery distance. This system becomes useful when the distance is up to 200 miles or less. Distance is also the deciding factor between liquid and gaseous trailers. Hydrogen transport costs are typically in the range of 1–4 ct/kW h (0.3–1.3$/kg). Because of the specific physical and chemical properties of hydrogen, pipelines must be made of non-porous, high quality materials such as stainless steel; therefore the investments in a hydrogen pipeline for a given diameter are up to two times higher than those for natural gas pipelines [11]. The discussion in this section clearly shows that transportation of hydrogen may not be technically as challenging as other components of hydrogen economy, but nevertheless it is a very important component of hydrogen economy infrastructure and would require substantial investments.

7. Future aspects

With the emergence of a broad based ‘advocacy coalition’ [108] comprising a diverse range of academic researchers, politicians, business and civil society organisations, the concept of ‘hydrogen economy’ has received considerable attention in recent years, promoting hydrogen as a means of delivering a sustainable and secure energy system [109]. Presently, there are three major technological barriers that must be overcome for a transition from a carbon-based (fossil fuel) energy system to a hydrogen-based economy. First, the cost of efficient and sustainable hydrogen production and delivery must be significantly reduced to bring it on par with other alternatives. Second, new generations of hydrogen storage systems for vehicular applications must be developed to provide adequate driving range. Finally, the cost of fuel-cell and other hydrogen-based systems must be reduced along with improvement in their useful life [61].

The major future markets for hydrogen transport and delivery depend primarily upon four factors: (a) the future cost of hydrogen, (b) the rate of advances of various technologies that use hydrogen, (c) potential long-term restrictions on greenhouse gases, and (d) the cost of competing energy systems [110,111]. Hydrogen holds the promise as a sustainable fuel of the future with many social, economic and environmental benefits to its credit. It has the long-term potential to reduce the dependence on fossil oil and lower the carbon and criteria emissions from the transportation sector [112].

With every new technological transition, understanding of social cultural factors holds significance to understand the concept of socio- technical systems. In our predominantly fossil fuel based energy system, issues in relation to transport and mobility as well as household and equipment are important features to discuss. In terms of speed and range of vehicles, existing practices and technologies cannot be easily surpassed by upcoming new ways of transportation in society and thus transition to hydrogen economy will be rather slow. However reduced CO_2 emissions associated with hydrogen economy based on renewable will have an advantage over other methods.

Socio-cultural barriers with technological developments may well be overcome through economic means. Other strategies such as prohibitions and campaigns – all of which can be part of policies to promote a certain technological development (such as the spread of hydrogen as energy carrier) can be adopted. The kinds of barriers that are embedded in everyday practices and routines, in social norms and values, and in aesthetic preferences etc. have to be recognised and understood. The obstacles are serious but not unfeasible to achieve. Current architecture of the energy system and social practices need certain changes along with proper political-administrative support by way of public funding, investment and regulation.

8. Conclusion

Hydrogen is considered as the best energy carrier for automobiles. It is as versatile as electricity. It can be produced from a variety of sources both renewable and non-renewable. Currently, non-renewable sources are mainly used for hydrogen production but from the viewpoint of sustainability, it is important that renewable energy sources like solar, wind or biomass are used primarily for its production. Hydrogen is an important feedstock/energy carrier in today's world and it is used for a variety of applications such as ammonia production, hydrogenation of hazardous wastes, in petroleum refineries for desulphurisation and hydro-cracking, synthesis of methanol and ethanol, as rocket fuel, etc. One of its most important potential uses can be in the transportation sector for both IC engines and fuel cell technologies as it has many potential advantages over currently used technologies based on use of conventional fuels like higher energy conversion efficiencies and practically negligible emissions as in the case of fuel cells. There is vast experience of handling hydrogen in the industry, which reinforces the belief that it is a safe fuel, however, it needs to be fully validated to dispel any concerns about its safety among common people.

One of the major technical challenge in using hydrogen as a vehicular fuel is its on-board storage. Adequate quantities of hydrogen are required to be stored to provide a preferred driving range for any vehicle. This is a major challenge in view of very low gravimetric density of hydrogen. Various storage routes have been investigated such as compressed gas, cryogenic tanks, metal hydrides, carbon nanotubes, etc. Research is still underway in determining the most economical and efficient storage mechanism. The second most important challenge is the transport and distribution of hydrogen. This is an imperative factor while making a transition to the hydrogen economy. Currently, compressed tube trailers, cryogenic liquid trucks and compressed gas are the three prospective hydrogen delivery pathways used for the various applications.

The infrastructure requirement and financial resources allocated for the production and supply of oil and natural gas were enormous during the initial several decades of commercialisation efforts of this sector. It was more of a politico-economic policy and funding which brought oil and natural gas to its present state. Hence, it will require a huge initiative for replicating the same for hydrogen in the near future and the Governments of various countries must align their requirement of energy for the future in terms of increasing the usage of hydrogen as a transport fuel. Policy and regulatory measures apart from enhanced support for research and commercialisation efforts at the global level would certainly pave the way for making initial strides in embarking towards hydrogen economy, which promises energy security to the nations and clean and green environment to the people. The potential of hydrogen to be used in the transport sector is vast provided the right measures and pathways are taken to make it safe, trustworthy and robust.

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