

PRODUCTION, STORAGE AND PROPERTIES OF HYDROGEN AS INTERNAL COMBUSTION ENGINE FUEL: A CRITICAL REVIEW

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ABSTRACT

In the age of ever increasing energy demand, hydrogen may play a major role as fuel. Hydrogen can be used as a transportation fuel, whereas neither nuclear nor solar energy can be used directly. The blends of hydrogen and ethanol have been used as alternative renewable fuels in a carbureted spark ignition engine. Hydrogen has very special properties as a transportation fuel, including a rapid burning speed, a high effective octane number, and no toxicity or ozone-forming potential. A stoichiometric hydrogen–air mixture has very low minimum ignition energy of 0.02 MJ. Combustion product of hydrogen is clean, which consists of water and a little amount of nitrogen oxides (NO_x). The main drawbacks of using hydrogen as a transportation fuel are huge on-board storage tanks. Hydrogen stores approximately 2.6 times more energy per unit mass than gasoline. The disadvantage is that it needs an estimated 4 times more volume than gasoline to store that energy. The production and the storage of hydrogen fuel are not yet fully standardized. The paper reviews the different production techniques as well as storage systems of hydrogen to be used as IC engine fuel. The desirable and undesirable properties of hydrogen as IC engine fuels have also been discussed.

Keywords: Hydrogen, Production, Storage, Alternative fuel, Economy.

1. INTRODUCTION

The major two problems faced by the modern world are the acute fuel shortage and the environmental pollution due to emission from the combustion of conventional fossil fuels. Our fast depleting fossil fuel stores will not be able to sustain us long and we although have been in search for alternate fuels for fairly a long time, there hasn't been much success. The emissions caused by large amount of industries and vehicles nowadays are affecting the atmosphere and the earth and if steps are not taken to this effect, we may soon face serious problems.

Specially, motor vehicles face a serious problem due to fast depleting fuel sources and the emissions they are causing. Around the world, there were about 806 million cars and light trucks on the road in 2007; they burn over a billion cubic meters (260 billion US gallons) of petrol/gasoline and diesel fuel yearly. Motor vehicles are unique in a sense that they cannot be operated on all fuels e.g. coal because in motor vehicles design, fuel-economy plays important part. Majority of motor vehicles today run on Internal Combustion(IC) engines running either on petrol or diesel. Though through recent developments battery powered motor

vehicles with minimal emissions have emerged as a new concept, they still lag behind in performance and cost effectiveness and hence, are not popular.

Hydrogen, in the recent past have been thought of as a fuel in IC engines because of its certain properties like lowest molecular weight, high infusibility etc. What appeals more is the combustion product of IC engines running on hydrogen would be ordinary water. Research is being undertaken to this effect because there are still some shortcomings and in near future we may find motor vehicles on streets that have IC engines running on Hydrogen. In this report, we are going to present prospects and facts about viability of hydrogen as fuel in IC engines.

2. PROPERTIES OF HYDROGEN

Hydrogen, the lightest element, is a colourless, odourless, tasteless and nontoxic gas found in the air at concentrations of about 100 ppm (0.01%) [1]. It is the most abundant element in the universe, making up 75% of normal matter by mass and over 90% by number of atoms [2]. The properties that contribute to its use as a combustible fuel are:

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. As little as 4% hydrogen by volume; produces a combustible mixture with air [3]. Hydrogen has very low ignition energy (0.02 MJ). Hydrogen is detonable over a very wide range of concentrations when confined, however, unlike many other fuels; it is very difficult to detonate if unconfined. 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. It facilitates the formation of a uniform mixture of fuel and air. If a hydrogen leak develops, the hydrogen disperses rapidly. Thus, unsafe conditions can either be avoided or minimized. Hydrogen also has very low density causing some problems when used in an internal combustion engine as pointed out by Shoko et al. [4]. A very large volume is necessary to store enough hydrogen to give a vehicle an adequate driving range. The energy density of hydrogen-air mixture is low and it results a lower power output.

In comparison with an engine burning gasoline, the emission of nitrogen oxides is far less for the engine fueled by hydrogen. The product of hydrogen combustion with air is water vapor and negligible pollution when the peak temperature is limited. According to Nada et al. [5], some nitrogen oxides are formed at very high combustion temperatures (~2300 K); but, the auto ignition temperature of hydrogen is only 858 K. A summary of chemical and physical properties of hydrogen and gasoline is given in table 1 taken from the work of Muradov and Veziroglu [6].

3. SOURCES OF HYDROGEN

All primary energy sources can be used in the hydrogen-producing process. Currently, the primary route for hydrogen production is the conversion of natural gas and other light hydrocarbons. Coal and petroleum coke may also serve as raw materials for hydrogen production in the future. As shown in above approximately 96% of the hydrogen produced comes from fossil fuels' conversion, such as natural gas reforming. The production of hydrogen from fossil fuels causes the co-production of carbon dioxide, which is assumed to be the main responsible for the so-called "greenhouse effect". These processes use non-renewable energy sources to produce hydrogen and are not sustainable. Therefore, renewable energy sources and technologies for hydrogen production will be necessary in the coming decades.

Hydrogen can be produced from renewable energy sources such as biomass, but yields are low. If hydrogen conversion efficiency could reach 60–80%, based upon a maximum theoretical conversion of 12 mol-H₂/mol-hexose, Hydrogen production from wastewater could have great potential for economical near-term hydrogen production from renewable energy sources.

Table 2 shows the percent share of raw materials in hydrogen production. Hydrogen can also be produced from water by using a variety of energy sources such as wind, solar, geothermal, hydropower, and nuclear energy. Nuclear energy has the potential to play a significant role in a sustainable hydrogen economy.

Table 1: Chemical and physical properties of hydrogen, methane and gasoline

	Hydrogen	Gasoline (H/C=1.87)
Molecular weight(g/mol)	2.016	~110
Mass density (kg/N _A m ³) at P=1atm T=0 ⁰ c	0.09	720-780 (liquid)
Mass density of liquid H ₂ at 20 K(kg/N _A m ³)	70.9	-
Boiling point(K)	20,2	310-478
Higher heating value(MJ/kg)(assumes water is produced)	142.0	47.3
Lower heating value(MJ/kg)(assumes steam is produced)	120.0	44.0
Flammability limits(% volume)	4.0-75.0	1.0-7.6
Detonability limits (% volume)	18.3-59.0	1.1-3.3
Diffusion velocity in air (m/s)	2.0	0.17
Ignition energy (ml) -At stoichiometric mixture-At lower flammability limit	0.02	0.24
Flame velocity in air (cm/s)	10	n/a
Toxicity	265-325	37-43
	Nontoxic	Toxic

Source: Muradov and Veziroglu [6]

Table2: Percentage share of raw materials in hydrogen production

Source	Bcm ³ /yr	Share (%)
Natural gas	240	48
Oil	150	30
Coal	90	18
Electrolysis	20	4
TOTAL	500	100

Bcm³: billion cubic meters

Source: Kothari et al. [13]

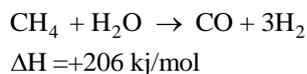
4. HYDROGEN PRODUCTION METHODS

Hydrogen can be produced by a number of processes, such as thermo-chemical processes, electrochemical processes, photochemical processes [6], photo-catalytic processes, or photo-electrochemical processes. Thermo-chemical processes for hydrogen production involve thermally assisted chemical

reactions that release the hydrogen, e.g., from hydrocarbons or water. The advantage of the thermo-chemical process is that its overall efficiency (thermal to hydrogen) is higher (η -52%) and production cost is lower [6].

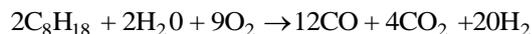
Today, hydrogen is produced almost exclusively from fossil fuels, through steam reforming of methane (SMR) [7, 8] or partial oxidation (POX) of hydrocarbon fuels [9]. SMR is currently the most popular process for producing hydrogen from natural gas. Almost 48% of the world's hydrogen is produced from SMR, which is the most common and least expensive method of producing hydrogen, with energy consumption rate of only about 1.23–1.35 GJ-NG/GJ-H₂ [10]. The SMR process requires high process temperature and the most common practice for providing the needed heat for the process is via burning natural gas. Steam reformation of natural gas (or methane from other sources) produces a hydrogen rich gas that is typically on the order of 70–75% on a dry basis, along with smaller amounts of CH₄ (2–6%), CO (7–10%), and CO₂ (6–14%) [11]. The SMR is a three-step process to produce hydrogen. Methane is first catalytically reformed at elevated temperature and pressure to produce a syngas mixture of H₂ and CO. A catalytic shift reaction is then carried out to combine CO and H₂O to produce the H₂ product. The hydrogen product is then purified by adsorption. The reforming step is described by the following reaction [12]:

Reforming reaction:-



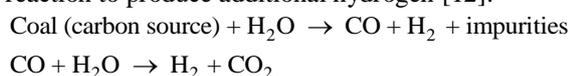
POX of hydrocarbons is an exothermic reaction with oxygen and steam. The amounts of oxygen and water vapor are controlled so that the reaction proceeds without the need for external energy [13].

An example reaction for this process is:

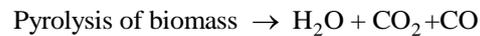


Hydrogen can also be produced by the gasification of coal, and while these processes are less mature than SMR process, they are relatively well established. It is noteworthy that hydrogen from coal only accounts for 18% of the world's hydrogen production, and that the complex and expensive gasification process it undergoes presents the greatest drawback for its widespread production. Its energy consumption is about 1.54–1.69 GJ-coal/GJ-H₂ [14]. Artificial water gas (CO + H₂) from coal can be reformed to hydrogen. Hydrogen and oxygen concentrations in coal increase as coal rank goes down.

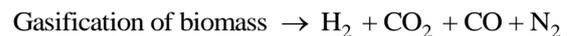
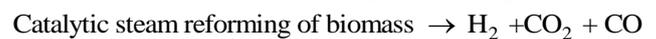
The water vapor (steam) can be further shifted to hydrogen by establishing conditions to drive the reaction to produce additional hydrogen [12]:



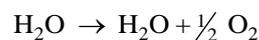
Hydrogen can be produced from biomass by pyrolysis [12–15], gasification [16, 17], steam gasification [16, 18], steam reforming of bio-oils [15], and enzymatic decomposition of sugars [17, 19]. Hydrogen is produced from pyrolytic oils produced from the pyrolysis of biomass [14]. The main gaseous products from biomass are the following:



+ Hydrocarbonages



The net reaction for producing hydrogen and oxygen by water electrolysis is given by:



5. HYDROGRN STORAGE

Hydrogen storage is one of the major issues affecting the future hydrogen economy. The traditional hydrogen storage facilities, both for stationary and for 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/NA m³ (kilogram per normal cubic meter)) and a liquid (70.9 kg/NA m³).

5.1 Compressed gas storage

Hydrogen stored in high-pressure vessels could be the preferred storage type for fuel cell vehicles, for reasons of vehicle design, cost and efficiency, as well as environmental benefits [20]. The main advantages of compressed gas storage are reliability, indefinite storage time, easy to use, and affordable cost. Its main disadvantage is the low storage density which depends on the storage pressure. High-pressure storage results in higher capital and operating costs.

5.2 Liquid hydrogen storage

The main advantage of liquid hydrogen is its high density at low pressure, which enables light and compact vehicular storage and efficient delivery by truck. The main drawback of liquid hydrogen storage on-board vehicles is the high cost [21]. Liquid hydrogen storage is not economical at low production rates (due to the high capital cost of liquefier) and is difficult to compete with compressed gas at higher production rates unless longer storage times are required, when the lower capital cost of liquid hydrogen compared to compressed gas pressure vessels becomes the chief factor [22].

5.3 Hydrogen storage materials

The development of efficient methods for hydrogen storage is a major hurdle that must be overcome to enable the use of hydrogen as an alternative energy carrier. The development of high capacity, hydrogen storage materials that can be recharged under moderate conditions is a key barrier to the realization of a hydrogen economy.

Several studies report the development of hydrogen storage materials such as metal hydrides, Mg-based alloys, carbon-based materials, chemical hydrides [23], boron compounds [24], etc.

An optimum hydrogen storage material must have the following characteristics: high volumetric /gravimetric hydrogen storage capacity, fast absorption kinetics, near room temperature and ambient pressure operation, light weight materials, and low cost materials.

The advantages of storing hydrogen in the form of metal hydrides include high volume efficiencies, relative ease of recovery, indefinite storage capabilities without loss of hydrogen and a high degree of safety. Metal hydrides have the potential for reversible on-board hydrogen storage and release at the relatively low temperatures and pressures required for fuel cell vehicular applications. Hydrogen can be stored in the form of metal hydrides with negligible loss over time, but the tanks must be heavy and expensive, the storage rate at 2–9 MJ/kg (mega-joule per kilogram), meaning petrol is 4.5–21 times as energy dense as hydrogen within a hydride.

6. ECONOMICS OF HYDROGEN DELIVERY

Hydrogen delivery is important for a viable hydrogen economy, which requires an infrastructure to deliver hydrogen from where it is produced to the dispenser at a refueling station or stationary power facility.

Two types of hydrogen delivery are considered [25]: Hydrogen transmission (from a central hydrogen production plant to a single point), and Hydrogen distribution (from a central hydrogen plant to a distributed network of refueling stations within a city or region). There are three potential delivery pathways:

- (1) Compressed tube trailers,
- (2) Cryogenic liquid trucks, and
- (3) Compressed gas pipelines.

A combination of these three options could be used during various stages of hydrogen fuel market development. Tube trailers could be used during the initial introductory period because the demand probably will be relatively small and it would avoid the boil-off incurred with liquid hydrogen storage. Cryogenic tanker trucks could haul larger quantities than tube trailers to meet the demands of growing markets. Pipelines could be strategically placed to transport hydrogen to high demand areas as more production capacities are placed on-line.

For hydrogen delivery, the most important factors affecting the delivery cost (US\$/kg) are: Scale (or hydrogen flow rate into the city), number of stations, delivery distance. Scale is important for liquid hydrogen delivery systems because liquefiers have strong scale economies.

For pipeline systems, the pipeline capital cost contribution is strongly scale dependent. For compressed gas truck delivery there are mild scale economies in compression.

Number of stations determines the spatial extent of the infrastructure, and is particularly important for pipeline delivery costs. (For fewer stations, a less extensive pipeline network is required.) Delivery distance is related to the physical size of the city (expressed as a characteristic length such as the city radius, and is particularly important for compressed gas trucks and for pipeline delivery, and less so for liquid hydrogen delivery).

6.1 Hydrogen delivery by pipeline

The cheapest option of transporting hydrogen is by high capacity pipeline, which can cost less the 0.1 US\$/kg over 100 km [25]. Figure 1 shows the cost of pipeline delivery with distance at different pipeline capacities. Pipeline costs are composed of labor (45 % by weight), followed by materials (26 % by weight), right-of-way costs (22 % by weight) and other miscellaneous costs such as planning and management range of about 30–80 bar.

6.2 Compressed gas truck delivery

The delivery of compressed hydrogen gas via tube trailer trucks requires the compression of gaseous hydrogen to 180 atm (18.2 MPa) at the conversion facility with storage and trucks with compressed gas tube trailers to transport the hydrogen to the refueling stations [23]. A typical trailer might carry 300 kg of hydrogen, which represents about 1% of the total mass of the truck [24].

6.3. Cryogenic liquid hydrogen delivery

Delivering hydrogen as a cryogenic liquid requires the liquefaction of the hydrogen at the conversion facility with storage and delivery via tanker trucks. Tank trucks can carry between 400 and 4000 kg liquid hydrogen, a factor of ten more than tube trailers. Boil-off can be a problem, which typically runs at 0.3–0.6% per day. The primary barriers to using liquid hydrogen for delivery are the high cost and high energy use of liquefaction

The figure 1 shows the variation of delivery cost with delivery distance at two different pipeline capacities:

7. ENVIRONMENTAL BENEFITS HYDROGEN

Air pollution is a serious public health problem throughout the world, especially in industrialized and developing countries. In industrialized and developing countries, motor vehicle emissions are major contributors to urban air quality. The major emissions from motor vehicles include carbon monoxide (CO), nitrogen oxides (NO_x), hydrocarbons (HCs), lead, and particulate matter. One can attribute to transportation more than 70% of total global CO emissions and more than 40% of total global NO_x emissions. Almost 50% of total global HCs, around 80% of total global benzene emissions and least 50% of atmospheric lead emissions

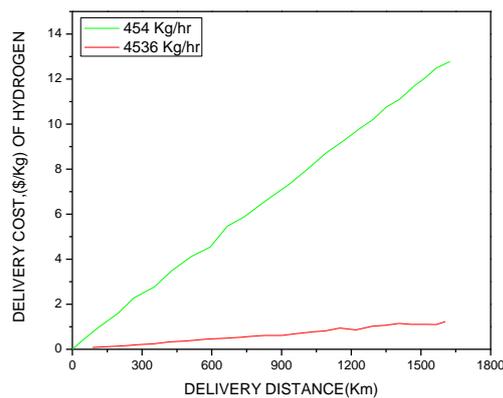


Fig.1. Relationship between delivery cost of hydrogen with the delivery distance at different pipeline capacities. *Source:* Williams et al. [25]

8. ADVANTAGES OF USING HYDROGEN AS A FUEL IN I.C. ENGINES

Many experts think that hydrogen has a major role to play as an energy carrier in future energy supply. Hydrogen as a future energy carrier has a number of advantages. One of hydrogen's primary advantages is that it can be produced from a variety of primary resources, one of which will most likely be readily accessible almost anywhere in the world. Another important advantage of hydrogen over other fuels is that its only major oxidation product is water vapor; its use produces no CO₂.

Hydrogen can be used as a transportation fuel, whereas neither nuclear nor solar energy can be used directly. It has good properties as a fuel for internal combustion (IC) engines in automobiles. Hydrogen can be used as a fuel directly in an IC engine not much different from the engines used with gasoline [19]. The blending of hydrogen and ethanol has been used as an alternative renewable fuel in a carbureted spark ignition engine [21]. Hydrogen has very special properties as a transportation fuel, including a rapid burning speed, a high effective octane number, and no toxicity or ozone-forming potential. It has much wider limits of flammability in air (4–75% by volume) than methane (5.3–15% by volume) and gasoline (1–7.6% by volume). A stoichiometric hydrogen–air mixture has very low minimum ignition energy of 0.02 mJ.

A hydrogen engine is easy to start in cold winter because hydrogen remains in a gaseous state until it reaches a low temperature such as 20 K. Such characteristics play a role to decrease engine cycle variation for the safety of combustion. However, it is frequently observed that the values of cycle variation for hydrogen-fueled engines with direct injection are higher than those of hydrogen-fueled engines with manifold injection or those of gasoline engines, due to a decrease in the mixing period by direct injection in the process of compressing hydrogen.

Combustion product of hydrogen is clean, which consists of water and a little amount of nitrogen oxides

(NO_x). With proper measurements it is believed that this amount of NO_x can be reduced, even attaining 1/200 as low as diesel engines [9].

9. DISADVANTAGES

The main drawbacks of using hydrogen as a transportation fuel are huge on-board storage tanks, which are required because of hydrogen's extremely low density. Hydrogen can be stored on-board a vehicle as a compressed gas, as a liquid in cryogenic containers, or as a gas bound with certain metals in metal hydrides [1]. However, because of the low density, compressed hydrogen will not be able to give a comparable range to that of gasoline. Hydrogen can achieve a reasonable density adsorbed in these metal hydrides, but the weight of the metals makes the system very heavy

10. CONCLUSION

Hydrogen is to be used as alternative transportation fuels so as to negate the concern for the greenhouse effect. Greenhouse gas emission reductions should be estimated on an annual basis. Where the levels from year to year vary significantly these should be specified on an annual basis. Hydrogen as a future energy carrier has a number of advantages. One of hydrogen's primary advantages is that it can be produced from a variety of primary resources, one of which will most likely be readily accessible almost anywhere in the world. Another important advantage of hydrogen over other fuels is that its only major oxidation product is water vapor; its use produces no CO₂. Hydrogen can help reduce carbon emissions, if produced from renewable energy sources and nuclear energy. The production of hydrogen from fossil fuels causes the co production of carbon dioxide, which is assumed to be mainly responsible for the so-called "greenhouse effect". These processes use non-renewable energy sources to produce hydrogen and are not sustainable. Therefore, renewable energy sources and technologies for hydrogen production will be necessary during coming decades. Hydrogen has good properties as a fuel for IC engines in automobiles.

It can be used as a fuel directly in an IC engine not much different from the engines used with gasoline. The problem is that while hydrogen supplies three times the energy per pound of gasoline it has only one tenth the density when the hydrogen is in a liquid form and very much less when it is stored as a compressed gas. The blending of hydrogen and ethanol has been used as an alternative renewable fuel in a carbureted spark ignition engine.

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