

HYDROGEN ENERGY FOR A CLEANER ENVIRONMENT

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At the onset of this new century, we are facing the early warning signs of an impending global environmental crisis. We are also becoming aware of the finite nature of our fossil fuel sources and their uneven distribution. These challenges favor a transition to a new energy system based on hydrogen, a clean energy vector. In this article, we discuss the challenges to the introduction of hydrogen on the energy market: production, infrastructure, safety, with special emphasis on hydrogen storage, as well as the solutions proposed to overcome them.

Keywords: Hydrogen; Fuel cells; Storage; Safety; Production; Infrastructure

INTRODUCTION

According to the Intergovernmental Panel on Climate Change (IPCC), the average global temperature has risen by 0.3°C to 0.6°C and the sea level by 10 cm to 25 cm during the twentieth century. The 10 warmest years of the century have occurred over the last 15 years. If this trend continues over the next century, the IPCC projects an increase in globally-averaged surface temperature of 1.4°C to 5.8°C, an increase in sea level of 90 cm, and a likely increase in precipitation intensity over the period from 1990 to 2100. The changes in climate could adversely affect human health, agriculture, water resources, and ecosystems. Most national and international agencies (Global Warming and Climate Change Policy Websites) have concluded that global warming exists, and that our use of carbon-rich fuel is responsible for global warming through the greenhouse effect.

In 1999, Canada emitted 4.9 metric tons of carbon per capita, compared to 5.6 in the United States and 2.2 in Japan. In the United States, according to the U.S. Environmental Protection Agency (2002), the largest source of greenhouse gas emissions (79% on average between 1990 and 2000) is fossil fuel combustion. Since the industrial revolution, the amount of CO₂ in the atmosphere has

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risen by 30%. The IPCC projects that the emissions of CO₂ from residential, commercial, and institutional buildings will rise from a level of 1.9 Gigatons of Carbon (Gt C)/year in 1990 to 5.3 Gt C/year in 2050. The CO₂ emitted by the transportation sector is expected to contribute even more to the total CO₂ emissions by 2050, increasing from 1.3 Gt C/year in 1990 to over 5.7 Gt C/year in 2050 (Climate Change: The IPCC 1990 and 1992 Assessments Reports).

The first steps towards addressing the CO₂ emissions problem at the international level are embodied in the Kyoto Protocol to the United Nations Framework Convention on Climate Change. Under the Kyoto Protocol, which Canada has recently ratified, Canada is called upon to reduce its greenhouse gas emissions 6% below the levels of 1990 in the commitment period 2008 to 2012. CO₂ emission reductions will be obtained through domestic emission cuts and pollution credit mechanisms such as the clean development mechanism, by investing in emission reduction projects in developing countries and in developed countries that have taken on a Kyoto target (joint implementation), and international emissions trading. Reaching these emission targets with the current fossil fuel-based energy system will be challenging for such a heavy energy consuming country as Canada. Going beyond Kyoto will likely require fundamental changes to the current Energy System.

In addition to its global environmental impact, the use of fossil fuels directly affects our immediate urban environment, to the point that certain cities, such as Mexico, have attempted to implement driving restrictions during periods of extreme air pollution. The combustion of fossil fuels emits pollutants, such as carbon monoxide, nitrogen oxides, volatile organic compounds, and particulate matter that directly affect the urban environment. Carbon monoxide is, of course, deadly to human beings. Nitrogen oxides, emitted by all internal combustion engines, are key ingredients in the formation of smog, which can cause lung damage and eye irritation. Volatile hydrocarbons contribute to ozone formation and thus to smog. Particulate matter may cause damage to lungs.

These challenges have opened a window of opportunity for a transition to a new energy system that will have no adverse impact on the environment or human health.

ENERGY TRENDS

Over the last 150 years, the trend in energy use has been towards reducing the amount of carbon in the dominant fuel and increasing its hydrogen content. We have gone from wood to coal to oil, and are currently increasing our use of natural gas. Each new fuel has contained more hydrogen and less carbon. As a con-

sequence, the fuels we have used have become progressively cleaner and with higher energy density. A general trend towards the increase of the H/C (hydrogen/carbon) ratio of the current dominant fuel can thus be observed, as well as a transition from solid fuels to gaseous fuels (Natural Resources Canada (2000)). Every transition between energy systems has mostly been driven by technological innovation, rather than depletion. Increased fuel efficiency has been achieved specifically through gains in the gravimetric energy density (the heat of combustion of wood is 25 MJ/kg, compared to 121 MJ/kg for hydrogen) and in environmental efficiency (the CO₂ emissions of wood is 31.1 g/MJ compared to 14.3 g/MJ for natural gas and 0 for hydrogen). As environmental issues become more critical in the energy sector, we are very likely to witness a drive towards completing this trend by pushing it to its natural limit: a hydrogen-based, clean, and renewable energy system.

The energy conversion device of choice of the petroleum era has been the internal combustion engine (ICE). Although internal combustion engines can and have been adapted to hydrogen, the introduction of hydrogen on the energy market may well result in a change in energy conversion devices. The ICE's role as the prime energy conversion device is being challenged by fuel cells. Unlike the ICE, which runs on high temperature explosions, most fuel cells rely on relatively cool and clean electrochemical reactions. The fuel cell is composed of two electrodes (anode and cathode), a catalyst (a thin layer of platinum or platinum-embedded material), and a membrane. In the case of a proton exchange membrane (PEM) fuel cell, the technology under consideration to power cars, hydrogen reacts with the catalyst on the anode and is split into electrons and protons. The protons pass through a membrane to combine with oxygen on the cathode on the other side, producing water. The electrons, which cannot go through the membrane, are collected by an external circuit to produce a current and drive an electric motor. The only by-products of a fuel cell are electricity, water, and a moderate amount of heat. A hydrogen fuel cell is thus an electrochemical device that converts the chemical energy of hydrogen to direct-current electricity. Fuel cells can continuously supply electricity as long as they are supplied with hydrogen and air (or oxygen). The energy conversion (chemical to electrical) efficiency of a fuel cell can be as high as 50%, compared to 25% for internal combustion engines. In addition, a hydrogen fuel cell is essentially noiseless and does not emit harmful emissions.

With advances in fuel-cell technologies, hydrogen has become a serious competitor to hydrocarbon fuels. It stands now as the only fuel completely benign to the environment that can be used as an energy vector in a fully-sustainable energy system.

CHALLENGES AND SOLUTIONS

Despite its potential benefits, there are a number of problems with the introduction of hydrogen on the energy market: storage, safety, production, and infrastructure.

The Storage Issue

Perhaps the greatest hurdle to the widespread acceptance of hydrogen as an energy vector is its low storage density. The predominance of gasoline as the fuel of choice for automotive applications is largely based on its storage efficiency. In its liquid state, it offers convenient storage in light tanks that yield superior range, and fast and simple refuelling of the vehicles. Unlike gasoline or alcohol fuels, which are easily handled liquids at ambient conditions, hydrogen is a light gas and has the lowest volumetric energy density of any fuel at normal temperature and pressure. The density of hydrogen at ambient pressure and temperature is 8 times smaller than for methane, 15 times smaller than air, and 22 times smaller than propane. The combustion of hydrogen yields about three times more energy per unit of mass than such fossil fuels as natural gas, propane, or petroleum, and six times more than coal. Even though hydrogen has one of the largest energy contents of any combustible per unit of mass, it has one of the lowest under ambient conditions per unit of volume. To circumvent the hydrogen storage problem in fuel-cell vehicles and stationary applications, onboard reforming of liquid hydrocarbons was proposed. Reformers mostly shift the emissions to the fuel processor, and do not constitute a definitive alternative to advanced next-generation internal combustion engines. Life-cycle assessments performed by the Pembina Institute (2000) indicate that an ill-advised choice of fuel production for fuel-cell vehicles could lead to only modest greenhouse gas emission reductions, on the order of 10%. The greatest challenge, which also bears the promise of the greatest benefits, is to find a way to store hydrogen efficiently so that it can be used directly by a fuel cell.

Table 1 shows the US Department of Energy's (2003) stringent conditions for the acceptance of hydrogen storage in transportation. A vehicle powered by a

TABLE I DOE technical targets for on-board hydrogen systems^(a)

Storage parameter	2005	2010	2015
Gravimetric Energy Density	1.5 kWh/kg (0.045 kg H ₂ /kg)	2.0 kWh/kg (0.060 kg H ₂ /kg)	3.0 kWh/kg (0.090 kg H ₂ /kg)
Volumetric Energy Density	1.2 kWh/L (0.036 kg H ₂ /L)	1.5 kWh/L (0.045 kg H ₂ /L)	2.7 kWh/L (0.081 kg H ₂ /L)

^(a)Based on the lower heating value of hydrogen and a minimum of 300-mile vehicle range, for the complete storage system.

hydrogen fuel cell would require 3.1 kg of hydrogen to achieve a range of 500 km. This amount, when stored in a typical gasoline tank, would correspond to a hydrogen density of 65 kg/m^3 (including the storage system) and 6.5% by weight. Only liquid hydrogen is close to this target.

Possible approaches to vehicular hydrogen storage include classical storage techniques that are based on physical storage via compression or liquefaction, storage on a solid or a liquid through chemical or physical sorption processes such as metal hydrides, cryoadsorption on activated carbons, and adsorption on nanocarbon materials.

Compressed Hydrogen Storage

The storage of pure hydrogen as a compressed gas in high-pressure cylinders is the most standard and least complex storage system available today. Compressing hydrogen is similar to compressing natural gas. However, because hydrogen can cause embrittlement, there are restrictions imposed on the materials used. Conventional fiberglass-wrapped aluminium cylinders storing hydrogen at a pressure of 24.8 MPa have a volumetric storage density of 12 kg/m^3 and a gravimetric density of 2% by weight (including the weight of the storage system). Better storage densities are obtained from lighter carbon fiber-wrapped polymer cylinders (DOE 2004). These values remain below the US Department of Energy's stated targets for hydrogen, which are 62 kg/m^3 for the volumetric storage density and 6.5% for the gravimetric storage density. Dynetek recently achieved a storage pressure of 825 bars (81 MPa) in lightweight composite material cylinders, which may one day be used to supply hydrogen to 700 bars storage cylinders used by hydrogen-fuelled vehicles.

Liquid Hydrogen Storage

Liquid hydrogen at atmospheric pressure has a density of 71 kg/m^3 , which is three times higher than room-temperature hydrogen compressed to 34.5 MPa. Consequently, liquid hydrogen has received considerable attention as a vehicle storage method. However, a temperature of 20 K (-253°C) is needed to liquefy hydrogen. Liquid hydrogen is usually stored inside super-insulated Dewars, which have an inner pressure vessel. Some designs use insulation consisting of infrared reflecting films to lower thermal radiative transfer.

Liquid hydrogen storage faces two hurdles: dormancy and infrastructure impact. Dormancy concerns arise from boil-off losses (heat impact on the tank system). Infrastructure impact is mainly because of the high cost of the liquefaction process, which amounts to at least 30% of the lower heating value of hydrogen (see for instance Peschka (1998)). Furthermore, cryogenic storage requires a more

energy intensive and more advanced fuel delivery infrastructure than ambient storage methods. However, the cost of using liquid hydrogen as a transportation fuel is nearly twice that of gaseous hydrogen, because of the liquefaction process, increased fuel transportation costs, and more complex manipulation of the fuel.

Metal Hydride Storage

Metal hydrides are compounds in which hydrogen is absorbed by a metal under pressure and released when heat is applied. In metal hydride-based systems, hydrogen molecules are dissociated at the surface of the hydrides into hydrogen atoms and chemically absorbed into the material. Metal hydrides can store a significant amount of hydrogen in a small volume at high temperature.

The heat of reaction for hydrides can range from 9300 to 23,250 kJ/kg of hydrogen and operating pressures can reach more than 10 MPa, according to Amos (1998). Each alloy has different performance characteristics, such as life cycle and heat of reaction. In general, metal hydride systems for hydrogen storage can be classified as either high (above 300°C) or low (below 150°C) temperatures, depending on their operating temperature at modest pressures (0.1–1.0 MPa). The metals typically considered for the hydrides are Mg, Ni, Fe, and Ti. Some alloys have a limited lifetime, because of decomposition and pulverization, and thus can experience a rapid loss of their storage capabilities. The metal hydride alloy must be structurally and thermally stable in order to withstand a reasonable number of charge/discharge cycles. These systems are heavy and store 2–6% hydrogen by weight. The ideal metal hydride material would have high volumetric and gravimetric efficiencies, fast kinetics at low temperatures, and should be based on inexpensive and safe materials.

Carbon Adsorption Storage

Sorption on carbon-based materials offers a possible avenue for lowering the storage pressure of compressed gas fuels: hydrogen can be adsorbed in reasonable quantities on activated carbons with high specific areas (Chahine and Bose, 1994). However, the temperature must be lowered in order to attain a significant gain over compression. Experiments show that at 77 K and 17 bars, a density of approximately 40% that of liquid hydrogen can be achieved. This level of efficiency can be attained by using a densification process with a high surface area carbon (Benard and Chahine, 2001). Physisorption is also likely to lead to better dormancy (Gardiner and Bradley, 2003). The storage capacity of physisorption systems undergoes a loss of efficiency with increasing temperature. Extensive studies are underway to find new carbon materials for the storage of hydrogen by physisorption or chemisorption.

Comparative Analysis of Hydrogen Storage Options

In automotive applications, weight and size are critical factors and metal hydrides suffer from a considerable weight penalty compared with gasoline; however, they can be quite competitive with the electric battery. A comparison of various hydrogen storage methods for lightweight fuel-cell vehicles shows that a lightweight compressed-gas cylinder storing 12% hydrogen by weight at 34 MPa would weigh 32.5 kg and have a volume of 186 L (Ogden, 2002). A liquid hydrogen storage system offering the same range would have a weight of 28.5 kg and a total volume of 116 L. A metal hydride-based storage system would offer the smallest volume (100 L), but would also weigh the most (325 kg). A similar gasoline vehicle with an internal combustion engine would require only 25 L of gasoline for the same range, with a storage system weighting a total of 25 kg, including the tank. A study by Gardiner and Bradley (2003) confirms that a liquid hydrogen storage system would offer a smaller volume and would weigh less than a compressed or a cryoadsorption-based storage system. The volume and weight of a cryoadsorption storage-based system would be somewhat lower than a compressed gas storage system. Adsorption-based storage systems would, however, have a much better dormancy than a liquid hydrogen system and require a much lower storage pressure than a compressed storage system.

The problem of storing hydrogen is fundamentally different from the storage of gasoline. Gasoline tanks operate under ambient conditions, and the design of the storage system is relatively straightforward. For hydrogen however, the storage conditions are never ambient. A complex set of trade-offs is therefore involved in the choice of hydrogen storage technology. If cost is not factored in, the choice of a storage system will be application-dependent. Systems (such as stationary applications) that require small volumes, but impose no constraint on weight, are likely to benefit from metal hydride systems. Systems in which weight and volume are the driving factors would benefit from liquid hydrogen storage. If a low pressure storage system with long dormancy is required, cryoadsorption storage could be considered. Each storage method has advantages and problems, and the best choice depends on several factors: efficiency, size, weight, cost, and safety requirements.

Safety

Hydrogen has several properties that make safety one of the prime concerns of its use: a wide flammability and detonation range, a low heat of vaporization, a low minimum ignition threshold, and one of the largest heats of combustion per unit of mass. The accepted flammability range of hydrogen in air is 4.1% to 74.2% by volume. Detonations can occur for hydrogen concentrations between 18.3% and

59%. They require a strong ignition source, and are more likely to occur in a confined volume. The energy threshold to ignite a combustible mixture is a function of the concentration of hydrogen in air. The minimum ignition energy occurs close to stoichiometric conditions (30%), where it reaches 19 μJ . For hydrogen concentrations in air below 10% (vol/vol), the ignition energy is similar to that of typical hydrocarbon fuels. A hydrogen flame is nearly invisible and difficult to detect, because of the absence of soot.

Hydrogen leaks are colorless and odorless. Hydrogen is buoyant at room temperature. The density of hydrogen vapour at the normal boiling point is heavier than air. Cryogenic hydrogen gas remains heavier than air at ambient pressure up to temperatures of 190 K. Liquid hydrogen spills are thus likely to form larger vapor clouds that can remain close to the ground, with higher hydrogen concentrations than gaseous hydrogen leaks.

On the positive side, hydrogen is buoyant at room temperature, diffuses rapidly in air, and is difficult to explode in open, unconfined areas. The hydrogen molecule has a high diffusivity in air, almost six times larger than propane and close to 4 times larger than methane (Zittel and Wurster, 1996). Because of the small size of its molecule, it tends to leak more easily than other gases. Hydrogen molecules can also diffuse into steel and other metals. Depending on the material, it can cause embrittlement, resulting in structural defects. Susceptibility to hydrogen embrittlement imposes important restrictions on the choice of materials for the storage and manipulation of hydrogen.

Safety of hydrogen systems requires methods to ensure that hydrogen is safely confined in the vessels used for its generation, transport, storage, and end-user applications. Like any fuel, the manipulation of hydrogen has its inherent risks. Hydrogen is no more, and no less, risky than other fuels. The perception of risk in the general public stems from inaccurate depictions of the Hindenberg incident, which, incidentally, was shown by Bain and Vorst (1999) to have not been caused by hydrogen, as well as inaccurate associations with the hydrogen bomb. It is also rooted in the absence of clear codes and standards regarding the safe use of hydrogen. In the absence of specific codes and standards for hydrogen, natural gas standards were very often used, taking into account the specific properties of hydrogen.

However, the recent push for hydrogen standards by the International Standards Organization's Technical Committee 197 for hydrogen technologies and the International Electrotechnical Commission's Technical Committee 105 for fuel cell technologies will certainly contribute to the acceptance of hydrogen by the public. Demonstration projects, such as hydrogen-fuelled buses and cars, as well as hy-

drogen refuelling stations, will also play an important role in gaining the public's acceptance of hydrogen technologies.

Production and Infrastructure

Although hydrogen is the most abundant element in the universe, it does not exist in the pure state in any significant amount on earth and is almost always chemically-bound to other elements such as water, biomass, or fossil fuels. Molecular hydrogen must thus be extracted from compounds such as water or organic molecules. Various methods of production have unique needs in terms of energy sources (such as heat, light, and electricity) and generate specific by-products. Steam methane reforming represents the most common and least expensive way to produce hydrogen. It is based on a catalytic process that involves reacting natural gas, or other light hydrocarbons, with steam at a temperature of 700–1100°C to produce hydrogen and CO₂. About 48 percent of worldwide hydrogen production is based on steam metal reforming (Dunn and references therein, 2002). Partial oxidation of fossil fuels in large gasifiers is another method of hydrogen production thermally. It involves the reaction of a fuel with a limited supply of oxygen to produce a hydrogen mixture, which is then purified by pressure swing adsorption. Partial oxidation can be applied to a wide range of fossil fuels, such as natural gas, heavy oils, solid biomass, and coal. Its primary by-product is carbon dioxide. Biomass from recurring or renewable organic by-products from industrial and agricultural activities can also be used to produce hydrogen through pyrolysis, which is CO₂ neutral. This is a process in which biomass is decomposed by heat to form an oil that is then reformed with steam. The hydrogen produced from biomass is sensitive to the price and type of feedstock used, as well as the distance between production centers and distribution points.

Electrolysis, which involves the use of electricity to split water into hydrogen and oxygen, would open the possibility of a clean production cycle of hydrogen if electricity from renewable resources is used. According to Dunn (2002), about 4 percent of the total hydrogen produced comes from the electrolysis of water. This method is, however, not as efficient or cost-effective as the use of fossil fuels in steam reforming and partial oxidation processes for the production of hydrogen. It would allow, however, for more distributed hydrogen generation, except for the production of extremely pure hydrogen in small quantities (Dunn, 2002). Production of hydrogen by electrolysis is generally more expensive than by reforming of natural gas, although the level of gain will depend on the price of natural gas, the price of electricity, and on the possible presence of taxation measures designed to discourage the use of fossil fuels ("carbon taxes"). A life cycle analysis of the hydrogen production process suggests there are environ-

mental advantages for renewable electrolysis, as compared with natural gas reformation. Electrolysis from renewable energy would result in a very clean hydrogen cycle. The production of hydrogen through thermochemical splitting of water with heat from nuclear reactors is also being studied.

The present distribution infrastructure was designed for liquid fuels. A hydrogen-based energy system will not happen before a distribution infrastructure designed for a gaseous fuel with the particular properties of hydrogen has been set up. Specific properties of hydrogen to be considered are its propensity to cause embrittlement in certain metals, and the small size of its molecules and their rapid diffusion rate. Unlike electricity, natural gas, or gasoline, there is at present no widespread distribution system for hydrogen. Various possibilities for supplying hydrogen have been under study in the past few years (see, for instance, Ogden *et al.*, 1994 and references therein). Hydrogen could be produced at the point of use, or at a large centralized plant for distribution via truck or local gas pipeline. Onsite production of hydrogen avoids the problem of transmission and distribution. However, the cost of producing hydrogen is often lower at a large scale. Designing the total hydrogen energy system to give the lowest delivered hydrogen cost generally involves a trade-off between production costs (which would decrease with plant size) and transmission and distribution costs (which would increase significantly if an extensive transmission and distribution network were needed). The best solution depends on the total hydrogen demand (which determines the total production capacity needed) and the geographical location of the demand (which determines what kind of transmission and distribution system is needed).

CONCLUSIONS

There are still many obstacles to the introduction of hydrogen on the energy market. Other issues, such as ways to lower the cost of fuel cells, and the possible role of renewable alternative fuels, such as methanol, as a storage vector in hydrogen energy technologies must also be addressed. However, these obstacles constitute an opportunity for the development of new technologies and new materials. An energy system based on hydrogen will not happen without the proper storage and distribution infrastructure, and without reliable and safe technologies. Various storage options are being considered for hydrogen. Each has its pros and cons, and the choice of a specific storage option is very likely to be application-dependant. Every storage option is likely to find a niche application. The implementation of an infrastructure for the distribution of hydrogen will likely be solved progressively, by introducing hydrogen-based public transportation that can rely

on a centralized distribution infrastructure. Public funding will therefore play an important role. The early implementation of the infrastructure also requires a minimum degree of cooperation at the international level to ensure compatible hydrogen technologies. Therefore, international standards will play a critical role in the establishment of a hydrogen-based energy system. The simultaneous development of standards and technology will facilitate the early demonstration and implementation of the hydrogen technologies that will be required to move hydrogen into widespread energy applications.

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