SUSTAINABLE HYDROGEN PRODUCTION, STORAGE AND TRANSPORT PATHWAYS

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ABSTRACT

Hydrogen production, storage, transportation, and energy conversion constitute the foundation of a hydrogen energy system. Hydrogen is a gas that generally does not exist naturally in a pure usable form. The primary markets for this green hydrogen include the growing fuel cell transportation market with trains, trams, buses, and automobiles, as well as ammonia and the production of synthetic fuels from CO_2. Another application that is gaining momentum in the power industry is power-to-grid (P2G), where hydrogen is injected into the natural gas distribution network as a supplementary component to offset emissions and improve the heat of combustion. Today, hydrogen is mainly manufactured using a steam methane reforming (SMR) process with natural gas as the feedstock. Currently, global hydrogen production is estimated at approximately 119 Mt H_2/year, of which approximately 4% is produced via electrolysis, and the balance from fossil sources. There is a push for 'blue hydrogen', where the CO_2 produced in this process is sequestered in geological deposits; a process known as CCU (carbon capture and storage). Many countries are adopting this method of producing hydrogen at large scale including Australia, Canada, USA, Saudi Arabia, among others. The cost of production varies depending on whether or not the production is centralized or decentralized. This paper summarizes the most common methods of producing, storing and transporting hydrogen, and introduces the heat-to-hydrogen thermochemical production method.

Keywords: hydrogen production, storage, transport, pathways.

1 INTRODUCTION

Hydrogen production, storage, transportation, and energy conversion constitute the foundation of a hydrogen energy system. Hydrogen is a gas that generally does not exist naturally in a pure usable form. The hydrogen atom is made up of a nucleus with positive charge and one electron. The hydrogen molecule is made up of two hydrogen atoms and is the most basic of all molecules. At room temperature and under normal pressure, hydrogen is a colourless, odourless gas which is lighter than air and helium. Hydrogen burns with a light blue, almost invisible flame. At temperatures below −253°C, hydrogen is in a liquid state. It must be extracted or produced from other sources using various production methods. Thermochemical cycles like the copper-chlorine cycle developed at Ontario Tech University (previously known as UOIT) are promising alternatives for large scale hydrogen production. The Cu-Cl hydrogen process cycle generally involves four main steps: hydrolysis, thermolysis, electrolysis, and crystallization (or drying). The technology would displace considerable GHG emissions from conventional hydrogen produced via the steam methane reforming process. A key benefit of the Cu-Cl cycle is that all the chemical reactions occur within an internal closed loop and the chemical reagents and reactants are recycled on a continuous basis with near zero GHG emissions.

As illustrated in Fig. 1, the primary markets for this green hydrogen includes the growing fuel cell transportation market with trains, trams, buses, and automobiles, as well as ammonia and the production of synthetic fuels from CO_2. Another application that is gaining momentum in the power industry is power-to-grid (P2G), where a small percentage of hydrogen is injected into the natural gas distribution network as a supplementary component to offset emissions and improve the heat of combustion.

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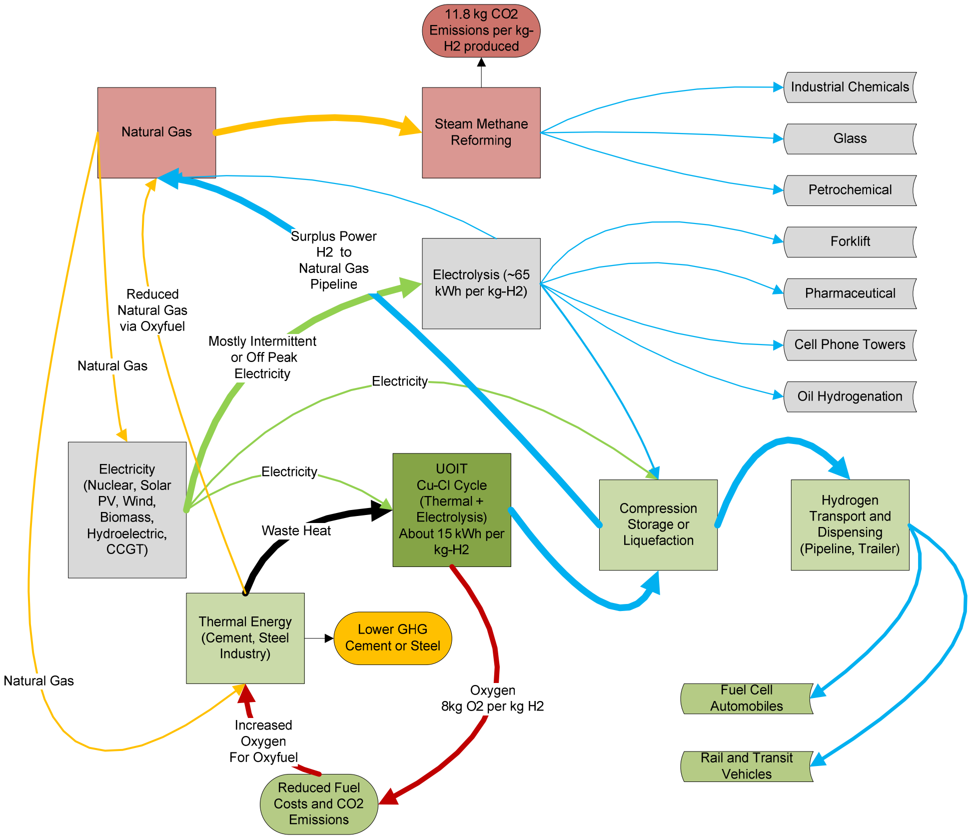

Figure 1: Large scale hydrogen production with copper-chlorine cycle.

2 HYDROGEN PRODUCTION

Hydrogen is currently manufactured using a steam methane reforming (SMR) process. Global hydrogen production is estimated at approximately 45,500,000 tonnes per year, of which ~4% is produced via electrolysis, and the balance from fossil sources [1]. The bulk of the global hydrogen production is currently produced on an industrial scale through steam methane reforming of natural gas and as a byproduct from a number of chemical industrial processes. Fig. 2 illustrates global hydrogen capacity, production and consumption as of 2017. Since then, the distribution has not changed significantly, but the total annual global production has now reached 119 Mt H_2/year [2].

During the SMR hydrogen production process, steam at a temperature between 700 and 1000°C is fed with methane gas into a reactor with a catalyst, typically at 3–25 bar pressure. The methane gas is the principal component of natural gas. In addition to the natural gas being part of the reaction process, an extra 1/3 natural gas is used as input energy to power the reaction. New methods are being developed to increase the efficiency and maximize the value of the steam that is produced as a byproduct. A large steam reformer which produces 100,000 tonnes of hydrogen annually can supply hydrogen for approximately 300,000 fuel cell vehicles. Steam methane reforming, however, emits enormous amounts of greenhouse gases into the atmosphere, estimated at 9–11 kg of CO_2 for every 1 kg hydrogen produced.

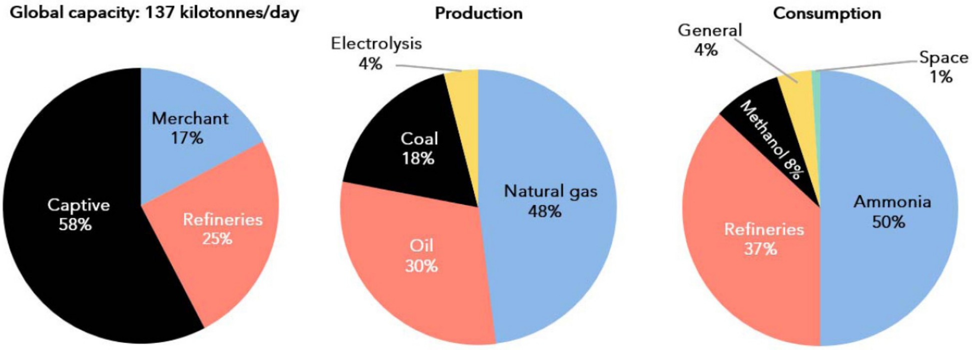

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Figure 2: Global hydrogen capacity, production and consumption.

2.1 Decentralized electrolysis production cost estimate

Figs 3 and 4 are representative graphs for decentralized and centralized hydrogen production. The dotted vertical line indicates the overall average hydrogen cost. The overall length of each vertical bar (purple plus yellow combination) indicates the relative weight of that factor to the overall price. The purple bar represents the relative impact the factor could have to decrease the hydrogen cost, and the yellow bar indicates the impact that factor could have to increase the cost. For example, for decentralized hydrogen the overall average cost to produce is \$5.20 per kg-H_2. Under the electricity price bar, if the cost of electricity was reduced to \$0.03/kWh, the cost to produce hydrogen could drop to \$4.20/kg-H_2 and if electricity increased to \$0.08/kg-H_2, the cost to produce would increase to ~\$6.50/kg H_2.

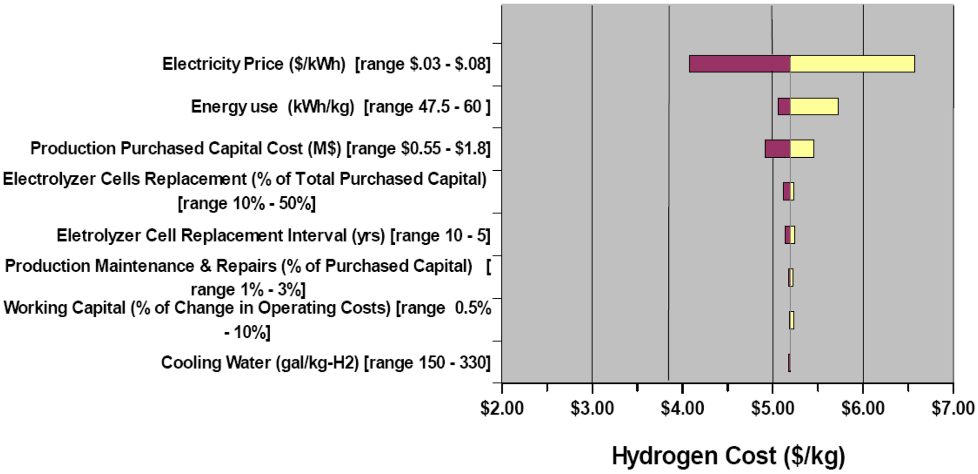

Figure 3: Decentralized hydrogen production cost breakdown [3].

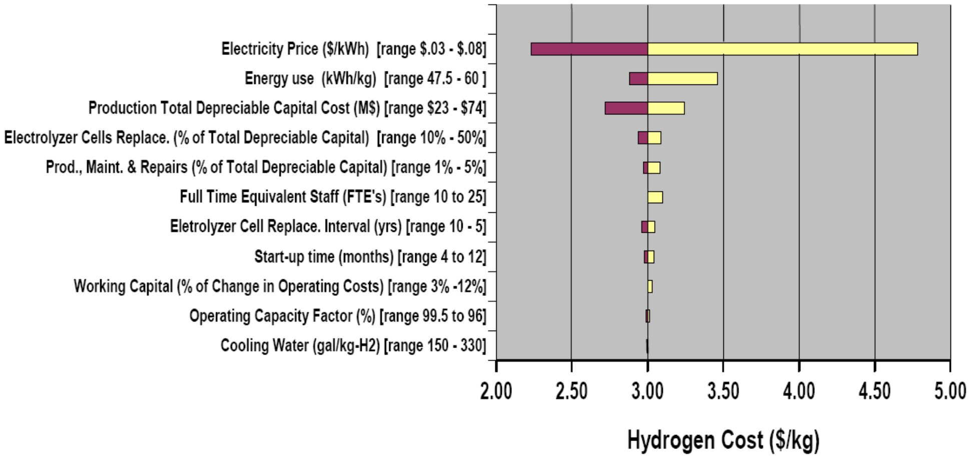

Figure 4: Centralized hydrogen production cost breakdown [3].

2.2 Centralized electrolysis production cost estimate

Large, centralized SMR hydrogen production facilities (those producing greater than 50,000 kgH_2 per day) have benefits and drawbacks with the opposite impact of distributed facilities. Centralized facilities have the advantage of economies of scale due to large quantities of hydrogen production but may have some risks. These risks include large initial capital investment requirements for facility construction and potentially large investments in delivery infrastructure depending on factors such as distance, geographic location, and existing infrastructure capabilities.

Large centralized steam methane reforming facilities can be built close to a supply of natural gas (RC (resource centred)) or close to an area with high hydrogen demand (MC (market centred)). The SMR facility is essentially the same in both cases. The salient differences are:

- There might be a better opportunity to sequester CO_2 in the case of the RC facility as, for example, depleted underground wells can be injected with CO_2.
- Hydrogen must be transported from the RC facility to the point of end use. In some cases, this may not be economically or logistically viable. MC facilities essentially cut down the distance for shipping hydrogen to end users.

Centralized hydrogen distribution systems would be like the system used to distribute gasoline today. Hydrogen is produced at large-scale facilities, possibly near refineries, and other sources of primary energy. The hydrogen would then be distributed to filling stations by pipelines and/or tanker trucks. Because hydrogen has low volumetric energy density, a given size of tanker truck would carry less energy in the form of hydrogen than it could for petroleum fuels. This increases transportation costs while reducing the energy efficiency of the entire process. Although pipelines are a mature technology for transporting fuels across great distances, current hydrogen pipelines are about 50% to 100% more capital intensive than other gaseous fuel pipelines due to additional inspection, safety and compression equipment requirements.

2.3 Decentralized steam methane reforming

Decentralized SMR facilities supplied by natural gas local distribution companies can be in urban areas and very close to customers. Long haul shipments of hydrogen are thus avoided. Distributed or decentralized SMR hydrogen generation occurs at a service station. This production method also requires equipment to separate and purify the hydrogen. Compact size PSA systems will be a key differentiating factor in the emerging hydrogen refuelling market, given the space premiums and footprint limitation involved in retrofitting hydrogen refuelling systems into existing service stations. Hydrogen can be produced at distributed locations near the end-user as well as at large centralized plants further away. Distributed facilities (those producing between 1,500 and 10,000 kg of hydrogen per day) can take advantage of existing natural gas transmission and distribution infrastructure and produce hydrogen on site, where it can then be purchased by the end-user, thus eliminating the need for potentially costly investments in hydrogen delivery infrastructure. However, the disadvantage is that small, distributed production facilities typically lack economies of scale, possibly have low efficiencies, and require a higher capital investment per unit of hydrogen produced. There is also risk associated with the potential for underutilization of the plant and unexpected downtime if redundancy or buffering storage is not built into the system. By contrast, an unexpected shutdown at a small, distributed plant will have only a localized impact, affecting a relatively small number of consumers.

2.4 Alkaline electrolysis

Alkaline electrolysis is a mature technology and has widespread commercial installations. The alkaline water electrolysis is frequently used due to its relative low cost, durability, and technology maturity. The anode and cathode materials in these systems are typically made of nickel-plated steel and steel respectively. Proton exchange membrane (PEM) electrolysis has been a suitable alternative for alkaline electrolysis. PEM electrolysis is built around a proton conductive polymer electrolyte. The cell consists of an anode (oxygen production) and a cathode (hydrogen production) and a PEM in between, by which the two gaseous components are separated. PEM technology is increasingly being applied in fuel cell technology, in which the exact opposite reaction of the electrolysis reaction occurs. Commercially available production units with upper capacity of tens and perhaps hundred MW electric are available and rapidly improving in performance and reliability. Fig. 5 shows that the conversion of electricity into hydrogen as an energy carrier is between 30% and 42%. This does not include additional energy for compression, transportation, storage and dispensing of hydrogen.

2.5 Solid oxide electrolysis (SOE)

SOE can provide an alternative to alkaline or PEM electrolysis. SOE is unique in that the process can produce synthesis gas (H_2 and CO) from an input of power, water and CO_2. Moreover, the operating temperature range (from 700°C to 1,000°C) in which this technology operates is significantly higher than alternatives but enables the splitting of water with an overall energy efficiency in the 50%–90% range. SOE fuel cells had a rocky history with the testing of a 250 kW Westinghouse system and the demise of Fuel Cell Technologies (Kingston, Ontario) with their 4 kW system. The CuCl hydrogen production process may be able to tap into high temperature heat source from SOE in the future.

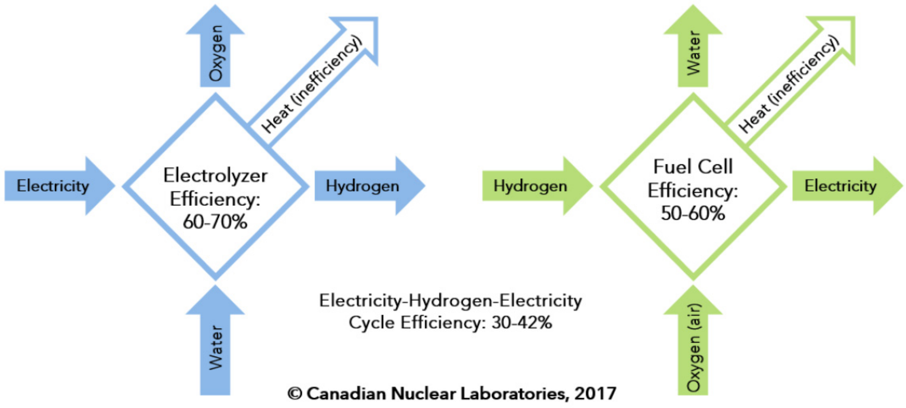

Figure 5: Hydrogen production via electrolysis has 30%–42% cycle efficiency.

2.6 Thermochemical water splitting cycles

Thermochemical water splitting cycles are one of the most promising clean alternatives to traditional hydrogen production methods, as they use water as a feedstock, with no external emissions to the environment [4]. Feedstock to the process is steam produced by waste heat or other energy source and copper-chlorine compound with electricity used to a much lesser extent compared to conventional water electrolysis [5]. Over 200 thermochemical cycles have been previously identified in the literature to produce hydrogen [6]. Lewis and Taylor [6] conducted a survey and reported that the Cu-Cl cycle is one of the leading methods for sustainable, green hydrogen production. A future commercial Cu-Cl plant would utilize thermal energy from sources such as nuclear, solar, waste/process heat, or other industrial heat sources. This includes heat recovery from the emissions of power plants, industrial petrochemical plants, steel recycling, or cement production.

The Cu-Cl cycle is a system of chemical reactors which allow for waste heat to be used as the primary energy input in producing hydrogen. This contrasts against electrolysis, which uses only electricity. To do this, the Cu-Cl cycle employs a copper and chlorine salt which undergoes several chemical decompositions throughout the process. This Cu-Cl salt starts in the hydrolysis step as solid $CuCl_2$, which then reacts with high-temperature steam at 400°C and forms an intermediate compound (Cu_2OCl_2) and HCl gas. The products of this reaction carry hydrogen and oxygen separately, with Cu_2OCl_2 carrying oxygen, and HCl carrying hydrogen. The Cu_2OCl_2 is heated to its melting point at ~500°C, releasing oxygen gas and forming aqueous CuCl as a byproduct. The CuCl and HCl then react in an electrochemical cell forcing hydrogen gas to be released from the HCl and liberating chlorine (Cl), which binds with CuCl forming molten CuCl2. The CuCl2 is then sent back into the hydrolysis step, beginning another cycle to be repeated. A schematic of the Cu-Cl cycle is presented in Fig. 6. The equations representing the chemical reactions in the Cu-Cl cycle are presented below:

$$2\mathrm{CuCl}_{2(s)} + \mathrm{H_2O}_{(g)} \rightarrow \mathrm{Cu_2OCl}_{2(s)} + 2\mathrm{HCl}_{(g)}, \tag{1}$$

$$2\mathrm{Cu_2OCl}_{2(s)} \rightarrow 4\mathrm{CuCl}_{(l)} + \mathrm{O}_{2(g)}, \tag{2}$$

$$2\mathrm{CuCl}_{(aq)} + 2\mathrm{HCl}_{(aq)} \rightarrow \mathrm{H}_{2(g)} + 2\mathrm{CuCl}_{2(aq)}. \tag{3}$$

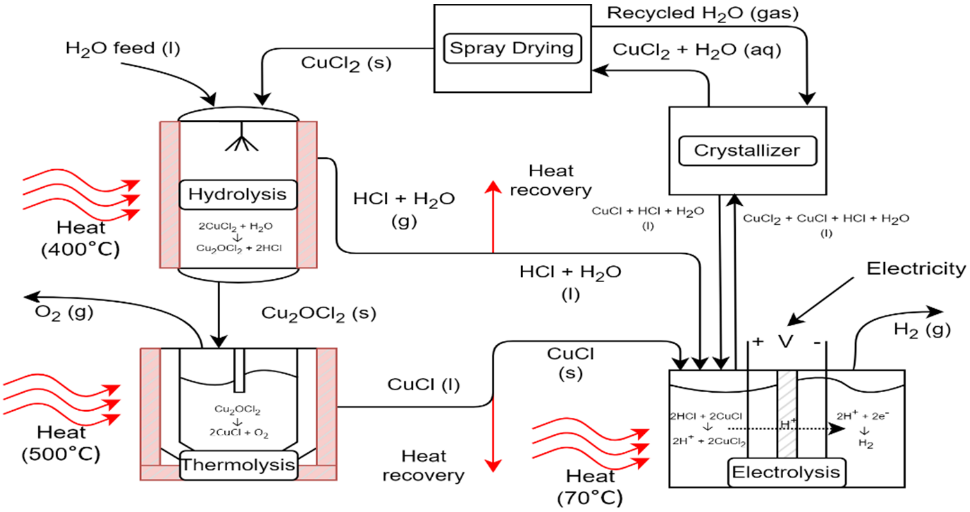

Figure 6: Schematic of processes in the Cu-Cl cycle.

3 HYDROGEN STORAGE

Hydrogen is a substance with high ratio of energy content to weight. However, the energy content compared to volume is rather low. This poses greater challenges with respect to storage compared to storage of liquid hydrocarbon fuels. The US Department of Energy determined that an energy density of 6.5 wt.% hydrogen and 62 kg hydrogen per m^3 must be achieved for a hydrogen storage system of appropriate weight and size to facilitate a fuel cell vehicle driving distance of 560 km. There are essentially three options for hydrogen storage in transportation applications:

1. It may be compressed and stored in pressure tanks;
2. It may be cooled to a liquid state and kept cold in a properly insulated tank; or
3. It may be stored in a solid compound.

3.1 Compressed hydrogen

Storing hydrogen under pressure has been done successfully for many years. The main materials for hydrogen tanks are steel and aluminium core encased with composite fibres. In stationary systems where weight and size are not decisive factors, steel tanks are a good solution, but for vehicles, traditional pressure tanks are problematic regarding both weight and volume. There has been considerable breakthrough in the past few years in the development of new types of composite tanks which can store hydrogen at 350 bar pressure and at the same time meet the current safety standards. This type of tank has a storage capacity of 10–12 wt.% hydrogen, whereby the weight of the tank no longer is a problem. Significant advances are also being made on tanks which can store hydrogen at 700 bar pressure. This will reduce the tank volume, which is necessary to achieve the desirable driving distance.

3.2 Liquid hydrogen

Hydrogen can be stored as a liquid (LH2) at 20 K (−253°C) in super insulated tanks. The equivalent of 30%–40% of the energy value of liquid hydrogen is required to liquefy it. The liquefaction process uses a combination of compressors, heat exchangers, expansion engines, and throttle valves to cool the hydrogen to the desired temperature. A concern with liquid hydrogen storage is minimizing hydrogen loss due to boil-off. Para and ortho are two molecular forms of hydrogen, depending on the electron configuration of the atoms. At the boiling point of hydrogen almost all the molecules are para-hydrogen, but at room temperatures the concentration is 25% para-hydrogen and 75% ortho-hydrogen without a catalyst, the conversion from ortho to para is slower than the conversion from a gaseous state to liquid state. Hence, after the hydrogen has been liquefied, the ortho-to-para conversion takes place and releases heat. To prevent this, a catalyst is used to facilitate the conversion while the mixture is cooled. Hydrogen boil-off occurs because any heat transfer to liquid hydrogen at the boiling point results in the evaporation of hydrogen. To prevent boil-off all sources of heat are eliminated. Highly insulated cryogenic containers are used to store the liquid hydrogen to prevent heat transfer from exterior sources.

3.3 2.3 Metal hydride

Hydrides are compound which contain hydrogen and one or more other elements. Certain metals and metal alloys can absorb hydrogen under moderate pressure and temperature, creating hydrides [7]. A metal hydride tank contains, in addition to a heat manipulation system, granular metal which absorbs the hydrogen. The heat system draws heat away when hydrogen is filled into the tank and applies heat when the hydrogen is taken out of the tank. The hydrogen is released from the metal hydride when heat is applied. The required heat may be drawn from excess heat produced by the fuel cell [8]. From a safety perspective, metal hydride tank is a very safe. In the breach, the loss of pressure in a punctured tank will cool down the metal hydride, which will then cease to release hydrogen. Several metal hydrides are available commercially, representing a good solution for hydrogen storage where the weight factor is not a problem. For vehicles, the problem with metal hydride is the high weight compared to the amount of hydrogen stored. Work is being done on finding cheaper metal alloys which can absorb large amounts of hydrogen, and at the same time release the hydrogen at a relatively low temperature. The International Energy Agency's (IEA) metal hydride program has a goal of 5 wt.% absorbed hydrogen and hydrogen release at < 100°C. $NaAlH_4$ is a promising metal hydride and is also reasonably inexpensive. It has a 4 wt.% hydrogen capacity, and 150°C release temperature.

4 HYDROGEN TRANSPORTATION AND DELIVERY

Once hydrogen is manufactured at a central facility, there are several technologies to bring it to market. These include: (1) Cryogenic liquefied hydrogen; (2) Compressed to 5,000 psi and 10,000 psi (350 bar and 700 bar); (3) Pipelines; and (4) Solid state hydrogen transport. Several global factors must be taken into account when transporting hydrogen. In terms of technology, the energy intensity required to transport hydrogen is a principal economic concern. Factors in the economic decision involve assessing the various technology, hydrogen feedstock prices, distances to market, and volume of hydrogen to be transported. Other issues include the physical rate and quantity at which the hydrogen can be transported. Moreover, leakages occur with pipeline and cryogenic methods of transport, and this limits the economic range between supply and consumption.

For hydrogen to have a positive net energy impact, it is necessary to minimize energy associated with transportation and storage.

4.1 Cryogenic liquefied hydrogen

This transportation method increases the amount of fuel on board a delivery vehicle but requires the hydrogen to be stored at a temperature of at least −253°C. Heavily insulated tanks are required to maintain the very low cryogenic temperatures but eventually heat will seep into the tank and the hydrogen will boil off and return to its natural gaseous state. Therefore, the insulated tanks must also be pressurized to allow containment of the boiled off gas. Liquid hydrogen storage in cryogenic containers offers a higher mass to volume ratio than gaseous hydrogen.

4.2 Compressed hydrogen

Transportation of hydrogen in pressurized gas storage in tanks is currently the most mature transportation technology. Composite gas storage tanks are commercially available at 350 bar pressure. In the early 2000s, tanks at 700 bar were demonstrated and certified. The very high-pressure tanks utilize lightweight tank materials, including carbon fibre reinforced composites. The principal drawback for transportation applications involving high pressure gaseous transpiration is the small mass of hydrogen that can be stored within a finite volume. For example, when hydrogen is compressed to 700 bar, its energy content (4.4 MJ/l @ 700 bar) is significantly less than that for the same volume of gasoline 31.6 MJ/l. Also, significant energy is required to compress the gas, and this depends on both the initial and final pressures of the hydrogen. Ongoing research and development are focusing on novel reliable, strong, and low-cost materials. A better understanding of the mechanics and mechanisms associated the weakening and failure of materials, such as hydrogen embrittlement, is also being developed.

4.3 Hydrogen pipelines

In situations where there is centralized hydrogen production in place and continuous market demand for hydrogen, pipelines can make the most economic sense. For example, a densely populated urban centre with many fuel cell vehicles would benefit economically from the delivery of hydrogen via a pipeline. Hundreds of kilometres of gaseous gas pipelines have been operational for many years in North America and Europe. Several hydrogen pipelines have been in operation for many decades. Pipelines are suitable for the transmission of hydrogen gas at about 75 bar pressure, about the same as natural gas pipelines. Higher degrees of regular maintenance of hydrogen pipelines, together with special construction with low carbon content steels and welds, would be required to mitigate potential of hydrogen embrittlement. Hydrogen pipelines with critical minimum volume throughputs (e.g., 100,000 kg H_2 per day), are cost competitive with cryogenic transport of hydrogen. This is primarily due to the very high energy intensity for both cryogenic and pressurized hydrogen transport, together with the significant ‘boil off’ losses in the case of cryogenic.

4.4 Solid state hydrogen

An alternative transporting hydrogen either as a compressed gas or liquid forms, a solid storage or metal hydride. However, due to the light weight of hydrogen relative to the storage media, energy and weight penalties result when transporting hydrogen in this form. There is also an additional energy cost incurred during placing (adsorption) and removing (desorption) of hydrogen to the hydride [9], [10]. Metal hydrides have the advantage of providing more energy dense storage of hydrogen than either hydrogen liquefaction or compression, but the downside is they are quite heavy. MacDonald and Rowe [11] examined thermal coupling with energy converters (fuel cells) using a numerical model that was capable of dynamic simulations capable of modelling cyclical loading and represent accurate operating conditions. An experimental investigation was completed [12] using commercially available and proprietary metal hydride alloys from an industrial partner to validate the model.

5 CONCLUSIONS

Hydrogen as a clean fuel has many benefits for society, human health and the environment. The exhaust product that results from burning hydrogen is water vapour. On its own, hydrogen is a clean, non-toxic fuel. It represents a potentially major solution to the problems of climate change and depleting reserves of conventional fuels. Furthermore, increasingly stringent environmental regulations require cleaner transportation fuel production with lower content of sulfur and nitrogen compounds, which requires higher levels of hydrogen. This long-term trend is expected to continue especially as cleaner fuel specifications are progressively introduced by governments around the world. Hydrogen is an integral component for the vast majority of clean fuel standards compliance since tighter and cleaner fuel specifications emerged in the late nineties.

Choosing the right routes for hydrogen production is critical, and it determines the sustainability of hydrogen. There are several other routes to produce hydrogen in a cleaner and sustainable way; two ways to change this status quo: one is to combine carbon capture and storage (CCS) The thermochemical cycle utilizing waste heat has low cost and low environmental impact. For nuclear electrolysis and thermolysis, it is more competitive in terms of cost than under other energy sources. It is worthwhile to examine the technological maturity and safety of nuclear energy and expect it to become the main driver for hydrogen production in the future.

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