A Review on Hydrogen Energy

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Abstract

Hydrogen is the cleanest fuel among the existing with high calorific value ranging from 120 to 140 MJ/kg. It is being considered as 'a fuel of the future' from the global warming perspective due to very low to zero carbon emissions. Hydrogen energy is becoming a key component in bringing about the energy transition to ensure a sustainable future. Due to its very high potentials to capture the market in several fields, including automobiles, power generation, chemical, petrochemical and steel industries, and domestic uses, a lot of research has been going on and several innovations have been made in the technologies related to hydrogen production. It can be produced using fossil fuels and renewable sources which include production of H_2 from natural gas, coal, nuclear, biomass, solar, wind, hydroelectric, and geothermal energy. Among these, every approach has its own advantages and disadvantages along with some practical and commercial viability challenges. Therefore, while keeping several opportunities and future prospects of the hydrogen economy in mind, in this techno-economic review, we will be presenting different hydrogen production technologies along with their practical challenges and commercial aspects for different applications while projecting their future scope.

Keywords: *Hydrogen, Hydrogen Energy, Green Hydrogen, Renewable Energy*

Introduction

The world has been craving for a greener and cleaner energy due to the increasing global energy demands with added greenhouse gas emissions, and hydrogen is the most suitable candidate with applications in almost all the sectors ranging from aviation to transportation, shipping, fertilizers, stationary power, steel industry, petroleum and many more [1]. Since hydrogen has high calorific value about 120 to 140 MJ/kg, it can be an ideal candidate as a fuel for deep decarbonization of the global economy [1-5]. Various studies suggest that hydrogen from renewable sources could become a cost-effective solution in the upcoming decades, which could eventually transition into hydrogen based renewable energy economy. The hydrogen based economy could alter the energy balance among energy producing and energy consuming nations in the world by replacing the hydrocarbon society. Hydrogen has enormous geopolitical implications, and technological advances and competition in energy industries are the major motivations for exploring hydrogen [2]. Being a secure domestic fuel, hydrogen when used in hydrogen fuel cell powered vehicles, it will drastically cut down the emissions of air pollutants, nitrogen oxides, carbon oxides, sulphur oxides and other local pollutants. Although the cost of hydrogen and fuel cells are decreasing globally yet they are expensive compared to the conventional hydrocarbon-based fuels and systems. With recent global summits on global greenhouse emissions and promises made by different nations to lower the carbon footprint, the renewable energy technologies based on solar, wind, and hydro have started to emerge as a new hope in decarbonizing the global power sector despite of many challenges [3]. This is where hydrogen also has the potentials for generation, storage and transportation while utilizing the renewable sources [3]. Usually, large amounts of energy is produced during the day time with solar powered systems, and can be utilized in the later part of the days for generation of hydrogen through electrolysis[6] . Thus the surplus power generated during the day time can be converted into hydrogen for fulfilment of other energy applications as well as in the later hours of the day. Thus, hydrogen is going to act as suitable candidate for global transition into a cleaner energy economy. The current estimates of hydrogen production worldwide is around 70 million tonnes per year following different types of production technologies which are shown in Fig. 1 [6]. Among different approaches, following are the three major technologies that have the capability to produce clean hydrogen – (a) Steam methane reformation (SMR) with carbon capture, (b) Electrolysis of water, and (c) Hydrogen from renewable biomass [5]. Although there are other technologies which are known to be commercially successful, but from the global greenhouse gas emissions point of view, above techniques have garnered a great attention in the recent past and hence this article will also focus more on these three approaches while projecting their capabilities along with limitations and future prospects.

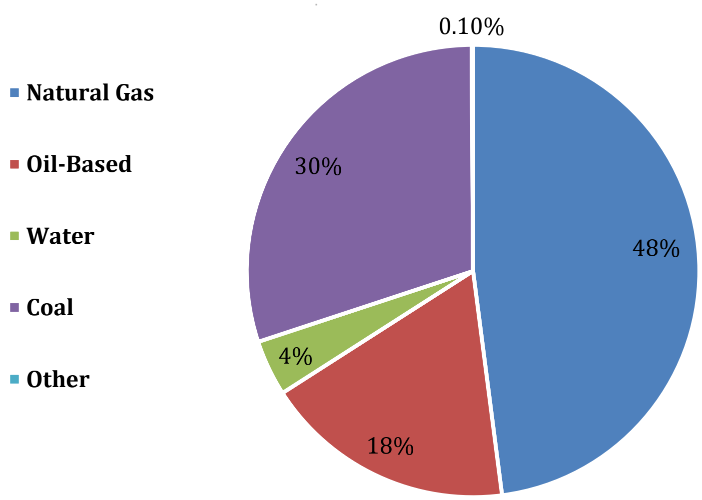


Figure.1. Overview of Hydrogen Production worldwide by various technologies [7]

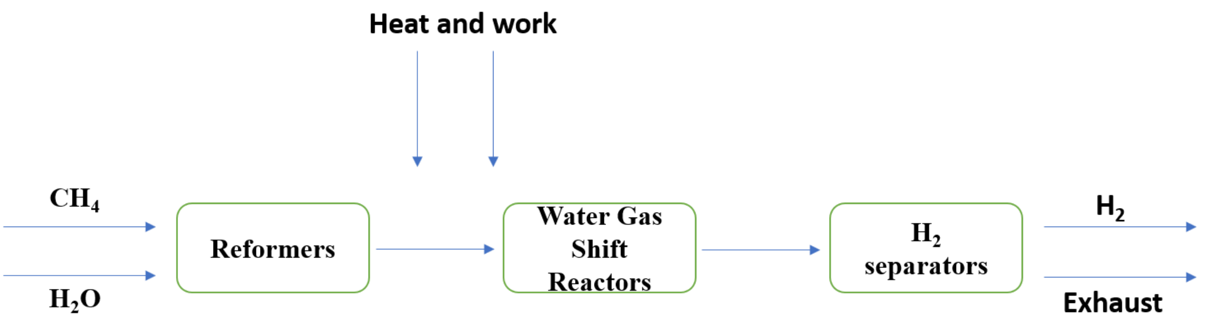
(a) SMR with carbon capture: Half of the overall demand of hydrogen across the globe is fulfilled by natural gas, which typically contains ~94% of methane and 6% of ethane, which also behaves in a similar manner to that of methane. The process of SMR produces both hydrogen and CO_2 but with capture of CO2 it can be converted into a green process. The initial step of SMR is endothermic in nature, but as hydrogen carries out high heating-value, the overall reaction is counter-balanced in the overall energy outcome [8]. The process of SMR includes two major reactions. In the first step, Methane is allowed to react with steam in presence of high temperature catalyst. Due to the endothermic nature of this reaction, heat must be supplied to the reformer which is achieved around 900-1200 K in presence of Ni-based catalyst with pressure ranging between 5-25 bar [5, 9]. The reaction in this step can be written as below:

$$CH_4 + H_2O\ (g) \rightarrow CO + H_2 \qquad \Delta H_R = +25 MJ/Kmol\ (CH_4) \qquad \text{Eq. 1}$$

In the second stage, the above produced syngas is passed through water gas reactor (WGS) converting CO into CO_2 and H_2 through an exothermic reaction in presence of water as shown below

$$CO + H_2O\ (g) \rightarrow CO_2 + H_2 \qquad \Delta H_R = -40 MJ/Kmol\ (CO) \qquad \text{Eq.2}$$

Finally, hydrogen is separated from the WGS reactor, which can be then utilized for generation of electricity or transported through pipeline systems to the energy requiring locations. A schematic for overall SMR is shown in Fig. 2.



(Schematic diagram for SMR [8])

SMR is a well-established technology for hydrogen production at present for almost all the industrial applications. The CO_2 capture in the final stages of SMR can help in reduced carbon footprint of SMR process, which could play a vital role in decarbonization of the economy. As progress in carbon capture area is speeding up every day, improvements in the SMR are being observed [13]. The efficiency of SMR technologies have shown to be around 65 - 75% [10] in the industries. However, it could be improved to 86 - 87% with increased costs incurring under zero export steam conditions [11 - 12].

2. Electrolysis of water

The process of electrolysis refers to decomposition of water into its basic constituents i.e., hydrogen and oxygen. It is carried out using electrolyzers with a set of electrodes (anode and cathode), a separator, and an electrolyte while utilizing electricity to breakdown the water into hydrogen and oxygen [6,14,15]. However, electrolysis can be perused with different electrolytes and electrolyzer setup. Some of the typical electrolysis methods used for production of hydrogen are discussed below

2.1 Alkaline Electrolysis*:* electrolysis of water using alkaline electrolytes is generally carried out due to their high conductivity. Alkaline electrolytes consist of 30wt.% KOH or NaOH solution which circulates through the electrolytic cell continuously. Platinum coated nickel cathodes are used against metal oxide (such as tungsten, manganese, or ruthenium oxides) coated Nickel or copper anodes [1,14,16]. The redox reaction at anode and cathode are shown below:

Reaction at anode:

$$4OH + O_2 \rightarrow 2H_2O + 4e^- \qquad \text{Eq.3}$$

Reaction at Cathode:

$$4H^+ + 4e^- \rightarrow 2H_2 \qquad \text{Eq.4}$$

Overall Reaction:

$$2H_2O \rightarrow 2H_2 + O_2 \qquad \Delta H = -288 kJ/mol \qquad \text{Eq.5}$$

Alkaline electrolysis is most suitable for stationary applications and the pressure required for this process is approximately 25 bar [17]. Alkaline electrolyzers show a maximum efficiency between 50-60%. It is a well-established technology as of today, however many challenges still persist in terms of cutting down the overall cost and improvement in efficiency [6].

2.2 Proton exchange membrane (PEM) electrolyzers: PEM electrolyzers have evolved significantly with advancements in fuel cell technologies. In PEM electrolyzers absence of electrolyte makes the overall design and mechanism very simple [16]. Generally the electrodes are made of iridium, Pt black, rhodium, and ruthenium etc [18], whereas a Nafion membrane is used as separator between the electrodes [19,20] .Water supplied at the anode is broken down into protons and oxygen, and the protons diffused through the PEM membrane recombine with electrons at cathode result in the release of hydrogen gas. The redox reactions in the PEM electrolyzers are shown below [14,17,21]

Reaction at anode:

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2 \qquad \text{Eq.6}$$

Reaction at cathode:

$$4H^+ + 4e^- \rightarrow 2H_2 \qquad \text{Eq.7}$$

Overall reaction:

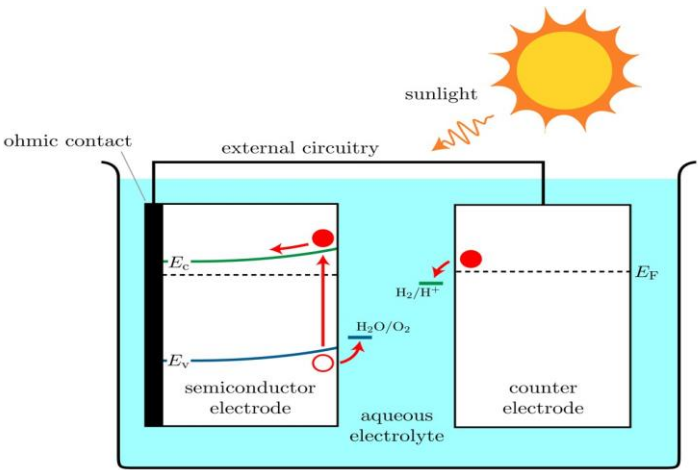
$$2H_2O \rightarrow 2H_2 + O_2 \qquad \text{Eq.8}$$

The PEM electrolyzers are designed to operate at high pressures up to several hundreds of bars and can be used both in stationary and mobile applications. However, their high cost, poor efficiency (55-70%) [19,22], and low capacity are apt to be improved. In contrast to the alkaline electrolyzers, PEM electrolyzers are a better bet for their safety, compact design and high operating pressures. At the same time advances in electrode material developments and cell stack design are expected to improve their overall performance significantly [6,18].

2.3 High Temperature Electrolysis: High temperature electrolysis is somewhat similar to alkaline electrolysis with low electrical energy demand while utilizing thermal energy support to breakdown the water into hydrogen and oxygen. This technology is primarily based upon high temperature fuel cells [16]. When compared with alkaline electrolysis, a non-corrosive solid electrolyte is utilized in high temperature electrolysis. Therefore, the problems related to electrolyte flow/distribution are not observed in this process [17][18]. Usually very high efficiency is observed due to reduction in overall potential between anode and cathode. The efficiency for these systems ranges between 85-90% [23]. Now a days nuclear and conventional combustion energy is also being utilized in high temperature water electrolysis. In addition to these, use of solar power is expected to improve the efficiency [24].

2.4 Photo-electrolysis or Photo electrochemical water splitting: water can be decomposed directly using sunlight to produce cleanest hydrogen along with oxygen as by-product using semiconductor materials or photovoltaic materials. A semiconductor electrode in combination with a metallic or semiconductor electrode is exposed to sunlight leading to the formation of photo electrochemical cell. A p-type and an n-type doped semiconductor materials are joined together resulting in the formation of a p-n junction. Rearrangement of the charges at this junction will produce a permanent electric field [15,16,17].

A photon with higher energy than the bandgap of semiconductor material strikes at the p-n junction, resulting in removal of an electron while leaving a hole at the junction. As electric field is present, both the electron and hole will be forced to move in the opposite directions leading to electricity. The same phenomenon occurs in the process of photo electrolysis in addition to decomposition of water giving away hydrogen and oxygen, which is depicted in Fig4.



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The performance of the system is analysed by the material of the photo electrodes and each layer of semiconductor. Various experiments have been conducted considering TiO_2, Fe_2O_3, and thin film WO_3 as photo electrodes[7]. The materials used for photo anode are n-GaAs, CdS, ZnS, and n-GaN while p-InP/Pt, CIGS/Pt, p-SiC/Pt are used as photocathode. Rossi et. Al. [7]performed several experiments of photo electrolysis using TiO_2 and cyanine chloride as semiconductor and sensibiliser, respectively, and concluded that use of sensibiliser increased the production of hydrogen. Photochemical catalyst with suspended metal complexes in addition to the semiconductors have also been used for photo electrolysis[7]. Nano-particles of low cost TiO_2, ZnO, and Nb_2O_5 have also been used to achieve high efficiency in the photo electrolysis. [16].

The efficiency of photo-electrolysis is affected by bulk and surface properties, imperfections in crystalline structure of photo electrodes, corrosion resistance and their ability to decompose the water. Although the photo electrodes used at present in PEC show very low efficiency but lot of research is conducted to improve their efficiency of PEC systems.

2.6 Geothermal Energy Electrolysis: Jonsson et. al.[8] utilized geothermal energy for water splitting experiments, where initially the water was heated to 200 ºC using geothermal fluid and the steam produced was further heated to about 900 ºC using the same geothermal energy for electrolyzing the water [16]. This study demonstrated a reduction of 19% production cost when compared with conventional thermal energy. Although geothermal energy is one of the cleanest energy sources available but replacement of fossil fuel with geothermal is not expected for use in high temperature electrolysis.

2.7 Wind electrolysis: Major developments have been observed in the area of wind energy in the past few decades, but due to geographical limitations, use of wind power in wind electrolysis is limited. Wind electrolysis can be carried out at isolated and remote locations where cost of electricity is relativity high [16]. Numerous developments have taken place in the area of wind electrolysis following which several wind electrolysis units have been setup. This is a renewable source but available at limited locations.

3. Hydrogen from Biomass:

Biomass can be obtained from wide range of available source's such as waste paper, animal waste, crop residue, corns, municipal solid waste, agricultural waste, aquatic plants, switch grass, saw dust, and many others. (ref). The yield of hydrogen produced from biomass is affected by composition and characteristics of biomass used. (ref). In addition to these, moisture content, reactor system, particles, temperature and heating parameters also affect the yield and efficiency of hydrogen production from biomass [6,17]. Here we discuss the technologies for production of hydrogen from biomass.

1. Pyrolysis and Co-pyrolysis
2. Biomass Gasification
3. Aqueous Phase Reformation
4. Microbial Biomass Conversion

3.1 Pyrolysis and Co-Pyrolysis:
In this process, raw organic material (biomass) is subjected to heat (temperature ranges between 500-900 ºC) and gasified between 0.1 - 0.5 MPa. On the basis of operational temperature, this pyrolysis is classified into:

- Low temperature pyrolysis (up to 500 ºC)
- Medium temperature pyrolysis (500-800 ºC)
- High temperature pyrolysis above (>800 ºC)

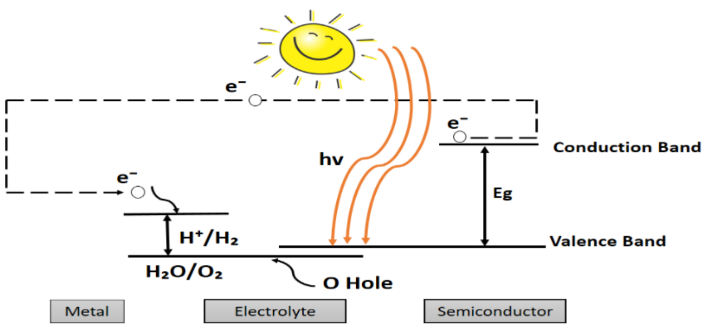
As the process of pyrolysis takes place in the absence of water, air and oxygen, a minimal carbon emission is observed, which significantly reduces the carbon footprints. As biomass can never be completely dry, a small amount of CO_x emissions is always emitted. The chemical reaction corresponding to pyrolysis is:

$$C_nH_m + \text{heat} \rightarrow nC + 0.5mH_2 \qquad \text{Eq.13}$$

Pyrolysis and Co-pyrolysis have the advantages, such as, simple and compact system design, reduced carbon emissions and fuel flexibility. Organic materials can be transformed into high energy content products using latest fast pyrolysis technology, which is considered ideal for lowering the CO and CO_2 emissions. A significant amount of solid carbon can be recovered with this technique that can be sequestered easily. Hence this technique is going to play a vital role in the near future for hydrogen economy outlook by 2050.

3.2 Biomass Gasification: It is a variation in pyrolysis process. The feedstock material is partially oxidized into a mixture known as producer gas, which contains carbon monoxide, carbon dioxide, methane, higher hydrocarbons, and hydrogen. Although the process of biomass gasification can be carried out with or without a catalyst, but due to the high moisture content, the efficiency of gasification process is very low. Superheated steam is used to dry the biomass at 900 ºC to achieve high hydrogen production yield. Large scale gasification reactors require large amount of biomass feedstock on a regular basis, which in turn requires tremendous number of resources. High logistic cost for biomass feedstock, massive biomass requirement with human resources are the current challenges that need to be addressed. Small scale biomass gasification plants with high efficiency may lead to cost reduction via biomass gasification, which is a mature and commercially available process that can lead to substitution for petroleum in the near future [25].

3.3 Aqueous Phase Reforming (APR): Carbohydrates or oxygenated hydrocarbons from renewable biomass sources can be used to produce hydrogen via a new technology termed as Aqueous phase reformation. In comparison to conventional alkaline phase steam reforming process, APR operates at relatively lower temperatures (220-270 ºC). Although group VIII catalyst can be used in APR but Pt-containing solids have shown the maximum catalytic efficiency. Researchers(ref) claimed that this technique was more efficient in conversion of biomass feedstock to hydrogen. Using APR based process an efficiency more than 55% using feedstock composed of 60wt% glucose in water has been achieved. (Figure showing mechanism)



Improvements in durability and catalytic activity are going to boost this technology in terms of cost and efficiency

3.4 Microbial biomass Conversion: The Organic matter is broken down by microbes resulting in the production of energy with formation of protons [17]. Microbial electrolysis cells (MEC's) in combination to small electric current can be used to harness the energy and protons obtained for hydrogen production. The chemical reaction taking place is shown below:

$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$ Eq.14

Dark fermentation is carried out by anaerobic microorganisms in which carbohydrate is converted into hydrogen and other by-products. As this technology is very much new, researchers are trying to improve the rate and efficiency of hydrogen production of the overall system. Different aspects including overall working of system, finding low-cost materials, and identifying most effective microbes for hydrogen production need to be addressed for improving the efficiency of this technology. Although MEC based systems have high potential for clean hydrogen production, but following areas need more developments:

- Optimization of reactor system
- Identification of suitable feedstock
- Enhancement of rate of hydrogen production
- Reduction of cost of reactor components
- Improvement of yield of hydrogen production

In the upcoming decades, MEC based systems are going to act as potential candidates with contribution towards greener and cleaner hydrogen economy [6]

While keeping the potentials and future prospects of all the above discussed hydrogen production technologies storage of hydrogen will also become a matter of concern for long term proliferation of hydrogen economy. In order to succeed in the implementation of hydrogen as fuel for different applications ranging from stationary to mobile currently available hydrogen storage technologies need to be critically looked upon while focussing on the challenges along with possible future improvements in prospects. Hence a short discussion on hydrogen storage is also provided below.

Hydrogen Storage: On the basis of mass, hydrogen has high energy content and it is approximately three times that of gasoline (about 44 MJ/kg). However, the situation gets totally reversed, on the volume basis where gasoline has comparatively very high energy density about 32 MJ/Litre when compared with hydrogen of 8 MJ/Litre. Storage of high-density hydrogen is a major challenge for applications in transportation sector. The storage options available right now needs to be expanded to larger volumes. Although for larger vehicles including trains, the storage volume issues do not seem to have a major impact, but whenever we look upon these issues in light duty vehicles, the storage hydrogen remains a critical challenge [6], [17].

Following fig. depicts different technologies available for hydrogen storage

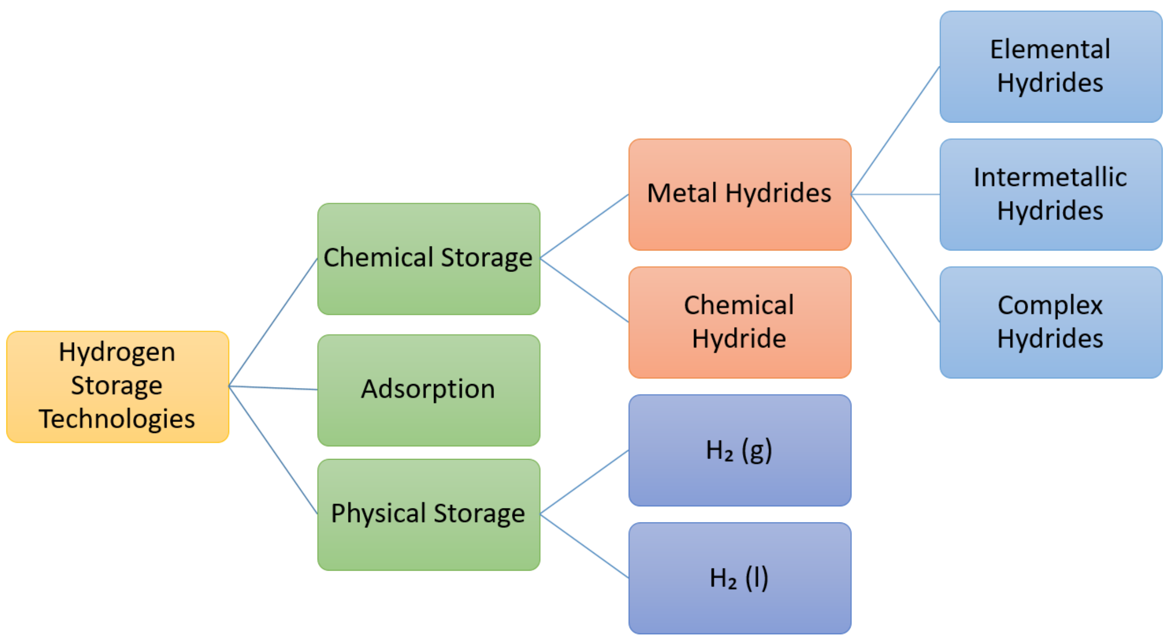


Figure: Technologies for Hydrogen Storage

Storage of Pure Hydrogen: Pure and molecular hydrogen can be stored in liquid or gaseous phase. Liquid or gaseous phase hydrogen storage and it is the only type of hydrogen storage which is currently being carried out at large scales. space industries across the globe are storing hydrogen in the form of liquid phase.

Storage of compressed hydrogen gas: Compressed hydrogen can either be stored above the ground level or below the ground level. The cost is significantly high for this storage and hence this method is not generally preferred. Although different methods for underground storage of hydrogen have been identified, but salt cavities are the most preferred one due to various reasons including minimal risk of contamination, low leakage rate, minimal/low construction cost, comparatively fast injection and withdrawal rates. Storage of hydrogen either underground or aboveground also depends on geographical parameters in addition to the existing factors.

Liquid Hydrogen Storage: Compression and condensation of pure hydrogen results in increased density. The process of Liquefaction of pure hydrogen at atmospheric pressure (1 bar) will result in increased density of saturated liquid hydrogen about 70 kg/m^3, with high energy consumption, which is a major concern.

Adsorption of Hydrogen: Hydrogen storage using different adsorption (with large surface area) such as porous polymeric materials, zeolites, porous carbon-based materials and metal-organic frameworks (MOF's) etc., is being suggested now a days. With improvement in efficiency and heat management, adsorption-based storage can play an important role in hydrogen storage.

Metal Hydride: Metal Hydrides can also be used to store hydrogen with formation of chemical bonds with hydrogen showing an efficiency of below 50%.

Chemical Hydrides: As lighter elements form chemical hydrides; hydrogen can be bonded with different chemicals for storage purpose. Due to liquid phase of chemical hydrides, storage and transportation of hydrogen is easily feasible. The suggested chemicals for hydrogen storage are formic acid, methanol and ammonia etc. Chemical hydrides-based hydrogen storage account for very low contribution in storage sector.

Considering different aspects which includes thermodynamic, physical and economic arguments, only very few hydrogen storage solutions exist globally, the first and initial successful technology for large scale storage is going to have a significant effect on further developments in the area of clean hydrogen infrastructure

Conclusions

Hydrogen can provide a sustainable solutions to climate change, rising sea levels, reduced agricultural production, water scarcity, and extreme weather events etc. Hydrogen is expected to play a vital role in transportation, steel production, powering societies, various industries including ammonia, chemical, and plastics etc. Developments in Hydrogen economy will also help in resolving issues, such as, oil import dependence, economic disruptions, and political and military conflicts etc. Hydrogen economy is going to help resolve air pollution, energy security and climate change etc. Governments across the globe are catalysing the role of hydrogen through green economy initiatives while providing grants, incentives and implementation of policies and regulations.

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