A comparative assessment of hydrogen production technologies and its storage – a review

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Abstract

This paper represents a review of hydrogen production systems using different methods, showing the importance and many parameters involved in producing hydrogen gas. Methodologies that are included in this review paper are water electrolysis, alkaline electrolysis, thermochemical water splitting, biomass, catalytic generation of hydrogen by ZrO2, polyethylene glycol, geothermal energy, wind energy, niobium-based photo catalyst, natural gas, artificial leaf, and biological production. Water electrolysis involves electricity breaking the water molecule into oxygen and hydrogen. A power supply is given to both positive and negative electrodes, dipped into the electrolyte and in alkaline electrolysis, an aqueous potassium hydroxide solution is used. The following method is thermo-chemical water splitting, a cycle loop of reactions with no greenhouse gas emission. It requires a high temperature to split the water molecule into oxygen and hydrogen. Biomass is a friendly method in which a low biomass concentration is used to avoid the polymerization of products. Zirconia is a catalyst used to increase the rate of gasification in biomass technology. Zirconia is also used in another method to degrade the polyethylene glycol in Inconel at high temperatures to produce hydrogen. Another reliable method used to produce hydrogen is the geothermal energy method which requires a PEM electrolyzer and is operated at a specific temperature range. The latest technology, an artificial leaf with a photovoltaic Si junction sandwiched by Co-OEC and NiMoZn catalysts, produced oxygen and hydrogen in the presence of sunlight and water after the formation of hydrogen stored in liquid and solid form by process of absorption and adsorption.

Keywords: hydrogen production; electrolysis; biomass gasification; renewable energy; geothermal energy; artificial leaf

Introduction

Safe, environmentally beneficial, and consistent energy materials are necessary for a high quality of life. Generally, the global market has no specific energy source that can rule the world globally [1]. In the past, we have faced many transformations from wood to coal, then coal to oil and then oil to gas which was a huge development in search of qualified human lifestyle transportation. Firstly, humans used fire as an energy source, which became essential to life. With time, we found a high energy source in coal mining which had high demand in that era. A new era will convert energy sources from oil and coal to fulfil human energy requirements [2]. Air aviation has significant concern towards atmospheric pollution [3]. Carbon emission in the atmosphere by the aviation industry is 2.1%, which is a relatively small contribution in the atmosphere compared to carbon emissions by goods and transport on roads, which amount to 11%. It is still getting significant attention because of contrails produced by jet engines. According to Graver, the aviation industry emits 918 million metric tons of CO_2 in the atmosphere, contributing significantly more at 2.5%. Researchers must develop highly efficient fuel for jet engines. Moreover, hydrogen cells and algae are being developed [4]. Reduction of emissions from engines is a practical challenge for the transport sector. The automotive industry has implemented various technologies and methods to resolve this problem [5]. For this purpose, many technical vehicles are introduced, such as electric vehicles, including battery electric vehicles (BEVs), hybrid electric vehicles (HEVs), and fuel cell hybrid electric vehicles (FCHEVs), to reduce the emission factor. But all these electric vehicles face many problems, such as the heavy weight of the battery, lower energy density of Li ions and sufficiently mining concern of lithium [6].

Hydrogen has been supposed to be a good energy source and is considered a green fuel for future transport on the road and aviation industry. Hydrogen oxidation will not create any pollutants in the environment [7]. Therefore, H_2 is a feasible substitute for fossil fuels in vehicles. For all of the problems faced by fossil fuel emissions, hydrogen can be a reliable source of energy [8]. Research shows that using hydrogen in vehicles reduces emissions and consumption, including lower price contribution.[9]. Hydrogen is an abundant element in the universe. It is three times more efficient than coal, gasoline and natural gas as it is a non-toxic, renewable, reliable and more significant fuel. Diverse energy resources produce hydrogen such as fossil fuel and renewable energy (RE). Fossil fuels produce blue hydrogen with carbon capture storage (CCS), green hydrogen can be produced by renewable energy and grey hydrogen can be generated by fossil fuels without carbon capture storage.[10]. Many systems are used to generate hydrogen gas as a fuel. Still, the most reliable pathway for the production of hydrogen is steam methane reforming. In this method CH_4 is extracted from natural gas and then heated in the presence of steam to produce hydrogen gas [11]. The second way to produce hydrogen gas is coal gasification, air is added into coal employing combustion to produce carbon dioxide. Then CO_2 is treated with the remaining carbon within coal to generate CO which is further reacted with steam to produce hydrogen gas [12]. The third method to produce hydrogen is water electrolysis where water is decomposed under electricity to produce oxygen and hydrogen [13]. Nowadays, hydrogen has outstanding advanced traction. Hydrogen has increased its demand three times since 1975, and its consumption is increasing day by day. Recent hydrogen technologies are getting investors' attention; the mandates and strategy incentives directly sustain hydrogen and worldwide spending on hydrogen fuel energy research [14]. The classification of hydrogen is considered blue, green, and grey. Generally, fossil fuels are used to generate grey hydrogen. More than 95% of global hydrogen is produced by reforming fossil sources, hydrogen can be generated two times by reforming the steam of neutral gas [15]. Dry hydrogen gas is produced by capturing carbon dioxide. Green hydrogen is considered to be a more reliable, environmentally friendly and renewable gas than other gases [16]. It has many advantages and that’s why it is commonly used in our daily life in areas such as electrical equipment, refining, fertilization sectors and production of many chemicals. Schematic diagram for the utilization and advantages of hydrogen is shown in Figure 1 [17]. Biomass, solar, geothermal, hydropower and wind are the major sources to generate green hydrogen. Among these sources, mostly, solar and wind are used for the production of green hydrogen. To generate green hydrogen, water splitting is one of the most frequently used methods employed for hydrogen production. Water splitting methods include electrolysis, photocatalytic water splitting, and thermolysis [18].

Generation of hydrogen by water electrolysis

Electrolysis is a process of breaking the molecule under electricity. In water electrolysis, electricity splits the water molecule into oxygen and hydrogen. For this purpose, two electrodes, an electrolyte (water) and a power supply are required to carry out electrolysis [19]. Here, battery is employed as a source of electrolysis, battery supplies direct current from negative to positive electrodes. At the cathode reduction occurs and at anode oxidation takes place as shown in Scheme 1. In this method, hydrogen is formed and then released, which can be used as fuel [20].

$$H_2O \longrightarrow 1/_2\, O_2 + 2H^+ + 2e^- \qquad E^0 = 1.23V / ENH$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad E^0 = 0.00V / ENH$$

Reactions occur at both electrodes, cathode, and anode, respectively.

$$2H_2O + 2e^- \longrightarrow H_2 + 2H_2O \qquad E^0 = -0.83V / ENH$$

$$2OH^- \longrightarrow 1/2\, O_2 + H_2O + 2e^- \qquad E^0 = 0.4V / ENH$$

This reaction is not spontaneous because this phenomenon requires an external power supply. The global reaction of water electrolysis can be written as follows:

$$H_2O + \text{Electricity} \longrightarrow H_2 + 1/2\, O_2$$

Scheme 1. Shows the water electrolysis reactions at the anode and cathode, respectively.

Alkaline electrolysis

Alkaline electrolysis happens when an aqueous solution of potassium hydroxide is used as an electrolyte, and electrolytic cells accommodate electrolyte (potassium hydroxide) [21]. These electrolyzers are commonly demonstrated in stationary applications and constructed to operate at a pressure of 25 bar [22]. Most industries run alkaline electrolysis and consider it an important process.
The following reactions that take place in alkaline electrolysis are shown in Scheme 2.
Electrolyte

$$4H_2O \longrightarrow 4OH^- + 4H^+$$

At Cathode:

$$4H_2O + 4e^- \longrightarrow 2H_2$$

At Anode:

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$$

Overall reaction:

$$2H_2O \longrightarrow 2H_2 + O_2$$

Scheme 2. Shows the alkaline electrolysis at the cathode and anode.

At the commercial scale, many electrolyzers are used and managed as cell stacks. However, a low-cost design for alkaline electrolyzers is required to enhance the efficiency and production of hydrogen by this effective method. The main components of the alkaline electrolyzer are shown in Figure 2 [21].

Thermo-chemical water splitting

A thermally driven chemical reaction series splits the water molecules into oxygen and hydrogen. This technology has been used widely for the past four decades and broadly studied in late 1980, but it lost its interest in the last decade [23]. It is a highly efficient and long pathway without greenhouse gas emissions [24]. This procedure has a cycle loop in which chemicals are recycled, generating hydrogen and oxygen, requiring a temperature taken from concentrated sunlight and heat wastage of the nuclear reactor [25]. The iodine/sulphur cycle is an example of thermochemical water splitting. R&D needs the captured hydrogen and lower emission of toxic substances to avoid side reactions and schematic diagram for the production of hydrogen by thermo- chemical water splitting metod as shown in Scheme 3 [25].

$$(850\ ^{o}C)\ H_2SO_4 \longrightarrow SO_2 + H_2O + 1/2O_2$$

$$(120\ ^{o}C)\ I_2 + 2H_2O + 2H_2O \longrightarrow H_2SO_4$$

$$(450\ ^{o}C)\ 2HI \longrightarrow I_2 + H_2$$

$$H_2O \longrightarrow H_2 + 1/2O_2$$

Scheme 3. Shows the iodine/sulfur cycle for the production of hydrogen gas [25].

Generation of hydrogen from biomass

Production of hydrogen gas from biomass (cellulose and glucose) is an environmentally friendly method [26]. Water plays a vital role as a reactant and suitable solvent to generate hydrogen from biomass as follows in Scheme 4:

$$C_6H_{10}O_5 + H_2O \longrightarrow 12H_2 + 6CO_2$$

Scheme 4. Generation of H2 by reaction of biomass and water.

Many researchers produced hydrogen by this method in sub and supercritical water. Low biomass gasification was observed at high biomass concentrations compared to low biomass concentrations because, at high concentrations, polymerization of decomposed products may occur [27]. However, active carbon in supercritical water can generate a high concentration of gaseous products from high biomass concentrations but less hydrogen produced [28]. In supercritical water, sodium hydroxide affects biomass gasification [29]. Gasification was observed three times more in the presence of sodium hydroxide than without alkali (NaOH) due to water gas in this reaction increasing hydrogen yield.

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Catalytic generation of H_2 with ZrO_2

Aldehydes and ketones as intermediates are produced in biomass gasification in the presence of supercritical water [30]. However, the gasification rate can be increased using zirconia as a catalyst in supercritical water [31]. A zirconia catalyst was prepared by calcinating zirconium hydroxide for 3 hours at 673 K. 1 M aqueous solution of sodium hydroxide, glucose, and cellulose was used in this reaction. In this reaction, a 0.3g catalyst was used. Stainless steel (SS316) container was used to carry out this reaction [32]. The total amount of samples in the container was 0.1g, and the amount of distilled water was 1.2g at 713 K for 9 to 15 min throughout [33]. After the completion of the reaction, insoluble water was separated by a membrane filter. The total amount of carbon dissolved in the solution was evaluated, and total organic carbon was detected. Diffractometer was used to detect the zirconia catalyst before and after the completion of the reaction [34].

Generation of hydrogen from polyethylene glycol

Polyethylene glycol is a water-soluble polymer, a non-ionic synthetic group; it has been used in various fields, such as pharmaceuticals and lubricants and plays a vital role as an antifreeze in automobile reactors [35]. In the past wide range of polyethylene glycol has been wasted in water, and its degradation is very challenging[36]. Under aerobic and anaerobic conditions, only 80% and 40% of polyethylene glycol was degraded in 5 and 10 days, which was very difficult [37]. Its complete degradation is very tough, even in wet air oxidation. However, catalysts like Ni, W, and Co are used to produce hydrogen from polyethylene glycol parent in wastewater along with the supported catalyst of ZrO2 in continuous flow Inconel at the temperature of 663K from one minute to 5 minutes [38]. It was studied that using a catalyst of Ni/ZrO2 in hydrogen production from PEG wastewater could reduce the chances of toxic products as intermediates. Therefore this heterogeneous catalyst can be used interestingly with high accuracy and stability [39].

Production of hydrogen from geothermal energy

Among all reforming energy resources, geothermal energy is a more reliable source with less ambient conditions. The stability of geothermal systems depends upon depth, properties of soil as well as grout material [40]. Geothermal energy is used in numerous applications, such as cooling, heating, and power generation [41]. Using a PEM electrolyzer, hydrogen can also be produced. Electrolysis of water is done with a specific temperature range which is considered an essential parameter that affects the operating cost and production of hydrogen [42]. It is observed that variation in temperature from 250 C to 70 0C will decrease the power required from 43.51 KW/Kg to 42.2 KW/Kg, nearly a three per cent reduction. First, heated fluid draws and passes through the geothermal power plant. After that, its residual heat will be used for the preheating of water. The air preheater is responsible for extracting all remaining heat in fluid just before injecting it back into the ground hole [43]. The temperature of geothermal fluid directly affects energy efficiency. Fluid flow rate also plays a vital role in energy efficiency. It directly affects hydrogen production, and it is considered that 0.25 g of hydrogen is generated at each Kg of geothermal water. Production of hydrogen using geothermal energy is a worthy case for more investigation and research-oriented for the future [44].

Hydrogen production from wind energy

Renewable energy sources are very important like solar energy and wind energy, and have a lot of advantages, such as environmentally friendly and economically beneficial solutions [45]. Interestingly, many countries adopted and applied technologies like wind power production and turbine technology employed for electricity production in the last few years [46]. Many methods are used commercially for electricity production, but their production through wind technology is considered very much beneficial and low cost effective [47]. Direct access to the production of hydrogen from wind technology is not an easy task. Many issues are considered to be overcome in future. The system used for hydrogen production from wind technology consists of a wind farm, power controller, rectifier and electrolyzer, as shown in Figure 3.

Firstly, the energy conversion process occurs in which rotation generates electricity, which is further supplied to the electrolyzer and includes electrodes to break the water molecules into hydrogen and oxygen. The efficiency of the rectifier used in this system is responsible for producing hydrogen [48]. Energy consumption of the electrolyzer is also considered a main factor for hydrogen generation during water electrolysis. Approximately 5-6 kWh/Nm3 energy is consumed during water electrolysis. 90% efficiency of the converter and 5 kWh/Nm3 energy consumption for the electrolyzer involved in hydrogen production were studied. 11.13 Nm3 energy equals one kilogram of hydrogen, and this relation is used to convert generated hydrogen from Nm3 to kilogram [49].

Niobium-based photocatalyst for H2 production

Non-renewable energy sources always have harmful impacts on the environment because they produce carbon dioxide gas and are responsible for ozone depletion [50]. Additionally, these sources are the causes of air contamination [51]. According to Researchers, the carbon dioxide ratio has increased by 2.3 ppm/year. In the last decades, it has been noted that many developed countries resist using fossil fuels due to environmental and health issues and also find substitutes for fossil fuels to tackle these problems [52]. Here, a lot of substitutes are available to overcome environmental issues like biogas substituting natural gas, charred bio waste replacing coal, and diesel being replaced by vegetable oil. Globally, the next generation could face problems due to present attributes, such as the non-availability of petroleum assets, and greenhouse impact can cause a big problem in the atmospheric situation [53]. The world should pay attention to balancing energy sources socially and economically, reducing the amount of carbon dioxide gas, and improving advanced technologies with lower emission of CO2 [54]. Many metal complexes have been used to produce hydrogen via the photocatalytic water-splitting method. However, niobium complexes are used due to their advantageous properties over other metal complexes, such as piezoelectric and photocatalytic [55]. In photocatalysis, electron-hole pairs are created to generate radicals for the electron-driving system. Electrons are excited from the valence band to the conduction band in semiconductors due to photon energy [56]. Electron holes are recombined by a reduction process, an important factor in hydrogen production and its evolution. Electronic and structural properties are responsible for controlling the reaction in photo catalyst process.

Cobalt catalysts such as noble catalysts can be used to increase the oxidation and reduction during photocatalyst process. It is noted that active metal over the support can diminish the activation energy required for the photocatalyst process [57].

Production of hydrogen by natural gas

Three different processes are mainly used to generate hydrogen by using natural gas:

- Partial oxidation
- Autothermal reforming
- Steam reforming process

by chemical combustion of methane which is responsible for the generation of hydrogen gas as shown in Scheme 5. However, carbon monoxide is also generated as a byproduct and the nature of this reaction is exothermic [58]. Hence this is profitable and sufficient because further heat will not be required as a reactor [59]. And carbon monoxide can also be used to produce hydrogen in the steam reforming process.

$$CH_4 + 1/2O_2 \longrightarrow 2H_2 + CO + \text{Heat}$$

Scheme 5: Combustion method to produce hydrogen and carbon monoxide.

Steam reforming is the process in which methane reacts to water vapours at high temperature and such reaction is endothermic reaction and it produces carbon monoxide and hydrogen. This chemical reaction requires 700-850 0C temperature and 3-25 bar pressure [59].

Biological production

Bio hydrogen is produced by many living organism, such as plants, bacteria and enzymes on an organic substrate [60]. It was noticed in 1990 that in the absence of sulfur, algae produced hydrogen instead of oxygen which was normal photosynthesis [61]. This methodology was considered renewable and carbon neutral, using algae deprived of sulfur in the bioreactor. Hydrogen and carbon dioxide are produced by this process and hydrocarbons are used on which bacteria are fed. Several methods have been used to separate the carbon dioxide and resulting in pure hydrogen [62]. The fermentation process is also known as the biological hydrogen production process in dark and light [63]. No light energy is required for the dark fermentation process. Still, photo fermentation needs light to proceed reaction, and Rhodobacter sphaeroides SH2C generates hydrogen by converting small fatty acids— constant hydrogen produced by this process in the dark and night [64]. Biocatalyzed electrolysis is a process used to produce hydrogen gas in which microbes are considered essential for the electrolysis process [65].

Hydrogen production by artificial leaf

Normally in natural leaf, during photosynthesis, carbon dioxide and water play an important role in producing carbohydrates from air and soil, respectively [66]. However, introducing an artificial leaf shows its unique quality to produce hydrogen and oxygen simultaneously by providing aqueous media [67]. By its construction, it has a photosynthetic membrane Si which stimulate light and generates a wireless electric current. Four holes move towards the side Co-OEC (oxygen evolving complex) and act as an anode where water splits and oxygen evolves. On the other side of the Si membrane, NiMoZn catalyst, which is electrodeposited and four holes generated by anode, captured in NiMoZn catalyst and hydrogen gas produced at the efficiency of 2.5%. A simple artificial leaf is a stand-alone device which is inexpensive and low cast pathway towards solar to-energy engineering.

Hydrogen generation by sodium borohydride

Sodium borohydride is economically beneficial and it has a high hydrogen density (10.6 wt.%), it is also favourable by hydrogen storage medium [68]. Sodium borohydride consists of four hydrogens and shows high reactivity towards water. Four hydrides carried by sodium borohydride and four protic hydrogen ions come from water to react. After this specific reaction, four hydrogen molecules are produced as shown in Scheme 6 [69]. As this reaction is exothermic during the hydrolysis, some borates are present in the steam and can be trapped using wash tank, which consists of water filled in the flask. Hydrogen production by hydrolysis is enhanced by metal-based catalysis such as Ni and Co [70]. It can also be accelerated by formic acid and acetic acid. During the reaction, a byproduct produced with hydrogen gas is sodium tetrahydoxyborate which is water soluble [71]. However, some drawbacks have been calculated from this reaction. The first one is the borates precipitated and clogged in the pipe resulting in an issue for further analysis. The second is maintaining the high temperature, as this reaction occurred at a high temperature. Furthermore, metal-based catalysts used in this reaction are not easily deactivated [72].

$$NaBH_2 + 4H_2O \longrightarrow NaB(OH)_4 + 4H_2$$

Scheme 6: Hydrolysis of sodium borohydride

Underground hydrogen storage

At large scale, several techniques have been applied for the storage hydrogen [73]. The first technique used at large scale is to develop salt caverns having rigid walls where hydrogen can be stored for long period with good stability. In 1972, the first salt cavern was built in the UK, which still works efficiently. Its volume can be increased concerning hydrogen storage, ranging from 100,000 to 1000,000 m3 with a pressure of 200 bar [74]. However, its development is not easy due to tightness, which is a main technical aspect along with surface installation [75]. Other ways for underground hydrogen are depleted deposits of natural gas, oil, and aquifers. These techniques need a porous structure, and more than 75% of hydrogen is stored worldwide in depleted deposits [76].

Liquid hydrogen

Hydrogen gas can be liquefied by decreasing temperature ranges from 20-21 k and ambient pressure [77]. After the liquefaction of hydrogen gas volume decreased, density approached 70.8 Kg/m3, similar to solid hydrogen density such as 70.6 Kg/m3. However, the liquefaction process consumes 40% of the energy consumed during this process. Liquid hydrogen is mostly used for special purposes such as space travelling [78].

Solid hydrogen

Besides the ways of hydrogen storage mentioned above, another pathway to store hydrogen is adsorption and absorption of hydrogen in solid material to formulate it. Mostly metal hydrides are used to absorb hydrogen in it and show more interest in absorbing the maximum of hydrogen gas as these (such as Pd) can sufficiently absorb 900 times its volume at 25 0C and atmospheric pressure [79]. However, complex hydrides (Mg2NiH4, LiAlH4, NaBH4, etc.) and chemical hydrides (LiH, NaH, CaH2, etc.) store the hydrogen by absorption phenomenon. But hydrogen extraction from these hydrides is difficult and challenging [80].
The adsorption process by a porous material such as carbon material and metal-organic framework is admirable and considered more applicable than the absorption process because thermal management can be avoided during adsorption [81]. However, this process is under research for commercialization due to hydrogen filling time when considering the storage of hydrogen and its capacity [82].

Conclusion and outlook

Multiple pathways were described for producing hydrogen gas through electrolysis, biomass, polyethylene glycol, zirconium catalyst, natural gas, wind energy and geothermal energy under various conditions. After production, hydrogen is stored underground through the salt cavern and depleted deposits technology. However, by liquefaction, adsorption and absorption way hydrogen is stored with fewer difficulties. Another cheap and low-cost manufacturing method, artificial leaf, showed a great revolution in the solar-to-energy conversion methodology with less cost. Hydrogen fuel is the future green fuel and has a lot of applications in many fields. At the commercial scale, many issues have been found and need to be improved by researchers and the government. Improvements in some methodologies may bring an extraordinary revolution to commercialize hydrogen production. Of all these methods described above, the latest and cheapest technology is artificial leaf which can be industrialized to overcome the energy crisis.

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