HYDROGEN: AS AN ALTERNATIVE ENERGY SOURCE AND ITS POTENTIALITY FOR BANGLADESH

As a partial fulfillment of the requirements for the Degree of MS in Renewable Energy Technology (RET)



Submitted to: Institute of Energy University of Dhaka

Supervised By: PROFESSOR DR. SAIFUL HUQUE. Institute of Energy Dhaka University

Submitted By:

MOHAMMAD HAFIZ AL ASAD Exam Roll: 508 Registration No: HA-226 Session: 2014-015

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DECLARATION

Candidate's Declaration

I confirm that this thesis represents my own work; the contribution of any supervisors and others to the research and to the thesis was consistent with normal supervisory practice. External contributions to the research are acknowledged.

Date: _____

MOHAMMAD HAFIZ AL ASAD MS student Exam Roll: 508, Registration No: HA-226 3rd Semester, Admission Session 2014-2015 Institute of Energy, University of Dhaka Dhaka, Bangladesh

Supervisor's Declaration

The MS level research on "Hydrogen; As an alternative energy source and it's potentiality for Bangladesh" has been carried out and the dissertation was prepared under my direct supervision. Herby I confirm that, to the best of my knowledge the thesis represents the original research work of the candidate; the contributions made to the research by researcher, by others of the University was consistent with normal supervisory practice, and external contributions to the research are acknowledged.

I believe the thesis to be in a suitable presentational form and is ready for examination.

Date: _____

DR. SAIFUL HUQUE. Professor, Institute of energy. University of Dhaka.

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DEDICATED TO

My Beloved Parents

Teacher and

Those people who are sacrificed their life for developing the science.

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Author September, 2016

Abstract

This thesis paper is not only delineate about the hydrogen as a sustainable versatile alternative future energy as well as its potentiality in Bangladesh to fulfill the energy demand in future and to mitigate the carbon emission. The Hydrogen, has the key prospective to become the ideal means among the range of renewable energy arena. Molecular of hydrogen has the highest energy content per unit weight among the known gaseous fuel (143 GJ ton⁻¹) and it is the only carbon free fuel which ultimately oxidize to water as a combustion product. Therefore burning hydrogen not only has the potential to meet a wide variety of end use applications but does not contribute to greenhouse emission, acid rain or ozone depletion as well. The use of hydrogen will contribute to significant reduction of these energy-linked environmental impacts thus it could be fruitful for increasing the acceptance of hydrogen as fuel. In 2011, Bangladesh was consume 1.09 quadrillion Btu energy as the reference of International Energy Statistics, February-2015. The energy we uses, 93.75% are from the fossil fuel, and 1.73% from hydro energy and rest of are imported. In average 58.81 million metric ton CO2 are emitted from the fossil fuel that we are uses per year in our country. In this scenario using the Hydrogen as an alternative energy source can play a key role to reduce the usages of fossil fuel and obviously to mitigate the carbon emission. The production, storage, utilization, percussion, environmental impact etc. are discussed in the point of view of Hydrogen an alternative energy source as well as its potentiality and prospective view of Bangladesh are also illustrate in this paper. We could certainly beseechers Hydrogen is the best choice of alternative energy and has fruitful potentiality in Bangladesh as I have seen in my research.

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Chapter - 01. About this thesis paper.

1.1 - Introduction

When the human race are began their race toward the civilization they discovered the essence and necessity of energy. As the civilization growing up, the technology developed simultaneously and a top headache issue comes as an obstacle of developmentation. That is none other than the alternative source of energy and to mitigate the demand of energy with harmless environmental impact. Now we cannot imagine a day without use of any sort of energy. Rise up from sleep to getting sleep energy is necessary. The fact is that the current total world consumption for energy is continuously expanding. It has expanded from 549 quadrillion British thermal units (Btu) in 2012 to 629 quadrillion Btu in 2020 and is expected to reach 815 quadrillion Btu in 2040, which is 48% increase from 2012 to 2040^[1]. Fossil fuels including coal, oil and gas alone are insufficient to meet the energy demand.

Renewable energy sources has been aide to this crisis. We already knew that the sun is the ultimate source of energy for our planet. The proper utilization of sun's energy could be the great solution of energy crisis but the fact is still we cannot invent such technology. However, photovoltaic cells, wind power, hydropower, biomass, ocean energy, geothermal energy, waste to energy are currently help us to fulfill the energy demand. But still those are not efficient enough cause of technological limitation and this is why scientists are bound to think another alternative source of energy. In this critical situation Hydrogen starts a new era in energy source cause of its energy content per mole. Molecular of hydrogen has the highest energy content per unit weight among the known gaseous fuel (143 GJ ton-1) and it is the only carbon free fuel which ultimately oxidize to water as a combustion product. Researchers dedicated their attention to bring in changes with the help of technology in the hydrogen industries.

This study combines Hydrogen as an alternative energy source as well as its potentiality for Bangladesh.

1.2 - Objectives of the study

This study is based on the overview of the following objectives:

- 1. Knowing the new face of Hydrogen as an alternative energy source and its properties, production, storing, utilization, precaution, environmental impact etc.
- 2. To know the energy scenario of Bangladesh.
- 3. To produce hydrogen by electrolysis.
- 4. Burning the hydrogen and compare the cost, burning rate, feasibility with wood and LPG to find the potentiality of hydrogen for Bangladesh.

1.3 - Thesis outline

The rest of the part of this thesis paper is illustrated as follows:

Chapter 2: The history of hydrogen, history of the fuel cell, some properties of hydrogen, some revolutionary invention and decision about hydrogen and fuel cell are describe in this chapter.

Chapter 3: Include hydrogen production, storage, utilization in global prospective percussion, environmental impact etc.

Chapter 4: Describe about present energy scenario of Bangladesh.

Chapter 5: In this chapter the scope of hydrogen utilization in Bangladesh are illustrate.

Chapter 6: Research Methodology are delineated in this chapter.

Chapter 7: In this chapter the required policy reformation for using hydrogen as an energy source are described.

Chapter 8: Future research scope of hydrogen has been discuss in this chapter.

Chapter 09: Conclusion.

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Chapter – 02.

Background of Hydrogen and its use as renewable energy.

2.1 ~ History of Hydrogen

The Latin name for hydrogen is "hydrogenium," originated from two Greek words, "hydro" and "genes," meaning "water" and "forming." Hydrogen, which is the first element in the periodic table of elements, having the atomic number 1, is a non-metal, colorless, odorless, highly reactive, self-burning characteristic gas that has all the qualities to be a fuel for our automobiles and a future energy source ^[1].

The first documented production of hydrogen was carried out by Theophratus Bombastus von Hohenheim (1493–1591) he was largely known by the name Paracelsus (Figure 2-1). He produced a gas by reacting metals with acids. He did not know what it was that he had produced, although he knew the gas was flammable.



Figure 2-1 Paracelsus -discovered hydrogen, but wasn't sure what he had discovered.

Some years later, gentleman scientist Robert Boyle (1627–1691) (Figure 2-2), best known for Boyle's Law looked at the reaction between iron filings and acids, rediscovering Paracelsus' earlier experiment. He published his findings in a paper: "New experiments touching the relation betwixt flame and air" in 1671. He called the gas that he produced "inflammable solution of Mars."



Figure 2-2 Robert Boyle -discovered hydrogen . . . again.

However, the first person to recognize hydrogen as a substance in its own right was Henry Cavendish (1731–1810) (Figure 2-3), who in 1766 noted that the gas was flammable, and that it produced water when it burned. Cavendish called the gas "flammable air" and published his findings in a paper titled "On Factitious Airs." For his endeavors, he received the Royal Society's Copley Medal. The leap that Cavendish made was to identify hydrogen as being different from any other gas. He did this by carefully measuring the density of hydrogen, and also looking at how much was produced when different amounts of metal and acid reacted. This systematic, thorough inquiry has earned Cavendish the title of the person who ultimately "discovered" hydrogen; however, this "flammable gas" was still without a name.



Figure 2-3 Henry Cavendish -decided hydrogen was a unique substance.

Antoine Lavoisier (Figure 2-4) has been called the father of modern chemistry. He discovered that the constituents of water were hydrogen and oxygen, and went a long way towards discovering the composition of the gases that make up air. He found that when hydrogen burned in the presence of oxygen, dew was formed. This built upon earlier observations by Joseph Priestley. Lavoisier gave the gas the name "hydrogen", which in Greek translates to waterforming.



Figure 2-4 Antoine-Laurent de Lavoisier.

However, for more than half a century, hydrogen has been used in many chemical processes in industry and as a rocket propellant. During that time, hydrogen was produced using a very robust infrastructure. Then, it was stored, transported, and utilized with understanding and respect for its physical properties in the different energy-consuming sector.

2.2 - History of the Fuel Cell

The recent flurry of activity by the scientific and engineering community has brought the fuel cell into the public eye. Many would believe that the fuel cell was a recent innovation, however, its roots can be traced back to as early as 1838. Fuel cells are believed to be a very modern, current technology by many people: however, their origins can be traced back to the work of Sir William Robert Grove (Figure 2-5).



Figure 2-5 Sir William Robert Grove.

Sir William Robert Grove is widely heralded as the "Father of the Fuel Cell." He was born in 1811, in Swansea, Wales. A Welsh lawyer who later applied himself to the mastery of science,

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he published a diagram in 1843 and made a primitive model known as the "Grove Gas Battery." (Figure 2-6).

Figure 2-6 The Grove Gas Battery.

The idea of fuel cells never really developed beyond a laboratory curiosity after this discovery; it was not really until much later, in 1959, that a fuel cell with a sizable power output 5 kW was developed by British engineer, Francis Thomas Bacon (Figure 2-7). Bacon's fuel cell used a different technology than Grove's earlier design. He used electrodes of nickel in a solution of potassium hydroxide, initially calling his invention the "Bacon Cell". We now recognize this family of fuel cells as "alkaline fuel cells"



Figure 2-7 Francis Thomas Bacon.

The first fuel cell vehicle can probably be accredited to Harry Karl Ihrig, who built a 15 kW fuel cell tractor in 1959 (shown in Figure 2-8) for Allis-Chalmers. The alkaline fuel cell used had a potassium hydroxide electrolyte and produced 20 hp power.

General Electric made a bold leap forward in the early 1960s by developing the proton exchange membrane fuel cell. This was used in the U.S. space program in the Gemini V. The PEM fuel cell was based on a TeflonTM (the material that we find on our nonstick frying pans) solid electrolyte, which was impregnated with acid.

The Apollo, Apollo–Soyuz, Skylab and Shuttle reverted back to Bacon's design of an alkaline fuel cell. Since these early days of the fuel cell the number of fuel cell technologies have grown, and our understanding of the material science of fuel cells has improved rapidly.

A number of technology application prototypes were developed in the 1960s by major vehicle and fuel manufacturers, to demonstrate how fuel cells could be used to provide power for transport applications. However, the 1960s was a time of cheap, plentiful oil when the world was not looking for a solution to future problems. The energy density of early fuel cells was not sufficient to allow practical vehicles to be manufactured beyond prototypes and demonstration vehicles.

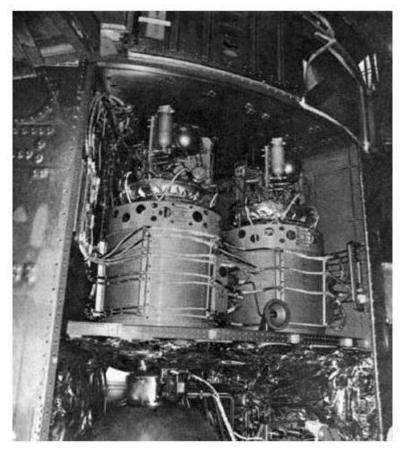


Figure 2-8 The alkaline "Bacon Cells" used in the Apollo missions. Image courtesy.

In 1993, Ballard Power Systems exhibited a fuel cell bus, which made important improvements on previous fuel cell vehicle applications by showing that higher power densities could be achieved with fuel cell technology. This has prompted a renaissance of major interest in fuel cell technologies. In the last decade, with an interest in cleaner, greener ways of doing things, driven by concerns over peak oil, energy security, and climate change, fuel cells have again been in the spotlight as a potential solution to some of our energy dilemmas.

In 2003, the first public hydrogen filling station was opened in Reykjavik, Iceland, which serves the three hydrogen buses in the city as part of the CUTE project. With improvements in the energy density of fuel cells, it is not only the big vehicles that can now use fuel cell technology, but also much smaller modes of transportation. In 2005, Intelligent Energy released the first fuel cell motorcycle, capable of travelling up to 50 mph, and with a range of 100 miles in an urban driving cycle.

2.3 - Some properties of Hydrogen.

| DATA | VALUE |
|------------------------|--------------------------------------|
| Chemical series | Nonmetals |
| Group | Period, Block 1, 1, s |
| Electron configuration | 1s1 |
| Electrons per shell | 1 |
| Appearance | Colorless |
| Density | 0.08988 kg/ nm ³ |
| Upper heating value | 12.745 MJ/nm ³ |
| Lower heating value | 10.783 MJ/ nm ³ |
| Ignition energy | 0.02 MJ |
| Ignition temperature | 520° C |
| Lower ignition level | (gas concentration in air) 4.1 Vol% |
| Upper ignition level | (gas concentration in air) 72.5 Vol% |
| Flame rate | 2.7 m/s |
| Melting point | 14.01 K (-259.14°C,-434.45°F) |
| Boiling point | 20.28°K (-252.87°C, -423.17°F) |

Some key properties of hydrogen is given below-

| Triple point | 13.8033°K, 7.042 kPa |
|--|--|
| Critical point | 32.97°K, 1.293 MPa |
| Heat of fusion (H ₂) | $0.117 \text{ kJ} \cdot \text{mol}^{-1}$ |
| Heat of vaporization (H ₂) | $0.904 \text{ kJ} \cdot \text{mol}^{-1}$ |
| Heat capacity (25°C) (H ₂) | $28.836 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ |
| Thermal conductivity (300°K) | $180.5 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ |
| Speed of sound | (gas, 27°C) 1310 m/s |
| CAS registry number | 1333-74-0 (H ₂) |
| Crystal structure | Hexagonal |
| Oxidation states | 1, -1 |
| Electronegativity | 2.20 (Pauling scale) |
| Ionization energies | 1st: 1312.0 kJ/mol |
| Atomic radius | 25 pm |
| Atomic radius (calc.) | 53 pm (Bohr radius) |
| Covalent radius | 37 pm |
| Van der Waals radius | 120 pm |
| Amount in atmosphere | 0.00005% |

| Gas * (m ³) | Liquid (liter) | Weight (kg) |
|--|----------------|-------------|
| 1 | 1.63 | 0.0898 |
| 0.856 | 1 | 0.0709 |
| 12.126 | 14.104 | 1 |

*m³ at 981 mbar and 15°C

2.4 - Some revolutionary invention and decision about Hydrogen and Fuel Cell.

1800 - Process of Electrolysis Discovered

As seen in history the first step has been began to access in hydrogen energy arena in 1800 AD. "English scientists William Nicholson and Sir Anthony Carlisle discovered that applying electric current to water produced hydrogen and oxygen gases. This process was later termed 'electrolysis'^[2]. The discovery of electrolysis was an important historical step in the development of hydrogen energy and the hydrogen fuel cell.

1838 - First Hydrogen Fuel Cell Developed to Generate Electricity

"William Robert Grove (1811 -1896)", a Welsh lawyer turned scientist, won renowned for his development of an improved wet-cell battery in 1838. The 'Grove cell', as it came to be called, used a platinum electrode immersed in nitric acid and a zinc electrode in zinc sulfate to generate about 12 amps of current at about 1.8 volts.

In 1800, British scientists William Nicholson and Anthony Carlisle had described the process of using electricity to decompose water into hydrogen and oxygen. But combining the gases to produce electricity and water was, according to Grove, 'a step further that any hitherto recorded.' Grove realized that by combining several sets of these electrodes in a series circuit he might 'effect the decomposition of water by means of its composition.' He soon accomplished this feat with the device he named a 'gas battery'– the first fuel cell^[3].

1960s - General Electric (GE) Develops Hydrogen Fuel Cells to Generate Electricity for Apollo and Gemini Space Missions

General Electric [GE] developed workable proton-exchange membrane cells [aka fuel cells] for use as power supplies in the Apollo and Gemini space missions. The cells were big and very expensive, but they performed faultlessly, delivering an unwavering supply of current as well as a very useful byproduct in space, drinkable fresh water.

Fuel-cell technology can be compared to that of a car battery, in that hydrogen and oxygen are combined to produce electricity. But while batteries store both their fuel and their oxidizer internally, meaning they have to be periodically recharged, the fuel cell can run continuously because its fuel and oxygen are external. Fuel cells themselves are stackable flat plates, each one producing about one volt. The size of the stack determines the power output" ^[4].

Jan. 23, 1990 - Congress Passes Act to Stimulate Development of Hydrogen Power

The US Congress passes the Spark M. Matsunaga Hydrogen Research, Development, and Demonstration Program Act of 1990 "to accelerate efforts to develop a domestic capability to economically produce hydrogen in quantities that will make a significant contribution toward reducing the Nation's dependence on conventional fuels".

The purposes of the Act were to develop "a comprehensive 5-year comprehensive program management plan that will identify and resolve critical technical issues necessary for the realization of a domestic capability to produce, distribute, and use hydrogen economically within the shortest time practicable; to direct the Secretary to develop a technology assessment and information transfer program among the Federal agencies and aerospace, transportation, energy, and other entities; and to develop renewable energy resources as a primary source of energy for the production of hydrogen" ^[5].

Oct. 9, 1996 - Hydrogen Future Act of 1996 Is Passed to Further Expand Hydrogen Power Development

The Hydrogen Future Act of 1996 expanded the research, and development, and demonstration program under the Matsunaga Act. It authorized activities leading to production, storage, transformation, and use of hydrogen for industrial, residential, transportation, and utility applications.

The long-term vision for hydrogen energy is that sometime well into 21st century, hydrogen will join electricity as one of our Nation's primary energy carriers, and hydrogen will ultimately be produced from renewable sources. But fossil fuels will be a significant long-term transitional resource. In the next twenty years, increasing concerns about global climate changes and energy security concerns will help bring about penetration of hydrogen in several niche markets. The growth of fuel cell technology will allow the introduction of hydrogen in both transportation and electricity sectors ^[6].

Feb. 2003 - President Bush Unveils the Hydrogen Fuel Initiative to Promote Hydrogen Fuel Cell Development

"The Hydrogen Fuel Initiative (HFI) increased federal funding for hydrogen and fuel cell research, development, and demonstration (RD&D) to \$1.2 billion over five years. With this increase in funding, the HFI accelerated the pace of RD&D efforts focused on achieving specific targets that would enable hydrogen and fuel cell technology readiness in the 2015 timeframe".

In support of the Hydrogen Fuel Initiative. President GW Bush stated: "Hydrogen fuel cells represent one of the most encouraging, innovative technologies of our era... let us promote hydrogen fuel cells as a way to advance into the 21st century... If we develop hydrogen power to its full potential, we can reduce our demand for oil by over 11 million barrels per day by the year 2040. So I'm asking Congress to spend \$1.2 billion on a new national commitment to take hydrogen fuel cell cars from the laboratory to the showroom...

Imagine a world in which our cars are driven by hydrogen and our homes are heated by electricity from a fusion power plant. It'll be a totally different world than what we're used to. The quality of life will be advanced. And people will say, gosh, I'm glad those folks went to Washington and were willing to think beyond the current"^[7].

Feb. 27, 2003 - Plans Announced to Build FutureGen, the World's First Zero Emissions Coal Power Plant

"On February 27, 2003, the President announced FutureGen as a cost-shared project between DOE [Department of Energy] and industry to create the world's first coal-fired, zero emissions electricity and hydrogen production power plant. The production of hydrogen was to support the President's Hydrogen Fuel Initiative to create a hydrogen economy for transportation. The original FutureGen plant was planned to operate at a commercial scale as a 275 megawatt IGCC [Integrated Gasification Combined Cycle] facility that would capture and store at least 1 million metric tons of CO2 per year".

[**Note:** On Jan. 30, 2008, US Secretary of Energy Samuel W. Bodman announced a "restructured" approach to the FutureGen project that focused on carbon capture and storage (CCS) technology and excluded hydrogen production as part of the project]^[8].

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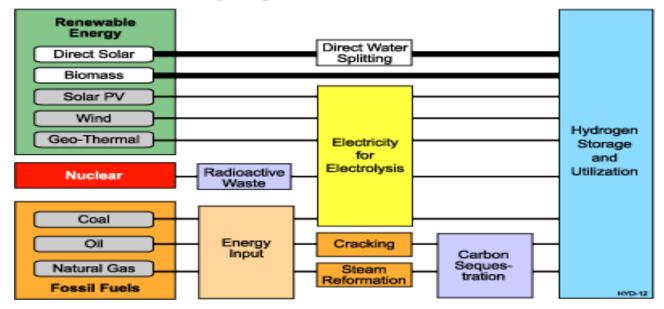
Chapter ~ 03.

Methodology of Hydrogen production and uses as energy source.

An important historical step in the development of hydrogen energy and the hydrogen fuel cell was developed in 1800 AD when English scientists William Nicholson and Sir Anthony Carlisle discovered that applying electric current to water produced hydrogen and oxygen gases. This process was later termed as 'electrolysis' as I mentioned previous chapter. However, the use of hydrogen as an energy source is not as much as easy as previously thought. There are several methods have been implemented to achieve the goal such as production, storage, utilization, percussion etc. Here I am going to describe all about those part by part.

Hydrogen is not an energy source, but is an energy vector or carrier. This means that it has to be produced from one of the primary energy sources: fossil fuels (coal, Oil, gas), nuclear, and renewable (solar, wind, biomass, hydro, geothermal and urban waste resources). All the energy we use, including hydrogen, must be produced from one of these three primary energy resources.

On earth, hydrogen is found combined with other elements. For example, in water, hydrogen is combined with oxygen. In fossil fuels, it is combined with carbon as in petroleum, natural gas or coal. The challenge is to separate hydrogen from other naturally occurring compounds in an efficient and economic manner. Following "Hydrogen Production Paths" (Figure 3-1) is the unique ways to produce hydrogen from the three primary energy sources.



Hydrogen Production Paths

Figure 3-1 Hydrogen Production Path.

3.1 - Production

Hydrogen can be produced by both renewable and nonrenewable sources of energy. Using diverse, domestic resources including fossil fuels, such as natural gas and coal (with carbon sequestration); nuclear energy; and other renewable energy sources, such as biomass, wind, solar, geothermal, and hydro-electric power using a wide range of processes could be the source of hydrogen production. The former has the advantage of being environmentally friendly whereas the latter has either carbon dioxide or some other form of carbon residue in the end product other than hydrogen. Hydrogen production using conventional sources, that is, coal, oil, and natural gas, is in practice these days, and research is ongoing to minimize the environmental damage caused by greenhouse gas emissions. One method by which greenhouse gases can be minimized is by using solar or some other form of renewable energy source as the primary energy requirement for the hydrogen production chemical reaction. Therefore, it is important to understand the renew-able energy sources first and then how these energy sources can be used for hydrogen production. Dincer^[1] has summarized various green hydrogen production methods that use renewable energy sources (Table 3.1). Careful reading of Table 3.1 shows that the primary energy required for the chemical reactions is generally electrical and thermal energy. The materials or chemicals used to generate hydrogen are principally water and fossil fuels. Organic biomass and inorganic compounds such as hydrogen sulfide are also used to produce hydrogen. Therefore, it is important to identify the sources of energy that can be used to fulfill the primary energy demands for environmentally benign hydrogen production.

The energy conversion from energy sources to process energy is equally important, as summarized by Dincer^[1] in Table 3.2. It is important to see that electricity may be produced by all the renewable energy sources. High-grade thermal energy can be produced by concentrated solar energy, biomass and recovery gas from landfills, etc., and low-grade thermal energy can be produced geothermally^[2].

| Primary energy | Hydrogen production method | Material resources | Brief descrip | tion |
|------------------------|--|----------------------------|---|---|
| Electrical energy | Electrolysis | Water | Water decon | nposition into O ₂ and H ₂ by passing a direct current which drives emical reactions |
| | Plasma arc decomposition | Natural gas | Clean natura | l gas (methane) is passed through an electrically produced plasma arc te hydrogen and carbon soot |
| Thermal energy | Thermolysis | Water | Steam is bro | ught to temperatures of over 2,500 K at which water molecule ses thermally |
| | Thermo-catalysis | H ₂ S cracking | Hydrogen sulfide | H ₂ S extracted from sea or derived from other industrial processes is cracked thermo-catalytically |
| | | Biomass conversion | Biomass | Thermo-catalytic biomass conversion to hydrogen |
| | Thermochemical processes | Water splitting | Water | Chemical reactions (including redox reactions or not) are conducted cyclically with overall result of water molecule splitting |
| | | Gasification | Biomass | Biomass converted to syngas; H2 extracted |
| | | Reforming | Biofuels | Liquid biofuels converted to hydrogen |
| | | H ₂ S splitting | Hydrogen sulfide | Cyclical reactions to split the hydrogen sulfide molecule |
| Photonic energy | PV electrolysis | Water | PV panels ge | enerate electricity to drive electrolyzer |
| | Photo-catalysis | Water | | mogeneous catalysts or molecular devices with photo-initiated elec- ection are used to generate hydrogen from water |
| | Photo-electrochemical method | Water | Contraction of the second s | l is used to generate photovoltaic electricity, which drives the water sis process |
| | Bio-photolysis | Water | | stems based on cyanobacteria are used to generate hydrogen in a d manner |
| Biochemical energy | Dark fermentation | Biomass | | ermentation in the absence of light |
| | Enzymatic | Water | Uses polysa | ccharides to generate the required energy |
| Electrical + thermal | High-temperature electrolysis | Water | Uses a thern cells | nal source and electrical power to split water in solid oxide electrolyte |
| | Hybrid thermochemical cycles | Water | | energy and electricity to drive chemical reactions cyclically with the esult of water splitting |
| | Thermo-catalytic fossil fuel cracking | Fossil fuels | | talytic process is used to crack fossil hydrocarbons to H ₂ and CO ₂ , CO ₂ is separated/sequestrated for the process to become green |
| | Coal gasification | Water | | verted to syngas, then H ₂ extracted and CO ₂ separated/sequestrated power spent) |
| | Fossil fuels reforming | Fossil fuels | | carbons are converted to H ₂ with CO ₂ capture and sequestration power spent) |
| Electrical + photonic | Photo-electrolysis | Water | Photo-electr | odes + external source of electricity |
| Biochemical + thermal | Thermophilic digestion | Biomass | Uses biomas temperat | ss digestion assisted by thermal energy for heating at low-grade ure |
| Photonic + biochemical | Bio-photolysis | Biomass, water | Uses bacteri | a and microbes to photo-generate hydrogen |
| | Photo-fermentation | Biomass | The ferment | ation process in facilitated by light exposure |
| | Artificial photosynthesis | Biomass, water | | engineered molecules and associated systems to mimic photosynthesis |

Table 3-1 Represents the Classification of green hydrogen production methods.

| Hydrogen production method | | Green energy source | Conversion path |
|---|----------------------------|--------------------------------|--|
| Electrolysis (green energy gen electrolysis) or plasma arc energy generates electricity | decomposition (green | Solar Geothermal Biomass | PV power plant or concentrated solar power (CSP) to generate electricity Power plant [organic Rankine cycle (ORC), flash cycle, etc.] Biomass power plant, internal combustion engines, fuel-cell plants |
| decomposition of natural g | | Wind | Wind power plants (grid-connected or autonomous) |
| | | Ocean heat | OTEC (ocean thermal energy conversion) plants |
| | | Other renewable | Tides, ocean currents, and wave energy converted into electricity |
| | | Nuclear | Nuclear power plants |
| | | Recovery | Landfill gas combusted in diesel generators |
| | | liceology | Industrial/other heat recovery used to drive ORC or other heat engines Incineration with pollutant capture drives Rankine power plant |
| Thermolysis | | Solar | Concentrated solar heat used to generate ultrahigh-temperature steam |
| Thermo-catalysis | H ₂ S cracking | Solar | Concentrated solar heat used to generate unranger temperature secan |
| Incluio-catarysis | 1125 cracking | Biomass | Low-grade biomass combustion generates the process heat |
| | | Recovery | Landfill gas combustion, high-temperature industrial heat recovery |
| | Biomass conversion | Solar | Concentrated solar heat at high temperature drives the process |
| | biomass conversion | Biomass | Auto-thermal process: reaction heat comes from biomass combustion |
| Thermochemical processes | Water splitting | Solar | Concentrated solar radiation generates high-temperature heat |
| Includencial processes | Water spinning | Geothermal | Geothermal-generated electricity to drive high-temperature heat pumps |
| | | Biomass | Dried biomass is combusted to generate high-temperature heat |
| | | Nuclear | Nuclear electric power used to drive high-temperature heat pumps |
| | | Recovery | Landfill gas combustion |
| | Gasification | Solar | Concentrated solar heat at high temperature drives the process |
| | Gusineuton | Biomass | Auto-thermal process: reaction heat comes from biomass combustion |
| | Fuel reforming | Solar | Concentrated solar heat at high temperature drives the process |
| | i dei teroining | Biofuels | Auto-thermal process: reaction heat comes from biomass combustion |
| | H ₂ S splitting | Solar | Concentrated solar heat used to drive the process at high temperature |
| | | Geothermal | High-temperature geothermal heat at ~200 °C drives the process |
| | | Biomass | Low-grade biomass combustion generates the process heat |
| 122 122 123 124 124 124 124 124 124 124 124 124 124 | | Recovery | Landfill gas combustion, high-temperature industrial heat recovery |
| PV electrolysis | | Solar | Solar radiation generates electricity through PV panels |
| Photo-catalysis | | Solar | UV and upper spectrum visible solar radiation drives the process |
| Photo-electrochemical | | Solar | All solar spectrum used by photo-electrochemical cell |
| Bio-photolysis | | Solar | All solar spectrum can be used |
| Dark fermentation | | Biomass | Biogas reactors are used for dark fermentation to generate hydrogen |
| Enzymatic | | Biomass | Polysaccharides are manipulated by special enzymes to extract hydroger |
| High-temperature electrolysis | | Solar | Concentrated solar power generates high-temperature heat and electricity |
| | | Geothermal | Geothermal electricity coupled to high-temperature heat pumps |
| | | Biomass | Biomass combustion generates power and high-temperature heat |
| | | Nuclear | Nuclear power used to generate electricity and high-temperature heat |
| | | Recovery | Recovered energy generates electricity and high-temperature heat |
| Hybrid thermochemical cycles | | Solar | Concentrated solar power generates high-temperature heat and electricity |
| | | Geothermal | Geothermal electricity coupled to high-temperature heat pumps |
| | | Biomass | Biomass combustion generates power and high-temperature heat |
| | | Nuclear | Nuclear power used to generate electricity and high-temperature heat |
| Dhata alasta bala | | Recovery | Recovered energy generates electricity and high-temperature heat |
| Photo-electrolysis | | Solar Biomann i othan | PV or CSP + electrolysis bath with photo-electrodes |
| Thermophilic digestion | | Biomass + other | Biomass energy drives the process; heat recovery or solar provides heat |
| Bio-photolysis | | Biomass + solar | Biomass + photonic energy drive the process |
| Photo-fermentation | | Biomass + solar | Biomass + photonic energy drive the process |
| Artificial photosynthesis | | Solar | Solar energy drives the hydrogen generation process directly |

| Table 3-2 Table 3-2 Production methods and energy conversion paths to produce "green hydrogen". |
|--|
|--|

3.1.1 - Categories of Hydrogen production and distribution.

Hydrogen can be produced from following three systems in terms of distribution-

- At or near the site of use in Distributed Production
- At large facilities and then delivered to the point of use in Central Production
- At intermediate scale facilities located in close proximity (25–100 miles) to the point of use in *Semi-central Production*.

There are three general categories of Hydrogen production

- Thermal Processes
- Electrolyte Processes
- Photolytic Processes

3.1.2 - Hydrogen production by Thermal Process.

Producing hydrogen by Thermal Processes can achieve by three different methods such as-

- Natural Gas Reforming
- Gasification
- Renewable Liquid Reforming

3.1.2.1 – Natural Gas Reforming : Synthesis gas, a mixture of hydrogen, carbon monoxide, and a small amount of carbon dioxide, is created by reacting natural gas with high-

temperature steam. The carbon monoxide is reacted with water to produce additional hydrogen. This method is the cheapest, most efficient, and most common for producing hydrogen. Natural gas reforming using steam accounts for the majority of hydrogen produced in the world wide annually.

A synthesis gas can also be created by reacting coal or biomass with high-temperature steam and oxygen in a pressurized gasified, which is converted into gaseous components—a process called gasification. The resulting synthesis gas contains hydrogen and carbon monoxide, which is reacted with steam to separate the hydrogen.

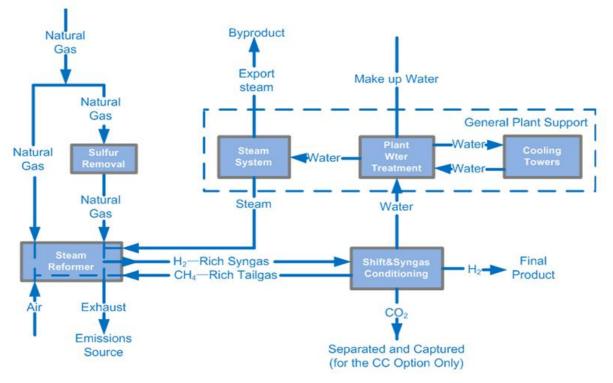


Figure 3-2 Production Hydrogen from Natural Gas Reforming.

3.1.2.2 - Gasification : In this process coal or biomass is converted into gaseous

components by applying heat under pressure and in the presence of steam. A subsequent series of chemical reactions produces a synthesis gas which reacts with steam to produce more hydrogen that can be separated.

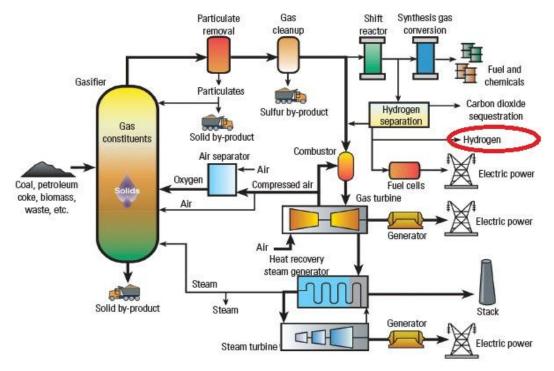


Figure 3-3 Production of Hydrogen from Gasification.

3.1.2.3 – Renewable Líquíd Reforming : Biomass is processed to make renewable liquid fuels, such as ethanol or bio-oil that are then reacted with high-temperature steam to produce hydrogen. This process is very similar to reforming natural gas.

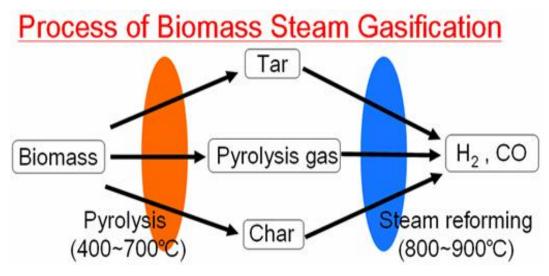


Figure 3-4 Production Hydrogen from Renewable Liquid Reforming.

3.1.3 - Producing hydrogen by Electrolyte Processes.

Water electrolysis is an electrochemical reaction where water is split into hydrogen and oxygen in the presence of a catalyst and applied electric field. As current density increases the cell losses due to membrane, electrode, and interfacial resistances dominate and are referred to as ohmic over potential. The splitting of water into O₂ and H₂ gases by electricity (generated by RSE resources such as biomass, geothermal, wind and solar energy) is an environmentallyfriendly process with the following reaction^[3].

$$H_2O + 2F \rightarrow H_2 + 1/2O_2$$
 (1)

F is the Faraday constant measuring 1 mol of electricity (96485°C).

The reverse of reaction (1) can be employed in combustion phenomena or HFC to generate electricity from hydrogen.

$$H_2 + 1/2O_2 \rightarrow H_2 + 2F$$
 (2)

In reaction (1), since the cost of water is negligible, the price of hydrogen yield from electrolysis process significantly depends on the cost of electricity. To augment conductivity

and consequently the overall rate of hydrogen yield from water electrolysis, an electrolyte is dissolved in water. In commercial electrolyzers, 30% Potassium hydroxide [KOH] (alkaline electrolysis) at 80°C is employed which is possible to recover and reuse it. The efficiency of alkaline electrolysis systems (AES) when ceramic micro porous separator is used, the electrodes are made of nickel, the cathode and anode coated in platinum and manganese oxide respectively is about 55–75%. In a typical commercial AES, pure hydrogen is produced by consuming 4.49 kWh/m³ of electricity.

Although hydrogen production by water electrolysis has shown promise, this technology still face challenges. In the current water electrolysis technology, the applied electrodes are usually coated with high cost platinum, which makes the process non-economic. Hence, elimination of such precious metals in water electrolysis process by utilization of nanomaterial's has attracted attention^[4]. To solve this problem, Matthew Kanan (*NIH Ruth Kirchenstein Postdoctoral Fellow. at MIT*), introduced a cobalt phosphate catalyst as a promising process to crack water molecules into its elements at atmospheric pressure by duplication of photosynthesis. In this system a conventional anode consisting of indium tin oxide is employed to split water. Application of abundant cobalt phosphate which is far cheaper than expensive platinum ensures lower price for electrolysis technology. Figure 3-5 shows typical method to produce Hydrogen by electrolysis.

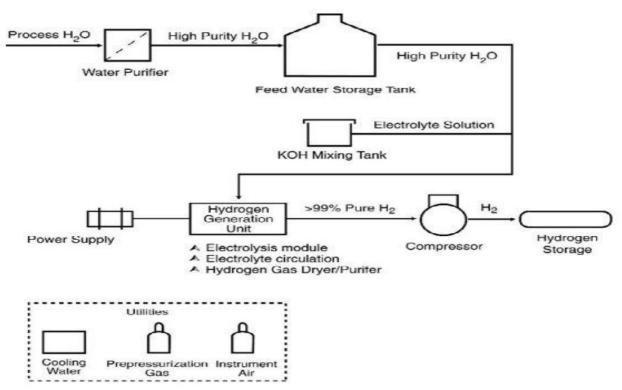


Figure 3-5 Production Hydrogen from Electrolyte Processes.

Figure (3-6) and (3-7) shows two different electrolysier design. First one is Unipolar (tank) electrolyzer design and the other one is Bipolar (filter-press) electrolyzer design. Both design are suitable for commercial use. Figure (3-8) shows Hydrogen costs via electrolysis with only electricity costs considered as international aspect.

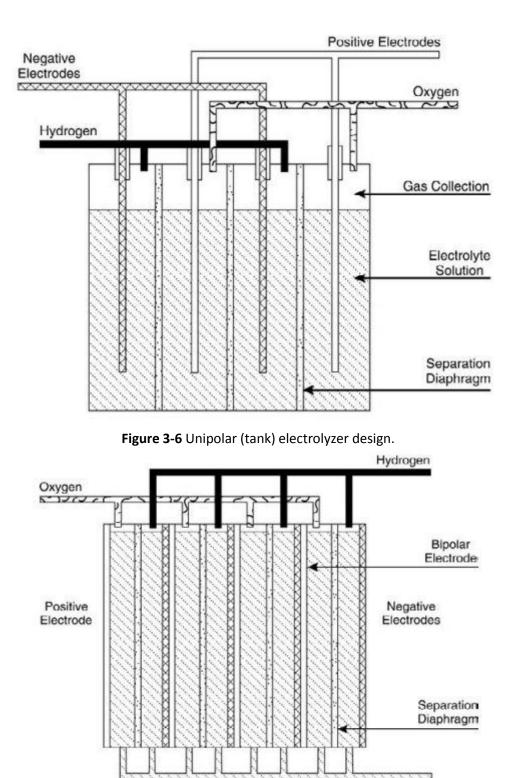


Figure 3-7 Bipolar (filter-press) electrolyzer design.

Electrolyte

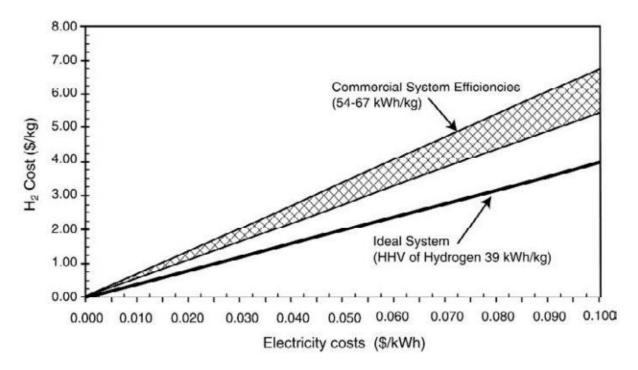


Figure 3-8 Hydrogen costs via electrolysis with only electricity costs considered.

3.1.3 - Producing hydrogen by Photolytic Processes.

Uses light energy to split water into hydrogen and oxygen is called Photolytic Process. These processes are in the very early stages of research but offer the possibility of hydrogen production which is cost effective and has a low environmental impact.

The "Solar Constant" is $1.37 \ge 10^3 \text{ W/m}^2$. So Earth receives $1.2 \ge 10^{17} \text{ W}$ insolation or $1.56 \ge 10^{18} \text{ kWh/year}$ in total. 1 kg hydrogen = 39.4 kWh. So sunlight represents $3.9 \ge 10^{16} \text{ kg H}_2$. Typical solar cell efficiency is 10% so midday electric power is 100 W/m², Annual energy harvest (N. Europe) 80kWh/m², or 2 kg. H₂. But 0.13% of earth's surface covered with PV panels of 10% efficiency =present world total energy demand! It's a matter of scale and economics! However electrolysis of water requires $\Delta V > 1.23 \text{ V}$ (1.45V adiabatic), i.e. three silicon PV cells in series^[5].

Hydrogen production from water splitting requires two molecules of water to donate fourvalence electrons to the oxygen nucleus and protons in a general reaction according to $2H_2O \rightarrow 2H_2+O_2$. This process consumes at least 4.92 eV of energy to generate one molecule of oxygen and two molecules of hydrogen. Additionally, a hydrogen separation method should be utilized to distinguish a pure hydrogen and oxygen stream^{[6][7]}. A typical photolytic process shown in Figure (3-9).

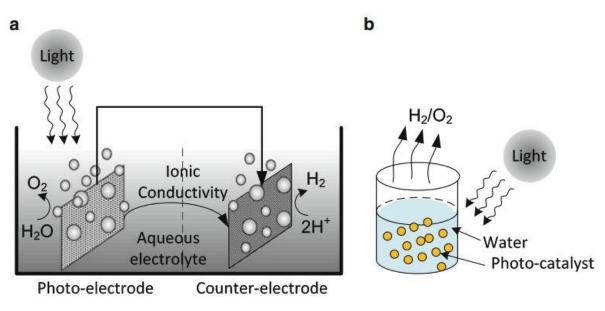


Figure 3-9 General configurations for photo-catalytic water splitting: electrode based (a) and particle based (b) (Modified from Baniasadi et al^[7]).

Another representation of photolytic process are given on Figure (3-10)

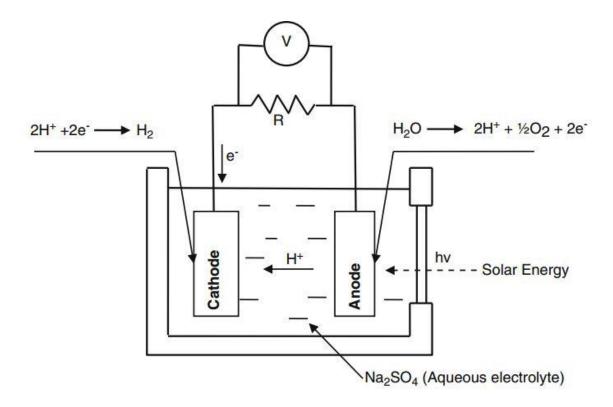


Figure 3-10 Schematic of solar photo-electrolysis (Modified from Fujishima and Honda^[9]).

Behind above delineated process there are some methodology to produce Hydrogen from renewable sources. Such as Hydrogen from *biomass*, *Biological hydrogen production*,

Hydrogen from biomass pyrolysis, Hydrogen from biomass gasification, Wind energy to hydrogen, solar energy to hydrogen, Hydrogen production from geothermal energy etc.

A graphical presentation of "Hydrogen production and storage pathway" has been shown on Figure (3-11), Figure (3-12) shows the "Pathways of biomass based hydrogen production" and an "Integrated system of electricity to hydrogen generation from wind power" is shown on Figure (3-13)

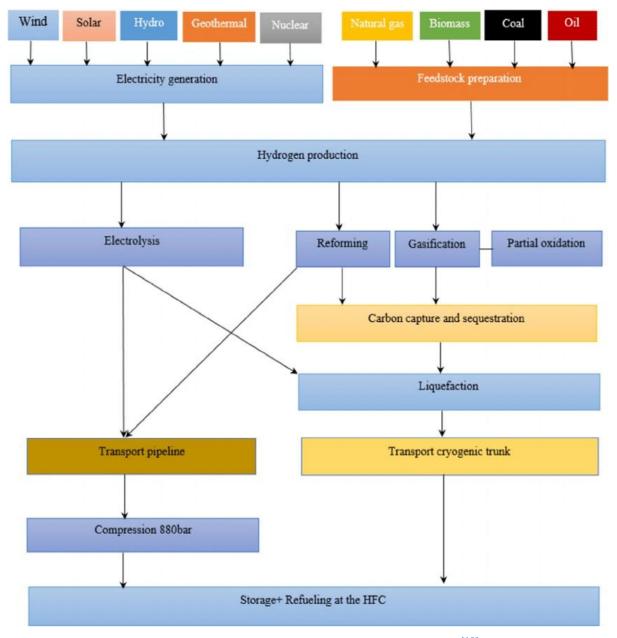


Figure 3-11 Hydrogen production and storage pathway^[10].

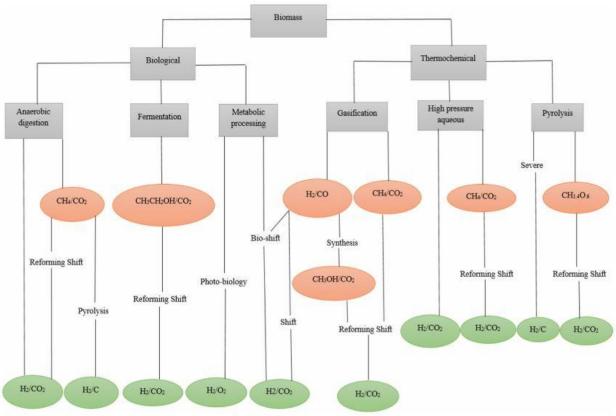


Figure 3-12 Pathways of biomass based hydrogen production^[10].



Figure 3-13 Integrated system of electricity/hydrogen generation from wind power^[10].

3.2 - Storage

The storage device is an important part of the hydrogen energy system. A big challenge regarding large scale use of hydrogen is storage. Hydrogen is quite difficult to store or transport with current technology. Hydrogen has good energy density by weight, but poor energy density by volume compared to hydrocarbons^[11]. For any kind of vehicle fuel system, it is desired to have at least a 500 km (300 miles) driving range^[12]. Developing a viable hydrogen storage system is becoming increasingly important for promoting a "hydrogen economy"^[13]. The gravimetric and volumetric storage should be high for those H₂ storage devices. Properties of good H₂ storing materials are lightweight, low cost, excellent kinetics of adsorption and desorption, and recyclability.

Hydrogen is an ultra-light gas that occupies a substantial volume under standard conditions of pressure, i.e., atmospheric pressure. In order to store and transport hydrogen efficiently, this volume must be significantly reduced^[14].

Hydrogen is the lightest gas in the entire Universe. One liter of this gas weighs only 90 mg under normal atmospheric pressure, which means that it is 11 times lighter than the air we breathe.

A volume of around 11 m^3 (which is the volume of the trunk of a large utility or commercial vehicle) is needed to store just 1 kg of hydrogen, which is the quantity needed to drive 100 km. For this reason, its density must be increased using one of the following techniques:

- High-pressure storage in the gaseous form
- Very low temperature storage in the liquid form (stored at -253°C).
- Hydride-based storage in the solid form

3.2.1 - High-pressure storage in the gaseous form.

Hydrogen is an ultra-light gas that can be highly compressed to reduce its specific volume.

The easiest way to decrease the volume of a gas, at constant temperatures, is to increase its pressure. So, at 700 bar, which is 700 times normal atmospheric pressure, hydrogen has a density of 42 kg/m³, compared with 0.090 kg/m³ under normal pressure and temperature conditions. At this pressure, 5 kg of hydrogen can be stored in a 125-liter tank.

Today, hydrogen is already being distributed in steel cylinders in which it is stored at 200 bar.

To further improve storage capacity, manufacturers are developing composite cylinders or tanks made of much lighter weight materials than steel, and which allow us to store hydrogen at a pressure of 700 bar.

Today, most car manufacturers have opted for the solution that consists in storing hydrogen in the gaseous form, at high pressure. This technology enables us to store enough hydrogen to allow a car that runs on a fuel cell battery to cover between 500 and 600 km between fill-ups. Figure (3-14) shows a Cryogenic hydrogen storage tank diagram.

Did we know? The value of 1 bar corresponding to atmospheric pressure is equal to the force exercised by one 1.5-liter bottle on a 1 euro cent coin. Pressure of 700 bar is 700 times atmospheric pressure; it is the force exercised by a 1.2-ton car on the same 1 euro cent coin.

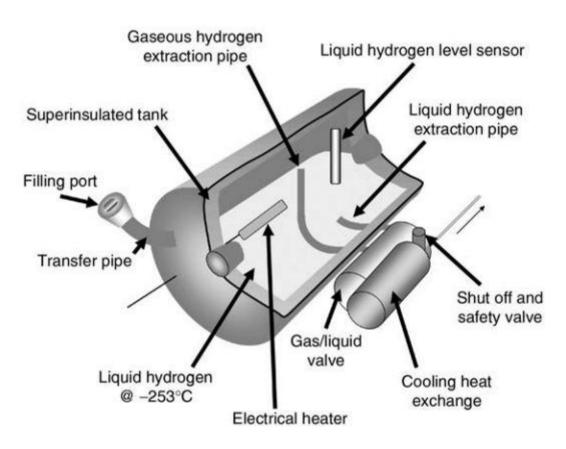


Figure 3-14 Cryogenic hydrogen storage tank diagram.

3.2.2 - Very low temperature storage in the liquid form.

A cutting-edge technique for storing a maximum of hydrogen in a restricted volume consists of transforming gaseous hydrogen into liquid hydrogen by cooling it down to a very low temperature.

Hydrogen turns into a liquid when it is cooled to a temperature below -250 °C. At -252.8°C and 1.013 Bar, liquid hydrogen has a density of close to 71 kg/m³. At this pressure, 5 kg of hydrogen can be stored in a 75-liter tank. In order to maintain liquid hydrogen at this temperature, tanks must be perfectly isolated.

Storing hydrogen in the liquid form is an option for just a limited number of applications so far, in high-tech areas such as space travel. For example, the tanks on the Arianne launcher, designed and manufactured by Air Liquid, contain the 28 tons of liquid hydrogen that will provide fuel to the central engine. These tanks are a genuine example of technological provess: they weigh only 5.5 tons empty and their casing is not more than 1.3 mm thick Figure (3-15).

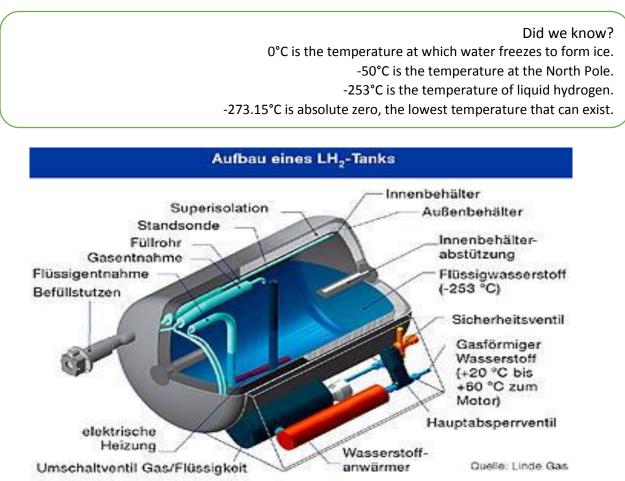


Figure 3-15 Very low temperature in the liquid form hydrogen storage tank diagram.

3.2.3 - Hydride-based storage in the solid form.

Storing solid hydrogen, i.e. conserving it inside another material, is also a promising avenue for research.

The methods used to store hydrogen in the solid form involve techniques that bring into play the mechanisms of absorption or adsorption of hydrogen by a material.

One example is to form solid metallic hydrides through the reaction of hydrogen with certain metal alloys. This absorption is the result of the reversible chemical combination of hydrogen with the atoms that comprise these materials. The most promising materials are composed of magnesium and alanates.

Only a low mass of hydrogen can be stored in these materials, which is currently the major downside of this technology. In fact, the best materials currently generate a ratio of hydrogen weight to the total weight of the tank of not more than 2 to 3%.

Before considering large-scale applications, it is also important to master certain key parameters such as kinetics (cell performance), and the temperature and pressure of the charge and discharge cycles of hydrogen in these materials. Figure (3-16) & (3-17) are the example of Hydride based H₂ storage system and Figure (3-18) shows a typical storage system for H₂.



hydrogen storage

Figure 3-16 Nano-composite materials for hydrogen storage.

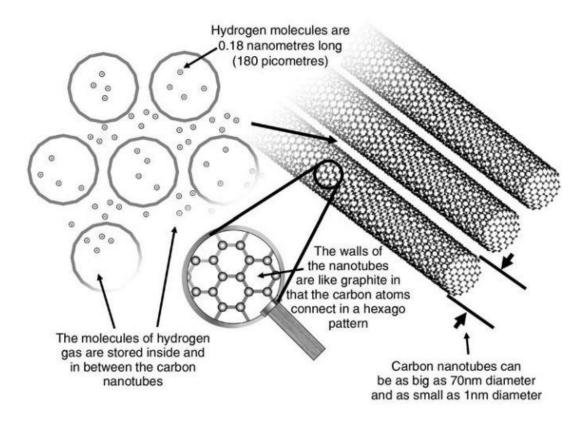


Figure 3-17 Hydrogen storage in carbon nanotubes.

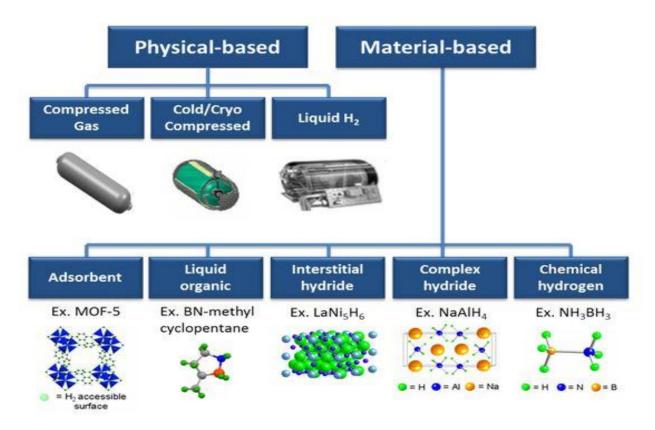


Figure 3-18 A typical storage system of Hydrogen.

At present, only three systems for on-board hydrogen storage are close to commercialization. They are compressed gas at high pressures (5,000 to 10,000 psi in composite cylinders), liquid hydrogen which requires a cryogenic temperature of -253° C, and materials-based storage in solids which involves the use of metal hydrides, carbon-based materials/high surface area sorbents, and/or chemical hydrogen storage.

The current status of various storage technologies in terms of weight, volume and costs is given below Table (3-3). These systems show a three to eight times performance gap in meeting the Department of Energy (DOE) goals.

| Storage Technologies | Weight (kwh/kg) | Volume (kwh/L) | Cost (\$/kwh) |
|------------------------|--------------------|-------------------|------------------|
| Chemical Hydrides | 1.6 | 1.4 | \$8 |
| Complex Metal Hydrides | 0.8 | 0.6 | \$16 |
| Liquid Hydrogen | 2.0 | 1.6 | \$6 |
| 10,000-psi Gas | 1.9 | 1.3 | \$16 |
| DOE Goals (2015) | 3.0 | 2.7 | \$2 |

Table 3-3 Current status of various storage technologies in terms of weight, volume and costs

3.3 - Utilization/Use in global prospective.

In the area of environmental preservation, the main use of hydrogen is to remove the sulfur that is naturally contained in oil to produce cleaner fuels. Hydrogen is a reagent used in many industrial sectors, including chemicals, textile fiber manufacturing, glass, electronics and metallurgy. Hydrogen is also used as fuel for some rockets and rocket launchers. Hydrogen, combined with a fuel cell, is also a great vector of clean energy, since it makes it possible to produce electricity directly onboard electric vehicles or in remote areas that are cut off from the power grid.

Hydrogen is used in a wide variety of applications such as:

Chemicals

- Ammonia and fertilizer manufacture
- Synthesis of methanol

- Sorbitol production
- General pharmaceuticals and vitamins

Electronics

- Polysilicon production
- Epitaxial deposition
- Fiber optics

• Metals

- Annealing/heat treating
- Powder metallurgy

• Fuels

- Petroleum refinement
- Liquid rocket fuel
- Some use in fuel cells

Food and float glass

- Fats/fatty acids
- Blanketing

3.3.1 ~ Energy extracting process from Hydrogen.

Hydrogen is a very versatile energy carrier. It can release energy in a number of different processes, among them following four process are most prominent.

- Direct combustion;
- Catalytic combustion;
- Steam production;
- Fuel cell operations.

3.3.1.1 – Direct Combustion : A mixture of hydrogen and oxygen with an appropriate proportion plus the presence of a trigger can release thermal energy until one of the two components is fully consumed $H_2+O_2/2 \rightarrow H_2O$ +heat.

The burning of hydrogen and oxygen is a traditional method for spacecraft propulsion, whereas the combustion of hydrogen and air is used more frequently in chemical and manufacturing industries. This direct combustion has many advantages. First of all, the wide flammability range of hydrogen allows the combustion of the gas immixture with other gases and creates a sensible reduction of the maximum flame temperature. Secondly, hydrogen can also replace traditional fuels in volumetric and internal combustion engines. The high speed of hydrogen flame can even benefit internal combustion engines by granting them a very high rotation regime. Furthermore, in comparison with fossil fuel combustion, hydrogen burning releases much fewer, if none at all, pollutants like carbon oxides (COx), particulate matter, sulphur oxides (SOx, recognized as carcinogenic agents) and nitrogen oxides (NOx, irritating but nontoxic agents).

Comparison among hydrogen, methane and petrol are given on Table 3-4.

| | Hydrogen | Methane | Petrol |
|--|-----------------------------|----------|---------|
| Mass (g/mol) | 2 | 16 | |
| Volumetric mass (kg/m ³) | 0.08 | 0.7 | |
| Density (kg/Nm ³) | 0.08988 kg/ nm ³ | 0.651 | |
| Boiling point (K) | 20.28°K | 111.7 | |
| Critical point (K) | 32.97°K | 190.6 | |
| Specific heat (kJ/kg K) | 175-6000°K | 2.26 | |
| Lower heating value (MJ/kg) | 110.9 | 50.7 | 44.5 |
| Lower heating value (MJ/Nm ³) | 10.1 | 37.8 | |
| Flammability minimal energy, ambient (mJ) | 0.02 | 0.29 | 0.24 |
| Flammability limits (by volume) (%) | 4-75 | 5.3-15 | 1.0-7.6 |
| Detonation limits (by volume) (%) | 13-65 | 6.3-13.5 | 1.1-3.3 |
| Auto-ignition temperature (°C) | 585 | 540 | 228-501 |
| Flame temperature (°C) | 2045 | 1875 | 2200 |
| Diffusion coefficient, in air (cm ² /s) | 0.61 | 0.16 | 0.05 |
| Stoichiometric flame speed (m/s) | 2.37 | 0.43 | |
| Explosive energy (kg TNT/m ³) | 2.02 | 7.03 | 44.24 |
| Detonation speed, in air (km/s) | 2 | 1.8 | |

Table 3-4 Comparison among hydrogen, methane and petrol.

3.3.1.2 – Catalytic Combustion : Hydrogen combustion is also possible with the presence of a catalyst, usually with a porous structure, to reduce the reaction temperature. However, compared to the traditional method, catalytic combustion requires a greater reaction surface. The only By-product of the reaction is water steam, since no NOxis yielded thanks to the low temperature. The process is therefore considered clean with very low gas emissions. The reaction speed can be easily controlled by managing the hydrogen flow rate. Since the reaction does not produce flames, catalyzed combustion is intrinsically a very safe procedure.

3.3.1.3 - Steam Production from Combustion : The burning of hydrogen and

3.3.1.4 - Fuel Cell: The opposite reaction of water electrolysis is the combination

oxygen can bring the flame temperature up to 3000°C and produce water steam, consequently more water needs to be injected to maintain the desired steam temperature, forming therefore saturated and superheated steam with an efficiency close to 100% without losing any thermal energy. The steam can be used in turbines and industrial and civil applications.

of H₂ with O₂ to generate water. This process releases part of the energy of electrolysis that was used to separate water into its elementary components. This happens in a device called fuel cell.

A fuel cell converts the chemical energy in hydrogen and oxygen into direct current electrical energy by electrochemical reactions. Fuel cells are devices that convert hydrogen gas directly into low-voltage, direct current electricity. The cell has no moving parts.

The process is essentially the reverse of the electrolytic method of splitting water into hydrogen and oxygen. In the fuel cell, the cathode terminal is positively charged and the anode terminal is negatively charged. These electrodes are separated by a membrane. Hydrogen gas is converted into electrons and protons (positive



Figure 3-19 13kW PEM fuel cell (Photo; Ballard Power Systems, Inc.)

hydrogen ions) at the anode. The protons pass through the membrane to the cathode, leaving behind negatively charged electrons. This creates a flow of direct current electricity between the terminals when connected with an external circuit. This current can power an electric motor placed in this circuit. The hydrogen ions, electrons, and oxygen combine at the cathode to form water, the only byproduct of the process.

The key element in a fuel cell is the ion (proton) exchange membrane. Its purpose is to separate the anode and cathode to prevent mixing of the fuel and oxidant and to provide an ironically conductive pathway for protons. Thus, its required properties are high ionic conductivity (and zero electronic conductivity) under cell operating conditions, long term chemical and mechanical stability at elevated temperatures in oxidizing and reducing environments, good mechanical strength with resistance to swelling, low oxidant and fuel crossover, pinhole free structure, interfacial compatibility with catalyst layers and low cost.



Figure 3-20 Honda FCX fuel cell vehicle, December 2002. (Photo: Ballard Power Systems, Inc.)

Fuel cells have the potential for excellent efficiency and can convert up to 75 percent of the energy in the fuel. When a fuel cell is used in an automobile, the automotive power train must be converted to electricity. Fuel cells may also be used as a stationary power source supplying electricity for a utility company or electricity to individual consumers.

In automobiles, there are two major advantages of a fuel cell versus an internal combustion engine. The

first is that the fuel cell is approximately twice as fuel-efficient (on a fuel-to-wheel basis). The second advantage is the next generation of automobiles may be electric-powered. Storing electricity for automotive use can only be done the by use of fuel cells. Battery technology cannot meet the weight, volume and range required for today's automobile.

On the negative side, a fuel cell will cost \$3,000 to \$5,000 per kW compared to \$50 per kW for an internal combustion engine. Thus, reducing a fuel cell's cost is the major R&D challenge.

A fuel cell can operate on industrial waste hydrogen, hydrogen from propane, or methane generated at the waste-water treatment plants. Ultimately, hydrogen obtained from renewable resources such as solar, wind, or biomass energy will provide a sustainable and clean source of hydrogen for fuel cell power generation.

There are five types of fuel cells available. Those are-

1. Polymer Electrolyte Membrane Fuel Cell (PEMFC) - A PEMFC fuel cell employs a solid organic polymer polyperfluorsulfonic acid electrolyte membrane and operates at temperatures of 60-100° C. PEMFC applications include electric utilities, portable power, and transportation. Its main advantages are that the solid electrolyte reduces corrosion, operates at low temperatures, and delivers quick start-up. Its disadvantages are that the cell requires expensive catalysts and the cell has high sensitivity to fuel impurities.

2. Alkaline Fuel Cell (AFC) - An AFC employs an aqueous solution of potassium hydroxide soaked in a matrix electrolyte, and operates at temperatures of 90-100°C. AFC applications include military and space, and it is the technology that has been used by NASA for more than 25 years. Its main advantage is that cathode reaction is faster in the alkaline electrolyte, resulting in high performance. Its disadvantage is the requirement for pure hydrogen, requiring expensive CO_2 removal from fuel and air streams.

3. Phosphoric Acid Fuel Cell (PAFC) - A PAFC employs a matrix soaked with liquid phosphoric acid. It operates at temperatures of 175-200° C. PAFC applications include electric utility and transportation. Its main advantages are that it has up to 85% efficiency when used in cogeneration of electricity and heat, and it can use impure hydrogen as fuel. Its main disadvantages are that it requires a platinum catalyst, has low current and power, and requires a large size and weight.



Figure 3-21 European fuel cell bus project, June 2002 (Photo: Ballard Power Systems, Inc.)

4. Molten Carbonate Fuel Cell (MCFC) - An MCFC employs a liquid solution of lithium, sodium, and/or potassium carbonates soaked in a matrix. It operates at 600-1000° C. The main MCFC applications are for electric utilities. Its advantages are its high efficiency, fuel flexibility and its ability to use a variety of catalysts. Its disadvantage is that the high temperature enhances corrosion and breakdown of cell components.

5. Solid Oxide Fuel Cell (SOFC) - An SOFC employs a solid zirconium oxide to which a small amount of yttria is added. It operates at 600-1000° C. Its main advantages are its high efficiency, fuel flexibility, ability to use a variety of catalysts and reduced corrosion. Its main

disadvantage is that the high temperature spurs breakdown of cell components. For transportation applications, the three key fuel cell challenges are cost (less than \$50/kW of engine power), durability (at least 5,000 hours) and rapid start-up (less than 30 seconds)^[15]. Figure (3-22) is Principle of Operation of Fuel Cell and Figure (3-23) shows how does a fuel cell work.

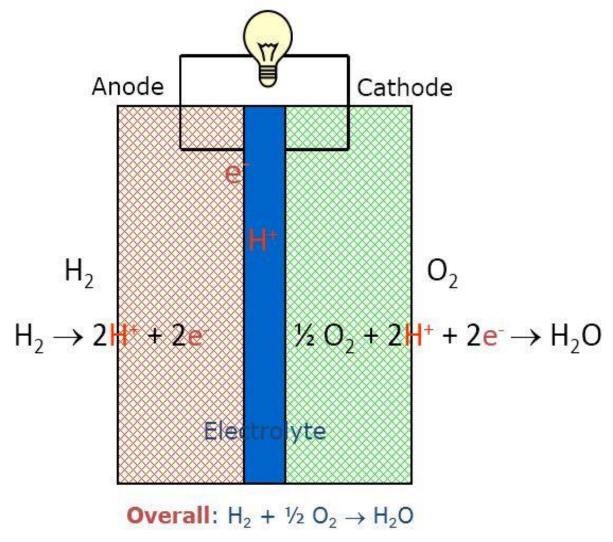


Figure 3-22 Principle of Operation of Fuel Cell

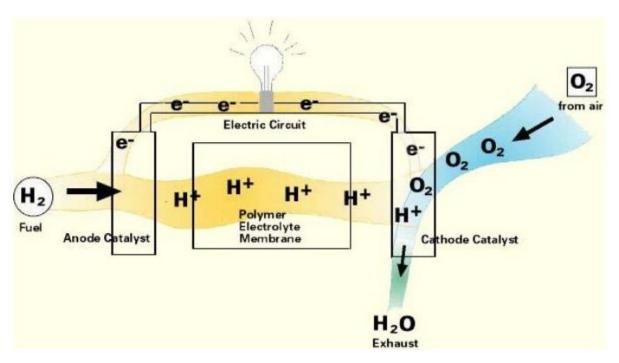


Figure 3-23 How does a Fuel Cell work.

3.4 - Percussion, Codes, and Standards.

A systematic assessment is required to evaluate potentially harmful effects of technologies and products. 'Technology assessment' aims at analyzing and evaluating the desirable and non-desirable consequences of technologies. The focus of such assessments should be 'ex-ante' i.e., prospective, future oriented^[16].

Hydrogen refill station is a highly risky area due to high pressure of compressed H₂ and high inflammable property. Therefore, safety measurement is required for hassle free operation of those filling stations and vehicles run by H₂. The safety inspections would be conducted using 'Risk Assessment Method'^[17], which is widely accepted as being an effective method of safety assessment. In risk assessment, thoroughly investigation of all accident scenarios is extremely important. Accident scenarios were identified using the HAZOP (Hazard and Operability Studies) and FMEA (Failure Mode and Effect Analysis) methods that are widely considered as effective ways of identifying the source of a risk^[18].

The detection of explosive conditions in hydrogen applications is important for both safety and economic reasons. Cost-effective hydrogen sensor technologies that deliver detection selectivity and sensitivity, dependability and durability, stability and reproducibility, resistance

to chemical degradation and real-time response are needed. An examination of the commercially available point-contact hydrogen sensors indicates the majority of these sensors fall into four main categories: catalytic combustion, electrochemical, semi-conducting oxide sensors and thermal conductivity detectors. All of these sensors depend on the interaction of hydrogen with palladium (Pd) or Pd-based alloys.

One kind of hydrogen sensor being developed at FSEC (Florida Solar Energy Center) is "Smart Paint." Smart Paint is a special powder that can be painted onto the surface of field lines, flanges, and joints of hydrogen pipelines or vessels to detect minute hydrogen leaks. The paint provides a visual method to detect and locate possible hydrogen leaks that may occur.

Vehicle applications require the development of new sensors with capabilities beyond those of commercially available systems. Areas of most interest include micro-machining and micro-fabrication technology to fabricate miniaturized sensors. In addition, new techniques that allow control and interrogation of each sensor and provide self-calibrating capability are needed.

Hydrogen, in vast quantities, has been used safely for many years in chemical and metallurgical applications, the food industry, and the space program. As hydrogen and fuel cells begin to play a greater role in meeting the energy needs of our nation and the world, minimizing the safety hazards related to the use of hydrogen as a fuel is essential.

DOE (Department of Energy, US) is working to develop and implement practices and procedures that will ensure safety in operating, handling, and using hydrogen and hydrogen systems. In addition, DOE (Department of Energy, US) is working with domestic and international organizations to identify the current gaps in the standards development process; facilitate the creation and adoption of model building codes and equipment standards for hydrogen systems in commercial, residential, and transportation applications; and provide technical resources to harmonize the development of international standards.

3.5 - Environmental impact.

The environmental impact and energy efficiency of hydrogen depends on how it is produced. The world's energy demand is ever increasing, and to fulfill that demand we often look for engineering solutions, that is, conversion of energy from one form to another. We convert one form of energy to another convenient form to use the energy better. This statement can better be understood by the following example: we convert chemical energy of fossil fuels to heat (thermal energy) first, and then the thermal energy is converted to electrical energy for our convenience to use it in our homes, offices, industries, hospitals, schools, etc. Such energy conversion activities come under engineering activities. Engineering activities are often associated with some environmental problems/issues, mainly the injection of greenhouse gas into the environment. Environmental damage caused by the green-house effect further causes global warming, which is responsible for climate change. Therefore, it is important to know how adversely engineering activities are affecting our environment. Environmental impact assessment is simply an indicator of these concerns.

Sustainable development can be defined as a mode of human development in which we use our resources to meet the needs of present the generation without affecting the environment and the needs of future generation. Sustainability assessment is an indicator of sustainable development. Energy, environment, and sustainable development can be referred to as three vertices of an equilateral triangle, as shown in Figure (3-24). If we come close to any vertex, for example, energy conversion, we move farther away from the other two points (i.e., environment and sustainability). Therefore, it has become very important for energy engineers and environmentalists to find the proper balance among the three factors^[19].

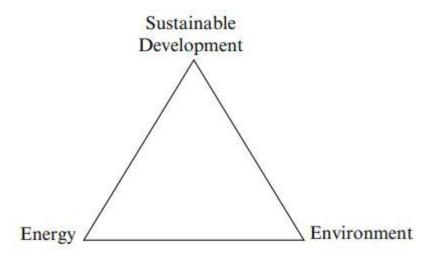


Figure 3-24 The triangle of energy, environment, and sustainable development

3.5.1 - Environmental Impact Reduction Factor.

As already mentioned, electricity is one of the energy inputs for hydrogen production; therefore, its generation cost, efficiency, and environmental impact become important parameters for environmentally benign and cost-effective hydrogen production. Table (3-5)

shows these parameters along with the efficiency of a hydrogen production system using an electrolyzer unit and the environmental impact reduction factor. The efficiency of hydrogen production is calculated by multiplying the efficiencies of electricity production and the electrolyzer unit (i.e., 52 %)^[20], whereas the environmental impact reduction factor (EIRF) can be given as

$EIRF = (gCO_{2coal} - (gCO_2) / (gCO_{2coal})$ (2.1)

Here, the numerator denotes the difference in carbon dioxide injection into the environment by conventional (coal-based) and nonconventional methods, and the denominator denotes carbon dioxide injection into the environment by coal-based electricity generation. No carbon dioxide is produced during the electrolysis of water, but it is produced during electricity production. Hence, EIRF is calculated by using the carbon dioxide emission by different sources for electricity production only. The value of EIRF remains between 0 and 1, where 1 represents the best technology and 0 the worst technology, for which the environmental impact is highest and lowest, respectively.

| Table 3-5 Mean price of electricity generation, efficiencies of electricity and hydrogen genera- | | |
|---|--|--|
| tion, average greenhouse gas emissions expressed as CO2 equivalent, and environmental | | |
| impact reduction factor (EIRF) for individual energy-generation technologies ^[21] . | | |

| | | Efficiency | | | |
|-------------------------|----------|-----------------|--------------------------------------|-----------------------|------|
| Energy sources US\$/kWh | US\$/kWh | Electricity (%) | Hydrogen production ^a (%) | gCO ₂ /kWh | EIRF |
| Photovoltaic | 0.24 | 4-22 % | 2-12 % | 90 | 0.91 |
| Wind | 0.07 | 24-54 % | 13-28 % | 25 | 0.98 |
| Hydro | 0.05 | >90 % | 47 % | 41 | 0.96 |
| Geothermal | 0.07 | 10-20 % | 5-11 % | 170 | 0.83 |
| Coal | 0.042 | 32-45 % | 17-23 % | 1,004 | 0.00 |
| Gas | 0.048 | 45-53 % | 23–28 % | 543 | 0.46 |

^a Hydrogen production considered here is by using electrolyzer unit only

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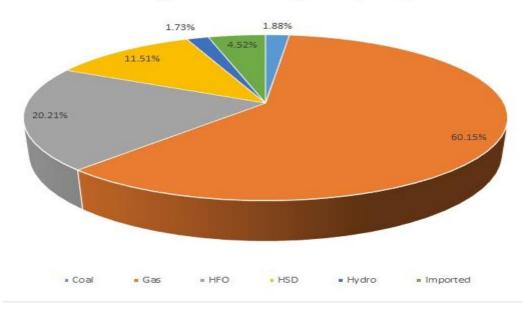
<u>Chapter - 04.</u>

Present Energy Scenario of Bangladesh.

Bangladesh is developing country has 147,570 km² area with a population of 170 million, and population density of 1,319/km², it is the world's eighth-most populous country, the fifth-most populous in Asia and the third-most populous Muslim-majority country. About 85% of the population lives in rural areas. Per capita energy consumption in Bangladesh is one of the lowest in the world. Its per capita energy consumption in 1997 and per capita GNP in 1999 were 197 kgOE (kilogram oil equivalent) and US\$ 370 respectively^[1].

In 2011, Bangladesh was consume 1.09 quadrillion Btu energy as the reference of International Energy Statistics, February-2015. The energy we uses, 93.75% are from the fossil fuel, and 1.73% from hydro energy and rest of are imported. In average 58.81 million metric ton CO2 are emitted from the fossil fuel that we are uses per year in our country^[2].

Different energy sources are usages in Bangladesh among them natural gas is 64%, Furnace oil 19%, Diesel 7%, coal 3%, hydro 2% and rest 5% are from imported as shown in Chart (4-1)^[2]. Bangladesh power development board give us the very recent energy statistics (Table 4-1) where shows Installed Capacity of BPDB Power Plants and Derated Capacity of BPDB Power Plants as on August 2016 data^[3].



Energy scenario of Bangladesh [2016]

Chart 4-1 Energy scenario of Bangladesh [2016]

| Fuel Type | Capacity(Unit) | Total(%) |
|----------------------------|--------------------------------|----------|
| | 0.00 MW | 0 % |
| Coal | 250.00 MW | 1.88 % |
| Gas | 7988.00 MW | 60.15 % |
| HFO | 2684.00 MW | 20.21 % |
| HSD | 1528.00 MW | 11.51 % |
| Hydro | 230.00 MW | 1.73 % |
| Imported | 600.00 MW | 4.52 % |
| Total | 13280.00 MW | 100 % |
| erated Capacity of BPDB Po | ower Plants as on September 20 | 016 |
| Fuel Type | Capacity(Unit) | Total(%) |
| | 0.00 MW | 0 % |
| Coal | 200.00 MW | 1.58 % |
| Gas | 7529.00 MW | 59.35 % |
| HFO | 2627.00 MW | 20.71 % |
| HSD | 1499.00 MW | 11.82 % |
| Hydro | 230.00 MW | 1.81 % |
| Imported | 600.00 MW | 4.73 % |
| Total | 12685.00 MW | 100 % |

 Table 4-1 Energy statics from Bangladesh Power Development Board [2016]

HFO: Heavy Fuel Oil HSD: High Speed Diesel

Reference

[1] http://www.buet.ac.bd/ces/energy-relateddata-bangladesh.htm (accessed August 17, 2016)

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<u>Chapter - 05.</u>

Scope of Hydrogen utilization in Bangladesh.

Since Bangladesh is a developing country and most of the energy sources are from fossil fuel that demand high cost as well as great contribution to carbon emission through the earth. Its per capita energy consumption in 1997 and per capita GNP in 1999 were 197 kgOE (kilogram oil equivalent) and US\$ 370 respectively^[1] which is too high in respect of Per capita \$3,581^[2].

Bangladesh has a great scope to migrate in renewable sources as well as hydrogen fuel energy arena. Comparatively hydrogen fuel demand a bit low cost rather than traditional fossil fuel.

Hydrogen is measured by the kilogram. 1 kilogram is 1 gallon of gasoline equivalent (gge). 2. 0.0015/gallon + 0.987/kg (gge) Refining Costs = 0.9885 = 1.00/kg (gge) using Atmospheric Electrolyses. Table (5-1) and Graph (5-1) shows the cost comparison between different fuels.

| National Average Price Between April 1 and April 15, 2016 | |
|--|---------------|
| Fuel | Price |
| Biodiesel (B20) | \$2.23/gallon |
| Biodiesel (B99-B100) | \$2.81/gallon |
| Electricity | \$0.13/kWh |
| Ethanol (E85) | \$1.84/gallon |
| Natural Gas (CNG) | \$2.02/GGE |
| Propane | \$2.77/gallon |
| Gasoline | \$2.06/gallon |
| Diesel | \$2.13/gallon |



Graph 5-1 Average fuel price in the USA from 2000 to 2015

Reference

- [1] <u>http://www.buet.ac.bd/ces/energy-relateddata-bangladesh.htm</u> (accessed August 17, 2016)
- [2] <u>"Bangladesh"</u>. World Economic Outlook Database. <u>IMF</u>.
- [3] Alternative Fuel Price Report, April 2016 (PDF) and U.S. Energy Information Administration
- [4] Clean Cities Alternative Fuel Price Reports

<u>Chapter ~ 06.</u>

Research Methodology.

Hydrogen could be produce by number of ways but among all procedure electrolysis perhaps the easiest way. The methodology I used to produce hydrogen in my institute's lab is described as follows.

6.1 - Required materials and instruments.

Following materials and instruments are needed to produce hydrogen in lab.

- ▶ 1. Volt meter for measuring input voltage.
- ▶ 2. Ampere meter for measuring the flow of current
- ▶ 3. Pyranometer for measuring solar irradiance.
- ▶ 4. Thermometer for measuring temperature of water.
- ▶ 5. Glue gun for jointing different materials such as bottles, pipes, etc.
- 6. Water, Sulfuric acid, plastic bottle, cable, Chula, led (anode), steel (cathode), drum, plastic pipe etc.

6.2 - Experimental setup.

01. Cutting the bottom side of some 500ml plastic bottle and enter a bar of led (anode) on it with cable connection and a steel bar (cathode) with cable connection. The crock of the bottle should two hole, one is blocked with cable out put another is pipe connected for storing hydrogen.

02. The bottles containing anode and cathode are immerged in a 2.5 liter bottle that are half fill with diluted sulfuric acid. All hydrogen output pipe should connected in parallel and three of anode and cathode are connect in series.

03. Three series connected anode and cathode are then connect in parallel Figure (6-1) and then anode are connect in positive line whereas cathode in negative 12 DC supply line.

04. After connecting DC supply the electrolysis could began and hydrogen will produce. It will store in a water filled drum via output pipe line.

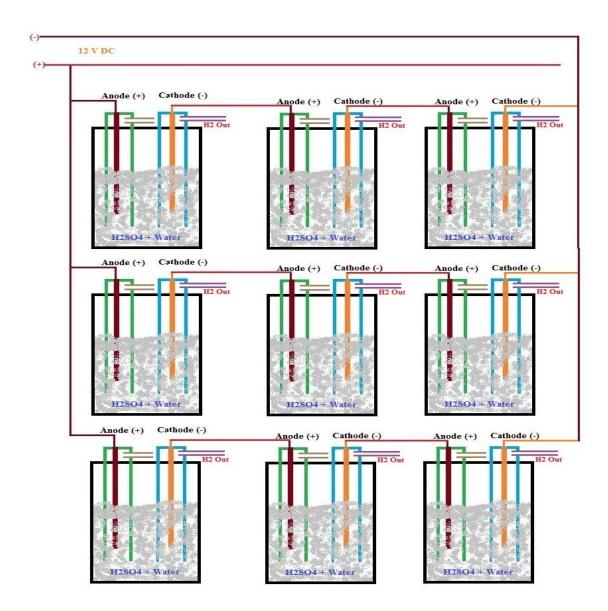


Figure 6-1 Connection diagram of anode and cathode to produce Hydrogen.

6.3 - Comparing burning rate with wood and LPG.

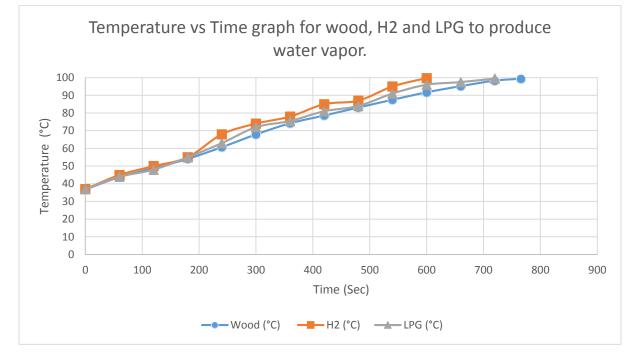
After sufficient storing hydrogen I have burned it for vaporing one liter of water and do the same for wood and LPG. The data have taken and then analysis. Figure 6-2 shows the boiling water by burning hydrogen.



Figure 6-2 Boiling water and measuring temperature .

| | Temperature | | |
|----------|-------------|---------|----------|
| Time (s) | Wood (°C) | H2 (°C) | LPG (°C) |
| 0 | 36.8 | 37 | 37 |
| 60 | 43.8 | 45 | 44 |
| 120 | 48.8 | 50 | 48 |
| 180 | 54.1 | 55 | 55 |
| 240 | 60.7 | 68 | 63 |
| 300 | 67.9 | 74 | 72 |
| 360 | 74.2 | 78 | 75.5 |
| 420 | 78.6 | 85 | 81 |
| 480 | 83.1 | 87 | 84 |
| 540 | 87.5 | 95 | 91 |
| 600 | 91.7 | 99.75 | 96 |
| 660 | 95.2 | | 97.5 |
| 720 | 98.3 | | 99.5 |
| 766 | 99.4 | | |

 Table 6-1 Temperature data of Wood , Hydrogen, and LPG for boiling water.



Graph 6-1 Temperature comparison of Wood , Hydrogen, and LPG for boiling in respect of time

6.4 - Techno-economic analysis.

Most of the technical items are got from the laboratory but some materials have been bought out from market. Following data will help to doing economic analysis.

| TOTAL | = Tk. 330.00 |
|----------------------|--------------|
| Others | = 50.00 Tk. |
| Led + Steel sheet | = 50.00 Tk. |
| Glue | = 30.00 Tk. |
| Plastic pipe | = 50.00 Tk. |
| Waste plastic bottle | = 50.00 Tk. |
| Sulfuric acid | = 100.00 Tk. |

Hence we use photovoltaic cell for electric supply thus we consider no cost for electric supply. So finally the cost for producing 0.5 Kg hydrogen is Tk 330.00, say Tk. 300.00

6.5 - Results and discussions.

- As we seen from the graph (6.1) to produce vapor from 1 liter of water, H2 needs 10 minutes, LPG needs 12 minutes and Wood needs almost 13 minutes. So the burning rate of H₂ is 1.21 and 1.3 times more efficient than LPG and wood respectively.
- Price of wood is Tk.10.00/kg, LPG is Tk.100.00/kg in our country and H2 is 300.00/Kg (Lab production)
- Though it is observed that costing of H₂ is more than wood and LPG and it tends to take decision H₂ is not efficient but this costing of H₂ is taken from lab production. The cost could be more less if it is product commercially. On the other hand wood and LPG both are emits CO₂ but H₂ has no CO₂ emission.
- There has also an opportunity to carbon trading by using H_2 as fuel.



Figure 6-3 Temperature comparison of Wood , Hydrogen, and LPG for boiling in respect of time



Figure 6-4 (A) Connecting solar panel, (B) Making hole on plastic bottle by soldering iron, (C) & (D) Bocking bottle cork by plastic glue gun, (E) Jointing pipe fettings on storage tank, (F) Observing electrolysis condition, (G) Fixing water line and (H) Hydrogen stroage tank.

<u>Chapter - 07.</u> Conclusion

7.1 - Conclusion.

It is clear from the above thesis that research on hydrogen fuel is going on throughout the world. Much attention has been given on sustainable production and lightweight H₂ storage device as well as its ecofriendly utilization. In contrast to conventional energy sources (coal, oil, natural gas), it is carbon free and hence environmentally friendly. The countdown for conventional sources of energy has already begun as they are depleting fast. Therefore, hydrogen is a perfect candidate to fulfill the energy needs of humans for the future. In addition to the aforementioned qualities, hydrogen is quite challenging as an energy source or fuel because of its availability. Although hydrogen is naturally present on the Earth in the combined state in both organic and inorganic compounds, for example, as water and hydrocarbons, it is scarcely present in the free and molecular state. Therefore, elemental hydrogen is artificially produced, and hence its safe and environmentally benign production is most important. When considering environmentally friendly hydrogen production, the obvious choice for the input energy is renewable energy, mainly solar energy.

Mitigating in new technology is a common phenomenon around the world. The uses of H_2 as an energy source is dramatically increasing in developed country. Analysis of different data such as cost, area of utilization, environmental impact, hazards etc.; give us the result of bright potentiality of hydrogen as a promising alternative energy source for Bangladesh. To sustain the natural resources and environment, in near future hydrogen base energy source should implement in every energy sector. As it is seen in this research, hydrogen is 1.21 and 1.3 times more efficient than LPG and wood respectively. Price of wood is Tk.10.00/kg, LPG is Tk.100.00/kg in our country and H_2 is 300.00/Kg (Lab production).

Though it is observed that costing of H_2 is more than wood and LPG and it tends to take decision H_2 is not efficient but this costing of H_2 is taken from lab production. The cost could be more less if it is product commercially. On the other hand wood and LPG both are emits CO_2 but H_2 has no CO_2 emission. So, all research evidence showing that hydrogen could be the best choice of alternative energy source for Bangladesh.

7.2 - Policy Reformation.

This policy sets the overall framework for the improved performance of the energy sector. The objectives are to provide energy for sustainable economic growth, ensure optimum development of all the indigenous energy sources (oil and gas, coal, hydropower), ensure sustainable operation of the energy utilities, ensure rational use of total energy sources, ensure environmentally sound energy development programs, encourage public and private sector participation in the development and management of the energy sector, bring entire country under electrification by the year 2020, ensure reliable supply of energy to the people at reasonable and affordable price, and develop a regional energy market for rational exchange of commercial energy to ensure energy security. The report provides a series of recommended energy policies on the following areas: non-renewable energy, petroleum, marginal gas field development, renewable and rural energy, power, rural electrification, and demand estimation and planning.

Government should take different campaigning programs to promote the use of hydrogen as fuel instead other fossil fuels. Government could subsidies to those organization which already working for promoting hydrogen energy sector as well as can emphasis more investment in this sector.

7.3 - Future Research Scope.

The overall challenge to hydrogen production is cost. For cost-competitive transportation, a key driver for energy independence, hydrogen must be comparable to conventional fuels and technologies on a per-mile basis. In order for fuel cell electric vehicles to be competitive, the total untaxed, delivered and dispensed, cost of hydrogen needs to be less than \$4/gge. A gge, or gasoline gallon equivalent, is the amount of fuel that has the same amount of energy as a gallon of gasoline. One kilogram of hydrogen is equivalent to one gallon of gasoline.

Storing of hydrogen is a great obstacle to scientists due to its very low weight. Though hydrogen transportation are still not easy and people are pretty anxious to use it as a fuel for its high flammability. A number of scopes are abundant in hydrogen energy sector. Reducing the production cost, user friendly and safety using technology, developing the storing technology and reducing storing cost, transportation, devolving the efficiency of fuel cell etc. are some example of future research scope among many more.