Potential of Hydrogen Fuel for Automotive Applications

Dileep Kumar
Research Scholar: Electrical Engineering Dept.
VJTI
Mumbai, India
dknayak@vpmthane.org

S.K. Mahajan
Director: Technical Education,
Govt. of Maharashtra, India

H.A. Mangalvedekar
Prof.: Electrical Engineering Dept.
VJTI
Mumbai, India

A.C. Gangal
Head: Mechanical Engineering Dept.
V.P.M.'s MPCOE,
Velneshwar, Dist. Ratnagiri, (MS), India

Abstract—*This paper explains various aspects related to hydrogen and its possible use as automotive fuel for Fuel cell vehicles. This area has excellent research potential and experts around the world strongly feel that this could be the future fuel. However before hydrogen fuel becomes a reality, technological innovations are expected for the society to accept this for sustainable development. This paper is an effort to provide the details of this very interesting area of futuristic significance. To overcome fossil fuel deficit and to provide an inexhaustible, pollution free option hydrogen can become ideal choice. It provides the properties of abundance, convenience, cleanliness and renewability.*

Keywords—Hydrogen energy; production; storage; safety; sustainability

I. Introduction

Energy plays an important role in human activity. The standard of living and prosperity of a nation depends on the natural resources, increase in generation capability as well as the usage of power. The energy requirements are increasing due to rapid industrialization and enhanced inflow of electrical gadgets in the society. In the developing countries, energy demand rises at the rate of 9% per annum and unless the generation capacities are incremented, they may face energy deficit conditions.

We get around 80% of our energy from conventional fossil fuels like oil (36%), natural gas (21%) and coal (23%). The oil and natural gas resources are in the mid-depletion region and the coal reserves will last for couple of centuries.

The basic trends, which are a cause of concern and demand responsible precautions are:

i) The traditional forms of energy are depleted rapidly.

ii) The increased use of fossil fuels has drastic impact on ecological balance. It has resulted in the increase of carbon dioxide, nitrogen oxides and other greenhouse gases. This has led to environmental issues like seasonal imbalances, decrease in food production, flooding of continental coastal areas, melting of glaciers, rise in sea levels and global warming.

II. Present Energy Options

India is a vast country with different geographical conditions, which are conducive for variety of renewable energy generations[1]. The energy conservation, savings and management is being discussed and implemented so as to optimize the use of energy within every organization. The awareness is already created among the general public as well as industrialists. This has also resulted in the search for alternatives to the fossil fuels in the areas of solar, wind, biogas, biomass, biodiesel, tidal, nuclear and hydrogen energy. Different levels of research are in progress in all the areas with some matured technology available in the areas of solar heating, cooking, rural electrification etc. However these attempts are inadequate to meet the raising energy demands.

III. The Indian Fuel Situation

The transport vehicles use petroleum products. Increase in these vehicles has increased the dependence on fossil fuels. The cost of transport fuel as well as production has steadily increased over the years. This has become a major concern and it is essential to find alternative to petroleum fuels. India depends on import for around 70% of its fuel. The excessive dependence on petroleum fuel has increased the pollution levels as well as the health of population especially in the urban areas.

TABLE I. Natural gas demand and supply in India (million cubic metres per day)[a][2]

	1996/97	2001/02	2006/07	2011/12
Demand	52.1	117.8	167.1	216.4
Production	49.3	71.2	57.5	43.8
Gap	2.8	46.6	109.6	172.6

TABLE II. OIL DEMAND AND SUPPLY IN INDIA (MILLION BARRELS PER DAY) [a][2]

Year	Crude production	Crude imports	Petroleum products demand	Self-Reliance(%)
1997/98	0.69	0.62	1.68	39
2001/02	0.74	1.57	2.10	33
2006/07	0.80	2.20	2.89	26
2011/12	0.90	3.31	4.06	21

a. Compiled from Website of Ministry of Petroleum, Govt. Of India

The statistics provided in the Tables I and II are the indicators of growing deficit in natural gas and crude oil. Last decade has witnessed spurt in the demand but without much increment in local production. The gap is being taken care by the import from oil rich countries. Increase in crude oil prices has put excessive stress on prices of transport fuel. This has cascading effect on costs of other commodities. There has been considerable increase in the cost of essential commodities too which is affecting the life of general public at large. The trend can lead to unaffordable situation soon unless our dependence on conventional fuels is reduced with various energy-efficient disciplining measures and switching over to renewable sources.

The fuel prices depend on global trends leading to vulnerable economy of the country. It is crucial to have viable alternatives for sustainable and continuous fuel supply. The use of Biodiesel has provided some useful results, however as on date this is a non-viable option & still in the early research stages. In this connection matured hydrogen technology, as a fuel in future can be an excellent alternative.

IV. HYDROGEN ECONOMY: FUTURE ENERGY

One of the possible alternatives to the transport fuel is the use of hydrogen. Technologists working in this field feel that Hydrogen Energy System will be a solution to the projected global crisis in energy supply.

It would be very appropriate to mention that the renewable energy areas have many options and each on its own may make the system sustainable depending on the geographical and climatic conditions. Almost all the renewable systems are eco-friendly and help in maintaining pollution levels under check. Solar, wind, tidal, biogas option are clean energy options and a matured technology is the need of future energy.

It is too premature to consider hydrogen as a prospective candidate as there are large numbers of issues related to production, storage and safety to deal with. This paper discusses some of these issues.

The 1980's saw developments in fuel cell technologies, one of the fundamental units of hydrogen based application systems. The developed countries invested hugely on fuel cell technologies, to make it cost effective and visualized the fuel cell vehicles. Some of the European countries, US and Japan are promising hydrogen economy by 2020, even though it seems unrealistic at present. The abundantly available solar energy is yet to be utilized due to inefficient technology and discouraging cost factor.

Hydrogen is the simplest element; an atom of hydrogen consists of only one proton and one electron. It is also the most plentiful element in the universe. Despite its simplicity and abundance, hydrogen is always available in the combined form with other elements. Water, for example, is a combination of hydrogen and oxygen (H_2O). Hydrogen is also found in many organic compounds, such as hydrocarbons that make up many of the fuels, like gasoline, natural gas, methanol, and propane.

Hydrogen is a colourless and odorless gas. It is a light element with molecular weight of 2.016 amu. It is 14 times lighter than air. Its calorific value is 3 times higher than the other fuels with very low ignition energy. The combustion process does not result in toxic pollutants because the by-product is water. Hydrogen can be produced from water through electrolysis. In a fuel cell hydrogen can be combined with oxygen to produce electrical energy, water and heat. Hence it is a clean and renewable source without any harmful pollutants.

The gravimetric energy density of hydrogen is 120MJ/Kg which is thrice compared with energy density of petrol which is 44MJ/Kg. However the volumetric density is poor with 0.01MJ/L compared with 32MJ/L of petrol. The various properties of hydrogen are given in Table III.

TABLE III. PROPERTIES OF HYDROGEN [b]

Property	Value
Molecular weight	2.01594
Density of gas at 0°C and 1 atm.	0.08987 kg/m^3
Density of solid at −259°C	858 kg/m^3
Density of liquid at −253°C	708 kg/m^3
Melting temperature	−259°C
Boiling temperature at 1 atm.	−253°C
Critical temperature	−240°C
Critical pressure	12.8 atm.
Critical density	31.2 kg/m^3
Heat of fusion at −259°C	58 kJ/kg
Heat of vaporization at −253°C	447 kJ/kg
Thermal conductivity at 25°C	0.019 kJ/(ms°C)
Viscosity at 25°C	0.00892 centipoise
Heat capacity (Cp) of gas at 25°C	14.3 kJ/(kg°C)
Heat capacity (Cp) of liquid at −256°C	8.1 kJ/(kg°C)
Heat capacity (Cp) of solid at −259.8°C	2.63 kJ/(kg°C)

b. Source : Kirk-Othmer Encyclopedia of Chemical Technology. Fundamentals and Use of Hydrogen as a Fuel. 3rd ed., Vol. 4, Wiley, New York, 1992, 631p

V. PRODUCTION OF HYDROGEN

Hydrogen can be produced from water. It is the lightest, efficient, cost effective and clean fuel, if the matured technology is developed. This is realistic since over 72% of the globe is covered with water and byproduct again is water.

In other words Hydrogen economy starts and ends with water. Use of hydrogen can avoid most of the harmful gases, acid rains, and pollutants. It can afford the development of clean and adequate energy for sustainable growth.

A. Hydrogen from fossil fuels

Industries which use hydrogen in large scale generate hydrogen from chemical methods basically by steam reforming of natural gas, coal gasification and reforming of heavy oil feedstock's. The natural gas is very common and economic method using endothermic steam reforming process.

$$CH_4+H_2O \longrightarrow CO+3H_2\uparrow \quad (1)$$

Further to maximize the hydrogen yield, externally heated bed reactor is used for water gas shift reaction.

$$CO+H_2O \longrightarrow CO_2+H_2\uparrow \quad (2)$$

It is required to have several gas purification stages. One of the important climates affecting factor is the release of carbon monoxide and carbon dioxide gases which are harmful. Coal is the largest releaser of toxic gases and natural gas is the least.

B. Hydrogen separation by electrolysis

This is one of the common laboratory methods. Development of electrolysers has several phases. Manufacturing electrolysers for the production of pure hydrogen is proven technology with many commercial electrolysers available to operate at room temperatures using concentrated electrolytes. High pressure electrolysers provide comparable efficiencies including compression work for storage. Electrolysis is basically splitting water into its constituent's hydrogen and oxygen using electricity. In this process, hydrogen forms at the cathode and oxygen forms at the anode of an electrolytic cell when a fixed dc voltage is applied. A separator between the anode and the cathode called diaphragm is used to prevent mixing of hydrogen and oxygen without blocking the ion flex towards electrodes. For industrial electrolysers series of cells are interconnected using a peripheral equipment to maintain electrolytic cycle, product gas separation and electrolyte cooling.

C. Solar Hydrogen

Solar hydrogen is one of the important steps of hydrogen economy. Here hydrogen is produced using renewable means such as solar / wind power. Water is supplied with energy to separate hydrogen and oxygen.

$$H_2O + \text{Energy} \longrightarrow H_2 + ½\, O_2\uparrow \quad (3)$$

This is a direct method without any pollutants or harmful byproducts. This is generally electrochemical water splitting. This method is still a subject of research but can be highly efficient.

D. Hydrogen from Biomass

In renewable and non-fossil production number of combinations is thought of including hydro-power, solar thermal or wind power plants. Biomass or organic waste can be converted into Hydrogen using stored solar energy.

The photo biological method involves exposure of microbes to sunlight which help to split water to produce hydrogen.

Quantity of hydrogen produced depends on the need of the industry or application. The large scale production as well as storage and transportation are expensive and complex. The delivery infrastructure of hydrogen needs high pressure compressors for gaseous hydrogen and liquefaction for cryogenic hydrogen. The methods involve significant operating as well as capital costs.

VI. HYDROGEN STORAGE

This is one of the important hurdles in the implementation of hydrogen fueled applications. Due to the lightness of hydrogen the size of the storage medium becomes impractically large. This has opened many areas of research for storing hydrogen in various forms. The US DOE has issued various storage goals for the experts in the field to achieve for storage optimization. However, none of the materials tested so far have reached close to the DOE set targets which are given in Table IV.

TABLE IV. DEPARTMENT OF ENERGY (DOE) USA HYDROGEN STORAGE GOALS (www.energy.gov)

Storage Parameter	Units	2005	2010	2015
Specific Energy	K Wh/kg	1.5	2.0	3.0
Wt%	Kg H_2/kg System	4.5	6.0	9.0
Energy Density	K Wh/1	1.2	1.5	2.7
	gm H_2/1 System[c]	36	45	81
Storage System Cost	$/k Wh	6	4	2
	$/kg H_2 capacity	200	133	67
Refueling Rate	Kg H_2/min	0.5	1.5	2.0
Loss of usable H_2	(g/hr)kg stored	1	0.1	0.05
Cycle Life	Cycles(1/4 to full)	500	1000	1500

[c.] For reference, liquid H_2 density is 70gm/l

A. Gaseous Storage(Fig. 1.)

Hydrogen can be stored as cryogenic liquid or compressed gas and can be transported by high pressure trucks or gaseous pipelines. Most prototype vehicles store hydrogen in composite tanks at high pressures of around 5000 psi to 10000 psi. Due to low weight volume ratio, the tanks for gaseous storage become bulky.

The best vehicles for applications of gaseous fuel are those with less space constraints and less rapid acceleration. Larger vehicles with space for accommodating hydrogen tanks find it convenient for implementation.

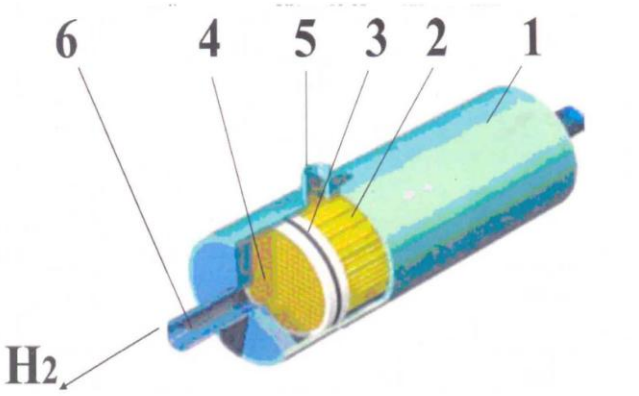

Fig. 1. Schematics of vessel for storing hydrogen in a version with accumulating structure of porous material[3]

1. Body
2. Hydrogen Accumulator
3. Heater
4. Hydrogen Collector
5. Safety Valve
6. Tube for Hydrogen supply and release.

B. Liquid Storage(Fig. 2.)

Cryogenic or liquid storage needs extremely low temperatures (-253°C) and liquefaction needs around 40% of energy contents. It is the best method for high gravimetric densities.

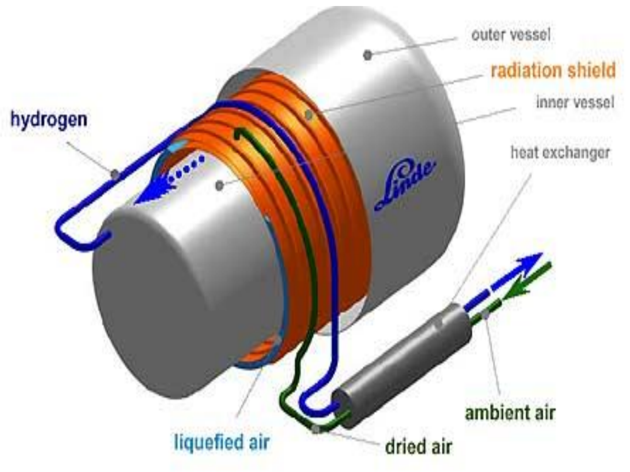

Fig. 2. State-of-the-art Liquid Hydrogen Storage (www.linde.com)

C. Solid State Storage

Solid state is apparently safe method of storage for on board applications. Even though most mature techniques today are cryogenic or gaseous storage, key issues is the safe fuel for a hydrogen based vehicle. The solid state materials offer increased safety as in case of tank ruptures; they won't result in large energy releases. This method will also benefit stationary and steady applications.

Gas-on-solid adsorption is inherently safe and potentially high density storage. Different solid state materials are recommended, each having advantages as well as limitations. Many intermetallic compounds such as Magnesium, Nickel and complex chemical hydrides such as $NaAlH_4$ and carbon based materials have promise of high storage density and safety factors.

From the storage point of view, classical intermetallic compounds have too low gravimetric hydrogen storage capability. Light weight metals such as Li, Be, Na, Mg, B, Al in their compounds are in various stages of research for improving Kinetics, adsorption/desorption temperatures, reversibility of hydrogenation of these compounds. The metals alloys, their characterization for weight percentage improvements are showing promising results. It is expected that many of these compounds may satisfy the DOE targets simultaneously. It seems a feasible alternative since most of the experimentations are laboratory standard and done under idealized conditions. However the transport application expects investigation for physical stability, chemical stability, thermal conductivity, and cycle life under operating conditions. Tolerance of impurity levels under realistic conditions for heat and mass transfer should also be addressed.

The successful gas on solid state hydrogen storage should have following attributes:

- Low cost recyclable / rechargeable vessels.
- Near ambient temperature/ pressure operations.
- Fast recharge/ discharge kinetics.
- Impact safety.
- Tolerance to trace poisoning

The characteristics of various recommended materials for solid storage are explained below and given in Fig. 3.

- **Metal Hydrides**
  - e.g. MgH_2, Mg_2NiH_4
- **Chemical Hydrides**
  - e.g. Amino Boranes
- **Complex Chemical Hydrides**
  - e.g. $NaAIH_4$, $LiBH_4$, $Mg(BH_4)_2$
- **Carbon- based materials**
  - e.g. CNT, AC, CNF
- **Hybrid materials and composites**
  - e.g. MOF

Fig. 3. Few recommended materials for solid state storage

1) Hydrides: Hydrides are compounds of hydrogen bound with metals that allow solid state hydrogen storage. Some of the prominent metal alloys are magnesium-nikel, Magnesium-copper, iron-titanium etc. When heated these materials absorb and release hydrogen. Efforts are made to reduce the operating temperature below 80ºC.

2) Chemically stored hydrogen: This uses non-metals. Even these materials are becoming increasingly popular due to improved hydrogen to material weight ratio of storage media. In these materials it is desirable to store large amount of hydrogen in the lighter units.

3) *Storage of Hydrogen in Carbon based Materials:* The special hydrogen adsorbing characteristics of carbon nano materials make them suitable as storage device. Due to high surface area and capillary, carbon nanotubes have high storage capacity. There has been limited progress in improving the storage performance in carbon materials with respect to DOE targets. The carbon nanotubes have some of the special attributes in addition to their property related to hydrogen storage. Some of the abilities include better mechanical strength, conducting / dielectric behavior. The carbon nanostructures are usually grown on metallic surfaces by the catalytic action of one or more transaction metals. Many new methods are recommending carbon as a storage medium through nanostructures. Different approaches are used to shape carbon into microscopic cylindrical structures called nanotubes. These are available in three different forms as shown in Fig. 4. Single-walled carbon nanotubes have remarkable forms of elemental carbon. Multi-walled nanotubes are developed for the bulk storage of hydrogen. The gravimetric hydrogen storage capacity in purified multi-walled nanotubes is much higher than single-walled carbon nanotubes.

There are many questions still to be answered regarding the efficient storage of hydrogen at lower temperatures and the possibility of increasing the gravimetric storage capacity of hydrogen in carbon nanotubes. Even the activated carbon which is amorphous variety with large surface area due to the presence of carbon nanoparticles[4].

The adsorption in carbon nanostructures generally occurs through one of the two mechanisms viz 1) Physiorption and 2) Chemisorption[5].

a) Physiorption: In this mechanism, the hydrogen molecules are adsorbed inside of a nanotube mesh due to Van der Waal's attractive force between carbon and hydrogen. Theoretically there is no limit to the percentage of hydrogen stored in multiple layers[5]. The room temperature and atmospheric pressure puts limits on the adsorption. The available effective surface area for adsorption is crucial for increasing storage quantities.

b) *Chemisorption:* The hydrogen molecules are conveniently bonded to the carbon atoms of the nanotubes[5]. Each carbon atom in the nanotube is hybridized and bonded with three other carbon atoms resulting in a dangling in bond. This permits only one hydrogen atom chemisorbed per carbon atom. This limits the maximum storage to 7.7% by weight. The desorption of hydrogen in chemisorption is more difficult than physiorption.

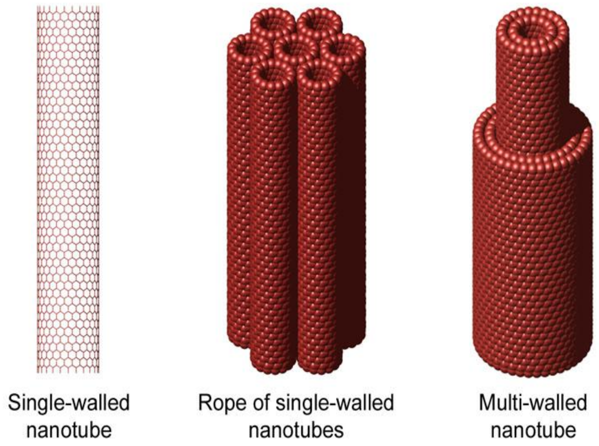

Fig. 4. Schematics of carbon nanotubes for hydrogen storage

The fundamental understanding of the physical mechanisms indicates that the inter-molecular forces account for considerable hydrogen adsorption and storage in carbon nanopores. However the change in carbon nanostructure compositions and structural changes are likely to enhance the hydrogen storage capacity. Further hydrogen storage is enhanced when the molecules are disassociated into atoms which easily penetrate into nanopores. If the nanotubes are annealed in higher temperatures in the range of 1700°C to 2200°C, there is significant improvement in storage. In Carbon nanotubes, amorphous carbon, nanofibres nanorods etc, the adsorption kinetics are reasonable and desorption is easily / thermally reversible. As of now, adsorption process requires cryogenic temperatures and the sample performances are inconsistent.

VII. Applications using Hydrogen

Hydrogen is high in energy and fuel cell technology is used for sourcing electrical power to applications. Here it is necessary to have a hydrogen storage medium and then to deliver energy in a usable form. Applications can use fuel cell as a battery which is constantly replenished by adding hydrogen and oxygen as fuel to prevent the fuel cell performance deterioration.

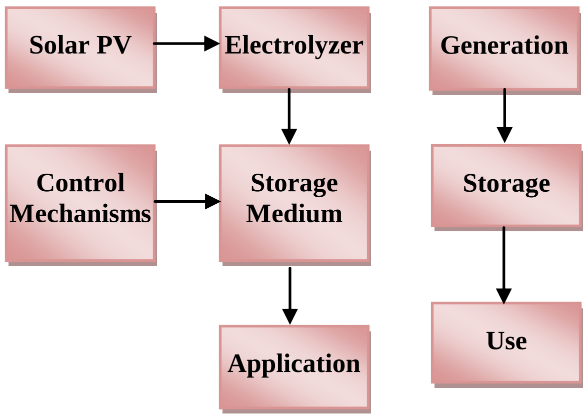

Fig. 5. Basic Schematic Diagram of a Hydrogen Based Application

The hydrogen based application requires hydrogen generator and storage medium (Fig. 5.). The solar PV is used for generating electricity for electrolysis of water to generate hydrogen. The control mechanisms ensure storage and distribution without leakage.

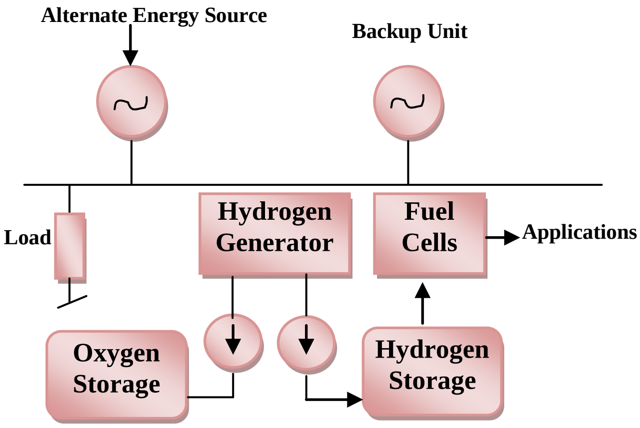

Fig. 6. Hybrid System With Backup Energy Source[6]

The hydrogen storage in combination with other energy sources is a useful operational technique for optimization (Fig. 6.). The above scheme is useful for both stationary and mobile applications. The hydrogen and oxygen are provided as input to the fuel cell. This is an important building block of vehicular applications. The backup source is provided to permit continuous functioning of the system.

VIII. Safety issues in Hydrogen Transportation

Hydrogen has been in use for over decades in chemical industries. The safety record has been excellent in production as well as transportation. Hydrogen is different in properties and hence before it is accepted for mass scale use in vehicles, safety procedures need to be redefined. Current storage pressures of compressed natural gas, CNG are 3600psi, while that of compressed hydrogen is 5000 and 10000 psi. Storage of hydrogen in cryogenic tanks requires extensive insulation, and is a source of frostbite in case of accidental release or rupture of the nozzle. A system that is airtight is not hydrogen tight due to hydrogen's lightness. This requires new materials for seals and fuel lines. Regular exposure to hydrogen leads to hydrogen embrittlement resulting in cracks and leakage through metal and nonmetallic components. Even moisture content may lead to tank embrittlement and formation of cracks. Safety issues are getting attention and much progress shall be made for making hydrogen economy a reality.

IX. Safety issues related to hazards in handling and storage

- Storage tank failures: Results in the release of hydrogen due to material failures. Release of liquid/gases form results in fire and explosion. Excessive pressure caused by heat leaks, failure of pressure relied systems[7].
- Transfer Leaks: Deformed seals/gaskets, value misalignment, failure of flanges, and failure of construction materials such as vacuum jacketed lines.
- Collision during transportation: May result in disastrous effects as spills cause fire and explosion.

X. Hazard Elimination and Control

High-level hazard elimination can be achieved by proper design process and use of safety devices through routine functional checks for maintaining their level of protection. Using warning devices, warning signals may be provided to help the workers react promptly and correctly to a hazardous situation. Safe operating procedures and safety training programmes should be developed to eliminate hazards and reduce their risks to acceptable levels through design selection. Personal protective equipments can be used to prevent injuries and illnesses. Typical Hydrogen Storage device model schematic will be prepared with trial values for mathematical modeling of safety analysis.

Conclusion

Hydrogen can be stored for long periods of time without significant losses. Presently, hydrogen is stored as a cryogenic liquid or compressed gas, and transported by cryogenic liquid or high-pressure trucks; and, to a limited extent, by gaseous pipelines. In future, it could be stored and possibly transported in chemical and metal hydrides, carbon nanostructured materials, and high surface area adsorbents. In such forms, hydrogen would be more amenable to safe and efficient distribution and storage. Hydrogen as a renewable fuel offers many advantages subject to addressing of various related issues. It would be a cost effective ecofriendly solution to replace depleting fossil fuel sources.

References

[1] Dileepkumar, Usha Raghavan, "Socio Economic Aspects of Hydrogen Energy-Indian Perspective", Hydrogen Technologies for Energy Production, 6-10 February 2006, Moscow, Russia, pp.27-28

[2] G.A. Pujare, Gauri Paranjape, "Energy Scenario", Proceedings of National Seminar on Alternative Energy Sources, 27-28 August 2005, pp.1-4

[3] V.G. Gnedenko, I.V. Goryachev, N.K. Zhevago, A.F. Chabak, "On-board Hydrogen Accumulator for Vehicles", Hydrogen Technologies for Energy Production, 6-10 February 2006, Moscow, Russia, pp.97-98

[4] A.S.Biris, A. R. Biris, D. Lupu, D. Buzatu, J. Darsey, M. K. Mazumder, "Use of Carbon Nanostructures for Hydrogen Storage for Environmentally Safe Automotive Applications", 0-7803-8486-5/04/$20.00 © 2004 IEEE, pp.953-956

[5] Soumik Banerjee, Sohail Murad, and Ishwar K. Puri, "Hydrogen Storage in Carbon Nanostructures: Possibilities andChallenges for Fundamental Molecular Simulations", Proceedings of the IEEE | Vol. 94, No. 10, October 2006, pp.1806-18014

[6] Magnus Korpaas, Ragne Hildrum, Arne T. Holen, "Optimal Operation of Hydrogen Storage for Energy Sources with Stochastic Input", 0-7803-7967-5/03/$17.00 ©2003 IEEE.

[7] Etim U. Ubong, "Safety Issues In Hydrogen Transportation", 0-941783-23-5/03/$17.0082003 IEEE, pp.395-401