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State-of-the-Art of Storage and Handling issues related to High Pressure Gaseous Hydrogen to make use in Internal Combustion Engines.

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Abstract: The purpose of this paper shall be to provide fundamental safe guards for installation, storage, piping, health related issues in use and handling of compressed gaseous hydrogen. And mainly focusing on stationary, portable infrastructural application under different National and International standards like, Bureau of Indian Standards (BIS) New Delhi, India, Petroleum and Explosives Safety Organization (PESO), Nagpur, India, Central institute of Mining and Fuels Research (CMRI), Dhanbad, India, International Electro technical Commission (IEC) Switzerland, National Fire Protection Association (NFPA) Massachusetts, USA, International Organization for Standardization(ISO), Switzerland. Further, also considered the supply of the gaseous hydrogen to an internal combustion engine.

Index Terms: Codes and Standards, Gaseous Hydrogen, Handling, Hazardous Signs, Internal Combustion Engines, Safety Aspects, Storage.

1.0 INTRODUCTION

Consumption Pattern of fossil fuels are increasing day by day and the reserves are coming down exponentially. At this present scenario, meeting this demand of Energy using Fossil fuels is really a great challenge. As per the report of the Central Pollution Control Board(CPCB), consumption of fossil fuels in India in transport, Industry, commercial and other domestic and agriculture by 51%, 14%, 13%, 18% and 4% respectively. Of these contributions, transport alone considered more than 50%. In 1951 total vehicle population is 0.3 million whereas as per the statistics of the same by 2000 it had been increased to 50 million. More over the emission levels already given an alarm and needs to be concentrated to reduce these without any doubt. Some statistics of such pollution from Indian Transport sector considered in the following table.[1]

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Table (1). Total Emissions from the Indian Transport for the year 2003-2004 in Gg [1]

Sl.No	Description of Fuel	CO_2	CO	NO_x	CH_4	SO_2	PM	HC	NO_2	NM VOC
1	**Shipping**									
	High Speed Diesel	782.28	10.66	8.527	0.533	-	-	-	0.0064	2.13
	Light Diesel oil	162.18	2.21	1.767	0.011	-	-	-	0.0013	0.442
	Fuel Oil	510.19	6.55	5.24	0.033	-	-	-	0.0039	1.31
2	**Railways**									
	Coal	5.280	0.0155	0.0121		0.0421	-	-	-	-
	High speed Diesel	5186	70.67	56.64	0.353	-	-	-	0.0424	14.13
	Light Diesel Oil	6.360	0.0867	0.0693	0.004	-	-	-	0.0001	0.0173
	Fuel Oil	25.04	0.3215	0.2572	0.0016	-	-	-	0.002	0.0643
3	**Aviation**									
	High Speed Diesel	85.860	1.17	0.9359	0.0058	-	-	-	0.0007	0.2340
	Light Diesel Oil	6.360	0.0867	0.693	0.004	-	-	-	0.0001	0.0173
	Fuel Oil	222.23	2.835	2.2828	0.0143	-	-	-	0.0017	0.5707
	Aviation Turbine fuel	7294	2565	8.7331	6.549	-	-	-	-	-
4	**Road Transport**	243816	3032	2213	126.78	709.09	153	723	-	-
	Total	**258103**	**5692**	**2298**	**133**	**709**	**153**	**723**	**0.0568**	**18.92**

Reduction in oil reserves and increase in GHG emissions and utilization of fossil fuels from transport, power,, industries, commercial, domestic and agriculture sectors causes think on alternative fuels. This paper mainly focused on Indian context only. As economy of India is increasing, energy needs also increasing in the same fashion but present fossil fuels are unable to cater the needs of present and future requirements.

As different alternative fuels available, Hydrogen is one such clean fuel by that almost all GHG will be zero. A lot of research is going towards the make use of this clean fuel. But Hydrogen is not simple to use as of like fossil fuels and needs to be special concentration required in storage and handling of hydrogen as a fuel. This paper focus is limited to utilization of high pressure Gaseous Hydrogen. Recently Ministry of New and Renewable Energy (MNRE), Government of India, Delhi launched "National Hydrogen Road Map" in 2006 and given different aspects towards sustainable development through suitable guidelines, pathways which will help in understanding the importance of usage of this Hydrogen in Transport, Industry, Power, commercial, agriculture and even in Academia also, through this the Indian Government is also expecting that nearly one million vehicles will run by hydrogen and nearly 1000MW will be produced by using this Hydrogen fuel only [2].

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equivalent to 18.3 MB of fossil fuels per day only in transport sector by 2040 [4]

2.0. HYDROGEN

Hydrogen it covers nearly 70% in the Universe but in the form mixture of Hydrogen and Oxygen. Even hydrocarbon fuels also contain hydrogen for example conventional petrol and diesel also contains four hydrogen atoms for every one carbon atom. This pure hydrogen is derived from the process called either Electrolysis or water or by reforming from gaseous or liquidous hydrocarbons [3]. In USA itself by 2007, through this reforming process nearly about 10 million tones of hydrogen was developed to meet the demands of industrial and transportation sectors and are expected to produce the hydrogen through this reforming

This pure gaseous hydrogen is not having any colour, taste, odor. This is a non corrosive in nature to materials and non toxic to human beings. This is considered to be second to be the second widest flammable gas mixture with air at a range of 4 to 75 % by volume. Where as diesel fuels vapor will ignite in a range of 0.6 to 5.5%, Natural gas is in the range of 5to 15% and the Gasoline of 1.4 to 7.6%. When considering the ignition energy in air, the hydrogen is 0.02 mJ whereas for gasoline this ignition energy is 0.24mJ., i.e., nearly hydrogen takes less than one twelth of the energy to ignite the hydrogen mixture when compared to gasoline.

Table (2). Properties of Hydrogen and other fuels

Description	Hydrogen	Gasoline	ULSD	Methane (CNG)	Ordinary Diesel	Ethanol	Jatropa oil	DEE	LPG	Biogas
Density (kg/m^3)	0.081	4.4	876	0.6512	830-850	789	917	713	2.24	1.1
Mol. Wt	2.016	107		16.043	142	46.07	800	74	44.1	25.46
Auto ignition temp (^{0}C)	500	257	250	537	280	423		160-170	493-549	700
Boiling Point (^{0}C) at 1 atm	-252	25-225	180-345	-162	180-340	78	286	34	-42	
Ignition energy in Air (MJ)	0.02	0.24	NA	NA				NA		
Flame temp in air (^{0}C)	2045	2197	NA	1918					1980	1911
Lower flammability limit (vol% in air)	4	1.4	0.6	5	1	4.3		1.9-2	2.2	7.7
Upper flammability (vol% in air)	74	7.6	5.5	15	6	19		36-48	9.5	23

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Buoyancy: Gas or vapor density relative to air	0.07	2-4%	4-5%	0.6	6.5	1.51	27.12	2.5	1.51	0.863
Carbon Constituent	NA	85-88		75	86	50-52			82	
Hydrogen Constituent	100	12-15%		25	13	13-15			18	
Lower heat of combustion (MJ/kg)	119.93	44.5	43	50.02	42.3	26.9	39.774	33.9	46	
Burning Velocity in air (m/sec)	2.65-3.25	0.37	NA		0-3	NA		NA		
Specific Heat Ratio of NTP gas	1.383	1.05		1.308						1.303
Diffusion coefficient in NTP air (cm^2/sec)	0.61	0.005		0.16				NA	0.11	

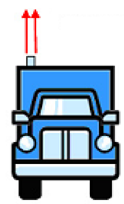
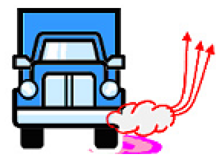
A small static electric spark causes hydrogen air mixture may ignite in the combustible range. If any leakage in the hydrogen flow system causes electrostatic charge and this is enough to ignite the leaking hydrogen [5]. Soot is the main cause of visibility of flame, where as the hydrogen flame not producing any sort of soot and virtually not visible. And this flame is in the range ultraviolent rays rather than normal light spectrum. Hence, the hydrogen flame is not visible in day light.

As hydrogen is not having any odour, taste and colour, leakage will not be identified by the humans. In general, hydrocarbons are mixed with some sort of sulphur content wantedly to detect the leakage by smell it, whereas mixing of sulphur to hydrogen makes the gas poisonous and not suitable in many applications. With reference to this, Palladium type hydrogen sensors will be used to detect the leakage as per its Lower Explosion Limit (LEL) 0-100% range. Once hydrogen leaked from the working place where this sensor was mounted nearer to roof, then the catalysts brakes the chemical bonds of hydrogen and diffusion into catalyst causes changes in electrical properties of material gives signal to monitoring system. This monitoring system will display the leakage and subsequently the hooter will give alarm to make the attention the people who are working in that area [6-11].

Diffusivity

As hydrogen molecule is smallest and lightest, if leaking this gas will accumulate at the roof of the enclosed area. The diffusivity rate of hydrogen is 10 times more than petrol and other fuel vapors [12].

Table.(3) Leak Profile of Hydrogen and conventional Diesel Fuel [03]

Sl.No	Description	Gaseous Hydrogen	Liquid Hydrogen	Diesel Fuel
1	Pictorial Representation			
2	Rising into atmosphere	Quickly disperses in the form of Gas	Puddles appeared at leaked location. Later vaporizes	Puddles appeared. Vaporization is very less.
3	Visual detection	Not Visible	Visible in the form of Fog and frost	Visible in the liquid form
4	Smell/Odour	None	None	Yes
5	Flammability	Very very rapidly catches the Fire/Ignition	Very very rapidly catches the Fire/Ignition	Rapidly catches the Fire/Ignition
6	Flame	Invisible at day light.	Invisible at day light	Visible in the form smoke

As it posses the high diffusivity property, the burning velocity of hydrogen air mixture will take care at equivalence ratio Φ=1.8, whereas for the same burning velocity with hydrocarbon-air mixture takes place at Φ=1.1 [4]

In this context, researchers has to consider the all necessary safety related issues in handling the high pressure gaseous hydrogen. Glimpse on different issues are considered below

2.1. Storage area safety aspects
2.2. Handling area safety aspects
2.3. Combustion related safety aspects in Internal Combustion Engines
2.4. Health related safety issues

2.1. Storage Area Safety Aspects:

Maximum Allowable Quantity (MAQ): Maximum Allowable Quantity is the total quantity of hydrogen combined available in storage and usage areas.

The storage areas are classified into Gas cabinets, exhausted enclosures along with sprinkler and without sprinkler systems. If the gas storage is up to 28m^3 by volume, there is no requirement of gas cabinet, exhaust enclosures under sprinkled area.

Table (4) Storage area requirements as per the MAQ

Sl. No	MAQ of Hydrogen storage	Requirement		
		Sprinkled area	Gas Cabinet	Exhaust enclosure
1	< 28 m^3	No	No	No
2	>28< 56 m^3	No	Yes	Yes
3	>56<112 m^3	Yes	Yes	Yes

If the storage area is covered with sprinkler facility, then up to volume of 56m^3 MAQ of Hydrogen can be stored there is no requirement of gas cabinet and exhaust enclosures. [13]

2.1.1. Storage and Usage Area Construction:

As per ASTM E 136 standards approved 'Non Combustible' material has to use to construct the storage and handling areas. [14 &15]. The accessibly and approaching road leads to these areas must have 20ft to 50ft width road with 13.6 ft height clearance and having minimum radius of road width for the convenient of Fire safety vehicle to reach these places in an emergency. [16]

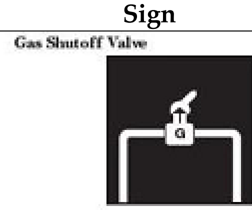
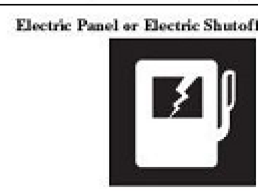
These buildings must be provided with exhaust ventilation at a distance not more than 1 feet from the ceiling because this hydrogen gas is lighter than air, causes any leakage of hydrogen reaches the roof and leads to electric accidents. If mechanical ventilation is provided, then rate of mechanical ventilation is not less than 0.3048 m^3/min/m^2. [17]. It is very essential to make use of Hazard identification signs in these areas all entrances where compressed gases stored, produced or utilized. And all these signs must be allowed to keep in a accessing mode to all people with in range of 25ft distance from the storage space. [19,20] as shown below.

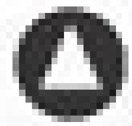
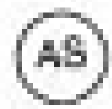
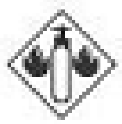
WARNING: HYDROGEN – FLAMMABLE GAS

NO SMOKING – NO OPEN FLAMES

Some such signs are given below [21]

Table.(5). Different Signs which must be available at the Storage site

Sign	Indication		Sign	Indication
	The Identification of areas where smoking is prohibited			The location of gas shutoff valve
	The identification of areas where the open fires are not permitted			The identification and location of an electrical panel or other electric shutoff devices

	For everyday use in working places and public areas:			Gas detector
	For everyday use in working places and public areas: supplementary text can be used to increase comprehension			Fully sprinklered area
	Flammable gas			Partially sprinklered area

Further, these buildings must be provided with suitable gas leakage sensors and monitors on the basis of Lower Explosion Limit (LEL) along with hooter and alarm as shown below by that if is there any leakage, then hooter will give an alarm by that, one can pay attention to control the leakage as soon as possible by shutoff of gas and electrical power supply [7-11]. One such implemented Gas sensors with its monitor was shown below.

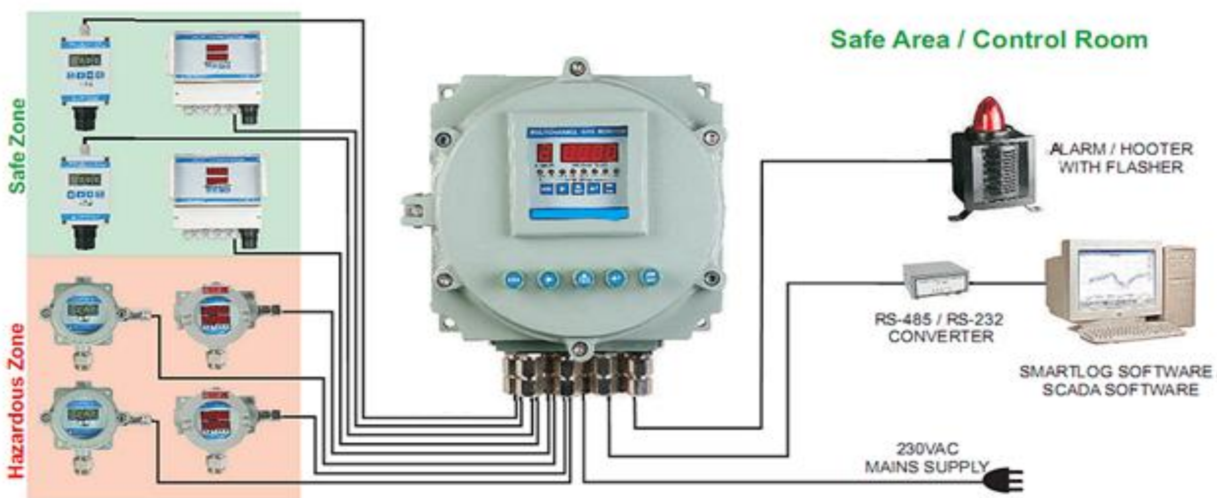


Fig. (1). Complete pictorial representation of Hydrogen Gas Leakage Monitoring system

2.1.2. Fire Extinguishers:

Fire: Fire is a chemical reaction in which a substance undergoes process of oxidation in presence of heat. The reaction is exothermic in nature, making this reaction is a chain reaction.

For gases, it is essential to keep class B type fire extinguisher but one has to keep class A for solid fire like wood, paper cloth etc and Class E for Electrically energized equipment. [21]

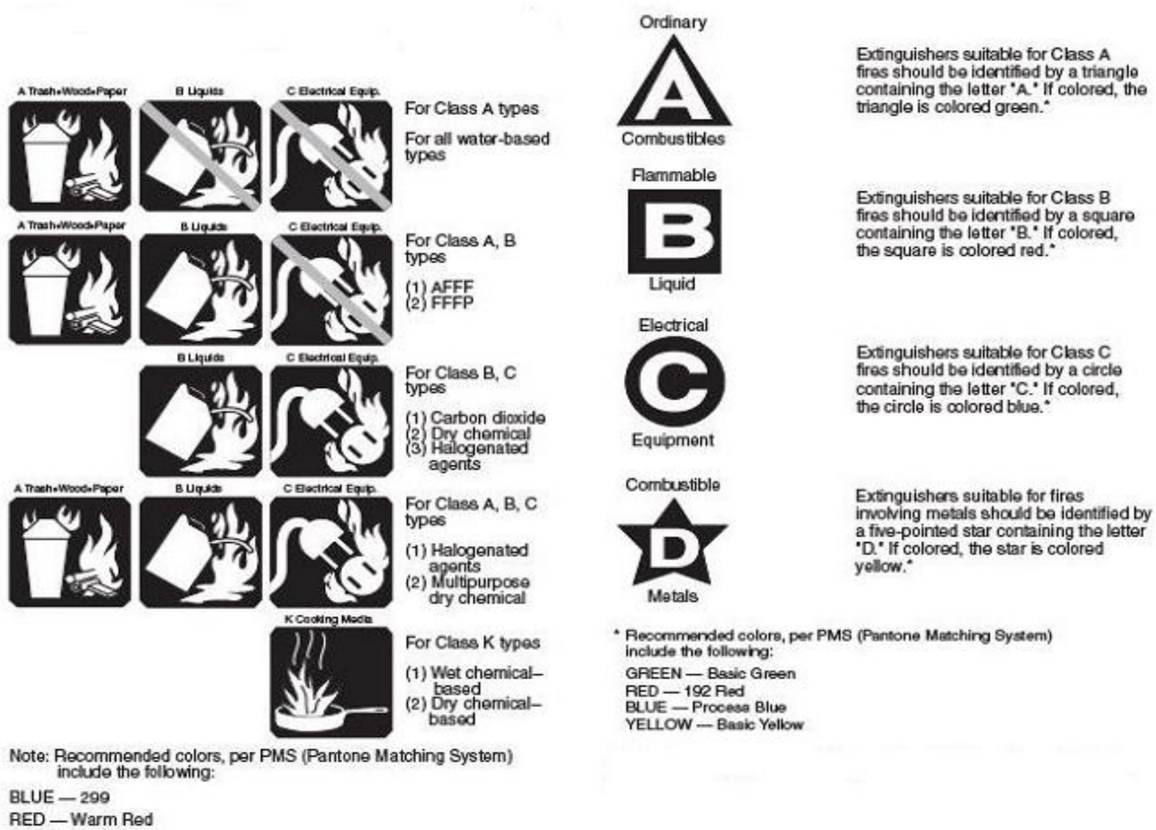


Fig.(2) Fire Extinguishers [21]

2.1.3. Electrification:

As per the requirement of usage of high pressure gaseous hydrogen different applicable standards are available. The scope of this paper is limited to minimum quantity of hydrogen storage i.e., less than the MAQ and the storage is confined to standard 47 Ltr water storage capacity with a pressure not exceeding 140 Bar. Hence Class I, Division2, Group B standard of NFPA is applicable to provide electrification in this area [22]

Class I represents that, Flammable gases are present in sufficient quantity in the air are responsible to ignite or explosive.

Division 2 represents that, flammable gases which are stored in a confined small cylinders and

Group B represents that, Flammable gases, which are present in sufficient quantity in the air having an experimental safe gap with less than or equal to 0.45mm. Hydrogen will be considered under this category.

2.1.3.1. Wiring:

Rigid metal or Steel intermediate Conduit will be used with Zero Halogen Fire Retardant (ZHFR) / Halogen Free Fire Retardant (HFFR) wire [22 & 23]

2.1.3.2. Luminaries

Luminaries and other heat-producing apparatus, switches, circuit breakers and plugs are potential sources of ignition are must be provided with suitable metal enclosures in classified locations as per the Class I, Division 2 Group B standards.. Further, Luminaries are protected from Physical damage by suitable guards or by location. Where there is a danger that falling sparks or hot metal from lamps or luminaries might ignite localized concentrations of flammable vapours or gases, suitable enclosures or other effective protective means shall be provided. [24]

2.1.3.3. Protection Concepts

There are varying types of equipment that can be used within these zones to ensure that the potential for an explosion is removed or greatly reduced. This equipment must be designed and manufactured in accordance with particular construction parameters known as protection concepts.

Table (6). Details of Protection Concepts

Type of Protection Method	Equipment Code	Description	International Standard	Suitable for Zones
Intended to prevent an ignition from escaping outside the equipment	Ex d	Flameproof protection	IEC 60079-1	1, 2

2.1.3.4. Ex d Flameproof

The equipment that may cause an explosion is contained within an enclosure which can withstand the force of an explosion and prevent transmission to the outside hazardous atmosphere. This method of protection also prevents the hazardous atmosphere from entering the enclosure and coming into contact with equipment.

2.1.3.5. Ingress Protection

Another consideration in the protection of equipment in hazardous areas is the safeguarding against the ingress of solid foreign objects and water. This is known as the degree of ingress protection and is commonly referred to as the IP Code. The relevant standard for the degree of ingress protection is IEC 60529. And the preferable one is IP 65.

Table(7). Details Ingress Progression 65

1st Numeral	Degree of Protection	2nd Numeral	Degree of Protection
6	Total protection against the ingress of any dust	5	Protected against water jets from any direction

Some such electrical equipment are given below

Fig.(3). Class I, Division 2, Group B Electrical Equipments

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This storage of compressed gaseous hydrogen must be separated with lot lines, public streets, open flames etc.

Table (8). Explosives Distance Maintained [27]

Sl.No	Description	Minimum distance maintained from storage space in feet
1	Lot Lines	45
2	Exposed persons other than those involved in servicing of the system	25
3	Air Intakes – Compressors	45
4	Unclassified Electrical Equipments	15
5	Utilities (overhead) including electrical power building services, Hazardous materials, piping	20
6	Ignition sources such as open flames and welding	45
7	Parked cars	25
8	Flammable Gas storage systems including other Hydrogen systems above the ground	20
9	Ordinary combustible including fast burning solids such as Ordinary lumber, excelsior, paper and vegetation other than found in maintained land scaped areas	20
10	Heavy Timber, Coal or other than slow burning combustible solids	20
11	Smoking	25

Table.(9). Separation of Cylinders by Hazard Class Gases [26]

Sl. No	Gas Category	Minimum distance maintained from storage space in feet
1	Toxic or High Toxic	20
2	Phyrophoric	20
3	Oxidizing	20
4	Corrosive	20
5	Unstable Reactive class 2, 3 and 4	20
6	Other Gases	No separation required

2.2. Hydrogen Handling System Issues:

This stored hydrogen as in confined cylinders must be designed, fabricated, tested and marked as per the standard testing procedures like ASME Boiler and Pressure vessel [28 & 31-34]. One has to ensure that under any circumstances these cylinders should not expose to a temperature not more than 52^0 C. And these cylinders must be protected from physical damage and falling from its position. These cylinders should be secured through standard securing procedures like guard posts, chains belts etc.

Use Cylinder caps whether the cylinders stored empty or fill. And these empty and full cylinders must be separated. Never allow the cylinder to fall down. If the cylinder fall down without cap, there is a possibility of turning this full pressurized cylinder into a rocket. One such incident shown below [43]

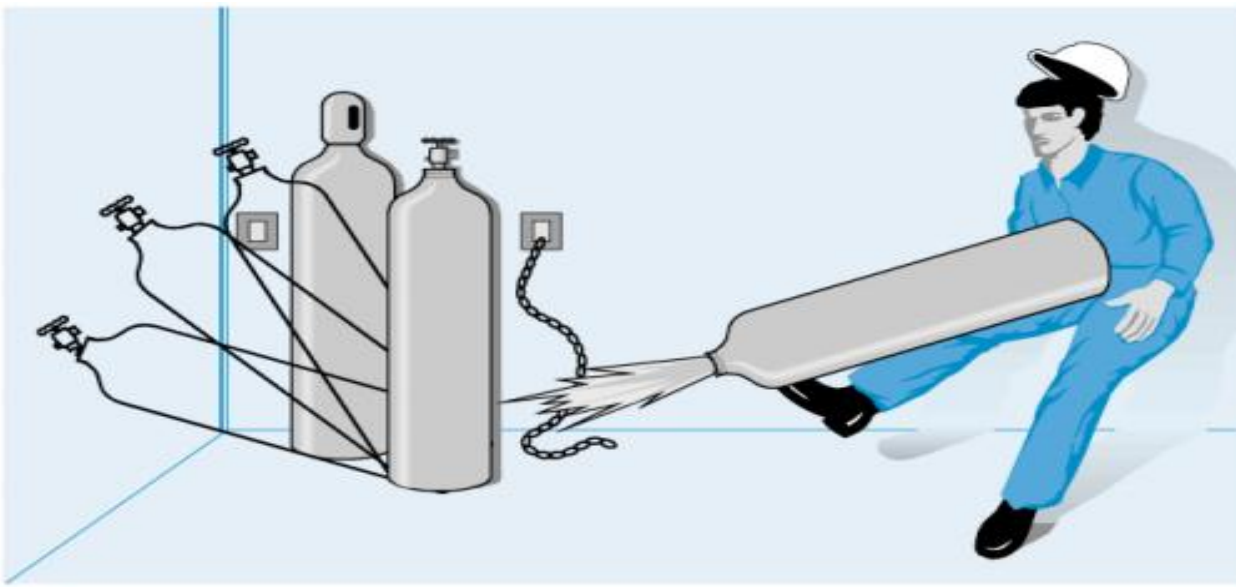

Fig. (4) . How Compressed gas Cylinder will turn into a Rocket

Cylinders are not supposed to drag even for small distances also. For smaller distances transportation also one has to use hand operated cylinder trucks [35]. Never allow the cylinders are subjected to mechanical shocks also. Cylinders must be positioned as per ISO Standard 11625 or Compressed Gas Association (CGA) Pamphlet Part-1.

Fig. (5). Cylinders Carrying Trolleys

While transporting the gas from the high pressure to low pressure at the working place like at engine test bench, one of the important component which is playing crucial role in bringing the high pressure to low pressure is the Pressure Regulator. Use standard SS316 material customizely designed and fabricated double stage regulators has to use. This double stage and single stage pressure regulator depends on the gas pressure requirement at the usage area. While safety checking of the regulator the operator has to take of the safety aspects as shown below [44].

Fig. (6). Safe method to operate the Pressure Regulator

And second most important is the Relief valve. If the pressure regulator is failed to sent the gaseous hydrogen at given low pressure, then there is a possibility of damage the hydrogen flow components in the flow line and great risk will be there if this gas leaked from these damaged components. Hence one has to use this relief valve and its outlet has to keep to the atmosphere by that any damage to regulator, this leaked high pressure gas will be entered into climate. This discharge procedure and the pressure relief valves must be in accordance with Compressed Gas Association (CGA) G 5.5, S 1.1 and NFPA standards. [29, 30 & 31]

It is very essential that other systems like tubing , valves and fittings must be designed and installed as per the standard procedures of NFPA and IFGC codes [32, 37-38 and 40]. It is always preferable to join the tube and different systems/components/devices with tube fittings only. Better to avoid BSP and NTP threads as much as possible when handling with gaseous hydrogen [36] . Further, it is advisable to go for annual maintenance by a qualified engineers as per the standard maintenance protocol mentioned in NFPA standards. These maintenance records has to kept for at least 3years. Never use Cast Iron material components for Hydrogen storage and transportations. It is always preferable to go for SS 316 material for this gas. All these components along with tubing installation must be inspected under pressure test at a pressure not less than $1\frac{1}{2}$ times of working pressure as per recommended standard procedures of NFPA, IFGC and ASME codes [41].

2.3. Engine Specific Systems:

While introducing this hydrogen into the engine, there is generally two modes most of the researchers adopted. Those are Manifold injection and the direct injection i.e, induction and injection modes.. This paper is mainly focused at the manifold injection. In this manifold injection, the delivery pressure of the hydrogen in the inlet manifold is nearer and just above the atmospheric pressure. Because this gas will be inducted by the pressure difference between the in and outside of the engine during suction stroke. Main problem of this induction technique is the backfire due to pre ignition and the hot spots of the combustion chamber. A lot of research was taken place in Indian Institute of Technology (IIT) Delhi under the guidance of Dr. L.M. Das. There are so many induction techniques like carburetion, port injection, Timed manifold Injection (TMI) available. With detailed investigation it is advised that through Timed Manifold Injection is the best induction techniques to control these undesirable combustion phenomena. Further, engine operation should preferably be carried out with well dispersed water sprays in the exhaust system by which this cooled exhaust will suppress the detonation. Even CO2 is also some times can be sent into this exhaust system bay that also this undesirable phenomena can be controlled. In the engine test cell, better have to some sort of Inertizer gases like Nitrogen, CO2, and Helium and fire extinguisher powders like Ammonium Phosphate or Potasium Chloride can be used t inert the inside atmosphere by that if is there any leakage of hydrogen can be get inertized though the Hydrogen is mixed with air in the combustible range. [46-48].Sometimes even delayed Port admission is also equally helpful like Timed Manifold Injection (TMI) and is very safe method of introducing the hydrogen in the engine [49].

2.4. Health Hazards:

The potential health hazard of the this hydrogen is much effecting when a victim had inhaled that, during leaking of this lightest gas immediately mix with the Air inside the confined area and replaces the oxygen causes the asphyxiation. Victim is unable to experience this situation also that he undergone to asphyxiation. Because of this oxygen deficient atmosphere the victim may experience symptoms like dizziness, nausea, vomiting and loss of mobility and unconsciousness. And there is no adverse effect on the skin. If this hydrogen is exposed to eyes, then eyes start irritation, at this situation, the victim must rinse his/her eyes immediately and has to continue for 15 minutes time.

Leaked hydrogen replaces the oxygen causes, asphyxiation in that particular area and predicting this situation is also very difficult. Because of this asphyxiation the victim will lose their consciousness without his/her knowledge. As victims exposed to this type oxygen deficient atmosphere experience symptoms like dizziness, salivation, vomiting and nausea etc. However exposed to skin will not have any type of adverse effect. [45]

3.0. CONCLUSION

Fossil fuels supply is unable to meet the demand of human needs. Day by day energy consumption is increasing exponentially but available reserves of these hydrocarbons are in extinct stage and moreover they are creating the pollution and had been reached to an alarm level. Researchers and industries started to think and work on Renewable fuels. One such clean fuel is the Hydrogen. But understanding this transition phase of Hydrocarbon to Hydrogen is a really good as well as challenging issues in its safety aspects especially in high pressure and gaseous storage and handling. In this paper, such raised challenging issues regarding safety issues considered and concentrated on different codes and standards of National and International agencies to make use this high pressure gaseous hydrogen in Internal combustion engines in a safe manner.

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