A Critical Review on Production, Storage, And Utilization Of Hydrogen Fuel In Automotive Applications

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Abstract: - Hydrogen fuel could be environmentally friendly when it is utilized as a sole fuel for automobiles. In this paper, an overview of hydrogen as an alternative fuel, with its use in IC engines and fuel cells, has been discussed in detail. We also presented a detailed study regarding hydrogen fuel production, storage, emission characteristics, and prospects. An ideal production method should ensure minimum emissions while also giving hydrogen in vast quantities. In contrast, the perfect on board storage method should be safe, less complex, and store enough hydrogen for reliable uses. All these things have to be carried out with economic feasibility. Modifications in engine designs can enable the application of hydrogen as the primary fuel, with an increase in engine efficiency and better environmental characteristics. Extensive research in hydrogen as an alternative fuel is the need of the hour and would take the automobile industry to a new era.

1. Introduction

The world energy demand is increasing rapidly with human comfort and day-to-day developments. The higher portion of this demand is being met by hydrocarbon energy sources like coal, oil, and natural gas. This leaves us with the daunting question of how long these fossil fuels will last and what would be their environmental impact.

Total global consumption of energy is expected to increase by 58 per cent between 2001 from 404 quadrillion British thermal units (Btu) and 2025, 640 quadrillion Btu, [1]. Figure 1 shows the world energy consumption history, which is projected up to 2025. Based on our current availability of energy resources, we can undoubtedly meet world energy demand up to 2035. But after 2035, there won't be any fossil reserves, so it's essential to find some alternatives, [2]. The two-petroleum crises of 1973 and 1978-80 showcased the fragility of modern industry. Fossil fuels, particularly petroleum which is produced by a small group of nations is vulnerable to this fragility, but this is a tailor-made situation to lure benefits of the finite nature of these fuels, [3]. Due to this limited availability, our energy supply pattern should undergo some radical changes. Changes that are more economical and relatively inexhaustible.

Then, another critical issue regarding energy utilization is its environmental impact. Environmental pollution is an issue of importance, and it should be dealt with seriously. Developing countries like India and China contribute around 200 million gasoline ICE two-wheelers on the world's streets. Many major cities of these developing countries contribute to a larger extent to the world's total air pollution, [4]. Carbon dioxide, oxide of nitrogen, oxide of Sulphur etc. forms after the reaction between carbon of burnt fuel and oxygen which is present in the atmosphere. These mentioned pollutants are caused because of sunlight or mixing with water. Other atmospheric compounds change their forms by undergoing a chemical reaction and then convert to become secondary pollutants, like aerosols, ozone, peroxyacetyl nitrates and various acids. The primary cause for global warming is Carbon dioxide. Carbon dioxide is the main constituent result of fossil fuel combustion. The concentration of CO2 is constantly growing with the usage of fossil sources. Figure 2 shows the variation of CO2 emissions from various sources.

These emissions shown above are responsible for a phenomenon called "Global warming". The average temperature of Earth is increasing because of this phenomenon. Figure 3 shows the increase in temperature.

Climate change affects human health and nature badly. Average temperature of the Earth over the past century has increased by about 1ºF; an additional rise of 2 to 6ºF is expected by scientists over the next century, [5]. This may change the Earth's climate drastically. Global warming motivates the sea level to rise. If sea level rises between several inches or feet, it will affect natural and artificial structures along the coastline. By the year 2100, 5000 square miles of dry land and 4000 square miles of wet land in the United States are estimated to be inundated due to a 50 cm rise in water level, [6].The flora and fauna of localities are affected when salt water reaches areas where it can be harmful. Other emissions like Sulphur, carbon monoxide are also threats to humanity. Many compounds when released in the atmosphere react with sunlight and lead to acid rains which further affects groundwater and also is the reason for ground level smog.

There are various ways available for handling this air pollution. One way is to change our transport patterns and the use of rail transport for transport of goods and humans rather than roadways. But rail transport installation is a money consuming process. Also, it is not possible to entirely avoid roadway transportation. Especially in hilly areas, roadway transport is unique. Another way of controlling pollution is to improve exhaust gas treatment technology and engine technology. The 3rd way is to change our fuel to give good engine combustion characteristics. For this, we have to go for alternative fuel. So, it's a big challenge for energy researchers to find alternative fuels which are inexhaustible and environment friendly.

Hydrogen is the simplest element which is composed of one electron and one proton. Hydrogen is the third most abundant element found on earth which also comprises 90 percent of the universe. More than 30% of the mass of the sun is composed of atomic Hydrogen, [7], [8]. Hydrogen, with its almost unlimited supply potential and being clean fuel with excellent combustion properties in the Internal Combustion engine is the ideal fuel to use for automotive applications. It emerges as an operationally and economically feasible energy source. Hydrogen can be produced rapidly in large quantities which are enough to power the world's automobiles in the near future. It can provide unprecedented efficiencies when used in existing Internal Combustion engines and also leads to reduction in levels of exhaust pollution. Combustion of Hydrogen does not contribute to emissions of SO_2, CO_2, CO, Furnas, dust and dioxins, [9]. Hydrogen produces water on combustion. Also, Hydrogen can be produced from water, which is available in plenty. It's a non-polluting fuel compared to conventional hydrocarbon fuels.

Hydrogen production currently accounts for 2% of the global emissions of carbon dioxide, while it's proposed to be the fuel of the future and as an alternative to current IC engine fuels, the emissions from its production must be kept under check to ensure that it fulfills its purpose of a clean fuel. This can be achieved by production of green hydrogen i.e., producing hydrogen via utilizing renewable energy, or in such a way that it does not lead to greenhouse emissions. Studies regarding the production of green hydrogen via electrical, thermal and biochemical processes have been conducted, but robust studies in improving the efficiency are the need of the hour. Electrolysis is seen to be the best method currently and is discussed thoroughly later. Studies for additives that would speed up the electrolysis process are gaining popularity and could be the key to making the fuel of the future a success.

Due to the qualities mentioned above, hydrogen is a promising fuel for IC engines for the long term. Many of its properties are excellently suited for using it as an IC engine fuel. It's a promising fuel to meet the world energy demand shortly. It's a 'UNIVERSAL FUEL' with continuous availability. The use of hydrogen as a fuel can led us to a cleaner relationship with the environment.

2. History of hydrogen

The formation of hydrogen is explained with the big bang theory, [10]. Hydrogen atoms are believed to have been formed as amongst the first atoms in the whole universe. The big bang theory claimed the universe to be extremely closely packed, hot and dense. Big-bang explosions occurred about 10-20 billion years ago, which led to expansion and hence cooling of the universe. This explosion led to the

production of a single fundamental force, which then sundered into gravitation, nuclear force and electromagnetism. This explosion was responsible for the creation of protons. Further, the combination of protons and neutrons lead to elements like hydrogen etc. The universe cooled about approximately 3000 °C during the years 300'000 to 1 million years after the big bang, which led to the combination of protons and electrons and hence formation of hydrogen atoms, [10]

The history of hydrogen discovery dates back to the 16th century when T. Paracelsus reacted with iron and acetic acid and hence obtained hydrogen, [9]. It was then named as 'burning gas' owing to its burning properties. A review of the history of hydrogen from 1660 till the development of the first hydrogen IC engine vehicle.

1660- R. Boyle reacted H_2SO_4 with Fe and hence obtained hydrogen, he also discovered the fact that hydrogen doesn't just burn in thin air.

1776- Henry Cavendish referred to hydrogen as a simple substance, and also highlighted its property of being lighter than air, later in the year 1781 he also evinced the production of water upon its combustion, but he was not aware that a water molecule consists of hydrogen, it was 20 years later to this incident that A. L. Lavoisier confirmed it and he called it 'hydrogen' (lat. Hydrogenium – forming water), [11], [12]

1783- The first practical usage of hydrogen dates to august 1783, when in Paris, J. A. C. Charles released a hydrogen balloon, [13].

Early 1800's to mid-1900 – Town gas was used for supplying heating and lighting in Europe and America, the gas was manufactured as product from coal. The composition of town gas is 50% hydrogen, 3-6% carbon monoxide, and the rest are predominantly methane. Providing heat and light to the civilized world it was celebrated like a wonder. It is displaced via a pipeline network of natural, [14].

1839 - Sir William Grove reversed the electrolysis process and hence led to the discovery of the first fuel cell. Drawing idea from Grove's original fuel cell, 4 of these cells were combined in series hence the voltage increased and even electrolyzed a cup of water. Thus, the creation of clean power (electricity) was obtained with the use of fuel cell while only leaving water as the by-product and also creating significant amount of power. Some

significant achievements in this field were the 200kW fuel sell by ONSI Corporation manufactured and Ballard Power Systems using fuel cells in U.S. and Canada generating 205 kW for usage in buses, [11], and, [15].

1911 – Directions for the development of ammonia and fertilizers via hydrogen and nitrogen gas were given by Carl Bosch. The innovation revolutionized agriculture via enabling development of synthetic fertilizers hence making feeding the rapidly growing population possible, [14].

1937 – The airship Zeppelin Hindenburg, supposed to land at Lakehurst, New Jersey, electrical discharge led to its ignition after it had travelled across the Atlantic via Germany. The airship burnt and crashed into the ground in a few seconds, 35 of the 97 people onboard died and the toll was 1 on ground. Owing this incident there was a stigma regarding hydrogen and it associated with the Hindenburg disaster even a lot of years later.

1959 – A fuel cell of capacity 5kW was produced by Francis Bacon produced in the same year, Harry Karl Ihrig demonstrated a tractor of 20 horsepower which was the first ever vehicle powered by fuel cell.

20th Century: Hydrogen was widely employed in ammonia production it was also used extensively in gasoline, heating oil and methanol production. Other uses were fertilizers, refined metals, lubricants, soaps and rocket fuel, [14].

Late 20th century/Dawn of 21st century – The National Aeronautics and Space Administration (NASA) and the National Advisory Committee for Aeronautics (NACA), and several universities and businesses employed hydrogen as rocket fuel and electricity source in the form of fuel cells. From 1980 automotive companies began testing Hydrogen fuel technology for cars.

1999 – This year marks the beginning of production of hybrid electric vehicles (HEV), the Toyota Prius and Honda Insight entered the US market.

2003 – Honda released its first fuel cell car for Los Angeles, [14], [16].

2005 – BMW produces internal combustion engine vehicle that runs on hydrogen.

3. Hydrogen production methods

There are various hydrogen production methods available, while their selection is a consequence of the feedstock availability, the quality and the quantity of hydrogen to be produced. Hydrogen production development in an economical and eco-friendly way is under progress, [17]. Efficient and economically feasible hydrogen production from a renewable source would be the pathway towards a viable "hydrogen economy". Hydrogen readily combines with other elements and hence is found in combined state in water, fossil fuels and biomass. Regarding the earth's atmospheric air composition, 1 molecule of hydrogen is present in about 15000 to 20000 molecules of air. At the same time, this data is subjected to altitude and a rise in the composition of hydrogen is seen with the rise in altitude. A source of gaseous hydrogen in the atmosphere is the gas emitted via charcoal mines and volcanos, [8]. Due to its high energy density, hydrogen can be efficiently and conveniently used for energy application with great ease. The flowchart of hydrogen production methods is shown in figure 4.

Following are the methods of hydrogen production technologies, to find economical and renewable means of hydrogen production which are emerging, giving hope to a promising future.

3.1 Fossil fuel resources

The use of energy from several types of resources like coal, natural gas, biomass, or coal, to release of hydrogen from their molecular structure via thermo-chemical process is the primary source of hydrogen production in the current scenario, [18]. Industrially majority of hydrogen is produced via hydrocarbon fuel and water, where in the hydrogen derived from water is also significant. The obtained syngas further undergoes catalytic processing, optimizing the produced hydrogen for further applications, [19]. Though hydrogen via fossil fuels is not eco-friendly, it provides high yields and is the most economical method currently available.

3.1.1 Hydrocarbon reforming process

Hydrocarbon reforming is the chemical process of converting hydrocarbon fuel to the final product of hydrogen via some reforming technique. This process leads to rearrangement of the molecular structure of hydrocarbon, and hence its properties are transformed. The reaction of hydrocarbon and the other reactant i.e., steam, leads to an endothermic reaction known as steam reforming. Hydrocarbon reforming governs production methods like the Bosh method, which employs coal gasification where coal reacts with the gas agent and is transformed finally to gas products under normal pressure with high temperature conditions, [14].

3.1.1.1 Steam natural gas reforming process

Hydrogen production from natural gas is essential for introducing hydrogen into the utility and transportation sectors. It can be achieved by limiting the cost of developing and conventional advanced hydrogen production processes that count on less expensive fossil feedstock, [17]. It is a two-step process. At first, to separate hydrogen from carbon atoms in natural gas (CH_4), natural gas is exposed to high temperature steam. Carbon monoxide (CO) and carbon dioxide (CO2) are produced. Secondly, the carbon monoxide conversion accompanied by steam is achieved to produce additional carbon dioxide and hydrogen. Natural gas is first passed through a Sulphur removal plant to reduce the Sulphur content to less than 5ppm to safeguard the catalyst. It is then mixed with superheated steam and fed to the reactor. Then CO is also reacted with steam. This stage is endothermic. Steam reforming process diagram is shown in figure 5.

$$CH_4 + H_2O \rightarrow CO + 3H_2, [9], [12]$$

$$CO + H_2O \rightarrow CO_2 + H_2$$
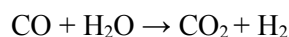
The removal of the remaining CO is achieved via absorption while the traces of water are also removed, leading to a 97% pure hydrogen. The ratio of methane to hydrogen obtained via this process is about 470 m3 to 1000 m3, respectively, while efficiency of 69% is achieved based on the heating values. At present times, this method is most efficient method for production of hydrogen, but it uses fossil fuels both in manufacturing and as a heat source, which is a significant disadvantage. Hydrogen produced by this method is not used as a fuel but is used in manufacturing fertilizers and chemicals and upgrading the quality of petroleum products.

3.1.1.2 Partial Oxidation Process

In this process, reforming for hydrogen production is achieved via an exothermic reaction of hydrocarbon and oxygen. It uses a lower ratio of oxidant to fuel with regards to

complete combustion, and hence the final products achieved are CO and H2 rather than CO2 and H2O. Recent development in this process has shifted considerable attention to partial catalytic oxidation (CPO), using catalysts like Ni and Pt, and, [20]. Partial oxidation process diagram is shown in figure 6.

$$CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2H_2$$

3.1.1.3 Auto Thermal Process

The combination of both steam reforming and partial oxidation is called auto-thermal reforming. In this process, the steam reforming is executed in oxygen. The determination of the hydrocarbon/oxygen/steam ratio governs the characteristics of the reaction. It has been observed that the use of high oxygen to hydrocarbon and water to hydrocarbon ratios can reduce coke formation, [21]. Auto thermal process diagram is shown in figure 7.

$$CH_4 + \frac{1}{2} O_2 + H_2O \rightarrow CO_2 + 3H_2$$

3.2 Renewable Processes

Achieving economic feasibility, lesser time for production and more significant quantities of products are significant challenges that renewable resources must cope with. The use of renewable processes for hydrogen production is the need of the hour. With fossil fuel resources decreasing and the environmental hazards caused due to use of conventional methods, renewable processes will inevitably take over the market.

3.2.1 Thermochemical Process

Thermal decomposition of water occurs only at a temperature above 5177°C, which is impossible to achieve nowadays. However, the execution of decomposition in two cycles allows decreasing this temperature to 3067°C.

$$CO + H_2O \rightarrow H_2 + CO_2 \quad \text{(at about 477 degrees Celsius)}$$

$$CO_2 \rightarrow CO + \frac{1}{2} O_2 \quad \text{(at about 3067 degrees Celsius)}$$

The profitability of this method is strictly connected with possessing the cheap source of carbon monoxide (for instance, gasification or incomplete combustion of coal) because the whole cycle is too expensive in realization, caused by the cost of achieving the temperature needed to decompose CO2. Throughout past years, around 20 different types of thermos-chemical circulation methods have been developed and further research is going on large scale, of which some have been tested run, [22].

3.2.2 Biological Methods

3.2.2.1 Co-fermentation of algae.

Production of hydrogen using algae is an up-and-coming technology and can be enhanced to achieve greater efficiencies and better economic feasibility. Co-fermentation with micro-algae, abundant with carbohydrates accompanied by an excellent C/N ratio, enhances hydrogen production performance. Pretreating the algal biomass with 2.5% dilute sulphuric acid at 135°C for 15 minutes affects a total yield of carbohydrate monomers of 0.268 g per gram of volatile solids. The increase in algal concentration leads to a gradual increase in specific hydrogen yield because of the consumption of carbohydrate monomers by the growth and reproduction of anaerobic fermentative bacteria. Increasing the concentration of algae also leads to an increase in the number of carbohydrate monomers available for hydrogen fermentation, [23].

3.2.2.2 Co-fermentation of Sewage Sludge

The process called dark fermentation is used to produce H2. Sometimes hydrogen is produced from the bacteria degrade carbohydrates and the corresponding reaction is called as dark fermentation, volatile fatty acids and carbon dioxide. It provides advantages such as low treatment cost, high production efficiency and operational simplicity. Sewage sludge has been one of the significant wastes for production of H_2 via dark fermentation because of its high organic content and high generation in treatment plants. But the problem with sewage sludge is that it does not attain high yields, and hence methods to increase the same have to be appointed. One such method is the addition of wine finesse; it is the final product of wine distillation; it has properties like low PH, high chemical oxygen demand and Biochemical oxygen demand. Studies have shown that for enhanced oxygen production, the PH should be between 5 to 6, the temperature for Thermophile and mesophile processes should be around 55 and 35 degrees, respectively. Wine vinasse has a greater concentration of soluble chemical oxygen demand when compared with sewage sludge, and hence their mixture magnifies the

concentration of soluble organic matter concerning sewage sludge alone. It has designated its mixture as a suitable substrate for hydrogen production. It is observed that the hydrogen production is increased by 13-14 times with the introduction of wine vinasse as compared to that of sewage sludge alone, i.e., to 43.25 ± 1.52 mL H2/g from 3.17 ± 1.28 mL H2/g. This method has a promising future and hence needs to be given importance and invested in, [24].

Cumulative hydrogen production from co-fermentation of sewage sludge with wine vinasse at different mixture ratios is shown in figure 8.

3.2.2.3 Effect of bio-augmentation

The study of the effect of bioaugmentation via 3 bacterial species on hydrogen production from an organic fragment of MSW was conducted at different bacteria/sludge correlations, maximum hydrogen production rate, the cumulative hydrogen production, and the lag phases were analyzed, showing that the highest cumulative volumetric hydrogen production was achieved via bioaugmentation by Bacillus subtilis, with sludge/bacteria correlation of 0.25.

Bioaugmentation reduced the lag phases and also led to the improvement in COD removal, the generation of volatile fatty acid was also enhanced, it also led to degradation of OFMSW, which is a complicated substance, and its bioconversion demands proper cooperation ff diverse bacterial consortia found in sewage sludge and anaerobic digesters, [25].

3.2.3 Photolytic Decomposition of water.

In this process the decomposition of water to gain hydrogen, is achieved via use of light in the form of energy to break down the molecules. Catalysts are used to promote the process, while water is normally the primary source of hydrogen production.

A study on hydrogen production in the presence of sacrificial methanol over Rh-loaded TiO2 at room temperature was conducted and it was observed that here water was not the primary source of hydrogen. This phenomenon occurred because protons obtained by methanol oxidation and water ionization could be reduced to hydrogen; this led to the astonishing discovery that hydrogen production was higher via methanol decomposition (~60%) than that

via water splitting (~40%). While in the case of Rh-loaded TiO2, the coupling of thermal and photo energies led to hydrogen production mainly via water. In thermo-photo catalytic reaction at temperatures above the boiling point of water, water molecules were reduced rather than protons, leaving hydroxyl ions as their byproduct. The hydroxyl ions hence produced would combine with the hydrogen ions generated via oxidation of methanol, leading to a high utilization rate of water. Thermo-photo catalysis achieved an impeccable increase in hydrogen production compared to room temperature photolysis, [26].

3.2.3.1 Solar assisted Photolytic decomposition.

Photocatalytic decomposition, as we know makes use of light for breaking down of molecules. Therefore, the use of sunlight to achieve photolytic decomposition shows great scope and provides a renewable method for hydrogen production. To use sunlight effectively concentrators are required. A Compound Parabolic Concentrator is one of the most advanced and reliable approaches for producing chemical energy from solar energy sources, the optimization and design of CPC can be achieved by the coupling of tubular reactors along with the CPC concentrator; the preliminary results show that hydrogen production sees a significant rise with the help of this design, [27]. Figure 9 shows the schematic representation of CPC with a round absorber and figure 10 shows the flow diagram of CPC's designing.

To further assist the optimization stated above, an attempt to hone the acceptance angle, the absorber tube diameter and the orientation of the concentrator was made. A North-south oriented, angle adjustable, single-axis tracking with low precision and truncated CPC having a concentration correlation of 4.22 connected parallelly with a down comer, a condensing tube and a riser to create a natural circulated solar hydrogen manufacturing system were set up, enhancing the performance of a photo reactor, [28]

3.3 Electrolysis Process

Electrolysis process of producing hydrogen is one of the best available methods at present time which is used widely and has

become more reliable with ongoing research. The hydrogen production by water as the raw material is the counter process to combust hydrogen and oxygen to generate water. Therefore, for splitting of the water it only needs specific amount of energy with a particular type. To split out the water by electricity supply, the production efficiency can be fixed from 75% to 85% generally, with the simple process and no pollution but heavy consumption of power. So, its application was restrained, [29]. The electrolysis process is commercially used to produce chlorine and caustic soda or potash, producing hydrogen as a by-product. Hydrogen production by water electrolysis is also a commercial process and is the most direct way of producing hydrogen through electrical energy. Advanced electrolysis using solid polymer electrolytes solar high-temperature electrolysis are the emerging technologies that form artificial systems. With addition of small amounts of potassium hydroxide/sulphuric acid, water is made electrically conductive. Electrical current is sent between the electrode which again leads to the dissociation of hydrogen and oxygen separately.

$$2H_2O + 2e- \rightarrow H_2 + 2OH- \text{ (on the cathode)}$$
$$2OH- \rightarrow H_2O + 1/2\ O_2 + 2e- \text{ (on the anode)}$$
$$H_2O + \text{electricity} \rightarrow H_2 + 1/2\ O_2 \text{ (globally)}$$

But this method is costly. To gain hydrogen employing this method, we have to provide more energy in the form of electricity (4.3 to 5.7 kW.h/m3) than we can achieve from the combustion of hydrogen (3 kW.h/m3). Furthermore, other forms of energy such as sun and wind energy or even nuclear energy can be used for electrolysis process, but again more research is needed to perform electrolysis with this kind of energy sources. Researchers from Ireland, where wind energy is abundant, tried hydrogen production from wind turbines. They showed an economical mode of preparing hydrogen from the wind where hydrogen acts as an efficient energy storage device. The following figure 11 shows the schematic of the Wind hydrogen system. A fuel cell is also accompanied by the system for getting electricity back while demand arises, [30].

3.3.1 Solar assisted Electrolysis

Electrolytic splitting of water for the production of hydrogen and water treatment is generally contemplated to be energy-consuming processes. If traditional energy sources are used for the two operations, it will lead to much environmental pollution and cost a lot. Using solar energy instead is a better option as it's renewable and environmentally friendly. The small organic molecule is primarily a pollutant in wastewater. It is also arduous to fully treat them via conventional methods because of high energy consumption. But these small molecules typically show a less redox potential. Therefore, they can be preferably oxidized on the anode. If included in wastewater, they would quickly oxidize and feed the electrolysis cell. Their oxidation transfers a certain amount of energy for the production of hydrogen. Hence a solar system of thermal & donor-modulated electrolytic water splitting for hydrogen and wastewater treatment can be constructed efficiently, [31]. It is observed that by utilization of collimated sunlight, hydrogen production can be enhanced up to 53% higher while 31% by conventional light and 16% by dark field. It is achieved because the polarizability and infinitival of sunlight result in strengthening the electric field in the electrolysis of water which enriches water splitting, [32].
The effect of sunlight in hydrogen production from water electrolysis is shown in figure 12.

3.4 Future

Nuclear assisted hydrogen production using water provides hopes for better production of hydrogen in the future, it employs the phenomenon of utilization of heat produced via the reactor for thermolysis of water. Currently this process involves certain risks while attempting to scale-up and the high corrosivity at excessive temperature also asks for consequential demand of materials and equipment used, [33]

4. Hydrogen storage

Ideal Hydrogen Storage should be defined by Heat Management, Cost Efficiency, Mass of the Tank, Complexity, Feasibility and many more potential properties or characteristics taking into account, [34]. The storage technology must be satisfied with the vehicle's performance,

range, and cost, [35]. Figure 13 displays the hydrogen storage method flowchart.

Storage is needed in a delivery system for two fundamental reasons.

> To match variations in demand with the economic requirement for the virtually steady rate of production and transmission necessary to maintain a high load factor in facilities.
> To accommodate temporary interruptions in production and transmission and the inability to make an accurate short-term forecast of demand, [7].

Hydrogen is a problematic fuel to store. Its energy density as gas is very low. The problem of storing Hydrogen has been one of the obstacles holding up its progress as a fuel.

4.1 Physical methods of hydrogen storage

Hydrogen gas can be stored physically in gaseous and liquid states. Hydrogen storage in gaseous form requires high-pressure vessels and require cryogenic temperature in a liquid state. The simplest and easiest method of storing hydrogen is physical storage which consists of three physical methods. The most reliable hydrogen storage methods are compressing hydrogen storage and liquid hydrogen storage. The following three physical methods are available and widely practiced for storing hydrogen.

1. Compressed H_2 storage

2. Liquid hydrogen storage

3. Cryo-compressed H_2 storage

4.1.1 Compressed H_2 storage

This technique uses compressed hydrogen gas as a fuel storage method is widely acceptable and reliable in automotive community due to the reliability and less complexity of the storage system, cost for hydrogen gas storage and transport when compared with the other conventional techniques. The method used to compress hydrogen is similar to the compression of the natural gas method, though the compressor needs a more acceptable seal as hydrogen is less dense. But, as hydrogen has a much lower density, this storage volume becomes very high. For example, at atmospheric pressure conditions, a gram of hydrogen gas occupies only around 11 liters of volume, so to build an effective storage system, the H_2 gas must be compressed and stored at very high pressures, [36]. Hydrogen gas is typically compressed to high pressures between 200 and 250 bar for storage in cylindrical tanks of around 50 liters. These high-pressure storage vessels are mainly made out of carbon/graphite compounds or aluminum alloys and can be used in small industrial projects or for transportation purpose. These tanks may be made from aluminum or carbon/graphite compounds and can be used for either small industrial projects or transportation. The pressure of 500-600 bars is required for compressing hydrogen to use it on larger scale, though some of the world's most giant compressed hydrogen tanks (about 15,000 cu meters) use pressures of only 12-16 bar, [37]. We would require 8.5 % of the same hydrogen volume energy content for compressing it to 5kpsi (34.5 Mpa) pressure, [35]. The refilling time of hydrogen and gasoline tanks are almost similar. Even so, hydrogen occupies more volume when compared with natural gas storage volume for the same energy equivalent quantity. By increasing pressure, fuel storage in the container can be increased, but parallelly cost will increase, inviting more safety issues. Further, lowering pressure to lessen this concern follows big storage system space. Compressed H_2 storage technique diagram is shown in figure 14.

In addition, due to its compact size hydrogen tends to leak. These leaks can be prevented or reduced by installing seals and valves on the containers. Hydrogen can also be stored in high-pressure storage tanks or even in the structure of pipelines onboard the vehicle. mined salt caverns, gas fields or depleted oil can serve as underground storage areas for gaseous hydrogen, [39]. A few numbers of companies have already developed aluminum made composite-type high-pressure vessels reinforced with plastic liner and carbon fiber layer outside the liner, which is applicable for compressed hydrogen storage at around or even higher than 35 MPa. Although a composite-type vessel with 0.113 H2-kg/kg (11.3 wt. %) of gravimetric hydrogen density has been developed, the light vessel's volume to store 5 kg H_2 is 250 lit (20 H2-kg/m^3) or more significant at a hydrogen pressure of 35 MPa.

Currently the carbon fiber system can store up-to 5000 pounds per square inch of hydrogen but 10000 psi is needed for better vehicle range. For safety purposes, burst strength of the specific tank must have at least twice the fuel pressure. On the other hand, tanks are made from materials that are either very expensive or very heavy. These tanks create packaging issues due to their large size, [40]. But still compressed hydrogen gas storage technique demands more advancement to meet volumetric and cost targets for storing hydrogen, [41].

4.1.2 Liquid hydrogen storage

The liquid hydrogen storage technique absorbs less space, and it is one of the compact methods to store hydrogen onboard. Since hydrogen does not liquefy until it reaches -253°C (423 Fahrenheit) at atmospheric pressure, at 20 K and 1 bar, 845cc of hydrogen can be stored in a 1cc capacity tank. Furthermore, the tank is not concerned about high internal pressure, so the container can be made relatively lightweight when compared to other storage tanks. However, in order to slow down hydrogen evaporation and to keep container cold, it must be super-insulated, [42]. But this process is both time taking and energy-intensive, resulting in losing around 40% of total hydrogen energy. High energy to mass ratio of hydrogen is three times to that of gasoline which is one of the primary advantages. Yamane and Furahama have investigated the effect of the fuel tank mass on the performance of engine, [43]. This study shows that the liquid hydrogen storage system has a range of 400 km with 100 kg of fuel tank weight. Liquid hydrogen fuel is employed in all space programs because of its high energy-dense property.

Nevertheless, it is laborious to store, and the insulated tank required must be significant and sizable. A significant amount of energy is required to decrease the temperature hydrogen to, after, even then again, the hydrogen gas will naturally "boil off," or vent, at a rate of about 3 per cent to 4 per cent per day, [40]. 5 kWh of electrical energy is required to cool one pound of hydrogen, [44].

Hydrogen storage tanks are made mainly for holding the cryogenic liquid rather than facing high pressures, [34]. Figure 15 shows the Linde cryogenic storage tank used in General Motors Company. It is double-wall cylindrical structure tank which is made of stainless steel and weigh around 90kg. At the temperature of -253°C, it is able to store 68 liters of net volume of liquid hydrogen with the maximum pressure of 0.6 Mpa inside. Dormancy or the time of first venting is the time period before liquefied hydrogen starts boiling off. The mentioned linde storage tank has a dormancy period of 3 days which means liquid hydrogen in the tank will boil off after the 3 days after the tank is being refilled. The rate at which hydrogen evaporates (boil off) is 4% per day for a 4.6 kg tank. However, the evaporation rate of LH_2 should be below 2 % per day, [45] to reduce the rate of fuel losses when the vehicle is not in function.

Liquid hydrogen refilling is done automatically by the use of robotic arm, self-servicing refilling of LH2 can lead to many problems like cold burns because of low temperature of liquid hydrogen. The picture mentioned below displays an automatic robotic arm filling liquid hydrogen to BMW 5 Series car in figure 16.

An LH2 storage technique was successfully built and tested by H. Rudiger. A study was performed during cool down and filling of the LH2. The study shows a satisfactory output of a net loss rate of 1.3% per day under steady-state conditions. It is worth mentioning that the cool down of the storage tank can be done in 9 minutes, where it takes another 7 minutes to fill it up to the maximum levels, [45]

Liquid hydrogen storage technique shares advantages of similar technology used in liquid natural gas storage, as happened in the case of compressed hydrogen. Liquefied hydrogen does not have the high weight penalty as seen with compressed hydrogen, but it is still bulkier and energy-intensive than gasoline storage. The storage tanks can become deplete if left for a while; therefore, excellent insulation of storage tanks is needed for hydrogen's low boiling point. Maintaining the extreme cold temperatures of LH2 during refueling and storing it onboard poses a significant technical, challenging and strenuous task, 25 per cent of boil off of LH2 occurs during refueling and 1 per cent lost per day for onboard storage. Liquid hydrogen is the most common method currently used for off board hydrogen storage because of the high energy density of liquid hydrogen. For example, this was used for the fuel cell demonstration at Chicago transit hydrogen refueling station for storing hydrogen. For storage on the roof of the bus, the liquid

hydrogen was pressurized into compressed hydrogen, [39].

When fluid is transferred between two containers, boil-off losses along the LH2 pathway may occur when it comes to contact with the heat of the environment. These losses can be determined by using thermodynamic models and MATLAB simulation, based on conservation of mass and energy law, [46]. Refueling LH2 into the storage tank of the specific vehicle requires both a heat exchanger and compressor, making it more expensive and complicated, [47]

The National Renewable Energy Laboratory (NREL) states that many industrial operations such as heat treating, food hydrogenation, glass manufacturing, brazing and semiconductor manufacturing are approached by deliveries of LH2, [44].

4.1.3 Cryo-compressed hydrogen storage

The traditional liquid hydrogen storage method requires properly-insulated and expensive cryogenic storage vessels to reduce the rate of boil-off process and eventually enhance dormancy period. Furthermore, gas to liquid transformation is not a cost-efficient process, leading to a costly and energy-consuming technique. Because of these reasons, this technique is not that efficient to use in future automotive applications because of the high cost and safety issues. So, a new method was developed to resolve the issues with the liquid hydrogen storage method, which is called a cryo-compressed storage method. This technique refers to hydrogen storage in a vessel at cryogenic temperature; further, it is designed to withstand internal pressure around 25-350 atm. Furthermore, these tanks can store hydrogen at higher densities than compressed hydrogen gas and liquid hydrogen storage. This technique is developed at the prototype level and may reduce the boil-off effect from cryogenic hydrogen. [48], [34].

A schematic developed at LLNL gen-3 cryo-compressed hydrogen storage tank system which is displayed in figure 17. Storage tank equipment requires a heat-exchange gas recirculation line and a tubing for filling and discharging of liquid and gaseous hydrogen. Significant balance-of-plant (BOP) components comprises of fill port, pressure regulator, pressure relief valves, control valves, transducers and rupture discs, and thermocouples. The weight of the storage vessel is 123 kg which can store 10.7 kg of liquid H2 at 1 atm pressure with a boil-off rate of 3-7 g/h, [49], [34]

4.2 Chemical methods

The hydrogen storage method should be safe, compact and meet the vehicle performance that users have come to expect. More work on old hydrogen storage techniques for reducing their cost and improving performance may give efforts to advanced chemical storage methods that can overtake old methods with more efficiency, [41].

Various researchers are developing chemical storage methods to make the storage method economical and flexible. Following are some of the results obtained for their effort, which is worth noting.

4.2.1 Sorbents

Traditional methods of storing hydrogen possess some limitations and disadvantages. When it comes to storage capacity of tank, it is observed that hydrogen storage by the means of solid form is more satisfactory than old conventional methods. Adsorption of hydrogen gives more pleasing results in terms of hydrogen storage capacity when compared with absorption methods of hydrogen storage. Adsorption is the trapping of atoms and molecules that collide on the respective material surfaces.

4.2.1.1 Metal organic frameworks

Metal-organic frameworks are receiving enormous attention from researchers from the past decade for hydrogen storage applications. MOFs are crystalline structure materials comprising of metal ions coordinated with organic ligands to form the structures. MOFs can be used in various applications such as batteries, gas storage, purification, super capacitors, photo catalysts. The characteristics of MOFs such as high surface area, porosity, low density, flexible and tenable porous structure makes it exceptionally most delicate material to overcome hydrogen storage problems.

The greater the surface area of MOF allows more hydrogen adsorption to occur, tending to increase hydrogen storage capacity. The porosity of MOFs is more when compared to other conventional materials. MOF, which owns high porosity, high surface to volume ratio and high surface area makes it foremost candidate for hydrogen storage application, [50]

Figure 18 below shows the unit cell structure of MOF-5 material. The yellow sphere represents the volume of the pore. Black, white and red spheres represent carbon, hydrogen and oxygen molecules respectively. In MOF-5 material, 60% open space is available for gas to be introduced. Hydrogen diffuses through the crystals on MOFs and gets stored, and the rate of diffusion depends on the diffusivity rate of hydrogen in the crystal and the size of the crystal, [51], [52].

4.2.1.2 Carbon based material storage

Carbon adsorption techniques are greatly affected by the affinity of carbon and hydrogen atoms. Activated carbon is one of the finest adsorbents for gases. Carbon sorption is a chemical process that relies on gas compression. Carbon is deposited inside the cylinder in powder, granules or pellets. The total amount of carbon that can be adsorbed increases by increasing the cylinder's gas pressure. Hydrogen with substrate of fine carbon particles which are held by molecular forces are pumped into the storage container, [53]

This storage method of hydrogen is successful as metal hydride storage technique and it is more advantageous when temperature gets lowered, where the distinction between chemical bonding and liquid hydrogen are worth to be appraise, [39].

One of the most exhilarate technology called carbon nanofiber technology for storing hydrogen fuel has come up with the astonishing capacity to store up to 70% of hydrogen by weight. Generally, a metal hydride storage tank possesses the capacity to store between 2-4 % by weight in a heavy structure, but if the new carbon storage technique shows satisfactory results, it is possible for hydrogen fuel cell vehicles to travel to range of around 5000 km before refueling it. So, for this technique refueling can be done through postal services which eliminates the problem regarding hydrogen refueling stations infrastructure. Everyone related to hydrogen community is avidly waiting for statement of further research and results in this storage technology, [40]

Due to low interaction energy between hydrogen and carbon nanotubes, they make it unacceptable for automobile applications. But still, it can be enhanced either by doping with heteroatoms or by incorporating light metal atoms, [54]. Early research reports concluded that carbon-based hydrogen storage techniques

possess exceptionally increased hydrogen storage densities which are more than solid hydrogen. However, this type of technology is not in use for commercial applications, currently. Also, there are many technical complications to overcome, including the manufacturing of nanotubes in reliable and commercial way, [40]. Further research is needed on this technique of hydrogen storage, considering the low cost of carbon materials.

Graphite storage material for storing hydrogen at higher capacities was advanced by researchers of Northeastern University in Boston, Massachusetts. By the use of this storage technique Hydrogen-powered cars could travel up to around 8000 kilometers before refueling it second time. At room temperature and under specific pressure value Graphite nanofibers can store up to three times their weight of hydrogen and are able to store ten times more hydrogen when compared to current storage techniques. Firstly, to remove metal impurities from the catalyst particles, nanofibers must first be washed with acids. To pump the nanofibers full of hydrogen it is the necessary condition to wash the nanofibers first, and after it is heated to around 900ºC and placed in vacuum condition to take out extra gases which are clogging up the slits. Secondly, at a pressure of approximately 120 atm hydrogen is pumped. Pressure of 40 atm is necessary to keep hydrogen stationary in tank and the gas can be released by reducing the value of pressure, gradually. According to Rodriguez, it can take between 4 to 24 hours to charge up the whole system. Rodriguez mentioned that, the nanofibers systems can be refilled 4 to 5 times at same capacity, [55].

4.2.2 Metal hydride storage

Neither gaseous storage technique nor Liquid storage technique is attractive in mobile applications when it comes to safety concerns and volumetric efficiency because of its bulkiness and hazardous nature, [56]. The potentially attractive alternative to these storage methods is Metal Hydride storage. Hydrogen form bonds easily with more than 80 metallic compounds, and establish a weak attraction that stores hydrogen until heated. It reacts with metals giving rise to binary hydride. Metal and liquid hydrides are the principal and safest methods known of bonding hydrogen chemically, as no hydrogen will be released

even if any accident happens with the storage tank. Gaseous Hydrogen gas can perforate the lattice structure of solid metals alloys and bind at various sites in the unit cell of the specific crystal because of the smaller size of molecules and higher diffusivity. It's just like how a sponge absorbs the water.

First, Hydrogen splits into H atoms at the surface of the specific metal, and then it enters the metallic matrix in the atomic form, jumping between interstitial sites after diffusing through the metal, [57]. In Metal hydride compounds, Hydrogen is stored by binding it to the material's surface. By the injection of hydrogen at higher value of pressure into the container of small particles, the material gets 'charged'. Heat gets released when hydrogen forms bond with the respective materials and after, this heat must be used back in to release the Hydrogen from its bond as shown in the reaction below, [40]. To store hydrogen at large volumes, it is essential to ensure that higher surface area must be available, to increase this surface area it is essential to use small granules of the base materials.

$$Hydrogen\ gas + Metal \xrightarrow{Heat\ absorbed} Metal\ hydride \xrightarrow{Heat\ liberated}$$
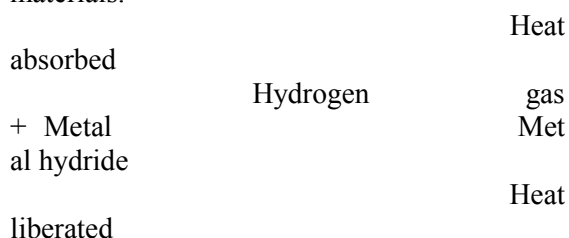
Figure 19 shows a typical hydride system. While hydrogen can diffuse over the metal surface, it gets absorbed and becomes a metal hydride. Also, it releases heat. For taking away the heat, cooling water is allowed to flow through the hydride tank. The enlarged diagram shows the hydrogen molecule's occupation inside the metal matrix.

After storing hydrogen, the hot water is circulated through the pipes if we need to extract hydrogen from the system. So, everything gets reversed, and hydrogen is evolved out of the system.

These metal hydride storage systems can be of low temperature which is less than 150°C or of high temperature which is more than 300°C. this method avoids safety concerns related to compressed and liquid hydrogen, since heat is required to release the hydrogen, it is slightly unsafe to handle, [39]. Technique of Metal hydrides are preferable because of their high

Hydrogen density per unit volume, which is substantially more than liquid hydrogen. Metallic hydride storage technique are one promising line of development.

The Materials suitable for storing Hydrogen should possess the following properties, [58].

> It should have a low atomic number.

> It should be inexpensive.

> It should have a high Hydrogen affinity to absorb it.

> It should respond to rapid temperature changes to Absorb and Desorption of Hydrogen.

The following are the material, which store Hydrogen in the form of hydrides, [58].

> Rare earth transition metals (RE)

> Titanium-iron

> Magnesium-nickel

> Zirconium-Manganese-iron intermetallic alloys.

> Vanadium alloy

Each has its advantages and disadvantages. RE alloys are easy to activate (rapid kinetics) and absorb large quantities of Hydrogen, but they become poisonous after a few absorption cycles. Also, they are very expensive. Magnesium alloys have a high capacity for Hydrogen absorption, but they are difficult to activate and required elevated temperatures. Also, its response is much slower. The titanium alloys probably offer the best compromise; however, they are heavy and require considerable activation before absorbing Hydrogen. In addition to this, Zr-Mn-Fe alloys are also being exploited as Hydrogen storing materials.

Liquid hydrides are substances like cyclohexane and methanol. For the ease of the transportation, they are just like liquid fuels but they must be partially oxidized or steam reformed to release the hydrogen which is held within.

There are many drawbacks of this method but one major obstacle to use this method commercially is that it absorbs only between 1.0 to 1.5 percent hydrogen by weight and the metal compounds used to bond the Hydrogen tend to be very heavy, [39]. Due to the high cost of metal hydride this hydrogen fuel system is not optimized for commercial use in current scenario. Currently, the required amount of metal Hydride for building up the storage tank costs between $7,000 and $18,000 per vehicle, [40]. Furthermore, there are numerous low-cost options are available but they are quite impractical to use commercially as these cheaper metals need very high temperatures to release the Hydrogen, [39].

Energy Conversion Devices (ECD) is one of the companies which is working on improvement of metal hydride hydrogen storage method. ECD's Ovonic proprietary magnesium alloy is a lightweight metal hydride, with a 7.0 percent by weight hydrogen content, which avoids some of the weight penalty encountered with other metal hydrides, [39].

The following Table 1 will give an idea about the three conventional techniques, which discussed before.

4.2.3 Chemical hydrides

Hydrides are the chemical compound in which hydrogen is bonded with any other element. Chemical hydrides are another type of hydride storage method for hydrogen. Chemical hydrides come up with a high energy density for storing hydrogen compared to conventional hydrogen storage methods. In metal hydrides hydrogen is bonded chemically, further they are much stronger than the physical bonds formed by the hydrogen. Chemical hydrides like LiH, $NaBH_4$, and $LiBH_4$ are highly hydrogen-containing materials with good stability, [59]. Chemical hydride hydrogen storage material is irreversible, and the reaction releasing hydrogen is generally exothermic, which leads to regeneration of fuel which is energy-intensive, [60].

4.2.3.1 Borohydride storage method

The borohydride storage system can store a considerable amount of hydrogen due to lithium borohydride's high volumetric and gravimetric hydrogen densities ($LiBH_4$). It is a reversible type of hydrogen storage material, [61].

$$LiBH_4 \leftrightarrow LiH + B + 3/2\ H_2$$

In Lithium Borohydride ($LiBH_4$), a boron atom is connected with other adjacent hydrogen atoms with sp3 hybridization and covalent bonds and form, $[BH_4]-$ and then it combines with $Li+$ by an ionic bond to form a $LiBH_4$ structure. As a consequence of strong bonds between atoms, as mentioned above, $LiBH_4$ shows good thermodynamic stability, [61]. $LiBH_4$ decomposes into LiH and B, accompanying the release of H_2 when heated around 573K, as shown in the above reaction. This decomposition of $LiBH_4$ into H_2 is a reversible process due to the endothermic nature of the reaction. Decomposition of $LIBH_4$ is a very much complicated process and difficult to understand. High operation temperatures, slow kinetics, and poor reversibility are some of the problems limiting the $LiBH_4$ storage technique. More work is needed on thermodynamic and kinetic properties to develop this technology fully, [62].

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 + \Delta H$$
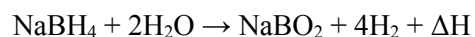
Another type of chemical hydride, Sodium borohydride ($NaBH_4$), is widely fascinating for hydrogen storage because of its high stability compared to other chemical hydrides, and it can be synthesized from common natural resources, [59]. For $NaBH_4$, the hydride is mixed in solution with water, and after hydrogen is released using a catalyst, as shown in the reaction above. This is a very reliable way of storage as hydrogen is produced. This method is pure and safer than gasoline for automotive use, [57]. Using coke, $NaBO_2$ could be recycled back to $NaBH_4$ with the minimum energy efficiency. Due to these reasons, chemical hydride hydrogen storage systems can be very effective. A study was of the $NaBH_4$ system was conducted by Millennium Cell in three fuel cell vehicles and two hydrogen internal combustion engine vehicles. The study indicates that the system is technically feasible and reliable for storing hydrogen for automotive usage, [35].

4.2.3.2 Ammonia borane storage method

Ammonia borane ($NH_3.BH_3$, AB) has become one of the effective methods for storing

hydrogen on-board due to its high hydrogen content, which is around 19.6 percent. Furthermore, it is in a solid-state and stable condition at ambient conditions making it more reliable for automotive applications. AB can be made to release hydrogen upon hydrolysis or methanolysis in the presence of a suitable catalyst, as mentioned in the reaction given below. Catalyst controls the strategy of the reaction to, at a greater extent controlling the release of hydrogen amount. So, further additional research is essential for choosing effective catalysts for these reactions to be worthwhile, [63].

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2$$
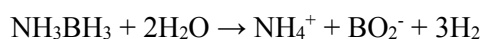
There are numerous methods available for dehydrogenation of ammonia borane, and the simplest elementary method is direct heating, AB thermally decomposes and being polymerized first to polyaminoborane $(NH_2BH_2)n$ to yield 1.1 equivalent H_2 and after to polyimiborane $(NHBH)n$ to give 1 equivalent H2 over a broad temperature range between 110 °C to 200 °C, [64]. This process is shown in figure 20 mentioned below:

5. Properties of hydrogen

NTP = 1 atm and 20 degrees centigrade.
NBP = Normal Boiling Point.
Table 2 gives the comparative data for hydrogen, gasoline, and methane. Hydrogen is the very first element existing in the periodic table. A hydrogen atom is consisting of one proton in nucleus and one electron which is spinning around its nucleus. When thinking chemically, the single electron present in hydrogen atom possess high reactivity. Due to his reason hydrogen always form pair as H2 instead of single H atom. Each proton present in H2 has a field and is associated with a "spin" which can be visualized and described mathematically. H2 molecules with have both photons in same spin are known as "orthohydrogen" and in which the protons have totally opposite spin are described as "parahydrogen". Orthohydrogen equips more than 75% of normal hydrogen at room temperature. This difference becomes more crucial at extremely lower temperatures while releasing heat in the process afterwards orthohydrogen becomes unstable and changes

to the more stable condition of parahydrogen arrangement. This heat can complicate hydrogen processes of low-temperature, specifically liquefaction, [66].
hydrogen has the lowest atomic weight possible among other substances and additionally own lowest density in both liquid and gas phase. Gaseous phase hydrogen has density of 0.08376 kg/m^3 and specific gravity value of 0.0696 which is approximately 7% density of the air. Water with density of 1000 kg/m^3 is used as a reference material for liquids with specific gravity of 1.0. liquids which hold specific gravity more than 1.0 are heavier than water and those who are less than 1.0 are lighter than water. Liquid hydrogen with specific gravity value of 0.0708 and density of 70.8 kg/m^3 is approximately 7% of water density, [66]. This lower viscosity enhances the problem of leakage when discussing about hydrogen storage. Because the volumetric leakage rate is either inversely proportional to the square root of the density or inversely proportional to the dynamic viscosity of the leaking fluid, [65], but as it has a low density and small molecular size, it has high buoyancy and diffusivity. These two factors determine the rate of mixing hydrogen with an oxidizer, [65]. Outdoors if hydrogen leaks will immediately diffuse with air and get diluted, thus avoiding the problem of the explosion, but in indoor conditions, it will immediately attain its ignition limit with air and readily ignite before monitoring the leak.

5.1 Flammability limit

Hydrogen has a very wide range of flammability limits compared with gasoline or methane, [65], [66]. It is interpreted that the flammability limit of hydrogen is from 4% to 75% of hydrogen in the air (mixture) at NTP, [67]; thus, hydrogen can be ignited over a very wide range of air-fuel mixtures, [68]. This wide range of flammability permits hydrogen to combust at very lean or rich mixtures, making it preferable for internal combustion engines, [69], [66]. Further, we can employ lean air-fuel mixture of hydrogen as an additional fuel in engine in order to reduce pollutant emissions due to wide flammability limits of hydrogen, making it more efficient, [70]. It is worth mentioning that in many leak situations, a lower flammability limit is the key parameter to determine whether it is going to ignite or not; in the case of hydrogen lower flammability limit is 4 times higher than gasoline and 1.9 times

higher than the propane making hydrogen engine more superior, [71].

5.2 Low ignition energy

Ignition energy is described as the energy necessary to sustain an ignition of a combustible vapor or gas mixture, [69]. Hydrogen has lower value of ignition energy of around 0.02 mJ, [71] which is nearly 10 times lesser than gasoline and 15 times than methane. So, it's easy to burn the hydrogen with a relatively weak spark. But in the meantime, any hot spot in the chamber becomes a source of ignition and results in unintentional ignition, which leads to preignition. Figure 21 shows the ignition energy variation of hydrogen and methane with equivalence ratio, [65], [66].

5.3 High flame velocity

Hydrogen possesses greater burning velocities than gasoline or methane at a stoichiometric ratio (Hydrogen possesses high flame velocity nearly 7 times faster than gasoline or natural gas, [72]).

As we tend towards a leaner mixture, flame propagation rates are reduced, and the high flame speed advances towards a thermodynamically ideal engine cycle, [68]. Fuel having high burning velocity has good antiknock qualities. So, this makes hydrogen a good SI engine fuel when knocking is concerned. Due to the high flame propagation rates, hydrogen has high octane number, and it's rated as good fuel for SI engine application, [65], [66].

5.4 High auto ignition temperature

Hydrogen owns remarkably higher auto-ignition temperature (958K) compared with hydrocarbons having long molecules, [67]. The enthalpy of combustion under mass basis is higher for hydrogen. But under volume basis, it's very low because of less density of hydrogen. So, achieving combustion with compression alone is difficult in hydrogen. So, it's not a good fuel for CI engines.

Due to the compression ratio is associated with the temperature rise, the auto-ignition temperature of hydrogen becomes a primary factor for determining compression ratio of the engine as shown in the equation given below, where T2 is the temperature achieved during compression, [68].

$$T_2 = T_1 (r^c)^{k-1}$$

5.5 Small quenching distance

Hydrogen has a very low value of quenching distance when compared with other fuels, which is 0.64mm. That is why hydrogen flames usually travel very close to the surface of the cylinder before they get extinguished, [68].

Additionally, burning velocity and quenching distance are inversely proportional and also quenching distance decrease with an increase in pressure and temperature, [67]. This makes the hydrogen flow back into the intake manifold of IC engines through a nearly closed intake valve and results in a flashback phenomenon, [65]. So obviously, hydrogen has a very low quenching distance than hydrocarbon fuels.

5.6 Motivity factor

Hydrogen is a good fuel to transport, as its very high Motivity factor. So that, it's used as a reference fuel for comparison. Motivity factor for fuel is defined as the following equation,

Here E denotes the energy of combustion of the fuel and volume is denoted as V. The subscript 'h' is used for hydrogen. For hydrogen, the mobility factor is the maximum value.

5.7 High diffusivity and low density

As a consequence of small size of the hydrogen molecule, it has a higher value of diffusivity when compared with other conventional fuels, and the diffusion coefficient of hydrogen in air ranges from $6.1E^{-05}$ m^2/s to $6.8E^{-05}$ m^2/s, [67]. There are two main advantages of the high diffusivity property of the hydrogen; the first one is that because of the high diffusivity of the hydrogen, it disperses more rapidly in the mixture making it more uniform and a preferable fuel for the direct injection method in SI engine. Secondly, if hydrogen leakage happens, it will not harm the engine and the environment as it will disperse in less time, [68].

There is one major drawback regarding this property. Hydrogen has a relatively low density compared to methane and other

hydrocarbon gases and is about 14 times less than the air, about 0.083764 kg/m³ at standard pressure and temperature conditions, [73]. As mentioned above, it has a very low density; there can be several problems related to hydrogen fuel storage in the vehicle to provide an adequate driving range.

5.8 Other physical properties

Pure hydrogen is tasteless, odorless, and colorless. The hydrogen flame is almost colorless. So, it's difficult to detect small hydrogen fires than hydrocarbon flames. But their visibility can be improved by adding impurities and moistures to the air. However, large hydrogen fires can be detected by producing convection currents and a "shadow effect", [65]. A stream of hydrogen from a leak is almost invisible in daylight. Hydrogen is non-toxic but by displacing the oxygen in the air it can act as a simple asphyxiant. Small leaks pose little danger of asphyxiation in an enclosed area, since hydrogen diffuses rapidly to fill the volume, large leaks of hydrogen can be a serious problem which need to deal with. Due to hydrogen's high diffusivity and buoyancy the potential for asphyxiation in unconfined areas is almost negligible, [66].

6. Hydrogen in IC engines

Research in progress in most developed countries on hydrogen in IC engines. Several researchers around the globe are working on this technology to make it comfortable for daily use. Hydrogen has a wide range of flammability limits compared with other fuels, making it reliable for IC engine use. However, several limitations come with hydrogen fuel. Broadly they fall into two categories.
1) Hydrogen in CI engines
2) Hydrogen in SI engines
3) Hydrogen as a supplement fuel with other fuels.

The first one is very familiar as hydrogen's properties are highly suited for SI engine mode operation. Anyhow, researchers are going around the world to operate in SI and CI modes.

6.1 Hydrogen in CI engines

CI engines can be used in applications where power output is high, vehicle traction is heavy, and stationary power supply units are required. The outstanding efficiency is the noticeable property of compression ignition engines, which motivates the researchers to work on the CI mode operation of hydrogen engines. There are two methods for feeding hydrogen into the CI engine. They are

1. Inducting the hydrogen through the suction process.
2. Direct injection of hydrogen into the cylinder.
The self-ignition temperature (SIT) of CI engine fuel is an important parameter that affects combustion by compression. The SIT of hydrogen is 858K (576ºC). This means it is challenging to ignite hydrogen by the compression ignition process. Due to this property, hydrogen is unsuitable fuel for conventional diesel engines. Attempts by several research workers have confirmed this. Researchers at Cornell University failed to achieve the compression ignition of hydrogen at a compression ratio as high as 29, [74]. So, for ensuring hydrogen combustion inside the cylinder, a secondary ignition source is necessary. The following are methods employed for igniting the hydrogen inside the cylinder
1. By introducing hydrogen into the air and using a spray of lower SIT oil like diesel to ignite the mixture by the Dual fuel mode. In this method, hydrogen is inducted into the air, compressed, and then ignited by a spray of secondary oil.

2. By injecting hydrogen directly into the cylinder at the end of

compression. Since the self-ignition temperature of hydrogen is very high, the gas spray is made to impinge on a hot glow plug in the combustion chamber-that is by surface ignition. This is because of hydrogen's lower ignition energy necessity.

6.1.1 Hydrogen Induction

The method of hydrogen induction is carried out as research work at IIT Madras, [75]. The Hydrogen was inducted in a single cylinder diesel engine (5 hp) with a combination of air and employed a pilot spray of diesel oil for the ignition of the mixture. This mentioned method is simple and flexible as the traditional diesel engine can be converted to work via this method. Here the Hydrogen was supplied to the inlet manifold of the engine. An exemplary control needle valve was used to adjust the flow rate of Hydrogen to any desired value. The diesel was injected directly into the engine with a conventional injector. The test was conducted with a constant engine speed of 1500rpm. The flowrate of diesel oil to engines was held at fixed values. Hydrogen was then introduced at a predetermined flow rate. Thus, the engine output was varied. The goal of this test was to evaluate the optimum amount of diesel to hydrogen. Another goal was to achieve engine operation with minimal injection of pilot fuel. The results show similar thermal efficiency of dual-fuel and diesel for the whole operation range.

Figure 22 shows the variation of brake thermal efficiency with increased hydrogen flow rates while keeping the pilot diesel flow rates constant. There is a smooth and robust rise in thermal efficiency with an increase in hydrogen induction for low diesel flow rates. At high flow rates of diesel, rise in thermal efficiency becomes less. At the highest tried rate of flow of diesel, practically no change in the thermal efficiency with induction of hydrogen was observed. Hence, overall, the hydrogen dual-fuel engine behaves similar to the standard diesel engine. The output of this engine is limited by knocking. The result has a directly proportional increase with the hydrogen flow rate. Beyond a specific value, highly violent combustion is observed because the hydrogen-air mixture is very. This was the

major shortcoming experienced in that experiment.

The researchers from IIT Delhi found a solution for knocking in the hydrogen induction technique in the CI engine, [74]. They also tried with the diesel pilot injector for igniting the gaseous Hydrogen. The objective of that work was to substitute the Hydrogen to the maximum possible extent without sacrificing the engine performance. After the severe test was conducted, the symptom of knock was noticed. For controlling this problem, diluents with various proportions were tried. Introduction of nitrogen, water and helium in the system as diluents in different ratios, in order to carry knock-free operation. In all these tests, the amounts of the specific diluents were evaluated for carrying out high knock-limited power output along with a maximum level of hydrogen energy substitution. The presence of such diluents improved the knock which limited engine output.

Via a study regarding comparison of the 3 diluents it was observed that conversion of engines to dual-fuel mode of 38% of full-load can be achieved without sacrificing performance parameters such as efficiency and power. The finest diluent for smooth engine operation was nitrogen. Only 30% of nitrogen by volume was utilized for carrying out engine operations at highest power output with maximum thermal efficiency while no knocking was observed. 10% of helium by volume of Hydrogen was observed to be best for operation of. Its further addition did not provide any significant improvement. Moreover, water was observed as a greater diluent in case of exhaust emission. With the help of continuous exhaustive tests, it was concluded that the maximum level of hydrogen-energy substitution is achieved at 2460 ppm of, that is about 66% in absence of any undesired combustion phenomenon. Negligible loss in efficiency and power was observed. In a study it was observed that the material is compatible and can be safely adopted in this configuration. Figure 23 shows the significant reduction in diesel consumption when water is used as a diluent, ensuring long-term application and fuel saving.

Though people find Hydrogen as a poor fuel for CI engines, some research recently done proved that compression ignition of Hydrogen is feasible. People from Sandia National Laboratories simulated the

combustion chamber TDC conditions and examined the ignitability of Hydrogen, [77]. The results show that the Hydrogen can be auto-ignited comfortably above the temperature of 1120K. But the ignition was observed to be insensitive to the pressure inside the combustion chamber. The dependency of fuel temperature on ignition delay was found to be less. Also, the oxygen concentration between 5 to 30% had not significantly increased the ignition delay. This is a desirable property as reducing the oxygen concentration reduces the NOx emissions. So reasonably good combustion with minor delay can be achieved with compression temperature above 1100 and 5 to 21% oxygen concentration.

An experimental analysis of the effect of pilot fuel injection operating pressure in Hydrogen blended compression ignition engine was conducted rendering that the use of 100% hydrogen in a CI engine isn't feasible to even at as high a compression ratio as 29 because it has a self-ignition temperature of 576 degrees Celsius and therefore dual fuel method is used, the experimental investigation of dual fuel mode rendered results that, after the addition of hydrogen, the thermal brake efficiency increases first and then decreases a bit, the nitrogen oxide formation occurs inside the combustion chamber because of the excess oxygen present and high combustion temperature which is favourable for the oxidation reaction, carbon monoxide is also found, while it's only present in exhaust engines. It's an outcome of incomplete combustion, which occurs because of insufficient air in the air-fuel mixture, [78]

Figure 24 shows the trend in Effect of Injection operating pressure on brake thermal efficiency. In compression ignition diesel engines, the investigation of hydrogen combustion under homogeneous charge compression ignition and hydrogen-diesel combustion in a compression ignition engine with various percentages of Hydrogen to study the engine's working gives the observations that, when low amounts of Hydrogen are added to the diesel engine, a shorter diesel ignition lag is observed, the compression engine ratio of a minimum of 16 is required, the knock is exceptionally high, and measures like leaning combustible mixture application should be adopted. The start of combustion is unstable. Moreover, it takes place early to bring about maximum brake torque. The addition of low quantity of

Hydrogen to diesel does not lead to knocking at levels that can damage the engine; it gives a soft engine run and may increase the durability of the engine, [79]

6.1.2 Dual fuel and its emission characteristics

The dual-fuel operation engine of diesel oil and Hydrogen was operated. Hydrogen was in the intake port while diesel was directly introduced inside the cylinder volume. The injection timing was iterated over a specific range; while the diesel fuel is advanced into the cylinder, the mixture of diesel and Hydrogen is better and mild initial combustion is observed. There was a decrease in NOx emissions due to lean premixed combustion sans the high-temperature region caused by the burning of gases. The mixing of Hydrogen led to reduced emissions of CO, CO_2 and HC in absence of exhausting smoke, but the breaking thermal efficiency was a bit lower than ordinary diesel combustion. It was observed that both NOx and smoke are negligible, and HC was standard when the injection timing was notably advanced, although the engine's operation became unstable. Ignition delay was observed in all conditions; heat release was similar to that of ordinary diesel operation, the combustion was very slow while heat release rate showed only one mild peak. Upon mixing Hydrogen with air, there was no exhaust smoke as Hydrogen does not have carbon atoms in its molecular structure, [80]

One of the methods employed for igniting the hydrogen inside the cylinder is using a spray of lower SIT oil like diesel to ignite the mixture by the Dual fuel operation mode. The impact of adding hydrogen to the CI engine fuelled with either RME (rapeseed methyl ester) or 7% RME blended diesel fuel (RME7) on ignition delay, and combustion process was studied, analysing hydrogen as secondary fuel of about 44% by energy. The analysis focused on engine performance, combustion properties, combustion duration, and toxic exhaust emissions. Positive trends were observed regarding maximum combustion pressure with increased hydrogen energy share. ISFC was observed to decrease with the increase in hydrogen energy share as shown in figure 25. An ignition lag was also observed. Another observation was the decrease in main combustion duration. Regarding the toxic exhaust emissions, the addition of hydrogen slightly reduced HC emissions at low loads,

while at higher loads, an increase in the emission of HC was observed. While in the case of NO, it's emission decreased up to 15% of hydrogen, a rise was observed after that. The addition of hydrogen was observed to increase the LHV of the entire combustion fuel, thus providing better conditions to obtain maximum combustion temperatures, [81]

Another dual fuel mode development that looked forward to advanced engine performance and reduction in emissions of smoke was observed in a study where hydrogen injection in the intake manifold as primary fuel was accompanied by indirect injection of Madhuca Longifolia oil. The engine's performance was observed to increase from 25% with 100% ML operation to 28.5% with hydrogen dual-fuel mode. However, this process resulted in knocking, thus leading to a direct impact on BTE. Hence, using the water injection method to extend the knock and increase hydrogen energy share was brought about. About 18% and 76% improvements were observed in BTE and smoke emission with 5% of water using mass fraction with H2. The hydrogen energy share was also increased from 6% to 8.5%, with 5% WI. The engine's overall performance was also observed to be improved via extending the knocking limit, WI and auto liquefied petroleum gas. Here, the primary fuel, i.e, hydrogen, was injected into the cylinder at the suction stroke while the pilot fuel, which was ML or diesel, was directly injected into the cylinder at the end of the compression stroke, leading to the initiation of combustion. The pilot fuel was injected first, acting as an ignition source for the air-hydrogen mixture. If the sequence was reversed, it resulted in knocking; the main reasons for knocking in a hydrogen-based dual-fuel engine were its wide flammability, less ignition energy and small quenching distance. Regarding the emission characteristics, it was observed that the smoke value decreased in the case of dual fuel mode compared to neat ML and Diesel. In the case of hydrogen being used as primary fuel, the emission decreased from 84% with 0% HES to 37% with 6.5% HES. The dual-fuel mixture of hydrogen and ML or hydrogen or diesel, through enrichment with ALPG and WI techniques to counter knocking, is one of the most promising concepts in the hydrogen CI engine, [82]

There is a drop in vibrations and noise levels with the addition of hydrogen, but at higher loads, the vibrations in the engine are seen to increase due to the active involvement of hydrogen in combustion. Thus, hydrogen addition is advantageous at mid-range and low loads. An increase in hydrogen combustion efficiency is also observed at higher loads, [83]

6.1.3 Direct Injection System and emission characteristics

Analysis utilizing a four-stroke, single-cylinder, air-cooled, stationary direct injection diesel engine of 4.4 kW and speed 1500 rpm with variable injection timings and hydrogen flow rates depicted that engine enriched by hydrogen gave minimum brake specific consumption and max brake thermal efficiency at around 70% load. The exhaust gas temperature was high because of enhanced combustion rates. An increase in NOx was observed due to this temperature rise which can be dealt with EGR, while other emissions reduced due unavailability of carbon in hydrogen gas, [84]

The combination of ABE port injection and direct hydrogen injection led to the formation of a layered state of the hydrogen-rich mixture around the spark-plug; this increased max cylinder pressure, max cylinder temperature, IMEP and the max heat release rate while there was a decrease in exhaust temperature. There was a distinct decrease observed in particle emissions, the combustion properties of ABE changed and an improvement in the test engine's power and emissions could be seen, [85]

6.1.4 Effect of waste exhaust heat on hydrogen production and its utilization in CI engine

One promising technology in the hydrogen CI engine is the use of waste heat in engine exhaust for producing hydrogen and its usage in CI engine, using a thermoelectric generator to convert the heat mentioned above to hydrogen gas with the help of PEM type fuel cell. By observation, we note that heat wasted from exhaust tends to increase with the increase in load, which improves the conversion efficiency of the thermoelectric generator, thus increasing the hydrogen flow rate. The induction of hydrogen helped achieve better brake thermal efficiency, an improvement of 10% compared to only diesel engine operation. It also helped reduce HC, CO and smoke emissions which contributed to a fall in diesel consumption, which is replaced by hydrogen. There is a slight increase in NOx emissions because of the rise

in in-cylinder temperature. The utilization of this system is achieved by storing hydrogen onboard in small containers, which would, in turn, reduce the weight of the vehicle and thus increase fuel efficiency, [86]

6.1.5 Thermal Efficiency of CI

For this investigation, the compression ratio was lowered from 18.25 to 16.9; this helped achieve a lower rate of heat release, max cylinder pressure, ringing intensity and max rate of pressure rise. Fluctuations in ignition delays are experienced with hydrogen enrichment while combustion durations also increase. It is observed that the enrichment of hydrogen firstly increases the brake thermal efficiency and then decreases the same of the low compression ratio engine; the ringing intensity is seen to increase with the rise in load and the amount of hydrogen, [87]

6.2 Hydrogen Supplementation

The successful commercial adoption of hydrogen as a fuel is still a long way off due to the current high cost of hydrogen and the high purity hydrogen needs of existing fuel cell technology. As a result of this predicament, a strategy for the earlier commercialization of hydrogen as a fuel is required. This technique entails combining hydrogen with other low-cost internal combustion engine fuels. As previously stated, hydrogen is an excellent fuel additive. It improves the combustion qualities of a wide range of fuels. The addition of hydrogen to a sufficient degree improves the lean limit of fuel combustion. It also increases the efficiency of low-flame-speed fuels by improving their flame velocity. In addition, employing hydrogen as a small-scale supplement fuel eliminates the difficulty of hydrogen storage. The impact of adding hydrogen to compressed natural gas (CNG), vegetable oil, and ethanol is described in depth here.

6.2.1 Hydrogen supplementation with natural gas

Natural gas or CNG vehicles are a potential alternative to gasoline vehicles in the short term. They are less polluting, and the fuel is widely available. However, natural gas has been run on a hydrogen natural gas mixture to reduce its pollutants further. Methane is the principal constituent of natural gas. The term "Hythane" denotes a specified proportion of this mixture. Hythane is a mixture of 20% by volume of H2 and rest CH4 and was trademarked by Hydrogen Consultants Inc. HCNG denotes it.

Natural gas has high SIT, mainly operating on SI engine mode. Much of the spark-ignition engines so far developed works in stoichiometric mixtures. Lean burn mixtures have some distinct benefits when running on long-term needs. It has high efficiency and lower NOx emissions. Also, the knock proneness of the lean mixture is relatively low. The lean mixture operates at higher compression ratios with less heat transfer. But a lean mixture suffers some severe drawbacks. The cyclic variation in lean mixtures is very high. Also, it has slow flame propagation, less complete combustion, and sometimes even flame failure may occur. Lean mixture results in reduced engine power. These shortcomings may sometimes over dominate the benefits of lean mixtures and lead to poor efficiency and emission control. So, to improve the engine's combustion speed with lean mixtures, we can go for spark advance, increase turbulence, and improve combustion chamber design. But these factors may alter the peak pressure and temperature, resulting in high NOx and penalties with high turbulence. So, the best solution is to use an additive to improve engine features to use lean mixtures.

Because of its particular properties, hydrogen is a good addition to methane or gasoline. An analysis of the parameters in Table 2 reveals that hydrogen can burn ultra-lean at a 1:0.1 equivalency ratio. Methane and gasoline, on the other hand, have equivalency ratios of 0.53 and 0.70, respectively. Figure 26 shows how hydrogen improves the lean limit of methane. With the addition of 10% hydrogen, the flammability constraints are enhanced.

The burning speed of a hydrogen flame (265 to 325 cm/s) is around seven times faster than that of methane or gasoline, resulting in a shorter burn. A hydrogen flame transfers less heat than a methane or gasoline flame due to its shorter burn period. The quenching distance of hydrogen is approximately 1/3 that of methane or gasoline (typically defined as the lowest spacing between parallel plates in which a flame will propagate, [89]). Based on flame temperatures in the air, hydrogen burns hotter (2318 K) than methane (2148 K) but cooler than gasoline (2470 K). Figures 27 and 28 show how adding hydrogen to methane improves flame initiation and propagation under two turbulent conditions (quantified by Reynolds number), and figure 28 shows how flame propagation speed varies for various equivalence ratios for

pure methane fuel and methane-hydrogen blends under two turbulent conditions.

Despite having a higher stoichiometric air-to-fuel ratio than methane (0.095) or gasoline, hydrogen occupies a larger fraction of volume in relation to air (0.290). (0.018). As a result of the low volumetric LHV of hydrogen, stoichiometric hydrogen-air mixtures contain somewhat less energy (approximately 2913 kJ/m3) than stoichiometric methane-air mixture (3088 kJ=m3) and stoichiometric gasoline-air mixture (3446 kJ=m3). For various equivalence ratios, [90], Figure 29 shows the variation in power produced by CFR engine with methane hydrogen blend. When compared to pure methane operation, the engine's power output is lower under stoichiometric conditions. The addition of hydrogen, on the other hand, boosts the engine's power output when the mixture is low. This is due to the fact that methane has a slow flame speed in lean conditions, and hydrogen speeds up the flame.

A full study on a 4.6-liter 8-cylinder production engine was conducted in 1996, [92]. The researchers looked at methane mixtures containing 0, 10, 20, 30, 40, and 50 percent hydrogen by volume. In the lean area at 1700 rpm, hydrogen addition increased NOx output while decreasing HC generation. The engine was tested at various speeds (1700, 2350, 3000 rpm) and loads in the case of a 30 percent hydrogen mixture with an equivalency ratio of 0.65. (brake mean effective pressures of 100 to 500 kPa). NOx production increased with increasing load and was found to be relatively independent of speed. The production of hydrocarbons was observed to decrease with increasing load, regardless of speed. At 2350 rpm, the thermal efficiency of the brakes was shown to improve when the load was increased. This instance did not examine various hydrogen mixes at varied equivalence ratios. The test was broadened in a follow-up publication, [93] to include 0, 30, and 100 percent hydrogen in methane mixtures in a one-cylinder research engine. At full load and 1800 rpm, the tests were conducted. The goal was to identify operating settings that produced NOx below the equivalent zero-emission vehicle (EZEV) limits without the use of a catalytic converter. While adjusting the spark time and equivalency ratio, NOx, power, and indicated thermal efficiency were measured. The 0 percent H2 mixture was tested with equivalent ratios ranging from 0.62 to 0.72, the 30% H2 mixture was tested with equivalence ratios ranging from 0.53 to 0.67, and the 100% H2 mixture was tested with equivalence ratios ranging from 0.35 to 0.45. The engine was determined to reach the EZEV limit for NOx of 8.9 ppm when operated with a 30% H2 mixture, an equivalency ratio of 0.53, and highest efficiency spark timing. The effect of engine speed or load was not investigated in this experiment. The partial burn restrictions were not attained despite the use of lean equivalency ratios. According to a study done on Wesport, the Westport HCNG engine modification reduced nitrous oxide (NOx) and non-methane hydrocarbon (nmHC) emissions by 50% when compared to exclusively natural gas operation on a steady-state heavy-duty test cycle, [94]. This was accomplished while maintaining the engine's performance and efficiency and resulting in a small reduction in carbon monoxide (CO) and methane (CH4) emissions. Furthermore, carbon dioxide (CO2) emissions have been cut by 7%. This means that, when compared to a bus with the most recent diesel engines certified to the US Environmental Protection Agency's 2002 emissions regulations, this bus would emit 65 percent less NOx, 80 percent less particulate matter (PM), and around 10 tonnes less greenhouse gases (GHG) each year. DOE, USA, performed an observation on a heavy-duty engine demonstrating that the CNG blend reduces NOx emissions by roughly 50%, [91].

The use of Moringa biodiesel as an additive in hydrogen–compressed natural gas (HCNG) engines resulted in a reduction in harmful gas emissions such as hydrocarbons and NOx. Five distinct Moringa biodiesel batches were tested in this investigation. The fuels had a fixed hydrogen-to-carbon ratio of 87:13 percent, while the HCNG–MB hybrid samples contained 0, 5, 7, 10, and 13 percent v/v Moringa biodiesel, respectively. The samples were labelled A, B, C, and D, in that order. The thermal efficiency of the brakes was found to be improved under higher engine loads, which improved the engine efficiency. The optimal fuel under ideal conditions is an MB–HCNG fuel combination with 10% MB. Up to the optimum value, which is defined by a fuel blend with 10% biodiesel in HCNG, a rise in BTE was seen, resulting in low BSFC. The BTE is affected by the fuel's inherent qualities such as calorific value, kinematic viscosity, cetane number, and low oxygen concentration. The

BTE decreases at low to medium engine loads, increasing brake specific fuel consumption and resulting in a rise in cylinder temperature at high engine loads. The emission of HC was found to be lower in mixed fuel than in unblended fuel. Furthermore, the emission was discovered to include at least 10% Morgana biodiesel blended gasoline. The incomplete combustion of fuel inside the combustion chamber causes HC emissions. The HC emission reduces as the engine load rises; this could be due to an increase in gas temperature, which helps to oxidise the unburned HC, [95].

Hydrogen enrichment between 10% and 30% by volume with natural gas was investigated in a study on a 1.5-litre 4-cylinder port injection naturally aspirated gasoline SI engine. The findings revealed that hydrogen enrichment leads to higher volumetric efficiency and thus greater power. Furthermore, at low speeds, the high enrichment factor is more advantageous in terms of power output, and exhaust emissions of CO, CO2, and unburned hydrocarbons drop as the infraction increases. In terms of enrichment benefits, a speed of 3000rpm was found to be ideal. At low speeds, the High enrichment fraction is proven to be more advantageous. As a result, the enrichment should be between 10% and 20% to maintain good BEMP. Furthermore, as enrichment progressed, UHC and CO emissions decreased. At 4000rpm, a dramatic decline in CO2 was detected, with a hydrogen proportion of 26 to 30 percent. As a result, a homogenous HCNG engine should be operated between 2000 and 4000 pm to reap the benefits of hydrogen enrichment, [96].

The impact of hydrogen addition on different aspects such as operating range, emissions, and efficiency in lean-burn natural gas engines at high specific loads was examined using a single-cylinder research gas engine with a displacement of 4.77 L. Even with tiny concentrations of H2, the results demonstrated that the addition of H2 has a substantial impact on the operating range and emissions; pre-ignition phenomena are restricting the operating range at richer circumstances with increasing H2 amounts. Furthermore, due to improved combustion, NOx emissions increased but unburned hydrocarbon (UHC) and formaldehyde (HCHO) emissions decreased. It may thus be argued that the reduction in THC emissions produced by enhanced combustion is greater than the reduction generated by a lower hydrocarbon content in the fuel. At a constant NOx emission, the efficiency increases as the operating conditions become leaner. Poorer NOx levels result in lower efficiencies, demonstrating a trade-off between NOx and efficiency. The effect of H2 addition on efficiency is more helpful at lower NOx emission levels, [97], but the effect of H2 addition on efficiency is more advantageous over the full air/fuel ratio.

The study investigated the impact of a high hydrogen volumetric ratio of 55 percent on performance and emission characteristics in a turbocharged lean-burn natural gas engine using a six-cylinder, single-point injection SI NG engine. The test was carried out under a variety of settings, including varied spark timing, surplus air ratio, and manifold pressure. It was discovered that adding hydrogen at a high volumetric ratio increased the lean burn limit, enhanced the engine's lean-burn ability, reduced burn length, and increased thermal efficiency. By delaying ignition timings from MBT spark timings, increased hydrogen addition was found to reduce COVimep (coefficient of variation of IMEP) at all ignition timings. The power indicated thermal efficiency and NOx emission increased as manifold absolute pressures increased, but flame development and flame propagation duration and COVimep, CO emission decreased. The addition of 55 percent hydrogen extended the lean limit to an excess air ratio of 2.5, compared to 1.71 for pure NG and 2.09 for 30 percent HCNG, [98], due to hydrogen's broader burn limit and high burn speed.

6.2.2 Hydrogen supplementation with ethanol

Ethanol is becoming more widely recognised as a renewable motor fuel. Locally grown vegetables, waste papers, grass, and tree trimmings can all be used to make it. However, ethanol has a lower calorific value than gasoline. As a result, ethanol-fueled engines produce less power than gasoline-fueled engines. Adding hydrogen in a smaller amount increases the charge's power density as hydrogen has higher calorific values, [99, 100, 101]. Research work on the Recardo E6/US carbureted single-cylinder engine shows that adding hydrogen with methanol improves the engine's performance compared with the gasoline engine of the same type. The experimental setup used is shown in figure 30. The ethanol was supplied to the carburettor like

conventional gasoline. The atomised ethanol was carried by the air stream. Hydrogen was supplied in the gaseous form after the venture and before the throttle valve. Then, this hydrogen ethanol blend was supplied to the engine.

The hydrogen ethanol engine was operated on stoichiometric mixtures with MBT and compression ratio varying from 7-12 at 1500 rpm. Gasoline fuel was used as a baseline for comparison. The effect of dual supplemented fuel on emission is better understood by the figure 31 and 32.

From the figure, the NOx concentration increases with hydrogen addition. This is due to the peak temperature produced by hydrogen combustion with a higher rate of pressure rise. Also, the time available for NO dissociation to N2 and O2 is becoming less with hydrogen addition. As shown in figure 32, adding hydrogen beyond 4% mass will give more NOx emission than a similar gasoline engine. So, for NOx free operation, the hydrogen percentage should not exceed 4. Also, it's clear from the figure that the ethanol addition decreases the NOx emission due to its higher enthalpy of evaporation, resulting in a lesser peak temperature.

As shown in figure 33 addition of hydrogen decreases the CO emission. This is because of the decrease in carbon atom concentration with an increase in hydrogen. Also, the addition of hydrogen improves the molecular diffusivity of the charge and improves the combustion efficiency.

The following figure 34 shows the Specific fuel consumption of dual-fuelled engines with increasing hydrogen percentage.

It has been noted that the alcohol-fuelled engine has poor SFC characteristics because of its low heating value. The addition of hydrogen with ethanol increases the charge heating value and thus lowers the SFC considerably.

The following trend in figure 35 shows the variation in power with hydrogen addition.

The alcohol engine develops 6% more power than the gasoline engine because of its high charge density and good volumetric efficiency. The hydrogen induction still improves the power because the combustion approaches constant volume mode with a higher burning rate. But more addition of hydrogen reduces the volumetric efficiency and reduces the power.

Considering all the above-said factors, a safe operating zone was developed for the hydrogen ethanol blend, [101]. The engine in this zone gives sufficient power with minimum SFC, NOx and CO emissions. The shaded area indicates the safe operating zone in the following figure 36.

The performance of a hydrogen-enriched ethanol engine under unthrottled and lean circumstances was investigated in a study. The engine utilised was a single cylinder that ran at 1400 rpm and was not throttled. The hydrogen volume percentages in the intake were maintained at 0% and 3%, respectively. To enable the engine to function under lean conditions, the ethanol flow rate was lowered for a particular hydrogen blending level. The engine efficiency was enhanced by blending hydrogen into the intake air, according to observations and findings obtained, and the highest thermal efficiency was improved by 6.07 percent after blending 3 percent hydrogen into the intake air. Following hydrogen enrichment and the use of a lean combustion strategy, both cooling and exhaust losses were reduced. After combining hydrogen, HC and CO emissions were reduced, while NOx emissions were raised. The energy of the mixture is reduced as the excess air ratio is increased; increasing the excess air ratio lowers the BMEP for both 0 and 3 percent hydrogen-enriched ethanol engines. Because of the lower BMEP, the engine torque may be adjusted within a certain range by altering the extra air ratio. This opens up the possibility of running the engine without a throttle and managing the load by adjusting the extra air ratio. It was also discovered that the 3% hydrogen-blended ethanol engine had a greater braking thermal efficiency than the pure ethanol engine. After hydrogen enrichment and the application of a small combustion strategy, both cooling and ventilation losses are reduced. After combining hydrogen emissions, HC and CO were reduced, while NOx emissions were increased. The strength of the mixture is reduced as the amount of excess air increases; increasing the amount of excess air lowers BMEP in both 0 and 3 percent hydrogen-powered ethanol engines. Due to low BMEP, engine torque may be adjusted within a certain distance by changing the air intake further. This opens up the possibility of using the engine without the throttle and loading the load by adjusting the volume of the extra air. It was also found that a 3% hydrogen-based ethanol engine has a higher braking capacity than a pure ethanol engine.

The addition of hydrogen helps improve brake mean adequate pressure only at lean conditions, [102].

Research has been done on the effect of adding hydrogen to ethanol to the Wankel mono-rotor engine in the open throttle area and the active ultra-lean state. The engine speed was maintained at a constant range of 3000 rpm with a fixed spark time of 15degree BTDC. Experimental results have shown that hydrogen enrichment improves the combustion process by reducing flame development and flame distribution times and reducing cycle variability. In addition, hydrogen supplementation helps increase IMEP and lowers COVimep at high temperatures and the fixed span time. Also, it was noted that when the hydrogen energy level increased from 0% to 18%, HC and mono carbon (CO) emissions decreased by 85.5% and 50%, respectively, while emissions. Direct CO_2 decreased by 32.6%. Wankel engine heat efficiency improved by about 14.12% by adding a fraction of 18% hydrogen to the ethanol fuel mixture, thereby lowering the BSFC by 27.91%, [103].

The use of pre-chambers can reduce burning time by 20% and increase thermal efficiency by 5%. In addition, it can reduce CO and NOx emissions by 12% and 33%, respectively, [104].

6.2.3 Hydrogen with vegetable oil

Vegetable oil is another good way to use IC engines. The engines have already been tested with various vegetable oils and got good results. Includes karanji oil, rapeseed oil, rice bran oil, cottonseed oil, Jatropha oil etc. But there are natural problems associated with vegetable oil engines. Vegetable oils naturally do not change well. Therefore, the evaporation of these oils is very bad. Also, due to the high viscosity, they provide high flow resistance. Unclaimed hydrocarbon chains in vegetable oils form a high humidity during burning. Vegetable oils pose a major hurdle as they create high carbon deposits and ring adhesions.

The work done on the IC engine lab IIT madras shows that hydrogen can be used effectively as a fuel supplement in vegetable oils to overcome vegetable oil limitations. In that work, hydrogen was added along with air and vegetable oils injected directly into the cylinder, [105]. The parameters for the operation, combustion, and discharge of emissions are calculated by the various major hydrogen components. The following figure 37 shows the differences in the efficiency of combustion of brakes with different components of hydrogen input weight and different load conditions.

The addition of hydrogen at part load is decreasing the efficiency. This is because the amount of hydrogen inducted at the part load will be low. This lean mixture won't get adequately ignited. So, the combustion efficiency will be lower. But, after 50% load, hydrogen improves the combustion efficiency. At 100% load, the efficiency is improved from 27.3 to 29.4 at 7% hydrogen mass share. Further Addition of hydrogen reduces the efficiency because the combustion becomes abrupt with hydrogen addition beyond a certain level.

The following figure 38 shows the variation of volumetric efficiency with the hydrogen addition.

The volumetric efficiency shows a reducing trend with hydrogen induction as hydrogen displaces some amount of air and thus reduces the mass of the charge in every cycle.

In partial loading, the addition of hydrogen reduces the maximum pressure. This is due to the very small mixture, and the ignition source is also not very powerful as the driver number is small. However, at higher loads, the addition of hydrogen increases the higher pressure as we expected.

Smoke is reduced by the addition of hydrogen. This is because the added hydrogen forms the same compounds, and burns much faster. Also, the whole mixture contains a small amount of carbon from which smoke can form. The release of unburned hydrocarbon also decreases with the addition of hydrogen. Hydrogen burning increases the temperature, leading to complete oxidation of injected jatropha oil.

Similarly, CO emissions indicate a downtrend with hydrogen induction. The only contradictory mechanism in the extraction curve was seen in NOx through hydrogen ingestion. NOx increases due to high temperatures caused by hydrogen combustion. Therefore, steps should be taken to control NOx emissions while hydrogen supplementation with vegetable oils.

Research is being done to investigate the effectiveness of hydrogen ethanol engines in both volatile and degraded environments. The engine used was a single cylinder and was running at 1400 rpm and under unchanged conditions. The hydrogen volume components

in the take are kept at 0% and 3%. The flow rate of ethanol is reduced to a given level of hydrogen bonding so that the engine can operate under mild conditions. By observation and results obtained, engine efficiency has been enhanced by hydrogen mixing and high temperature efficiency was improved by 6.07% after combining 3% hydrogen in the air you take. Both cooling and ventilation losses are reduced after hydrogen enrichment while using a low combustion strategy. HC and CO emissions are reduced, while NOx emissions increase after hydrogen synthesis. Energy concentrations are reduced by increasing the amount of excess air; an increase in the amount of excess air causes a decrease in BMEP in both 0% and 3% hydrogen-based ethanol engines. Reduced BMEP indicates that engine torque can be controlled at a distance by adjusting the air pressure. This provides excellent power to operate the engine under a fixed condition and to control its load by changing the excess air intensity. Also, it was noted that a 3% hydrogen-based ethanol engine experienced better thermal performance than a pure ethanol engine. The addition of hydrogen helps to improve the brake means the pressure is only effective in soft conditions, [106].

Research has been done on the effect of adding hydrogen to ethanol to the monorotor Wankel engine in the open throttle area and the ultra-lean operating state. The engine speed was maintained at a constant range of 3000 rpm with a fixed spark time of 15degree BTDC. Experimental results have shown that hydrogen enrichment improves the combustion process by reducing flame development and flame distribution times and reducing cycle variability. In addition, hydrogen supplementation helps increase IMEP and lowers COVimep at high temperatures and the fixed span time. Also, it was noted that when the hydrogen energy level increased from 0% to 18%, HC and m carbon CO emissions decreased by 85.5% and 50%, respectively, while direct CO2 emissions decreased. at 32.6%. The Wankel engine heat efficiency improved by about 14.12% by adding a fraction of 18% hydrogen to the ethanol fuel mixture, thereby lowering the BSEC by 27.91%, [107]. The use of pre-chambers can reduce burn time by 20% and increase thermal efficiency by 5%. In addition, it can reduce CO and NOx emissions by 12% and 33%, respectively, [108].

6.3 Hydrogen in SI engine

As mentioned earlier, Hydrogen is an excellent fuel for SI engine applications. Hydrogen is a perfect candidate for the SI engine because its highly desirable and unique properties are inherently suited for the SI engine. The wide burning limit, which gives less throttling loss, higher flame speed, good mixing, and high auto ignition temperature, highlights some of the properties. The fast-burning feature allows much more satisfactory high-speed engine operation; due to this stable lean mixture allowed in hydrogen fueled engines. There is no carbon monoxide, unburned hydrocarbons, smoke particulates and oxide of Sulphur, when it comes to the contribution of hydrogen fuel SI Engine. The broad research of Hydrogen fueled SI engines may lead to a superior engine and successful marketing of hydrogen engines. Researchers are receiving encouraging results worldwide while trying for a hydrogen-fueled spark-ignition engine.

However, there are some technical challenges to be faced before commercializing hydrogen engines in the market. The Backfire and Preignition are the two critical barriers in the way. People are suggesting some possible solutions, and still, it has to go more to eliminate these problems. Choosing an effective injection method, spark plug, catalysts, and engine design can lead to a worthier SI engine. Power developed by the engine gets reduced and a substantial amount of air gets displayed because of the large volume which is getting occupied by hydrogen. Additionally, NO_x emissions get formed at higher rates and increase in higher peak temperature is a consequence of higher burning rates of hydrogen.

6.3.1 Fuel metering system

The fuel metering system plays a magnificent role in the hydrogen-fueled spark-ignition engine. By choosing the correct way of fuel delivery system, some anomalies can be reduced, and the engine's efficiency can be increased, making it more suitable for H2ICE, [109]

The following are some of the fuel induction systems tried by the researchers for fuel supply to the engine.

1) Central injection method

2)	Manifold injection and intake port injection method

3)	Direct in-cylinder injection method

### 6.3.1.1	Carburetion/Central	injection method

Central injection method is one of the oldest, supreme and simplest methods of delivering the fuel to a hydrogen engine by using a gas carburettor. This system has many benefits over other fuel delivering techniques. At first, higher hydrogen supply pressure is not needed in the main injection method. Secondly, the carburettors or central injection technique is used on gasoline engines, on account of this standard gasoline engine is converted into a hydrogen engine easily. A figure describing fuel carburetion technique is displayed in figure 39 below.

Low mean effective pressure is occurred when compared to gasoline engines due to low density of hydrogen resulting in a displacement of around 30% of the aspirated air with external mixture formation and stoichiometric air/fuel ratios. For air displacement by hydrogen, enrichment beyond the stoichiometric ratio will not yield any improvement in IMEP. The maximum power produced by that engine will be approximately one third less than port fuel injected gasoline engines, [111]. With supercharging, the power output of the engine can be improved slightly. The charging pressure improvement is also limited by the peak pressure, which is determined by the mechanical limits of the engine. A diagram illustrating the volume occupied by hydrogen relative to the volume occupied by gasoline vapor in the combustion chamber is shown in figure 40.

Due to the anomalies like pre-ignition and backfire, it is more susceptible to irregular combustion and is one of the primary drawbacks while developing a central injection method. The disadvantage of central injection is that it is more susceptible to irregular combustion due to pre-ignition and backfire. The more significant amount of hydrogen/air mixture within the intake manifold compounds the effects of pre-ignition. If combustion happens while the inlet valve is open, the flame can propagate into the inlet manifold, and it can burn the fuel-air mixture, resulting in severe damage to the engine parts, [113]. So, carburetion gives rise to irregular and uncontrolled combustion and unscheduled points while running engine cycle which leads to disturbance in the engine cycle, making it less efficient, [114].

6.3.1.2 Manifold injection and intake port injection method

Apart from carburetion, hydrogen can be supplied through manifold injection. The manifold injection system is mainly divided into single and multipoint injection. In the single point manifold injection method, fuel is sprayed at one location at the Centre inlet of the engine's intake manifold, and in the multipoint manifold, injection fuel is sprayed at more than one location, [115]. An injector located on the inlet manifold continuously inject the hydrogen, and the air coming through the manifold mixes with the hydrogen and the mixture is supplied to the combustion chamber during the suction stroke. As the hydrogen has good diffusivity, mixing will be perfect. The technique is termed a continuous manifold injection (CMI), [74]. But, in continuous manifold injection, the hydrogen did not show a considerably different response from the carburetion method, [114].

In the manifold injection method, air-fuel mixing takes place into the manifold chamber and an ignitable mixture enters the cylinder. The mixture finds enough time to get in contact with the hot spots formed in the combustion chamber. Depending on the pressure oscillations in the manifold, more or less the mixture remains in the manifold after the inlet valve closes. The quality and amount of this mixture varies in every cycle. So, this mixture is responsible for most of the anomalies like backfire as it gets in contact with hot residuals just after the inlet valve opens.

An alternate approach was tried for eliminating the problems with continuous manifold injection. The method is called "Timed manifold injection" (TMI), [116]. With the test conducted in IIT Delhi, it was shown that over a wide range of speed of equivalence ratio with TMI, the engine was able to run smoother when compared to CMI. The system was designed in such a way that the intake manifold did not accommodate any combustible mixtures during the intake valve opening. This system ensures air induction

before fuel induction. This provided a pre-cooling effect and thus rendered the pre-ignition sources ineffective. It will help to dilute and quench the residual combustion products which remain after combustion in the combustion chamber near TDC. A hydrogen fueled engine acquiring the TMI method will benefit both the CI and SI engines. This method improves fuel distribution in the cylinder cycle, increases volumetric efficiency, reduces loss of fuel and reduces the risk of abnormal combustion, [115]. In the duration of the conducted test, it was concluded that the system possessed the unique capability of diesel-like quality governing and matching the thermal efficiency of a diesel engine while developing the specific power output of an SI engine. Variation of indicated thermal efficiency with equivalence ratio for TMI and CMI are shown below in figure 41.

Quality governing can be appropriately accepted with this manifold injection technique which is the primary advantage over the carburetion. As here, the air takes and fuel delivery rates are independent of each other. The figure 42 mentioned below illustrates the schematic diagram of the inlet manifold and intake port injection technique.

The hydrogen is injected through the injector near the inlet valve in intake port injection. Power output can be dominated by introducing more quantity of respective fuel in the stream of air, [110]. Fuel can be metered by two methods in the intake port injection process by changing injection time-span via controlling the signal pulse to the injector and by varying the injection pressure of the hydrogen, [117]. With this, an extremely rich but non-ignitable mixture enters into the chamber. As a mixing of hydrogen and air happens in the cylinder, hot residuals get diluted before mixing happens and backfire anomaly can be avoided totally. As a consequence of the charging effect of the injection pressure, port injection of the hydrogen over the valves evolves in an elevated cylinder pressure. If the end of injection is significantly before inlet valve close timing, this will lead to backflow in the following cycle. So, in order to prevent backflow, the injection should be timed.

In the intake port injection kind hydrogen engine, the backfiring problem is controlled up to some extent. But, the power loss due to poor volumetric efficiency is still there. The volumetric efficiency of port injected hydrogen engine is about 60%, but the same is about 90% for a gasoline engine, [118].

6.3.1.3 Direct injection in-cylinder injection

In the direct injection technique, at the desired pressure hydrogen is introduced immediately into the combustion cylinder when the intake valves are closed, at the end of the compression stroke. As the diffusivity of hydrogen has a higher value than other fuels, the merging of hydrogen with the available air inside the chamber is instantaneous. But due to less mixing time for fuel and air into the combustion chamber, the mixture can be homogeneous, [109]. The burning rates of fuel mutate expeditious pressure rise, knocking and reducing NOx emissions. As hydrogen will be introduced in the combustion chamber only after intake valves are closed, this technique intrinsically precludes the backfiring problem, but it does not entirely resolve the pre-ignition problem. This internal mixture formation can additionally improve power density by displacing more air present in the cylinder by the low-density fuel hydrogen can be prevented.

There are two types of injectors that we can utilize in a direct injection method. The first type of injector is a low-pressure direct injector (LPDI) which inserts fuel instantly when the pressure is low in the chamber and when the intake valve closes, and the second type of fuel injector is a high-pressure direct injector (HPDI) which introduce fuel when the pressure is high in the chamber at the end of the compression stroke, [113]. The Schematic diagram illustrating direct injection operation is displayed below in figure 43.

So far, the Direct injection system is the highly compatible injection method when compared to other injection techniques used for hydrogen as a fuel. The power output will be 42% over a hydrogen engine using a carburetor technique and 20% more than a gasoline powered engine, [109], [113]

The in-cylinder direct injection has been identified as the excellent fuel supply method as it does not have the problems of either abnormal combustion or power reduction. although, the thermal efficiency is low at low fuel/air equivalence ratios, and operation stability deteriorates, [119]. It's a highly complex task to design the injector for this. Also, the design of the injector is more

complicated due to lubrication between injector moving parts, [113], and the injector should be able to withstand a very severe environment inside the combustion chamber during a continuous engine functioning.

Another issue with direct injection methods is that the time it takes for mixing air with hydrogen after injection is extremely concise. This may result in higher level of emissions due to incomplete combustion. So, generally, the engine's thermal efficiency will be poor with direct injection. The following figure 44 shows brake thermal efficiency with TMI and low-pressure DI techniques.

The following figure 45 shows BMEP variation with speed for comparing TMI and low-pressure direct injection.

The in-cylinder injection inherently eliminates the problem of backfire as there is no combustible mixture behind the inlet valve. But complete combustion can never be achieved throughout the engine operation phase. So, the direct-injection system is one of the most realistic and less compromising techniques suggested by the researchers, [120].

A study was conducted by X. Liu et al. to compare in-cylinder pressure, efficiency, and engine-out emission of a port-injected and direct-injected dual-fuel combustion of hydrogen and diesel in a small-bore single-cylinder diesel engine at the same parameters. During the combustion process, by using a pressure transducer, in-cylinder pressure was recorded. The crank angle position was recorded and by using the rotary encoder, The crank angle position was recorded. Apparent heat release rate (AHRR), indicated mean effective pressure (IMEP) and indicated thermal efficiency were calculated by using in-cylinder pressure. Engine outlet emissions of NOx were recorded by a non-dispersive infrared (NDIR) gas analyzer, Carbon monoxide (CO) and unburned hydrocarbons were measured by using another NDIR gas analyzer. From the results, the peak in-cylinder pressure for port injection was recorded as 8.9MPa, and for direct injection, this value was 6.98MPa. Hence, this significant pressure ringing indicates the engine operation is unreliable and dangerous as this can cause severe damage to the engine parts. Low emission of unburned hydrocarbons and NOx is achieved in the direct injection technique compared to the port injection technique. However, using the pure hydrogen indirect

injection technique will lower CO emissions. Hence, the direct injection method is an effective and acceptable method for the SI engine, [121].

The trend in engine-out emissions of carbon monoxide, unburned hydrocarbons and nitrogen oxide is shown in figure 46.

6.3.2 Combustion anomalies

Hydrogen as a fuel in the IC engine is most likely to play a vital role in the automotive industry in the coming time because of its unique properties. But, with many advantages, there are some problems with the hydrogen IC engine. The major problem with the hydrogen engine is its undesirable combustion occurrence due to some properties of hydrogen. The exceedingly quick combustion rates of hydrogen lead to irregular and abnormal combustion, which leads to issues like knocking, preignition, and backfire, lessening the engine compatibility and restricting the engine's power output. These anomalies should be avoided to achieve superior engine performance. In this section of combustion anomalies, complications related to combustion in a hydrogen IC engine are listed and discussed briefly.

6.3.2.1 Knocking in SI engine

Knocking occurring in SI engines is one of the major barrier which is restricting the additional improvement of efficiency, increased power and limits the use of a wider range of fuels. Increased knocking intensity has a good relationship with a sizable quantity of end-gas and higher auto-ignition temperature, [122]. The onset of knock, which is caused mainly by the auto-ignition of the unburnt mixtures in the end gas region of the charge, involves exceedingly rapid rates of combustion of the fuel-air mixture, which is at any moment yet to be burned, extremely high cylinder pressure and temperature levels and increased emissions, increased heat transfer to the cylinder walls. After the flame front reaches the walls of the cylinder, knocking combustion involves an unexpected instant hike in pressure in the cylinder when the auto-ignition of the end-gas takes place. This sudden change of pressure affects the efficiency of the combustion and may cause high disturbance in performance of the engine and potential damage to the components of the engine when allowed to persist, [122]. The high amplitude pressure waves are the principal reason for the failure of the engine components due to a sudden increase

in mechanical stress. The frequencies of the oscillations accompanied with every resonant mode instantaneously following the knock depend on the geometry of the combustion chamber, position of auto-ignition and mean speed of sound, [123]. Accordingly, it is critically important to know the limiting conditions of its incidence under several sets of operating regions and conditions of designing to prevent the knocking. Knock-free operations are needed to be developed in order to improve the overall efficiency of the system. The following are the key factors affecting the knock in hydrogen engines, [124]

1. Spark timing
2. Compression ratio
3. Intake temperature

The figure 47 given below illustrates the effect of compression ratio on knocking.

The increase in compression ratio narrowed down the knock free operating region. So, the operating region is going to decrease with increasing CR. The rise in intake temperature further reduces the knock free operating region, thus imposing a suction temperature restriction. Also, advancing the spark timing enhances the knock. But the effect is lesser than that of the previous two factors. Thus, extreme care is needed in controlling the composition of the mixture for a satisfactory operation of an SI engine with hydrogen fuel. Furthermore, this is not as challenging when moderately low compression ratio and intake temperature are employed. To attain considerable engine performance while obtaining admirable power production, which is the primary concern of the controlling of engine combustions, a borderline knocking operation is worthwhile.

If we compare knocking in basic gasoline engine and H2 supplementation engine, it was found that the knock tendency of gasoline decreases notably as the air-fuel ratio increases. Leaning the mixture in the case of gasoline will reduce knock tendency, whereas at lean mixture condition, if hydrogen supplementation increases, it increases knock which is defined by the percentage of knocking cycles, [125]

S. Szwaja et al. conducted a study at Michigan Technology University to better understand the comparison of gasoline and hydrogen combustion in a SI engine. Here, analysis of hydrogen fuel combustion under knocking was compared with gasoline combustion. The compression ratio of 12:1 and stoichiometric air-fuel ratio was implemented. The single-cylinder CFR (cooperative fuel research) developed by the Waukesha motor company was selected for this study because of its robustness and versatile construction. One or two sensors are mainly used based on cylinder count and engine type. With the use of digital signal processing techniques, Each sensor can detect knocks from multiple cylinders. Many changes were created in the engine to achieve the study's essential conditions, like changing the compression ratio by modifying the piston; a latest intake manifold was also designed to assist distinct gasoline and hydrogen fuel injectors, electronic throttle, thermocouples and other sensors. A target-based rapid-prototyping system with electronic sensors and actuators was installed for monitoring and engine control. A diagram illustrating the CFR engine testbed is shown below in figure 48.

A small variance was observed in hydrogen and gasoline knocking. However, slightly higher frequencies were recorded in the case of hydrogen when compared with knocking of gasoline combustion. Apparently, skewness of the distribution lessened stoichiometric air-fuel ratio, when the overall knock level increased. Similar peak amplitude was seen in hydrogen and gasoline knock operation. From the results observed, it is concluded that hydrogen knock and gasoline knock can be treated as same for practical engine implementation, [123]

6.3.2.2 Pre-ignition

The distinctive properties of hydrogen-like wide flammability limit, low ignition energy and fast combustion speed are the main reasons for pre-ignition anomaly in hydrogen IC engines. As the mixture approaches stoichiometric ratio, the probability of pre-ignition increases eventually because of the generation of high cylinder pressure and temperature, [126] As the burning velocity of hydrogen is very high in value, it causes more heat transfer to the combustion chamber walls, which leads to extreme loss of heat to the coolant, [127].

The quenching distance of hydrogen is 0.64mm, which is very low compared to gasoline or other conventional fuels. Small quenching distance indicates difficulty in quenching flame, resulting in the generation of hotspots in the chamber, which later leads to pre-ignition or backfire phenomenon. Pre-ignition occurs during the compression stroke process when both valves are closed just before the spark plug ignites, [128]. The air-fuel

mixture ignites before spark plug ignition by contact with high-temperature areas in the combustion chamber, called hotspots. If there is a low risk of pre-ignition or knocking effects, we can increase the compression ratio, increasing thermal efficiency, [129].

Pre-ignition results in negative compression work, leading to decreased power output efficiency of the engine cycle. When pre-ignition occurs in the combustion cylinder, the temperature inside the combustion volume rises and therefore ends up with more hotspots, resulting in another earlier pre-ignition. This evolution of pre-ignition continues until backfire happens in the course of intake stroke, [127]. As the negative pressure work during pre-ignition decreases peak power by a significant amount, pre-ignition results in the generation of noise and vibration and eventually can stop the engine cycle. Also, it increases peak temperature in the chamber and will end up with high NOx emissions. Severe damage can take place to the engine components when pre-ignition occurs, [128].

6.3.2.3 Backfire Causative Phenomena

The high flame speed, low ignition energy and wide range of flammability limits make the phenomenon frequently called "backfire". This term refers to the uncontrolled combustion of the air-fuel mixture inside the intake manifold, resulting in a loud, and frequently damaging shock wave formed by burning the fuel. Backfire or the back flash is one of the critical problems researchers face while designing an efficient hydrogen engine. Pre-ignition and backflash phenomena occur due to the exact primary mechanism. The timing and positions of valves make a difference between these two anomalies. Pre-ignition happens throughout the compression stroke process when the intake and exhaust valve are closed. However, back-flash occurs while intake stroke when the intake valve is opened. The Backfire phenomenon depends on the valve's timings, air-fuel ratio, and hotspots occurrence in the combustion chamber. The primary mechanism of backfiring, or inlet charge combustion, is the same in both hydrogen and gasoline fuelled internal combustion engines. In either case, the inlet fuel-air mixture contacts a source of thermal energy of sufficient magnitude and intensity to initiate combustion during the period when the inlet valve is in the open position. The inlet charge can be ignited solely by the thermal energy of the residual gases, which remain in the combustion chamber at the end of the exhaust phase and mingle with the phase charge as the inlet valve begins to open. The hotspots inside the combustion chamber are also a significant source for producing backfire. Examples of hotspots are Spark plugs, exhaust valves, carbon deposits. Generally, this will be expected only in high-temperature engine operation. But, in hydrogen-fuelled engines, surprisingly, this backfiring occurs also in cold starting and idling conditions. This is because of the crevice volumes presented inside the combustion cylinder and the low ignition temperature of hydrogen. The space around the spark plug, small gap between the piston ring groove and cylinder, the gap between the nearly closed exhaust valve and combustion chamber contributes to the crevice volumes. A gasoline air mixture cannot burn in these small gaps. But hydrogen can burn here, but slowly. So, this slow-burning hydrogen continues to burn throughout the cycle and acts as a source of ignition for the new charge in the next cycle. Researchers found that the crevice volume present all over the spark plug has a more negligible effect on the backfiring problem, but the crevice volume in the piston top land and second land play a vital role towards the backfire anomaly. Backfire results in sudden pressure rise in the intake manifold section, which can be audible from the outside and harm engine parts intensively, [130]

Several changes in the ignition system and fuel are needed in order to control or prevent the backfiring problem, which includes eliminating centrifugal spark advance, reducing the spark gap, and eliminating cross-firing of cylinders by induced ignition sparks. With the solution mentioned above to control backfiring, water induction techniques can also be used to achieve considerable control over this problem. Water induction techniques include spraying of water into the combustion cylinder in order to quench the hotspots and to cool the flame which causes backfire. This method is reliable and has high efficiency to lower the flame temperature, which also reduces the production of nitric oxide emissions. With this for eliminating "hot-spots" in the combustion cylinder, the exhaust valves can be replaced with the sodium-cooled type. Also, as crevice volumes contribute to the backfire, a careful design is necessary to control the backfiring problem.

7. Hydrogen Fuel Cell Vehicles

In the vehicle industry, a hydrogen fuel cell is regarded as one of the new types of energy. It provides a number of benefits, including low emissions, low noise, extended durability, and ease of maintenance. However, it has drawbacks such as a slow dynamic response, a long start-up time, and soft output characteristics, [131]. As a result, supplemental energy sources must be linked to offer strong support for vehicles during high-power demand stages like climbing and acceleration, [132]. Batteries and super capacitors are two supplementary energy sources commonly employed in hydrogen fuel cell vehicles. However, the battery has drawbacks such as high temperature requirements, short service life, and high self-discharge rate, reducing the economy and reliability of hydrogen fuel cell vehicles; additionally, super capacitors have a low energy density, reducing the driving range of hydrogen fuel cell vehicles significantly, [131]. As a result of its high energy density, high charging efficiency, and low self-discharge efficiency, lithium batteries play an important role. The system structure of hydrogen fuel cell vehicles is depicted in Figure 49.

According to a study on Energy Management Strategy of Hydrogen Fuel Cell Vehicles, the control strategy can allocate energy between the hydrogen fuel cell and the lithium battery in a reasonable way to meet the vehicle's power demand, keep the lithium battery's SOC within a reasonable working range, and keep the hydrogen fuel cell system's working point in the efficient area, [131]. HFCs are garnering more attention as the environmental concern grows, particularly in the automotive industry. Alkaline anion exchange membrane fuel cell (AFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), and polymer electrolyte membrane fuel cell are some of the most important fuel cells (PEM C). Due to the expensive cost of Nafion and Pt catalysts, progress in HFC development and application is slow. Water management during the operation of HFCs is a critical concern. The effective transport of protons requires a high amount of hydration. Humidification is also critical; a lack of humidity causes membrane deterioration to occur more quickly. Internal humidification is based on exhaust gas recirculation; external humidification techniques include gas bubbling or water injection. Proton conductivity improves after UV irradiation on Nafion membranes. The optimum crosslinking of the -SO3H groups in the membrane is achieved by adjusting the dose of UV irradiation to achieve better proton conductivity. With increasing Nafion membrane thickness, the ideal dose for high proton conductivity steadily increases and approaches saturation near 183 mm, [133].

Limited knowledge of FCEV maintenance is the main reason for limited sales. Moreover, hydrogen storage, transportation, and refueling are not so prominent in many areas. The proton exchange membrane FC can work continuously in the steady-state for more than 40,000 h and rapidly produce hydrogen electricity, [134]. The possibility of hazards must be addressed to increase BEV and FEV sales. The following figure 50 shows the classification of some hazards.

Increase in driving range, reduction in emission and ease of refueling are some of the key points which attract customers. Leakage of hydrogen causes fire due to reaction with the atmosphere. So, proper storage of hydrogen is of utmost importance. High-pressure storage tanks must be thermally protected in order to avoid leakages. Tanks made of total carbon fiber can be preferred, which can store up to 950bars. The researchers have marked the silent operation of vehicles as a critical problem due to the possibility of a crash with pedestrians and cyclists. Securing batteries from a possible crash is also one of the most important focuses. Hydrogen storage technologies that give maximum range without reducing vehicle performance have gained more attention. Lithium-ion batteries outperform typical lead-acid batteries in terms of power and energy storage. Lithium titanate batteries, according to study, reduce vehicle weight and take up less space, allowing for additional cargo room. Compressed gas storage, metal hydride storage, pressured metal hydride storage, cryogenic liquid hydrogen storage, and chemical hydride storage are all options for storing hydrogen. The automobile industry has adopted compressed gas storage because it is more promising for vehicle applications in terms of volume and weight. Furthermore, it was discovered that a fuel cell with ultra-capacitors is more useful. The most promising commercially available hydrogen storage technique is composite

wrapped pressurized storage, which reduces storage mass and increases vehicle range, [136]. A study was done to see if a hydrogen fuel cell vehicle (HFCV) fitted with a thermal pressure relief system may spread fire to other automobiles (TPD). On the first day, two tests were performed. An HFCV was maintained next to a gasoline car in the first test, while three HFCVs were kept next to each other in the second test. The test findings showed that flames from the interior and exterior materials of the fire origin HFCV ignited the nearby vehicles, but not the hydrogen flames generated by TPRD activation, [137]. Both automobiles' windows were kept closed in the first test. The two automobiles were separated by about 0.8 meters. According to studies, the gasoline vehicle caught fire around 57 minutes and 26 seconds, or about 28 minutes after HFCV's TPRD was activated, [138].

Furthermore, it was discovered that the adjacent gasoline car was ignited by the HFCV burn-down flames, which spread from the exterior and interior fittings of the fire origin vehicle, rather than the hydrogen flames generated by TPRD activation. Three HFVC named A, B, and C were parked with a 10 cm lateral and 30 cm longitudinal separation in the second test. At 0 minutes after the commencement of the test, a burner ignited the rear bumper of HFCV-A, [137]. At 109 minutes, HFCV-B ignited in its right backside, [138]. HFCV-A burned down at 114 minutes, and HFCV-C caught fire at its front bumper and engine hood. The TPRD of the HFCV- A rear tank was activated at time 117 minutes, and hydrogen gas was expelled from the vent pipe. The fire quickly spreads from HFCV-A to HFCV-center B's section and HFCV-rear C's underfloor area, [137]. As a result of the hydrogen flames generated, the TPRD of adjacent vehicles activates, according to the results of the second test. The product carbon footprint (PCF) of hydrogen-powered vehicles has received very little attention.

According to a study, demand for urban last-mile delivery will increase by 78% by 2030, resulting in a 36% increase in delivery vehicles in metropolitan areas. As a result, making the switch to cleaner automobiles is critical. Automobile parts are also manufactured and assembled in many locations; some production techniques make measuring emissions difficult; as a result, calculating the carbon footprint becomes complicated. The environmental consequences of various electric vehicles (EVs) can be assessed using the life-cycle assessment (LCA) method, which is a method for calculating the environmental effects of goods and services over their entire production and value chains, [138], [139]. Vehicle life cycle assessments (LCAs) based on ISO standards (ISO:14040 2010) can be used to determine E's carbon footprint. The GREET (Greenhouse Gases, Regulated Emissions, and Transportation Energy Use) model, [138] could be used.

GREET1 - estimates the energy use and emissions associated with recovering the primary feedstock, transporting the feedstock, producing fuel from the feedstock, and transportation, distribution, and fuel use during vehicle operation.

GREET2 - estimates the energy use and emissions connected with automotive materials manufacture and processing, as well as vehicle manufacturing and assembly, [138].

A study was conducted on 54 drivers to review driving HFCEV. All the drivers drove various vehicles for a month.94% of the drivers found the fueling process to be simple and safe. Around 62% percent had to forgo at least one trip due to lack of hydrogen fuel. The average fuel economy was found to be 56.4 miles per kilogram. Refueling times were under 10 min. Most of the drivers reported that a sufficient number of refueling stations would significantly affect purchasing the HFCEV. Moreover, divers indicated a willingness to consider FCV purchase at or below the $40,000 ($US 2015) per vehicle level. Awareness campaigns exhibitions among the general public related to HFCV would be greatly beneficial, [140]

Currently, deterioration of air quality due to the transportation sector is the primary concern. The concentration of ozone and particulate matter have adverse effects on human health. The alternative propulsion system is the requirement of the current transportation sector to reduce the quantity of pollutants. Hydrogen is being seen as an appropriate alternative in light vehicles and heavy-duty vehicles, [135]. FCEVs operate with no emissions; also, they have more efficiency. Hydrogen production strategies such as methane reformation result in emissions. So, cleaner production methods such as electrolysis, pyrolysis, fermentation become more important. According to a study on a fuel cell hybrid electric car in NEDC driving cycle, employing an ultra-capacitor, 3.3% reduction in

fuel consumption and 20.2% decrease in the difference between initial and final State of Charge (SoC) in the battery pack can be achieved, [141].

8. Features of hydrogen fueled engine

- Less cyclic variations are encountered with hydrogen even for very lean mixture operation when compared with other conventional fuels. This leads to improved efficiency, reduced emissions, and smoother and quieter operation, [142].
- Hydrogen has a high burning rate. So, its octane rating is relatively high, [66]. Also, it has slow preginition reactivity.
- High burning rate also enables the engine at high rpm. So, hydrogen engines are suitable for high-speed operation.
- Less spark advance is usually preferred due to its higher burning rates, so that peak pressure occurring nearly at TDC results in good efficiency and output, [143].
- Hydrogen is an outstanding supplement in comparatively lower concentrations to some standard fuels such as methane. It will enhance the burning rate of poor fuels like biogas, producer gas etc.
- As hydrogen's freezing temperature is very low, it remains in a gaseous state in the regions where the temperature is relatively low. It enables good cold starting of the engine and also prevents the fuel-choking problem.
- Because of high-speed operation, hydrogen engine operation can be associated with lower loss of heat when compared to other conventional fuels. Only 17 to 25% of the thermal energy released during hydrogen combustion is lost to the environment due to radiation heat transfer compared to 22 to 33% for methane and 30 to 42% for gasoline.
- Hydrogen has high-energy utilization efficiency. Energy utilization efficiency is explained as the ratio of fuel utilization efficiency to hydrogen utilization efficiency. The advantage of hydrogen in terms of utilization efficiency for numerous areas of utilization is shown below in table 3.
- With the use of lean mixtures of hydrogen in air, achieving moderately high compression ratio operation is feasible, which allows higher efficiencies and increased power output. The higher auto ignition temperature also helps the engine to operate at a relatively high compression ratio.
- Since the energy transfer because of condensing a portion of water vapour can add up considerably to the thermal load output and the corresponding energy efficiency, Hydrogen engines are very satisfactory for applications in cogeneration.
- Hydrogen is a pure cleaner and green fuel of unique and satisfactory characteristics and properties, allowing continued and superior optimization of engine performance.
- The reaction rates of hydrogen are sensitive to the presence of a large variety of catalysts. This feature benefits to improve the efficiency of the combustion process and improve the treatment of its exhaust emissions.
- The heat transfer and thermodynamic properties of hydrogen fuel liable to produce high compression temperatures that improve lean mixture operation and consequently increases engine efficiency.
- The aspect ratio of 2 corresponds to the highest heat release, pressure and shortest combustion duration, while the aspect ratio of 1 corresponds to higher operating frequency and higher combustion efficiency. The piston speed is directly proportional to the aspect ratio, which directs the mean effective pressure and power output of PFLG, [145]

The majority of reactions in Hydrogen jets are seen to be taking place at the jets' boundary, despite the greater diffusivity and flammability of hydrogen. Hydrogen jets indirect injection compression engines do not significantly depict air entertainment and flame lift-off in the nozzle region, [146]

A decrease in excess air ratio from 2 to 0.85 leads to an initial increase and then a decrease in a hydrogen-fuelled rotary engine; improvement in thermal efficiency can be achieved by increasing MAP. With increasing load and decreasing excess air ratio, the flame propagation period is first observed to reduce and then increase while the thermal efficiency and work capacity first increase and then decrease, [147]

Use of gaseous fuel instead of liquid fuels prevents the problem of cold fuel evaporation, uneven distribution of the fuel to the different cylinders due to the presence of a liquid film on the walls of the intake manifold and the unwanted large variations in supplied air-fuel ratio during transient conditions such as acceleration and deceleration.

- Hydrogen extreme burning rates of hydrogen make the engine performance less sensitive to modifications to the structure of the combustion cylinder, the intake charges swirling effect and level of turbulence.
- Hydrogen can better tolerate the presence of diluents. This would allow better exploitation of low heating value fuel mixtures.
- Hydrogen used engines have long spark plug life because of the absence of carbon deposition over the spark plug, [148].
- It is possible for hydrogen to burn in leaner flames than natural gas or gasoline due to its wide range of flammability limits, [149].

Though storage of hydrogen on-board does have some problems, the application of metal hydrides showcases features like minimum energy loss regarding high levels of safety and storage, [150].

9. limitations associated with hydrogen fuel engine

Open literature published about the performance of hydrogen engines describes plenty of positive features of hydrogen fuel engines while ignoring the problems or limitations which come with the hydrogen fuel. There is indeed a need to overcome these anomalies or limitations to commercialize the hydrogen fuelled vehicles. Focusing equally on both positive and negative aspects of using hydrogen fuel can develop an efficient and reliable engine system. correspondingly, the list below highlights some important features of hydrogen:

- At 200 atmospheric pressure hydrogen is compressed gaseous state, at this state and the atmospheric temperature its energy is 5% that of the gasoline at the same volume. This is a significant challenge when it comes to transportation.
- The production cost of hydrogen is similar as compared to that of synthetic hydrocarbon fuels. The electrolysis process of hydrogen production makes the cost of hydrogen three times that of fossil fuels for the same energy, [151].
- Engines with hydrogen as fuel faced a reduction in power owing to its very low heating value with respect to volume in case of lean mixture operation. The volumetric heating value of hydrogen is 2890 J/l, and the same for conventional fuel is 3900 J/l, [151].
- The stoichiometric hydrogen fraction in the air is 30%, whereas gasoline is 2-3%. So, hydrogen occupies more volume in the chamber for combustion, so the power output reduces as it displaces more air, [151].
- Severe potential problems related to operation are seen to be associated with hydrogen due to uncontrolled preignition and backfiring in the hydrogen engine's intake manifold.
- The problems mentioned above are associated with increased intake manifold pressure and improper valve timings, hence damaging the engine, [152]
- Hydrogen engines can produce excessively high cylinder pressure, as shown in Figure 51.
- High temperature and pressure are generated due to higher burning rates of hydrogen when operating near stoichiometric mixture during combustion in engines. This would mean increased exhaust emissions of nitrogen oxides.
- Hydrogen in a compressed form is used as the best insulator in alternators. So, it needs high ignition voltage to

ignite the air-hydrogen mixture, which complicates the ignition system, [148].

• Hydrogen engines exhaust gas must possess lower energy due to greater part-load efficiency and lesser volumetric value, turbocharging of exhaust is hence less suitable in case of hydrogen engines, [151].

• Recirculation of the exhaust gas for exhaust emissions control can lead to major limitations.

• Fast burning of hydrogen leads to a rise in pressure at high rates in operation of the engine leading to high noise and vibration.

• Attention is required to avoid material compatibility issues in applications related to hydrogen engines.

• In case of applications in very cold climates, emission of steam exhaust can lead to icing problems and lower visibility and hence is undesirable.

• Road safety can be threatened, if hydrogen-air mixture leads to catalytic action due to sensitivity.

• Uncontrolled pre-ignition problems arise due to the lower ignition energy of hydrogen.

Corresponding to the condensation of exhaust water vapour, an increase in undesirable corrosion and lubricating oil contamination can be observed.

Durability problems related to lubricants may also increase.

Hydrogen will easily leak through the nearly closed valves, as its viscosity is relatively low. This will create a hazardous environment near the engine. Some potential for increased safety problems can always be observed with hydrogen operation.

Excessive cooling of the engine will make the product condense inside the engine and suppress the combustion.

Heat transfer may sometimes be high but sometimes they may be quite low owing to the conditions.

In the present scenario, the cost of a hydrogen engine is quite considerable.

In the case of hydrogen fuel cells, the usage of hydrogen demands high purity standards while the production methods influence contaminants like nitrogen, oxygen and water. The hydrogen then has to undergo drying and purification for its usage, [153]

Another issue associated with fuel cell application is that because of the short circuit and increase in membrane temperature, there can be leakage of the fuel cell, while the energy conversion ratio also hits a toll in the conditions mentioned above, [154]

The temperature and pressure-dependent chemical kinetics govern the rate of discharging and charging; as the equivalent pressure increases with temperature and the pressure drive for absorption decreases with temperature, the kinetic factors are countered and display a peak, and therefore, the temperature of the metal hydride bed must be maintained in a limit of 30K- 40K otherwise the recharging would be impaired, [155]

At high loads and high compression ratios, considerable percentages of hydrogen substitutions lead to an increase in NOx emissions (400 to 990 ppm).

Hydrogen enrichment also leads to an increase in exhaust temperature, which is bad for the engine, [156].

10. Pollutions in hydrogen engines

Hydrogen is more environmentally friendly than hydrocarbons. The only issue with hydrogen combustion is NOx emissions. As a result, lowering it becomes critical. The use of rich lean combustion to reduce NOx emissions has already been discovered to be successful. In rich–lean combustion, hydrogen has a greater effect on NOx reduction than methane, especially in situations with a higher richer side equivalency ratio, [157]. Backfire in a hydrogen engine can be avoided with a properly constructed timed manifold injection system. Significant pollutants such as CO, HCs, SOx, smoke, lead, or other harmful metals are not produced by hydrogen combustion, [158]. CO_2 dilution is an efficient approach to reduce NOx emissions. However, rising CO_2 levels result in an increase in HC emissions, necessitating the usage of the right amount of hydrogen. The addition of hydrogen to hydrocarbon fuel engines reduces cyclic fluctuations and speeds up combustion. The combustion of hydrogen-enriched natural gas engines is also influenced by valve timing. It was discovered that by reducing valve overlap, HC (hydrocarbon) and

CH4 emissions may be lowered by 41%, [159,160,161].

The most important part of hydrogen operation was to keep the engine running smoothly. The engine's smooth running without any odd combustion difficulties is clearly shown in figure 52 by the following typical pressure crank angle diagram.

In a hydrogen engine, NOx is the only relevant pollutant to be concerned about. However, the findings of trials with the hydrogen-supplemented engine have been published, and the levels of CO and unburned hydrocarbons in the exhaust have been assessed. In addition to unburned HC and CO, lubricating oil combustion produces traces of unburned HC and CO in the exhaust. The level of hydrogen peroxide in the exhaust of a hydrogen-powered engine has also been reported by several researchers.

Studies are being conducted all around the world to reduce NOx emissions. Water injection has been identified as one of the promising techniques for lowering the peak combustion temperature and thereby reducing NOx emissions. The following Figure 53 depicts a notable outcome with a SI engine. The level of NOx emissions was almost minimal for a Hydrogen driven SI engine with an equivalency ratio < 0.6 using "Timed manifold induction" procedures, as seen in this image.

The mechanism of NOx generation is well-known to be temperature-dependent. The lower temperature and slower chemical reactions in lean hydrogen engines impair the kinetics and reduce NOx generation. It was also discovered that the compression ratio has an effect on the degree of NOx emissions. NOx emissions showed a rising trend with equivalence ratio, peaking at roughly a 0.9 equivalence ratio. Because of the scarcity of oxygen, further enrichment leads to a drop in NOx. The NOx emission level is also influenced by the compression ratio. As illustrated in Fig. 53, an increase in compression ratio corresponds to an increase in NOx emissions. This is as a result of the rising temperatures. Remarkably, increasing the compression ratio and hence the temperature level typically resulted in a faster flame speed condition, which reduced the residence time. The researchers discovered that when two factors (such as increased temperature and shortened residence time) are combined, the effect of the former usually wins out, resulting in higher NOx levels and a higher compression ratio.

The combustion duration also has a marked effect on the NOx concentration. The combustion duration is affected by the parameters like speed, Equivalence ratio, Compression ratio and spark plug location.

The increase in engine speed and equivalence results in increasing flame speed and thus reducing combustion duration. The compression ratio increases resulting in high compression temperatures, resulting in high flame speed and ultimately lowering the combustion duration. A non-dimensional number defines the spark plug location. It's the ratio of the distance between the spark tip and nearest wall to the bore. It affects the flame travel and thus the combustion duration. Increasing the combustion duration reduces the NOx concentration. This is because of the reduction in peak temperature with increased combustion duration. Further, the combustion is complete. Decreasing the combustion duration beyond a certain limit also results in NOx reduction because of the minimized time for the product's exposure to peak cylinder temperature, [130].

NOx emissions can be drastically brought down in a multi-cylinder automotive engine through exhaust gas recirculation. A study carried out at University of California shows that it's possible to attain lower NOx emission with the stoichiometric operation of a hydrogen engine using EGR technology, [162]. They used the port injection fuel metering technique. Also, one throttle was used to control the airflow. A pipe from the exhaust line was taken and connected to the inlet through a manually controlled valve. Before that, the exhaust was cooled using a heat exchanger. The test was carried out at a constant engine speed of 1500 rpm. The comparison was between the two-operating strategies. One with lean burn condition and one with stoichiometric technique combined with EGR. In the lean-burn approach, the combustion chamber contains excess air. So, the A/F ratio of the charge is relatively high. In the EGR technique, this excess air is replaced by exhaust gas. This is done by throttling the air intake and allowing the exhaust to the inlet port. The following figure 54 explains this strategy.

Hydrogen should occupy 70% of the combustion chamber for a stoichiometric operation. If the charge is lean, i.e., F=0.4, then

the hydrogen portion is 14%, and the air needed for burning this Hydrogen is 34%. The remaining space, i.e., 52%, will be occupied by the air that doesn't take part in combustion and can be considered excess air. But in the EGR technique, the air supplied for combustion is the same, i.e., 34% for this same amount of fuel. But the rest of the combustion chamber is filled with exhaust gas.

The test was conducted with various amounts of fuel flow rates, and performance and emission comparisons were made between the lean-burn and EGR techniques. The following plot in figure 55 clearly explains the advantages claimed by the EGR technique.

The parameters associated with the EGR technique are denoted by the "EGR" prefix. The A/F ratio is not given for the EGR technique as it was always operated under stoichiometric conditions. The trend of curves shows that the efficiency and torque produced by the engine while operating with EGR is lesser than that of the lean-burn condition. This is because of the drop in volumetric efficiency of the engine when the hot exhaust is mixed with the incoming air. But if the emission is considered, the lean-burn technique produces heavy NOx when the ϕ increases. Particularly near the stoichiometric region, the NOx reaches an alarming level.

In contrast, in EGR operation, the NOx emissions are almost zero. This is because at all operating conditions, while EGR, the mixture is in stoichiometric condition, and there is no free oxygen to form NOx. This seems to be an excellent technique while we go for higher output. The only thing is that we need to sacrifice efficiency to obtain higher power and slightly lower emissions. The lean-burn strategy offers good efficiency and considerably lower NOx at lower loads. So, a good balance between the lean burn and EGR strategy will be good for high efficiency at low load and lower emissions at high load.

11. Current development and status of hydrogen automobile industry

In general, in every INDIAN city, air pollution is a major issue. The transportation sector is a significant contributor to escalating air pollution levels. India's National Development Plan (NDP) seeks to decarbonize the Indian economy by 33-35 percent by 2030, compared to 2005, [163]. From 2018 to 2025, the India hydrogen market is estimated to increase at a CAGR of 6.3 percent, reaching $81 million. Global energy demand is anticipated to boost thrice by 2050 compared to now, [164]. In the future, oil and gas production is unlikely to match predicted demand. Furthermore, renewable sources of energy have low efficiency as compared to conventional sources to power the electrical vehicle industry. That's why, energy sources like hydrogen should be encouraged in the automotive sector. Hence, the development and application of hydrogen fuel technologies are critical in meeting the rising demand.

One of the most poisonous elements on the planet is lithium. As a consequence, the use of lithium-based batteries poses a new concern. As a result, hydrogen technology is seen as one of the possible solutions. Building hydrogen stations that service captive fleets on hub-and-spoke missions in the early stages of deployment could assist secure high refuelling station utilisation and hence help get infrastructure construction off the ground, [165]. People must also be made aware of the advantages of implementing hydrogen. Additionally, much research is required to attain the required benchmark in hydrogen synthesis and storage. Vehicles with solar roofing, wind turbines on the side panel, and other technology that harnesses the benefits of renewable sources and hydrogen technology will be good areas to conduct research in

12. Conclusion

This review article on the production, storage, and utilization of hydrogen fuel in automotive applications can provide valuable insights and information for a variety of stakeholders. For policymakers and government officials, it can provide a comprehensive overview of the current state of hydrogen fuel technology and its potential as a sustainable alternative to traditional fossil fuels. This information can help inform decision-making related to policies and regulations surrounding the adoption of hydrogen fuel in the transportation sector. For industry professionals, this article can serve as a valuable resource for understanding the latest developments and trends in hydrogen fuel technology. This information can help inform strategic planning and investment decisions related to the development and deployment of hydrogen fuel systems. For researchers and

academics, the article can provide a useful summary of the current state of knowledge on hydrogen fuel technology and highlight areas for further study and exploration. Finally, for the general public, the article can help in better understanding of the potential benefits and challenges associated with the adoption of hydrogen fuel in the transportation sector. This can help inform personal decisions related to the use of hydrogen fuel and the role it may play in the future of transportation.

Hydrogen can be used in the automobile sector via application in internal combustion engines and fuel cells because of its wide range of flammability limits, low ignition energy and high diffusivity. The properties causing this drawback are small quenching distance, high flame velocity and low volumetric energy density.

The current scenario of hydrogen production involves extensive use of conventional methods which employ the application of fossil fuels and hence lead to emissions; for a sustainable global hydrogen economy to thrive, it is needed that the renewable methods are researched extensively and take over the production industry. Renewable methods such as photolysis electrolysis show high hopes for a better future.

Hydrogen storage for mobile use is complicated and has been a significant setback in its progress as a fuel. Currently, the most feasible methods for hydrogen storage are physical methods, of which compressed and liquid hydrogen storage are widely practiced. Research in chemical processes for storage show some positive prospects, but additional work needs to be done to achieve feasibility.

The use of hydrogen in IC engines is advantageous over conventional fuels regarding emission characteristics and engine efficiency. However, a few limitations such as knocking, preignition, and backfire have hampered its commercialization. Hydrogen in CI engines can be made possible via direct injection, and dual fuel modes as its use conventionally would not be feasible even at very high compression ratios. The use of hydrogen with other alternatives such as CNG, ethanol and vegetable oil has shown promising effects on various properties such as BMEP, BSFC, etc. Hence, hydrogen supplementation would be a reasonable step towards a cleaner future.

In contrast, application in SI engines is promising because of its unique and highly desirable properties. With the use of the direct injection technique in the SI engine, anomalies like backfire can be eliminated, while pre-ignition can be controlled to certain limits. The use of cold rated non-platinum spark plugs can also be employed to avoid combustion anomalies. With proper design and appropriate methods, hydrogen in IC engines can become a reality.

A fuel cell is more efficient as compared to a battery. Moreover, refuelling HFCV is much easier and faster than battery charging. HFCV takes less than 10 minutes to recharge. Also, FCVs have a range of about 300 miles. Since HFCV is portable, it dramatically benefits armed forces in remote locations. HFCVs are much lighter than other battery vehicles; hence, they are beneficial in heavy vehicles such as trucks.

The emission characteristics of hydrogen are much better than conventional fuels regarding CO, HCs, SOx, smoke, lead, or other significant pollutants. The only area of concern is NOx emissions. It can be reduced with the use of the appropriate method of injection and lean air-fuel ratio.

The social awareness regarding hydrogen as an alternative leading to sustainable energy utilization will drive us to a cleaner future. Research in the field of hydrogen infrastructure will make this a reality. Experiments to minimise NOx and for greener production are paths for the future, and the study must serve as a means of information to researchers for additional studies and experiments on production and utilisation of hydrogen.

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Declaration of interests

List of Tables:

Table 1. Comparison of various storage techniques, [58]

Material	No of hydrogen atom/unit volume (10^{-22} cm^{-3})	Weight % of hydrogen
H_2 gas	0.7	---
Liquid H_2	4.2	100
Liquid CH_4	6	25
Ti H_2	9	4
La H_3	6.5	2.1
TiFe H_2	6	1.8
La Ni_5 H_6	5.5	1.4

Table 2. Properties of hydrogen, [65], [66]

PROPERTIES	HYDROGEN	GASOLINE	METHANE

Molecular mass (Kg/kmol)	2.016	107	16.043
Triple point pressure (atm)	0.0695	------	0.1159
Triple point temperature (K)	13.803	180 to 220	90.680
Normal boiling point (K)	20.268	310 to 478	111.632
Critical pressure (atm)	12.759	24.5 to 27	45.387
Density of vapor at NTP (kg/m3)	0.083764	4.4	0.65119
Density of liquid at NBP (kg/m3)	70.8	700	422.6
Viscosity of gas at NTP (Ns/m2)	0.00000875	0.0000052	0.0000110
Viscosity of liquid at NBP (Ns/m2)	0.0000133	0.0002	0.0001130
Compressibility Factor of gas at NTP	1.0006	1.0069	1.0243
Compressibility Factor of liquid at NBP	0.01712	0.00643	0.004145
Gas constant R (kJ/kgK)	4.124157	0.077704	0.518251
Limits of flammability in air(%vol)	4 to 75	1 to 7.6	5.3 to15
Limits of detonability in air (%vol)	18.3 to 59	1.1 to 3.3	6.3 to 13.5
Stoichiometric composition (%vol)	29.53	1.76	9.48
Ignition energy (mJ)	0.02	0.24	0.29
Autoignition temperature (K)	858	501 to 744	813
Lower enthalpy of combustion (kJ/g)	119.93	45	50.02

Higher enthalpy of combustion (kJ/g)	141.86	48	55.53
Lower enthalpy of combustion (MJ/m3)	10.22	216.38	33.95
Higher enthalpy of combustion (MJ/m3)	12.10	233.29	37.71
Adiabatic Flame temperature in air (K)	2318	2470	2148
Specific heat (Cp) of NTP gas (kJ/kgK)	14.89	1.62	2.22
Specific heat (Cp) of NBP liquid (kJ/kgK)	9.69	2.20	3.50
Gama value of NTP gas	1.383	1.05	1.308
Octane number	130	87	125
Laminar burning velocity at NTP air(m/s)	2.65-3.25	0.37 to 0.43	0.37 to0.45
Quenching distance in NTP air (cm)	0.064	0.2	0.203
Flash point (K)	20	230	85
Flame colour	Colourless	Yellowish blue	Blue

Table 3 Utilization efficiency advantage of hydrogen, [144].

Application	Utilization efficiency factor
Thermal energy	0.90
Flame combustion	1.00
Catalytic combustion	0.80
Steam generation	0.80
Electric power, fuel cells	0.54
I.C. engines	0.82
Fuel cells/electric motor	0.40
Supersonic jet transportation	0.84
Weighted average	0.72
Hydrogen	1.00

Fossil fuel	0.72

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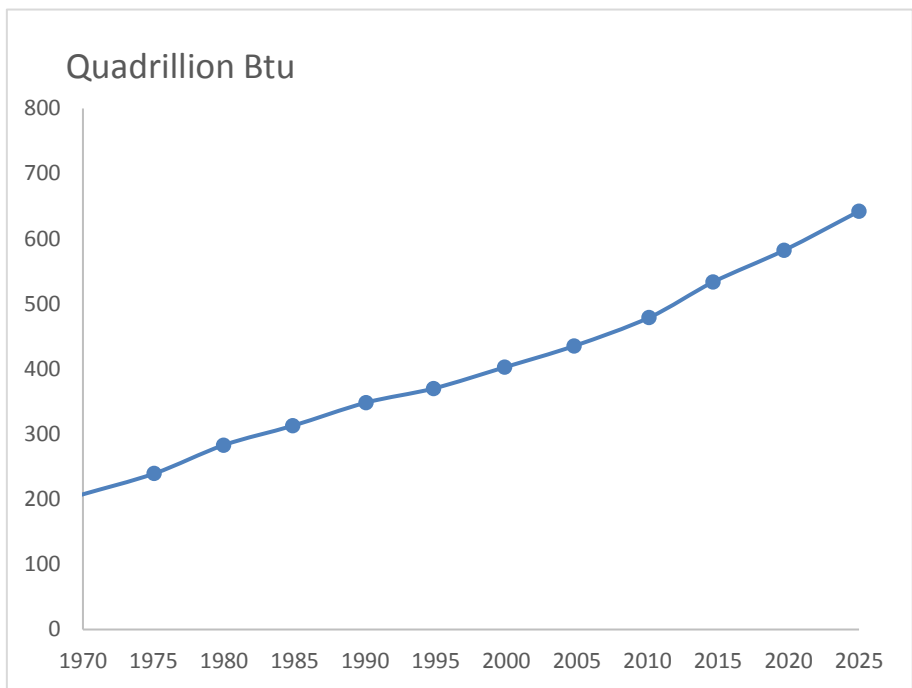
Fig 1. World energy consumption 1970-2025, [1]
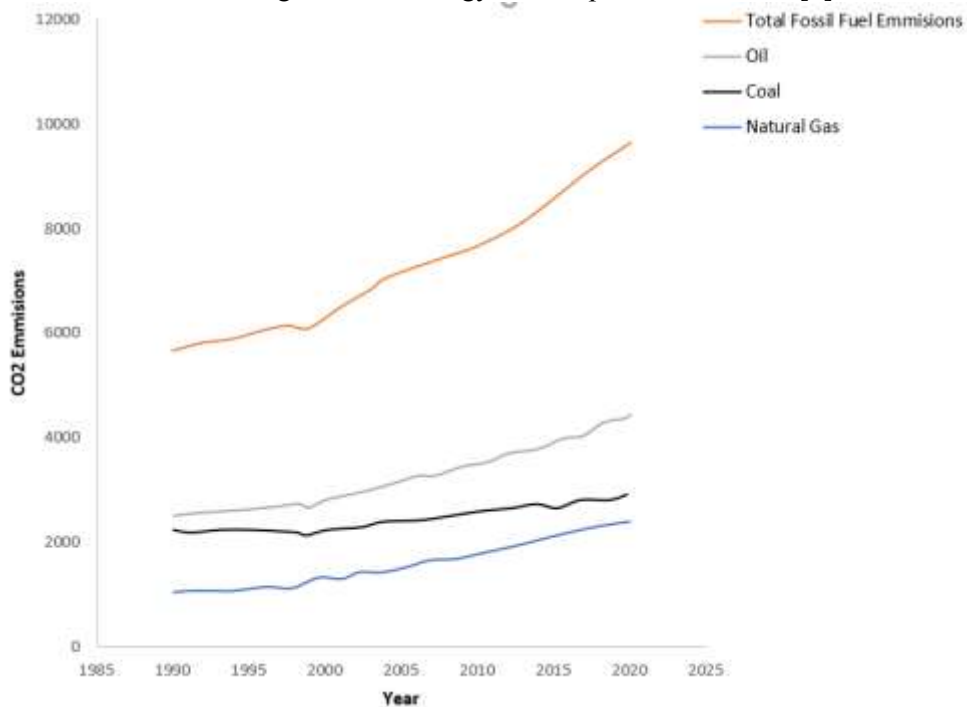
Fig 2. World CO$_2$ emissions (million metric tonnes carbon equivalent), [1]
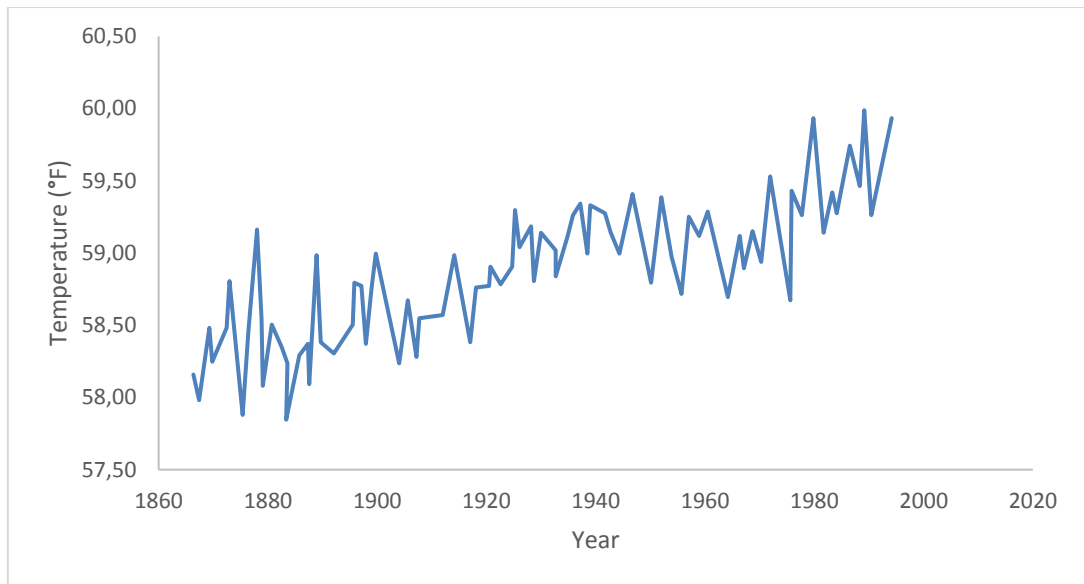
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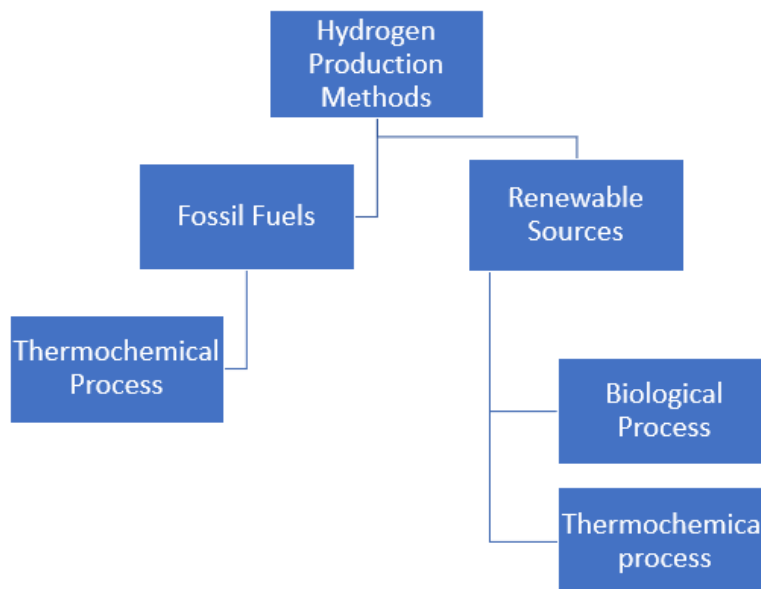
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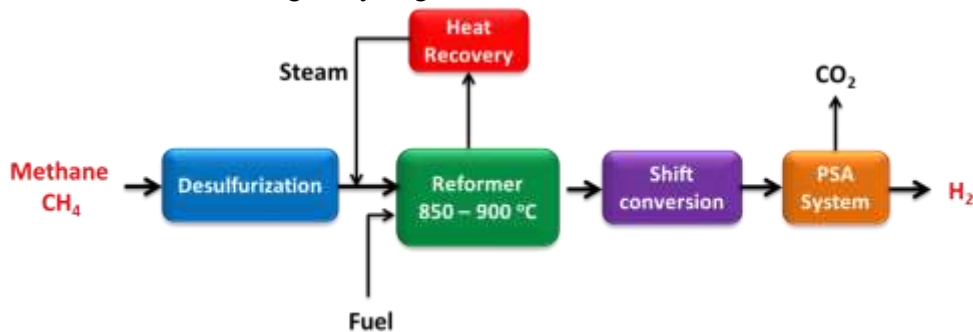
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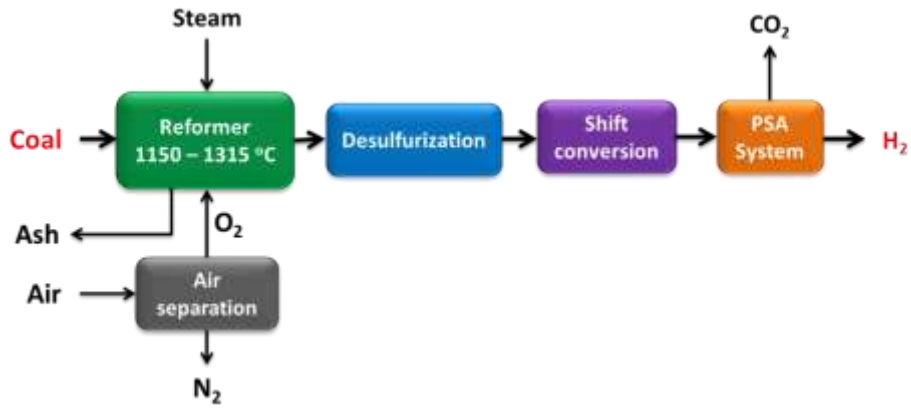
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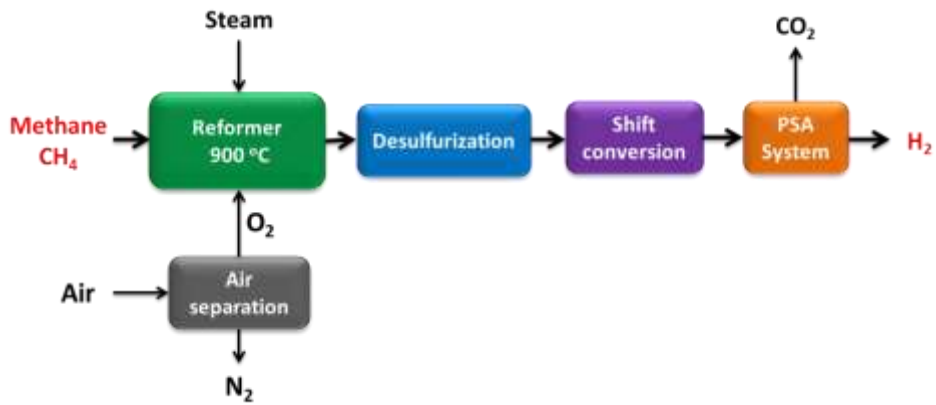
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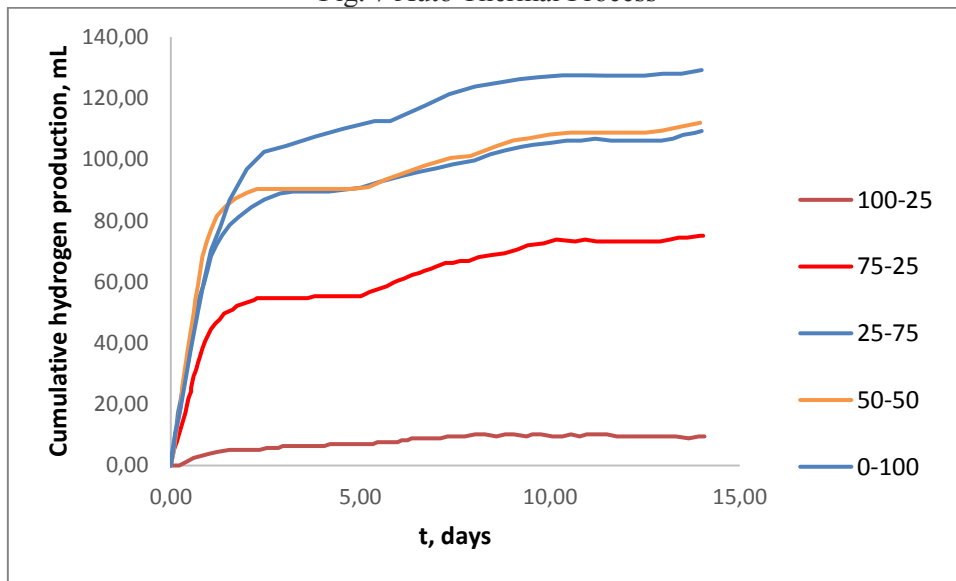
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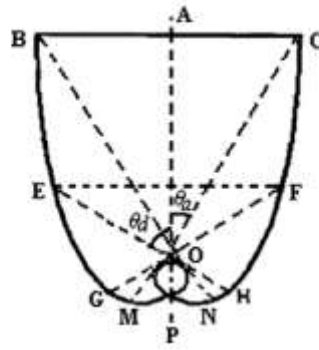
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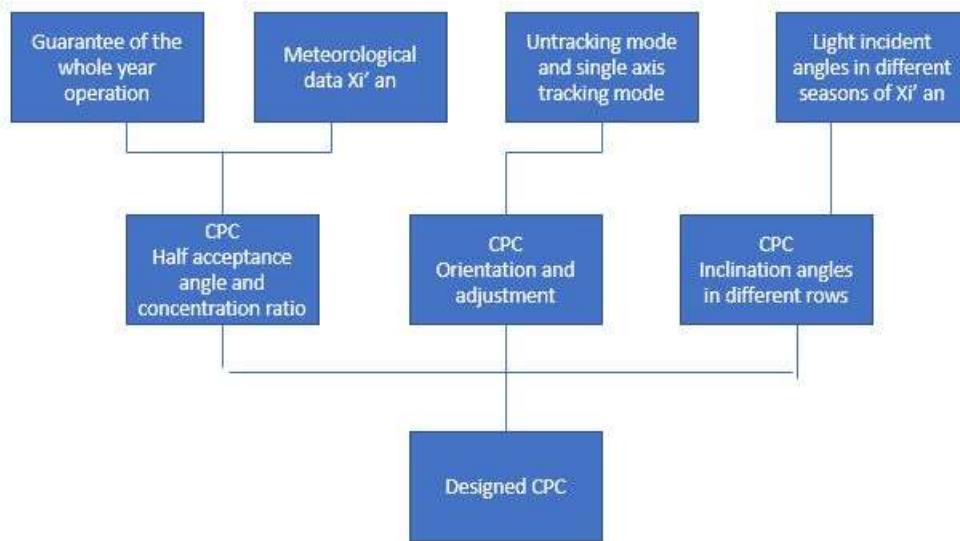
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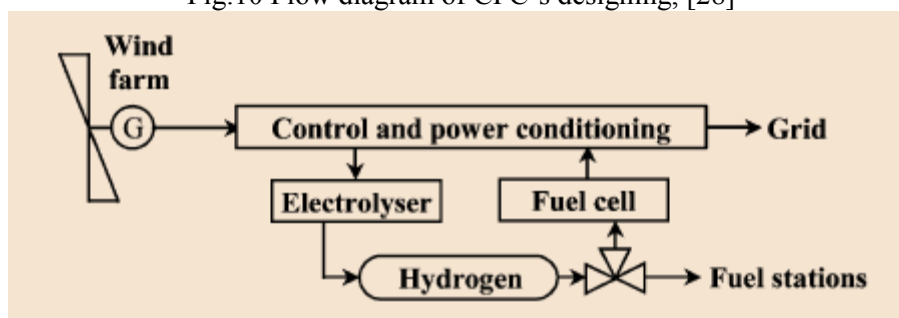
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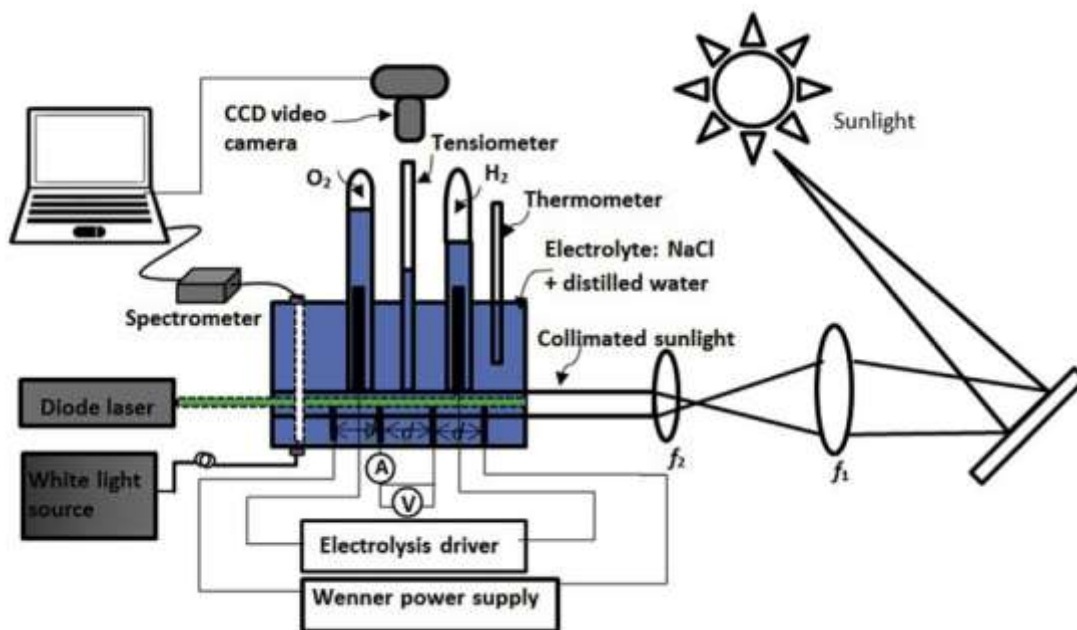
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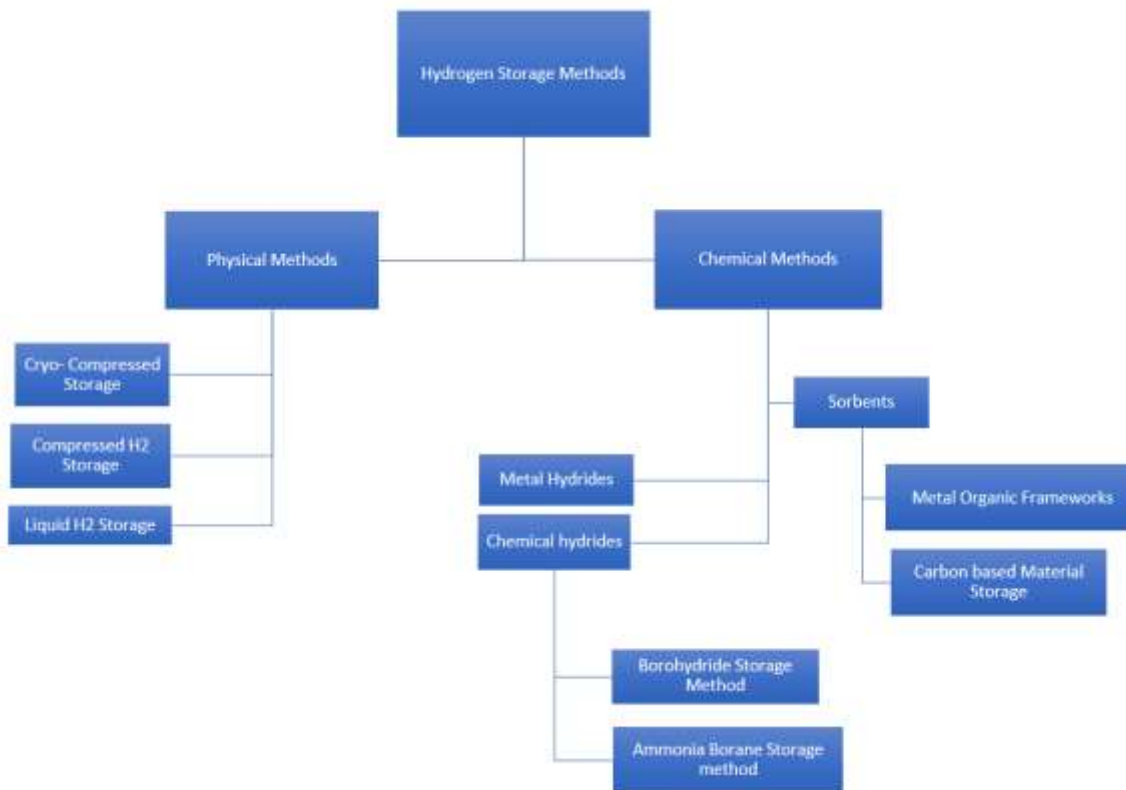
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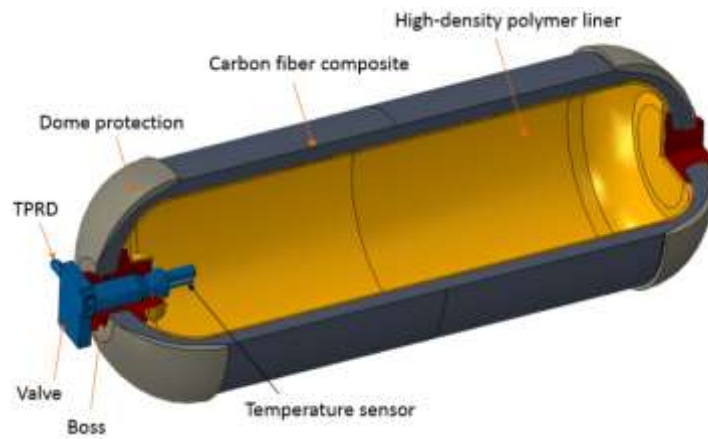
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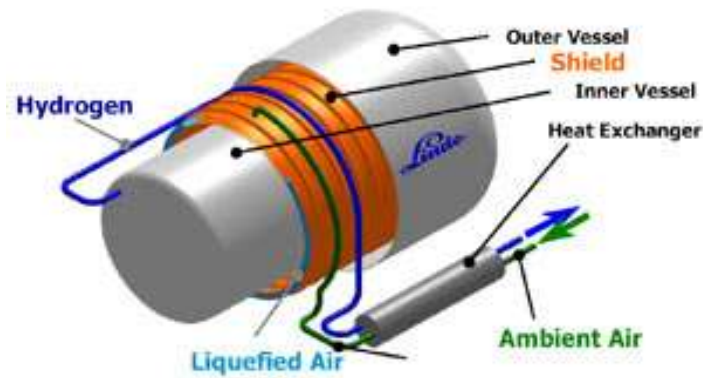
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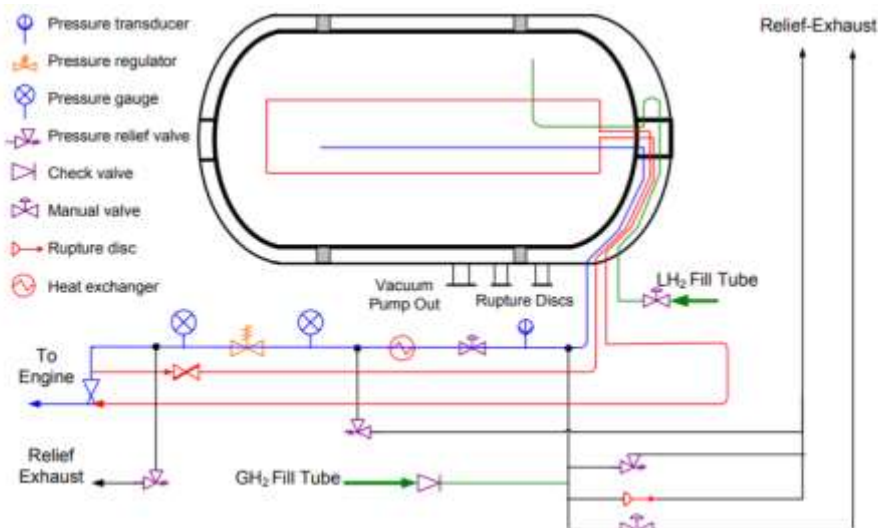
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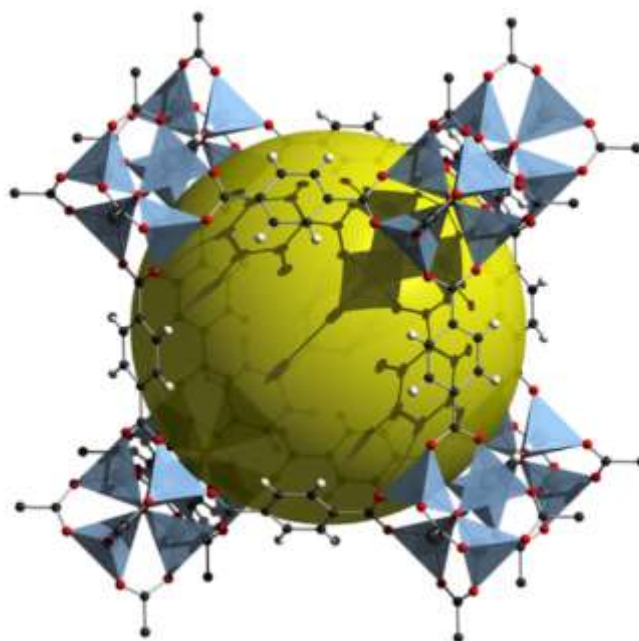
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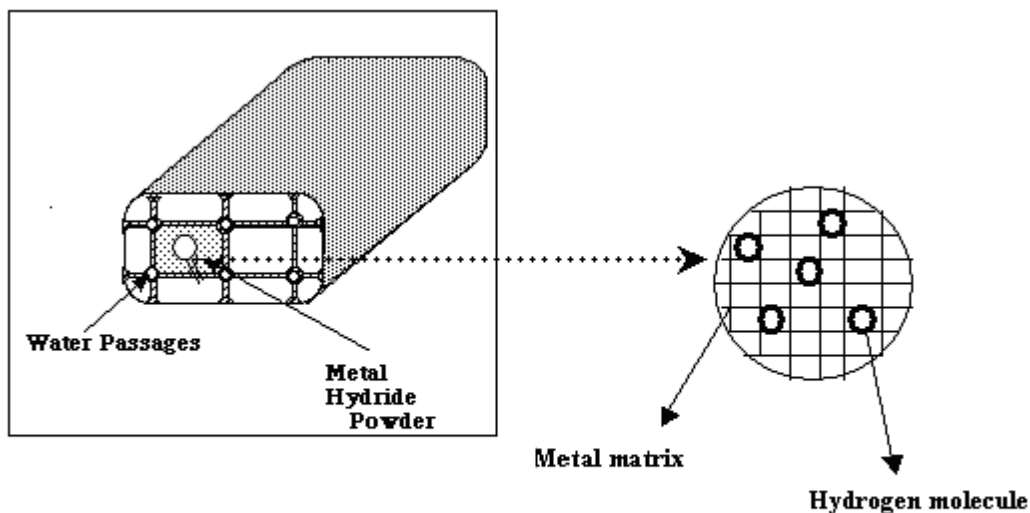
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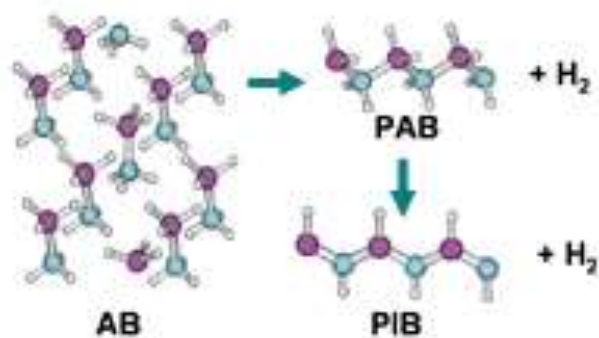
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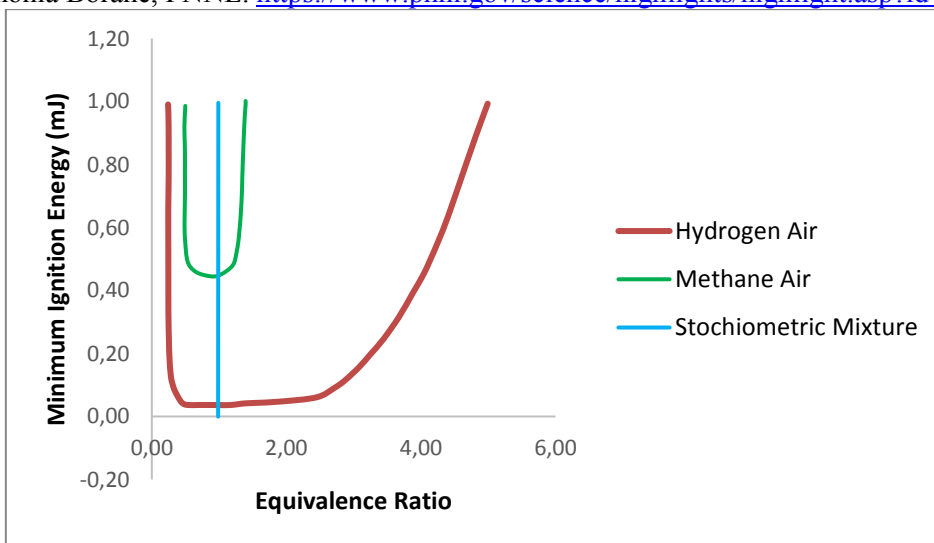
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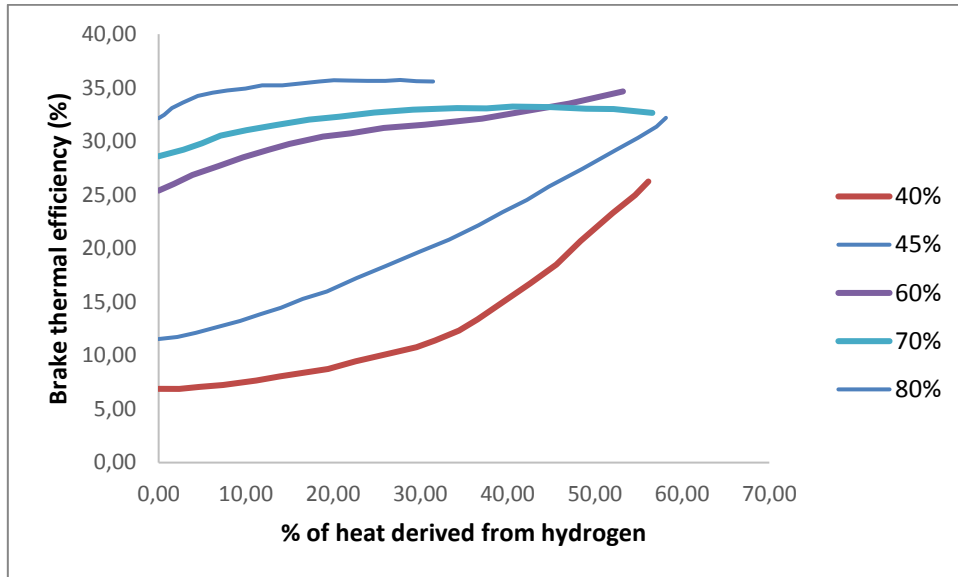
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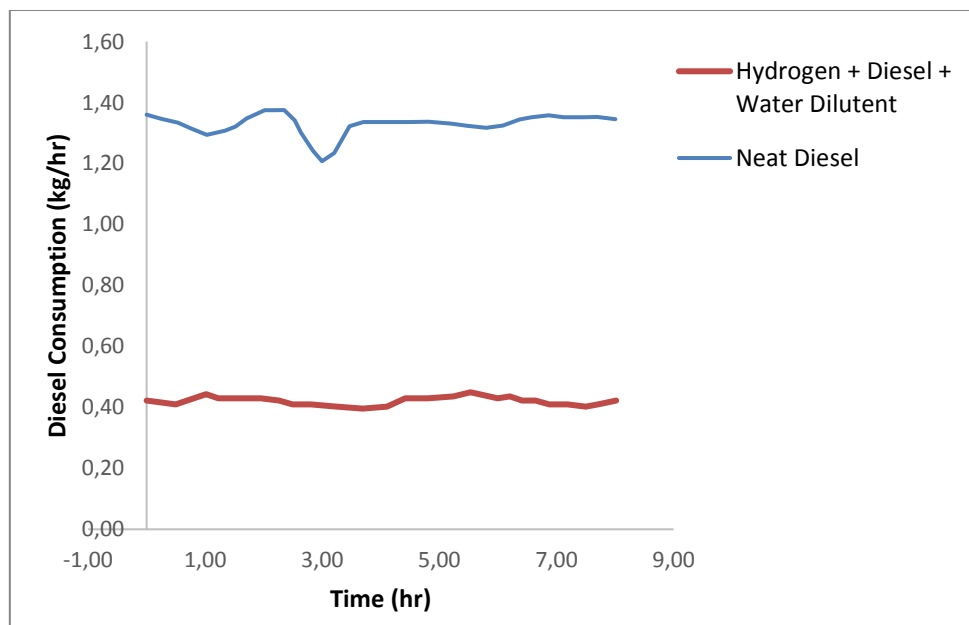
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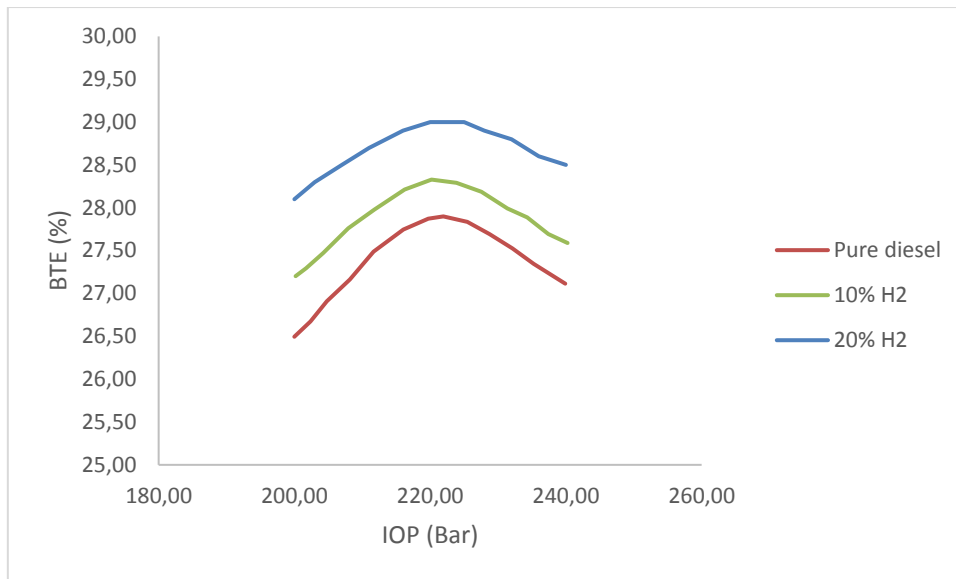
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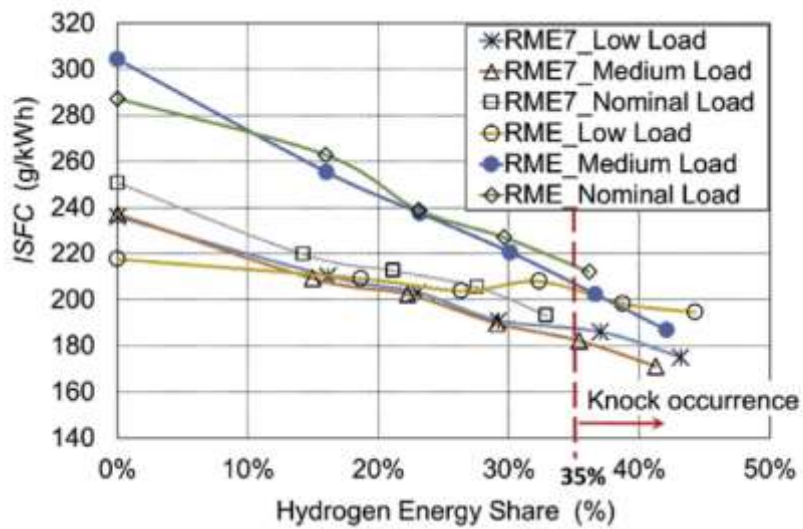
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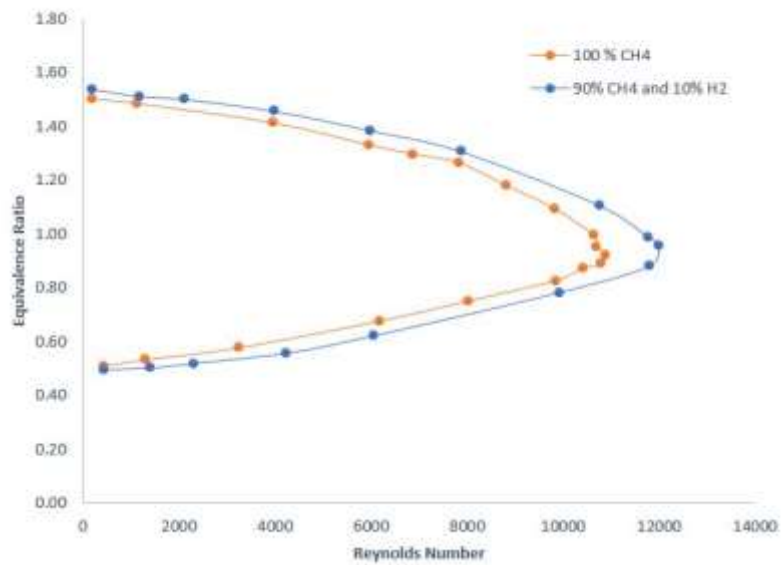
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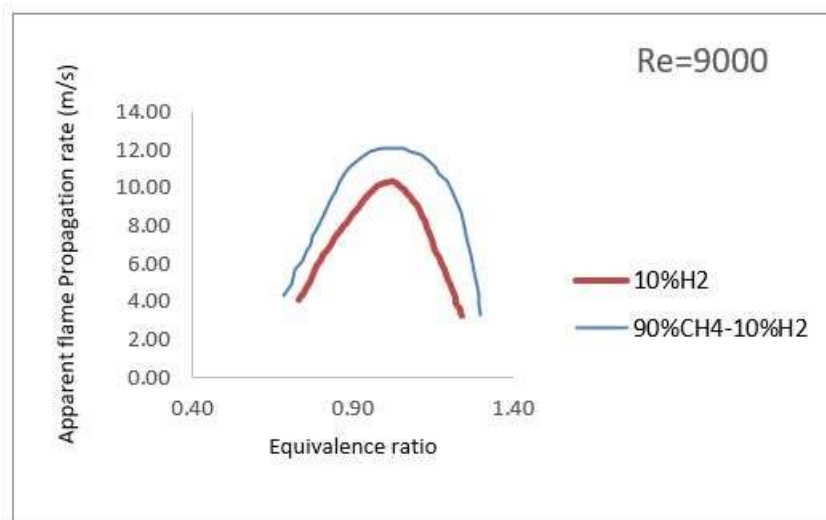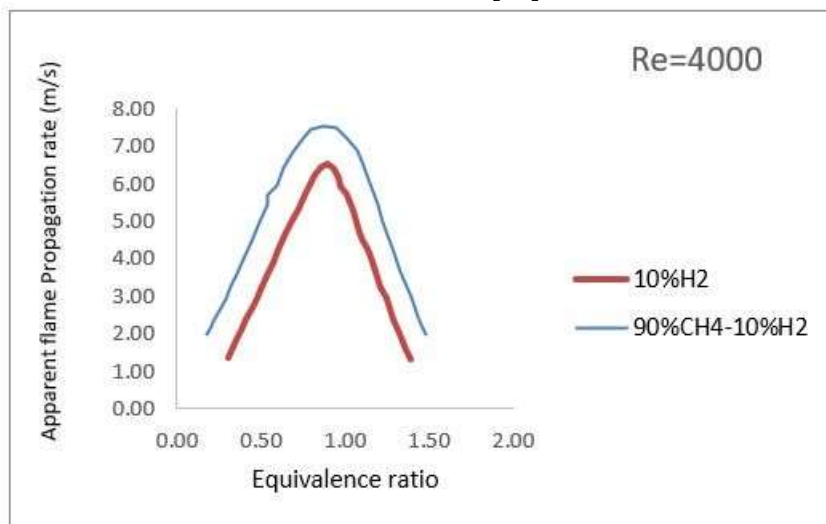
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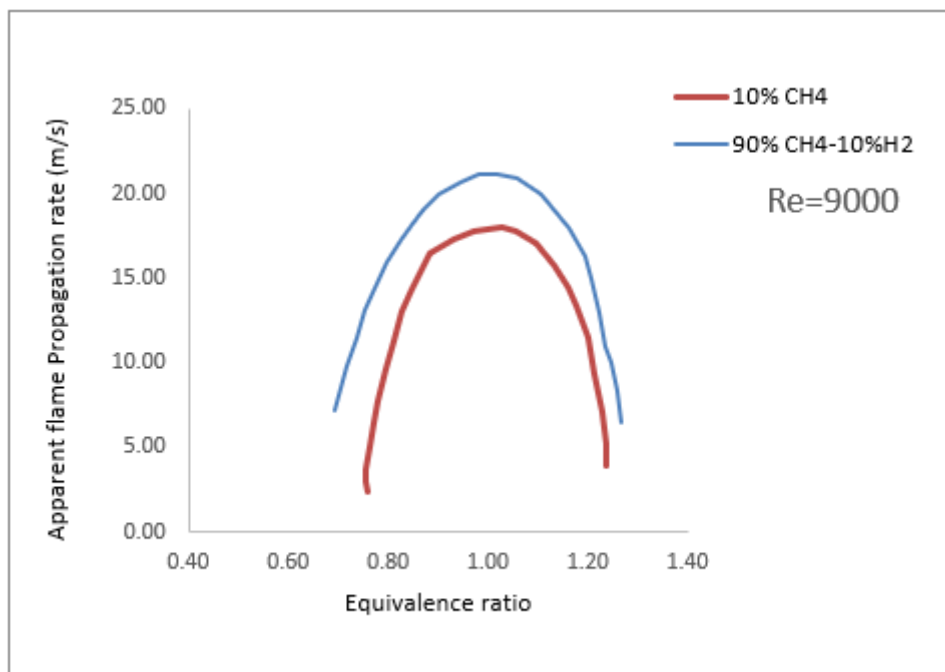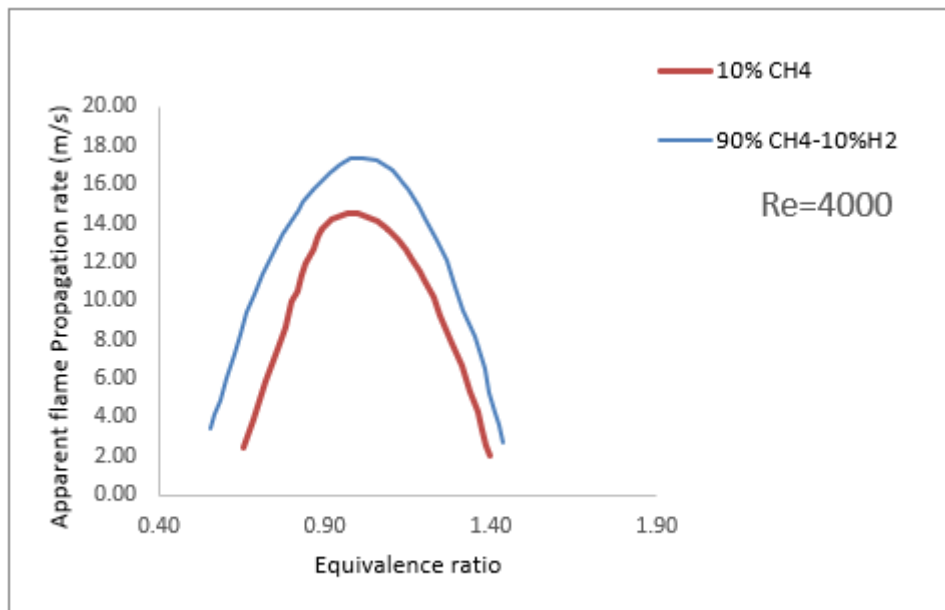
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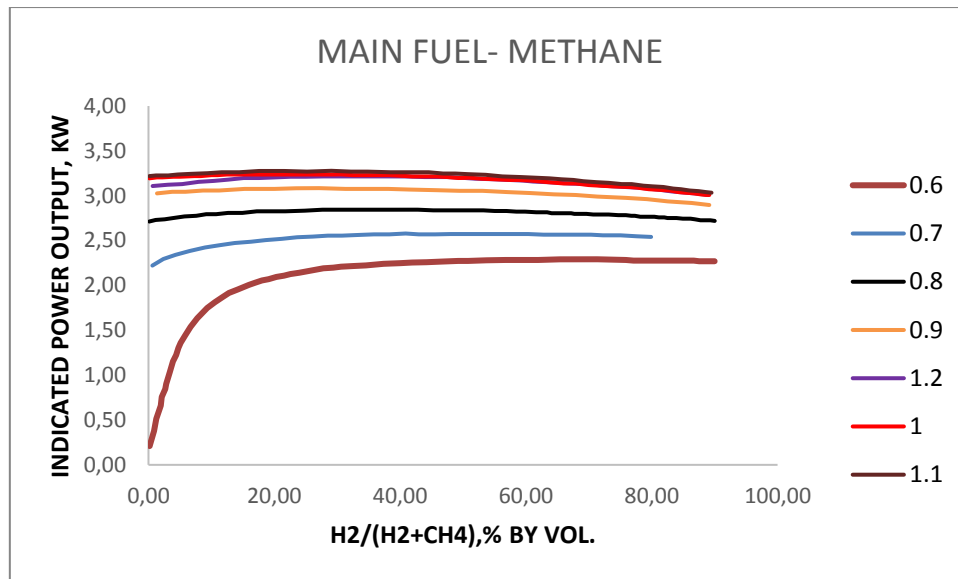
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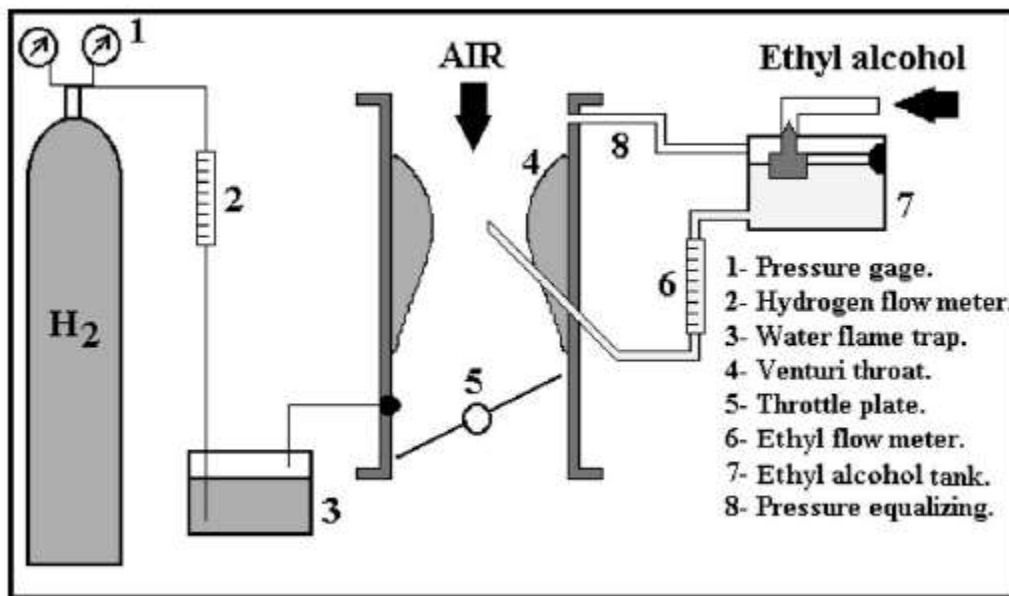
Fig 30 Experimental setup of engine with hydrogen ethanol fuel blend.
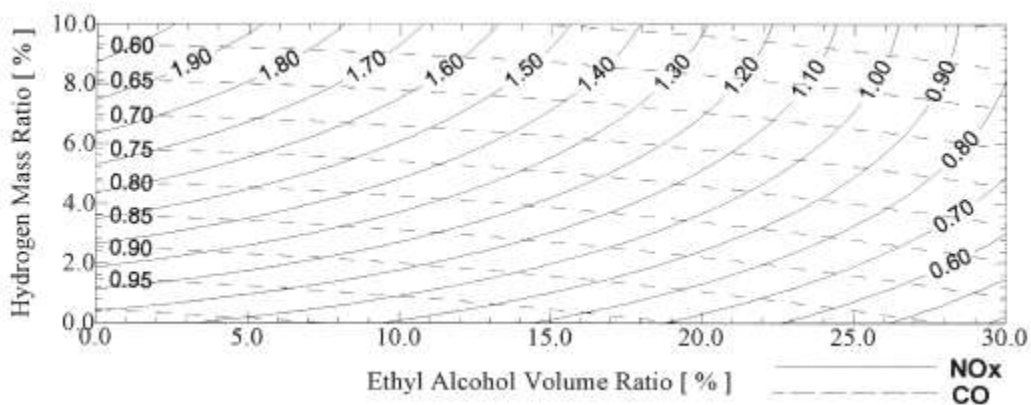
Fig. 31 Effect of fuel composition on CO and NOx, [101].
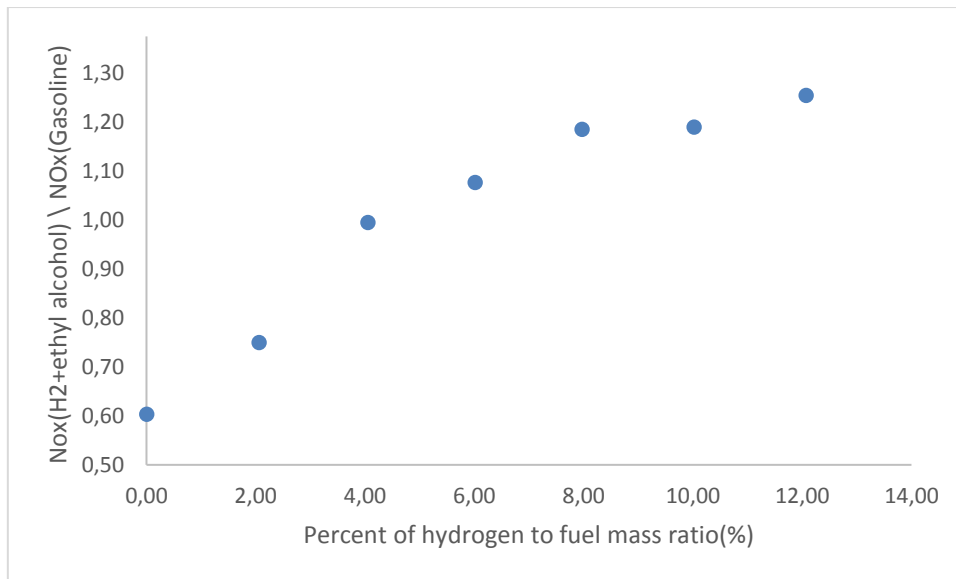
Fig. 32 Effect of hydrogen induction on NOx, [99]
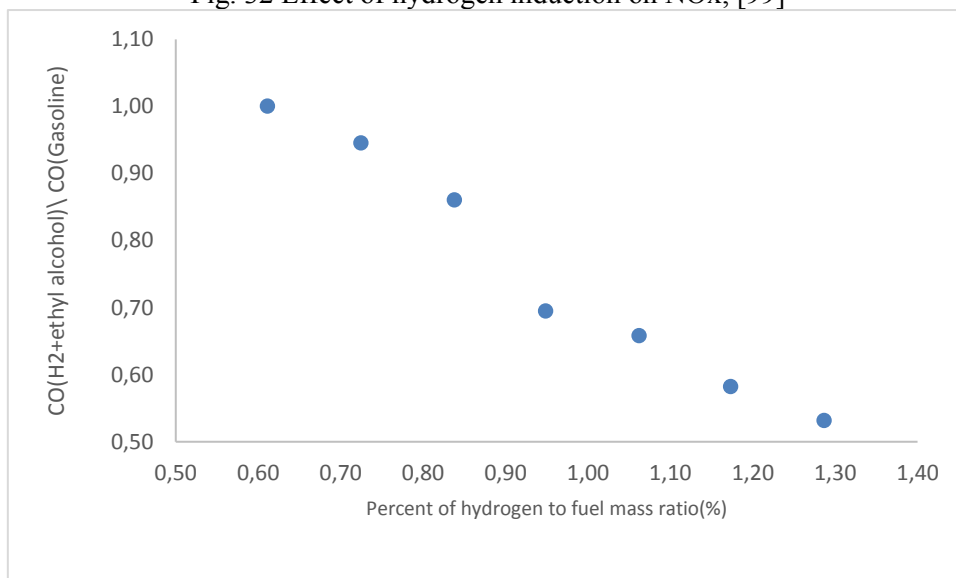
Fig. 33 Effect of hydrogen induction on CO emission, [99].
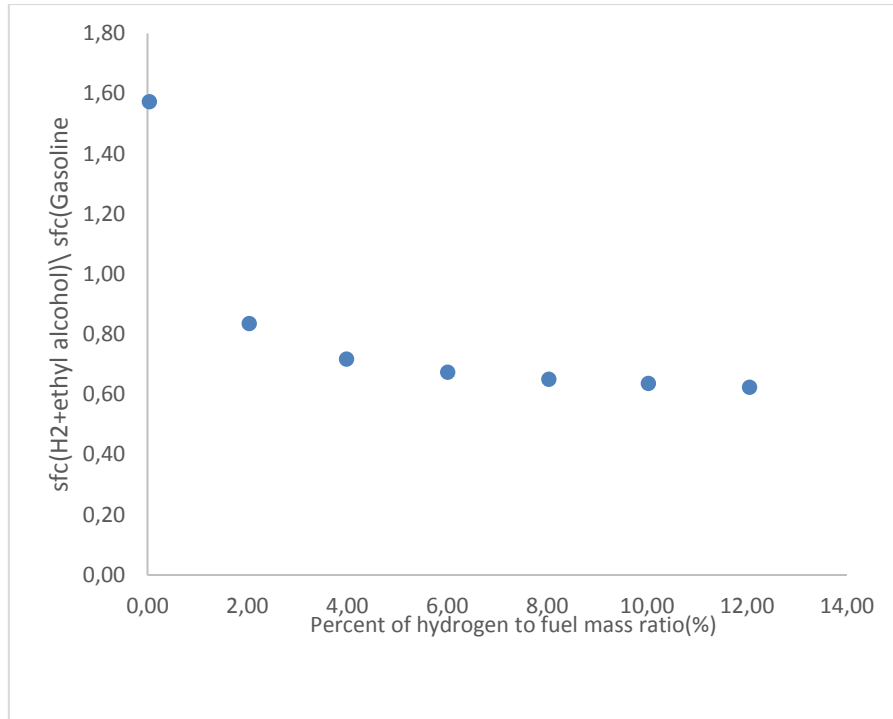
Fig 34 Effect if hydrogen induction on SFC, [99].
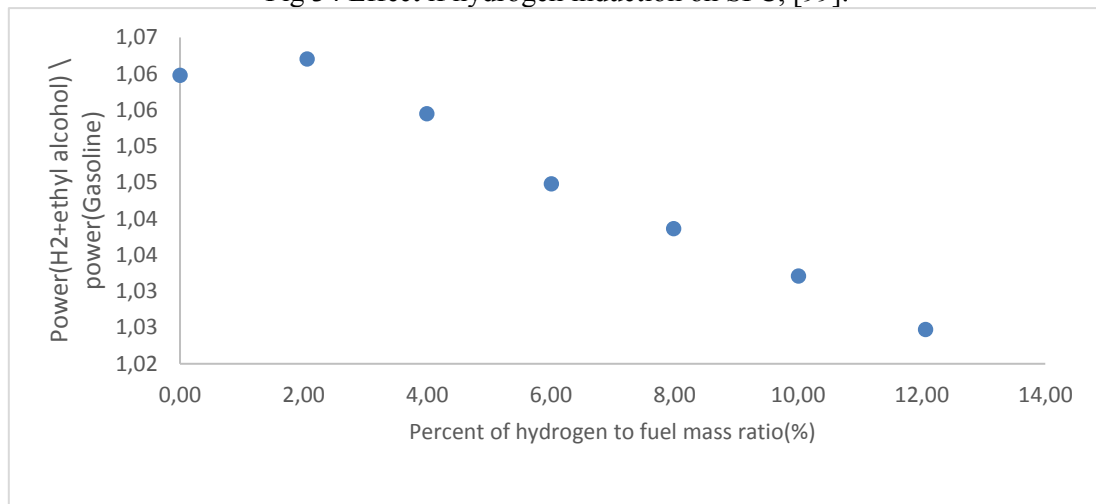
Fig 35 variation of power with hydrogen induction, [99].
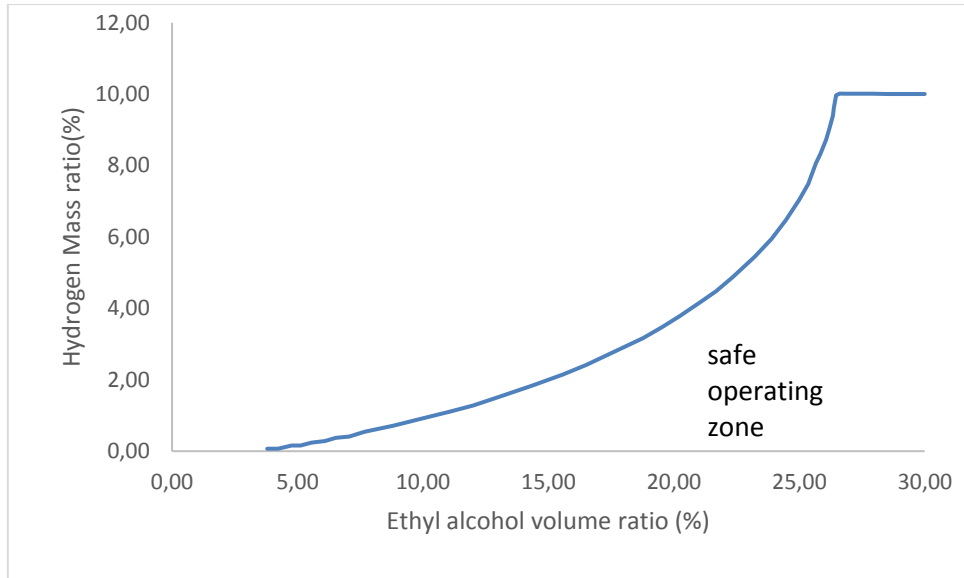
Fig. 36 Safe operation zone for hydrogen + Ethyl alcohol, [101]
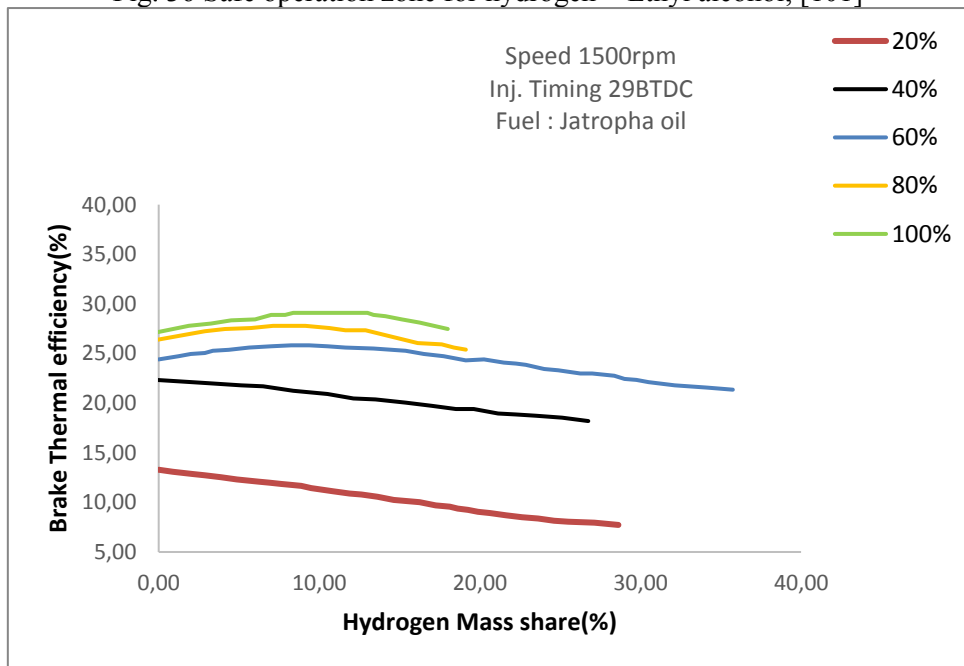
Fig. 37 Variation of Efficiency with different hydrogen mass share
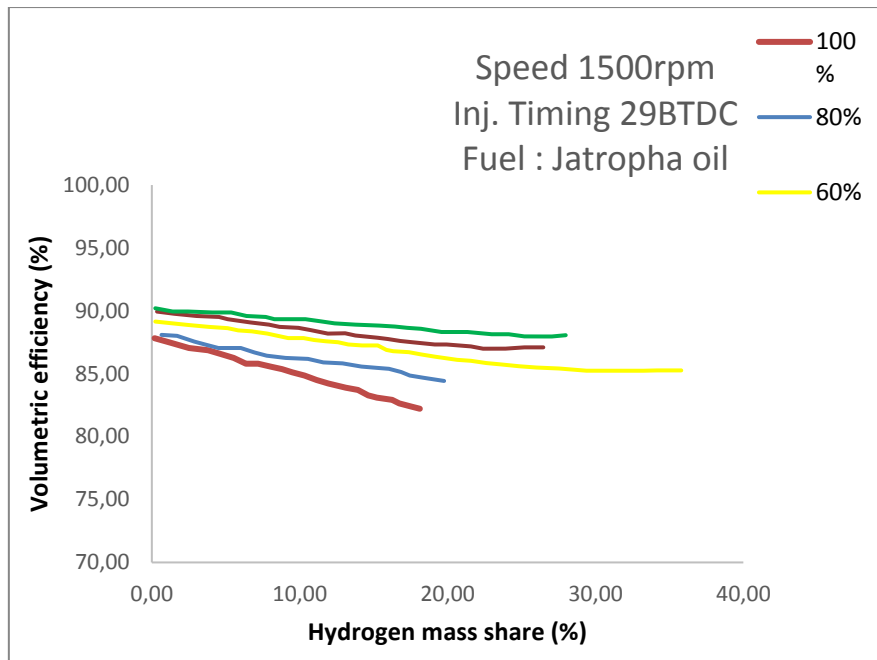
Fig. 38 Variation of volumetric efficiency with hydrogen induction.
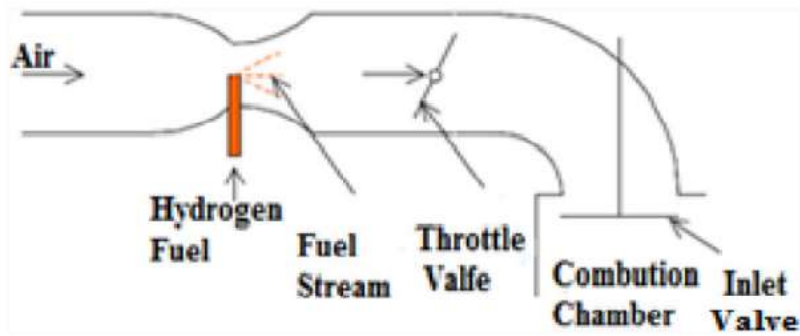
Fig. 39 Fuel Carburation method, [110]
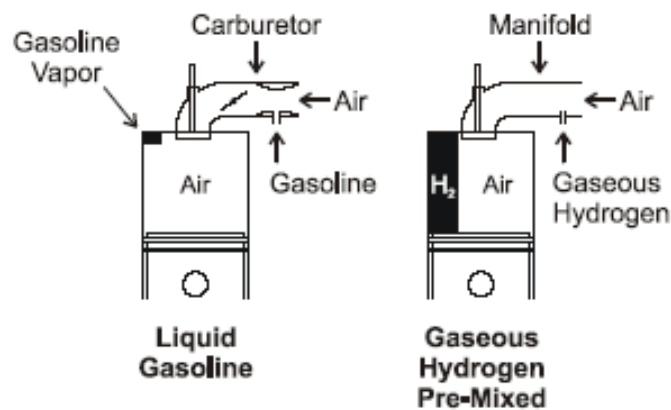
Fig. 40 Portion of combustion chamber occupied by the fuel, [112].
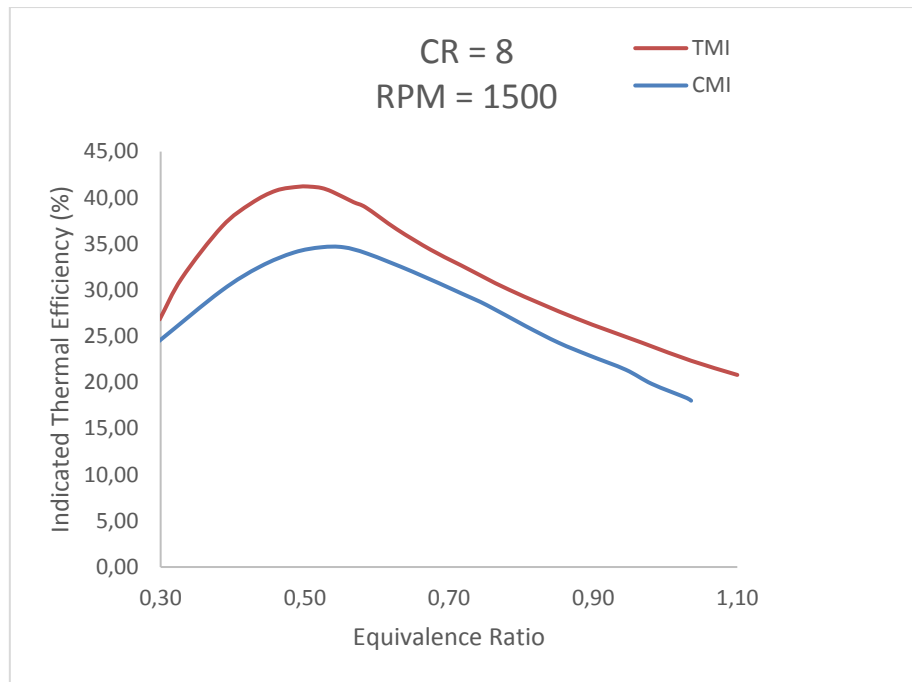
Fig. 41 Variation of ITE Vs phi for CMI and TMI, [74]
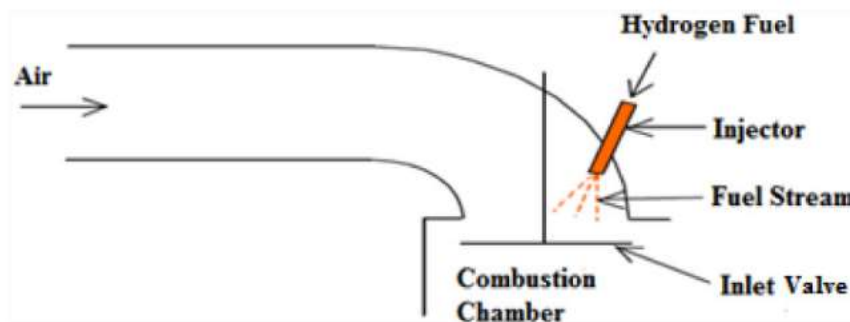
Fig. 42 inlet manifold and intake port injection method, [110]
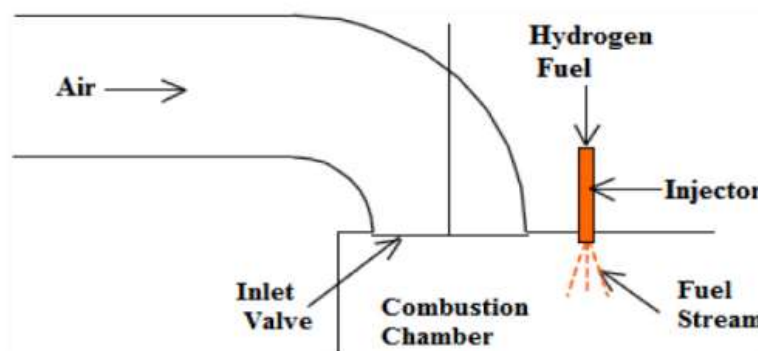
Fig. 43 Direct injection system, [110]
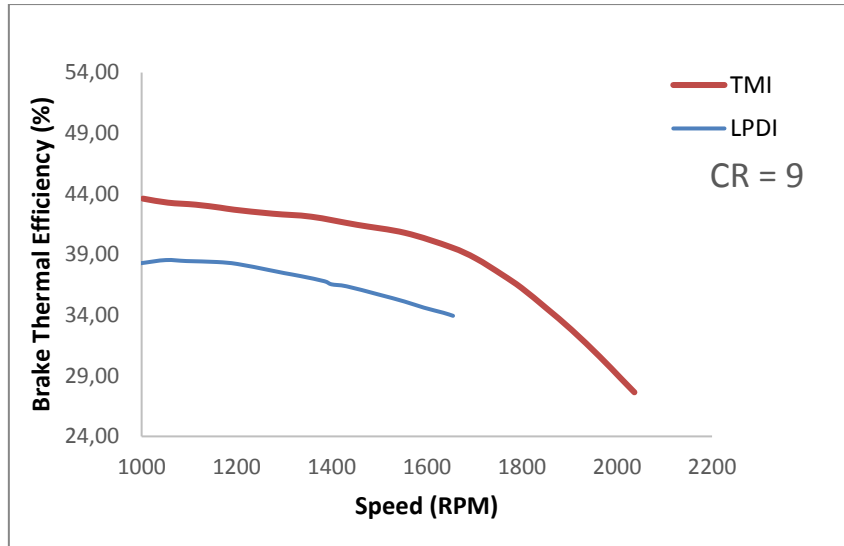
Fig. 44 Variation of BTE W.R.T speed for TMI and LPDI, [74].
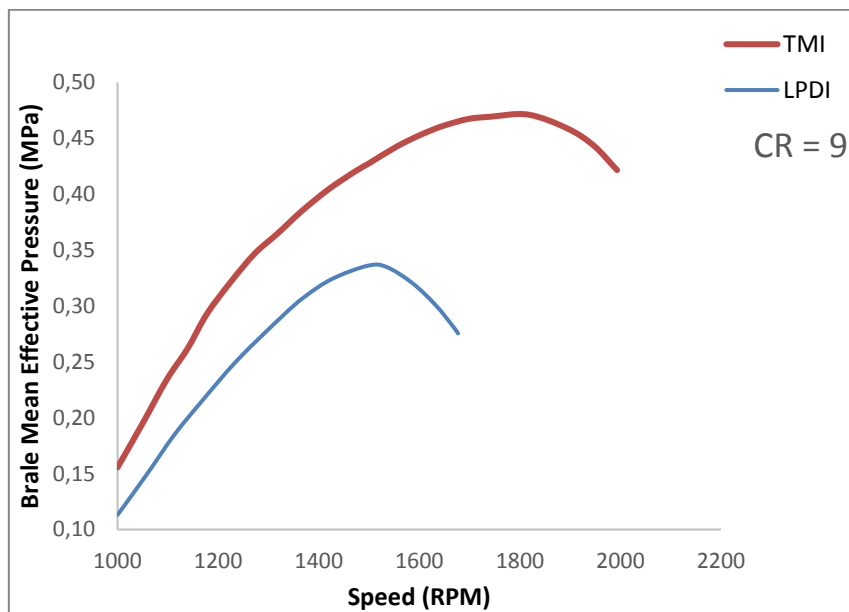
Fig. 45 variation in BMEP with speed for TMI and LPDI, [74].
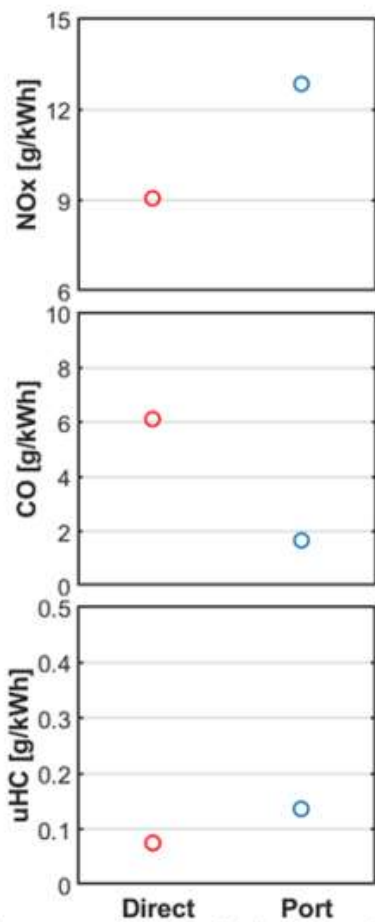
Fig. 46 Engine-out emissions of nitrogen oxides (NOx), carbon monoxide (CO) and unburnt hydrocarbon (Adapted from ref, [121])
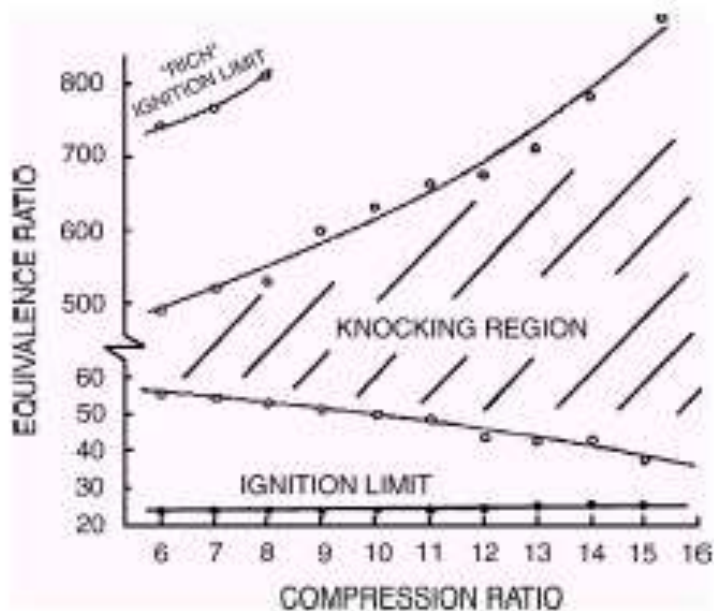
Fig. 47 Variations of operational limits for ignition and knock with compression ratio changes for hydrogen operation at ambient intake conditions, [124].
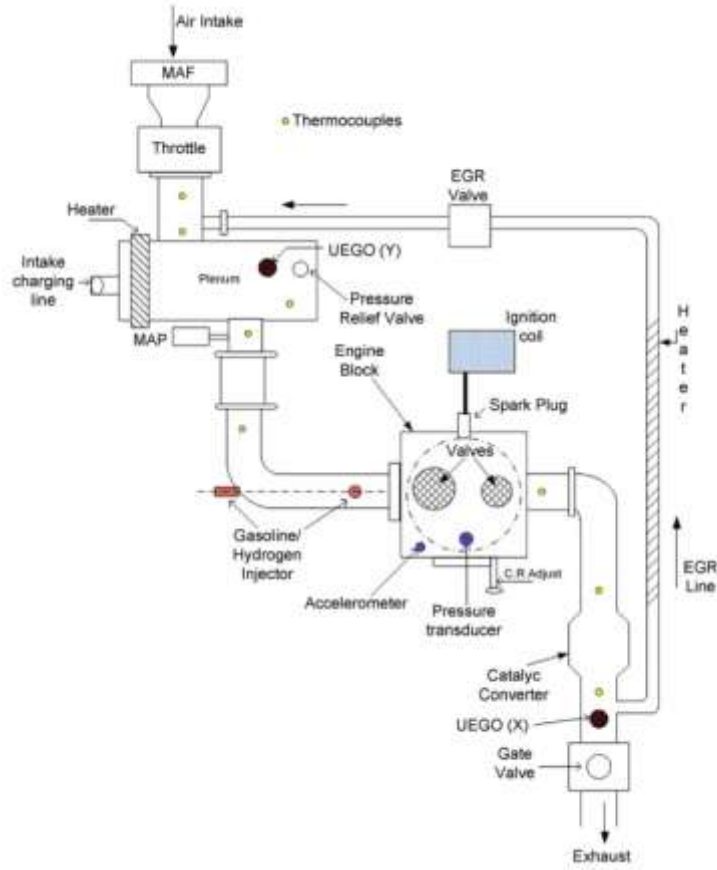
Fig. 48 CFR Engine test bed, [123]
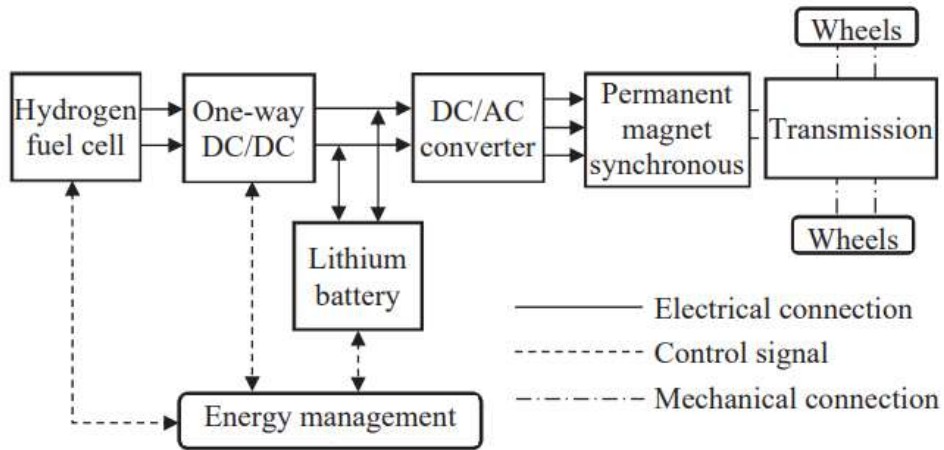
Fig. 49 System structure of the hydrogen fuel cell vehicles, [131].
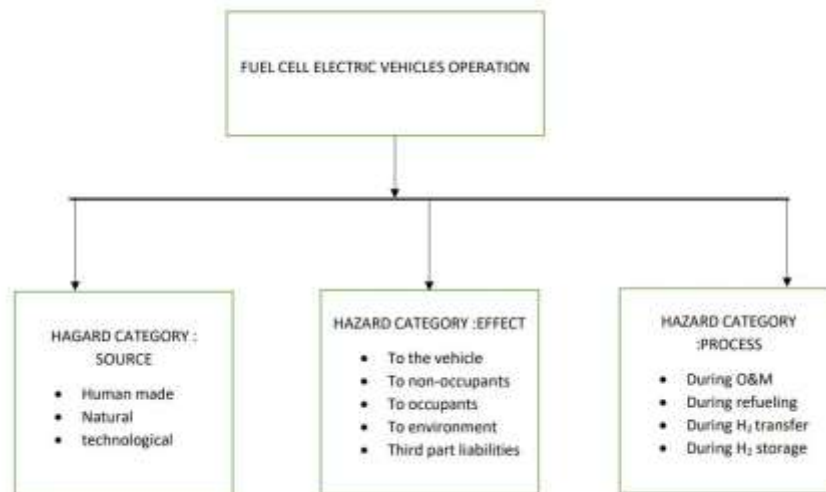
Fig. 50 FCEV hazard categories, [135].
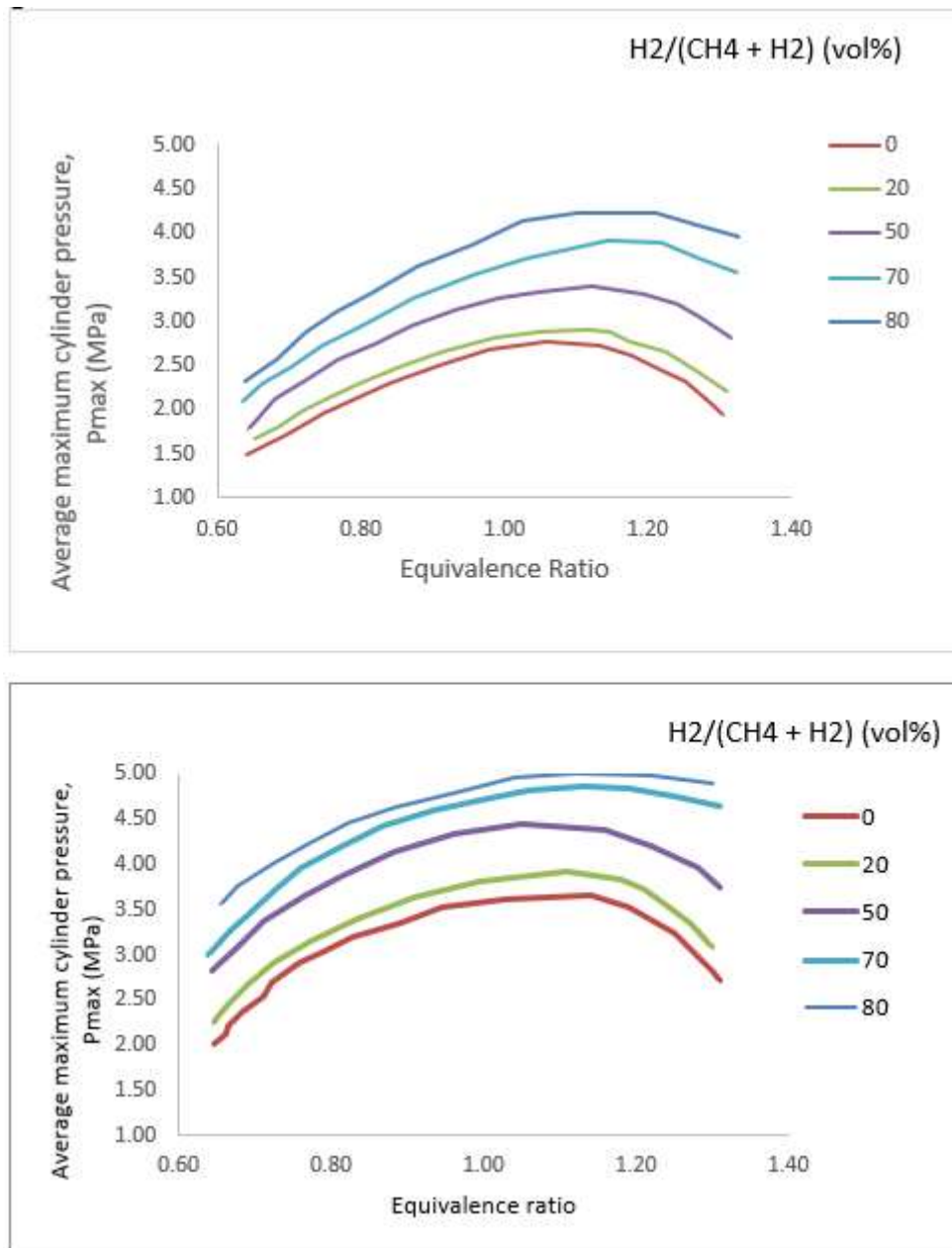
Fig. 51 Typical variations in the maximum cylinder pressure with changes in equivalence ratio when operating on a range of fuel mixtures of hydrogen and methane for two spark timings, [142,88].
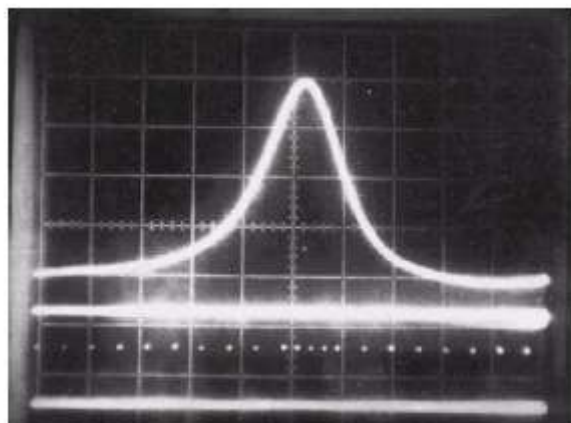
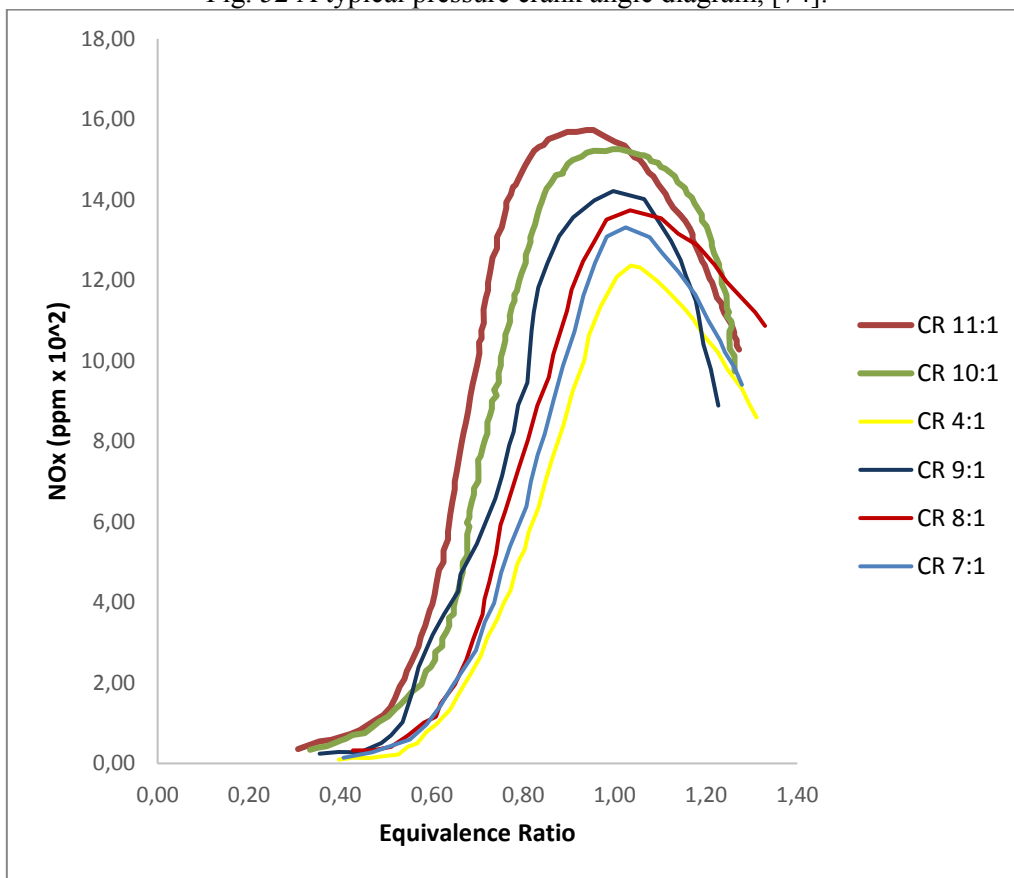Fig. 52 A typical pressure crank angle diagram, [74].

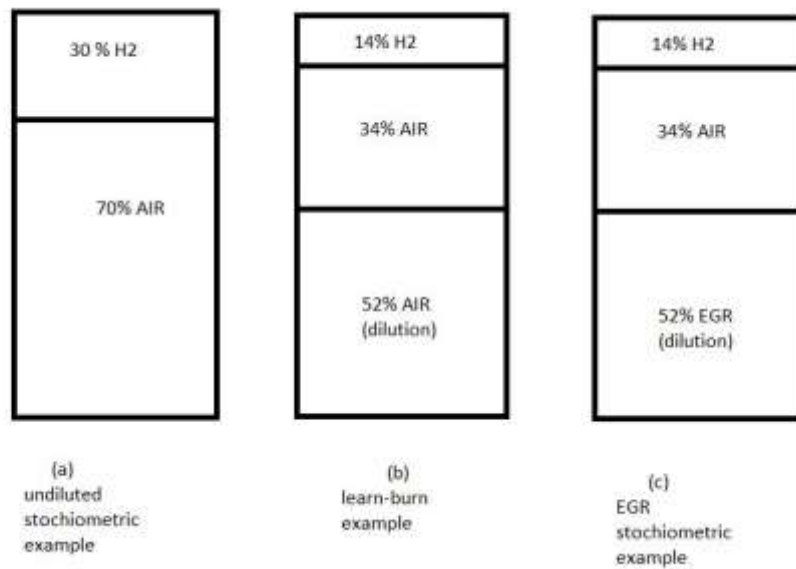Fig. 53 Variation of NOx concentration with equivalence ratio, [74].

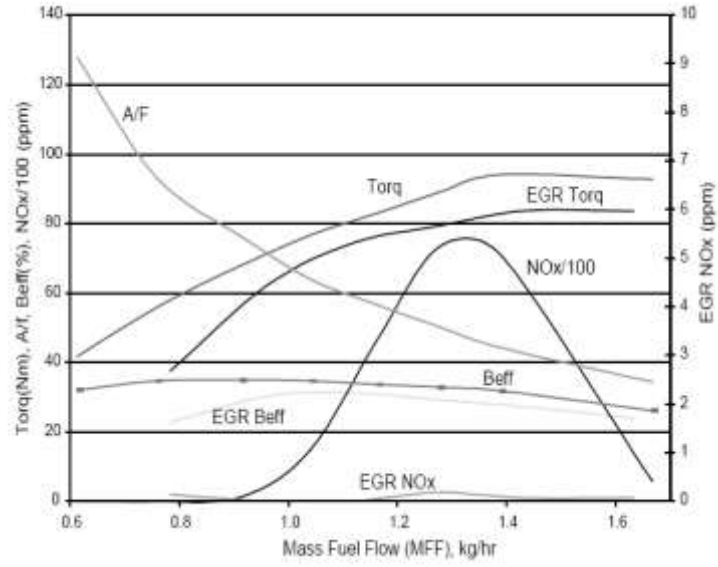Fig. 54 Volumetric portion of air, fuel and exhaust gas inside the combustion chamber.

Fig. 55 Comparison of Lean burn technique and EGR technique at 1500rpm.