CHAPTER 1

INTRODUCTION

1.1 GENERAL

The growing concern about depleting oil reserves, detrimental effects of greenhouse gas (GHG) emissions and the need to reduce emissions from vehicles and power plants are some of the prime factors that increase the necessity for development of alternative energy options (MNRE 2006). Among the various alternatives, hydrogen is a promising candidate, which would provide efficient and clean production of electricity, heat, and transportation requirements (MNRE 2006). Hydrogen is hovering to become a chief constituent in the energy-mix in the coming years to meet the growing energy needs for world's economy, while protecting the environment and guaranteeing energy security (MNRE 2006). It is envisioned that hydrogen will be available for an extensive range of applications including power generation, portable, transport, and heating applications. Hydrogen is principally suitable for meeting decentralised energy requirements of the country's population. However, the conversion to the hydrogen economy from the present economy based on fossil fuel will necessitate solutions to numerous challenges, specifically in the areas of production, storage, delivery and applications, and spanning infrastructure, technology, and large scale public awareness and acceptance (MNRE 2006).

Hydrogen economy is indubitably an effectual strategy to reduce the increasing amount of carbon in the atmosphere due to usage of fossil fuels. The growth of manufacturing sector in developing countries has increased the demand of fossil fuels. Nowadays, the major global challenge is to supply the clean fuels

to meet the future energy requirements through eco-friendly route. The efforts are in progress to reduce dependency on fossil fuels and encourage widespread use of cleaner fuels such as hydrogen. This is driving the research and development towards sustainable technologies for hydrogen production, storage, distribution, and utilisation. Hydrogen economy is a planned structure of utilising hydrogen produced from renewable energy sources with the advantages of a reduced dependency on oil and gas and reduced GHG emissions. According to the International Energy Agency, Global demand for energy is getting increased day by day and is expected to increase 40% by the year 2035. Figure 1.1 shows the regionalwise break-down of GHG emissions which is a contributing factor to climate change. From the graph, it is clear that China's contribution of GHG is very high compared with all other countries. It is followed by United States. India's contribution is 7%. The main challenge relying on all the countries is to reduce GHG emissions while satisfying the demand of energy.



Figure 1.1 Regionalwise break-down of GHG emissions (Oilsands 2014)

1.2 HYDROGEN ENERGY – INTERNATIONAL SCENARIO

A number of countries like Canada, Germany, Japan, UK, USA, etc., are supporting ample research, technology progress, and demonstration programme for developing and implementing hydrogen energy systems for stationary, portable, and transport applications. The main research focus in these countries is on producing fuel cells for automobiles and also for electricity generation by 2020 (MNRE 2006).

1.2.1 Canada

Canada has become a one of the renowned world leaders in developing hydrogen energy technologies. The Canadian Hydrogen Energy Industry is involved in almost all fields, including fuel cells, fuel cell systems, electrolysers, fuelling stations, storage technologies, and safety assessments. According to Canadian Hydrogen and Fuel Cell Association (CHFCA 2012), from 2003-2008, the Government of Canada invested \$170 million in the hydrogen and fuel cell sector through the hydrogen economy program. As a result, over the same five years Canadian industry raised and invested more than \$1 billion.

Today, most of the hydrogen production worldwide requires natural gas and releases CO_2 . Air Liquide Group of Canada is working to develop solutions that will enable to decarbonize the production of hydrogen. They are exploring various avenues to achieve it. Some of them are: use of renewable electricity for the electrolysis of water, biogas, and the capture and storage of CO_2 . In October 2011, the group started a hydrogen initiative program called Blue Hydrogen program. The objective of the program is that by the year 2020 at least 50% of the hydrogen used for energy applications should be produced without releasing any CO_2 . They are also innovating in the development of the infrastructure for the distribution and the storage of hydrogen by designing cylinders made of composite materials capable of resisting high pressure and efficient hydrogen distribution stations.

1.2.2 United States

In the US, the post war era witnessed more development in hydrogen technology. NASA in its spacecrafts used hydrogen based fuel cells for onboard production of electric power, water, and heat even in the 1960s. The first key international hydrogen conference was held in 1974 in Florida (Texas 2014). The conclusion of the conference was that hydrogen was the only solution to environmental problems and depletion of fossil fuels. In 1990s, the demonstration of commercial operated power generators based on fuel cells was carried out successfully.

	200	0 201	0 2020	2030	2040
	Public Policy Framework	Security Climate H2 safety	Outreach and acceptance	Publico	onfidence in hydro- gen as an energy carrier
nework	Production Processes	Reforming of natural	I gas/biomass Gasif Electrolysis using re Thermo-chemical splitt	ication of coal enewable and nuclear ting of water using nuclea	Biophotocatalysis ar Photolytics to split water
Industry Segments Public Policy Fran	Delivery	Pipelines Trucks, rail, garages	Onsite "distributed" facilities Integrated central-distributed networks		
	Storage Technologies	Pressurized tanks (gases and liquids)	Solid state (hydrides)	Mature technolo Solid state (carb	ogies for mass production
	Conversion Technologies	Combustion	Fuel cells Advanced combustion	Mature technologies	for mass production
Hydrogen Ir	End-Use Energy Market	• Fuel refining • Space shuttle • Portable power	 Stationary distributed power Bus fleets Government fleets 	Commercial fleets Distributed CHP Market introduction o personal vehicles	• Utility systems

Figure 1.2 DOE's vision about hydrogen economy (DOE 2005)

In 2002, U.S. Secretary of Energy, Spencer Abraham and major U.S. car manufacturers proclaimed a research plan called FreedomCAR which developed hydrogen technology for the production of light trucks and cars to assess the U.S. transportation system before transition to a hydrogen economy in full fledge. In 2003, the then President George Bush announced the hydrogen fuel initiative of \$1.2 billion for hydrogen technology development. The Bush government had requested nearly \$309 million for 2008 (Texas 2014). Now in 2014, the request is for a huge \$600 million (DOE 2014). Figure 1.2 prepared by DOE shows the milestones to be made in hydrogen energy implementation. It clearly gives the vision of DOE that the hydrogen power implementation would not begin to displace the petroleum fuels in a significant way before 2030 (DOE 2005).

1.2.3 Japan

The Japanese government is showing sky scraping level of dedication to green energy technology development since the Kyoto Protocol was signed in 1997 (Altenergy 2014). To minimize effects of GHGes on climate change caused by the emission, the Japanese government implemented a long-term plan called Cool Earth 50. The main goal of this plan is to reduce GHGes such as CO₂ emissions to 50% by 2050. Fuel cell technologies play a vital role in this plan (Altenergy 2014). To achieve the plan's goal successfully, the Japanese government is concentrating more on fuel cell vehicles (FCVs), stationary fuel cells, hydrogen production, and hydrogen storage technologies.

In July 2010, Japanese government revealed a plan to sell two million fuel cell electric vehicles by 2025, and install 1000 hydrogen fueling stations to support them. The Japanese government has set a goal of fuel cells powering 2 million homes by 2020. In 2012, the Japanese government invested approximately \$240 million in fuel cell and hydrogen energy projects. This was nearly twice the amout spent by the US during the same period. The investment details are shown in Table 1.1.

	¥ Billion	\$ Million
H2 infrastructure & vehicle demo.	3.01	37.71
ENE-FARM	9.0	112.77
$\rm H_2$ production, transport and storage	1.5	18.79
PEM systems	3.5	43.85
SOFC research	0.62	7.77
Industrial SOFC	0.9	11.28
Basic hydrogen research	0.8	10.02
Total	¥ 19.33	\$ 242.20

Table 1.1 Investment details of Japanese government (Fuelcells 2014)

1.2.4 European Union Countries

European countries have made momentous efforts, collectively and severally, in hydrogen-related research activities. Credibly the best-known project is Clean Urban Transport for Europe (CUTE) (Texas 2014). The project was carried out successfully between 2001 and 2006. European Commission (EC) and its member nations financed this project. Its plan was a demonstration project that used 27 fuel cell operated buses as public fleets in seven countries covering nine cities (Texas 2014). Friendly projects took place in China, Australia, and in Iceland. The CUTE project used natural gas as a prime source to generate

hydrogen and also in some instances the electrolysis of water (European Commission 2006).

1.3 HYDROGEN ENERGY – INDIAN SCENARIO

National Hydrogen Energy Road Map (NHERMP) prepared by Ministry of New and Renewable Energy (MNRE) has addressed various aspects of hydrogen economy. The key objective of the programme is to identify the routes, which will lead to a gradual induction of hydrogen energy in the country, speeding up the commercialization and facilitate establishment of hydrogen energy infrastructure in the country (MNRE 2006). The block diagram of total hydrogen energy system proposed by MNRE is shown in Figure 1.3. The Road Map has clearly pointed out that the production of hydrogen is a main area to be concentrated for hydrogen economy. It also insisted that the production of hydrogen should be made from other renewable sources such as nuclear energy, coal gasification, biomass, biological in addition to present methods of production of hydrogen.



Figure 1.3 Block diagram of total hydrogen energy system (MNRE 2006)

Road Map has planned to support the developmental activities to implement hydrogen usage in IC engines in addition to in fuel cells without further delay. It is predicted that about one million hydrogen fuelled vehicles would run on Indian roads and 1000 MW of power would be generated based on hydrogen technology by 2020 (Chemtech 2014). A schematic representation of transition to hydrogen economy is illustrated in Figure 1.4.



Figure 1.4 Schematic diagram representing transition to hydrogen economy (Chemtech 2014)

A schematic diagram showing processes for hydrogen production to meet for immediate supply, medium and long-term supply and for the periods beyond 2017 using various major energy sources for automobile sector, power generation sector, and for process industries like petroleum refining and fertilizers is shown in Figure 1.5 (MNRE 2006).



Figure 1.5 Schematic diagram of processes for production of hydrogen for the period beyond 2017 (MNRE 2006)

1.4 HYDROGEN PRODUCTION

Hydrogen production can be distinguished as follows (Lipman 2011)

- Captive hydrogen
- Merchant hydrogen
- On-purpose hydrogen
- By-product hydrogen

In captive hydrogen production, the hydrogen is produced and used onsite such as at oil refineries.

The merchant hydrogen is produced for delivery to other locations as an industrial gas.

On-purpose hydrogen means the hydrogen production being the main goal.

By-product hydrogen means the hydrogen being produced as a byproduct from another process such as chlor-alkali production.

1.5 HYDROGEN PRODUCTION METHODS

This section presents an overview of the technologies for hydrogen production. They are natural gas reforming; gasification of coal and biomass; and the splitting of water by water-electrolysis, photo-electrolysis, photo-biological production, and high temperature decomposition (IEA 2006). Figure 1.6 shows the various methods of producing hydrogen.

Electrolysis of water and natural gas reforming are well established technologies. These technologies can be used in the initial phases of implementing hydrogen economy for the automobile sector (Momirlan & Veziroglu 2002).



Figure 1.6 Hydrogen production pathways (EIA 2008)

For the industrial production of hydrogen, several technologies are now available. Water electrolysis was the first technology used on commercial basis even in 1920s (Marban & Solis 2007). From 1960s onwards, the commercial production of hydrogen swung gradually towards a fossil based feedstock.

Figure 1.7 exhibits the future pathway of hydrogen. The production of hydrogen from renewable sources on large scale is feasible only in the longer term (IEA 2006). In the near and middling term, the options are producing hydrogen through electrolysis of water and the reforming of natural gas and coal (IEA 2006). It is clear from the figure that large centralised hydrogen production plants are seemingly to be introduced in 2030s (IEA 2006). These plants will possibly be based on fossil fuels and/or biomass with technology of CO_2 capture and storage (IEA 2006).



Figure 1.7 Main hydrogen pathways: the long term perspective (IEA 2006)

1.5.1 Production from natural gas

At present hydrogen can be produced from natural gas by the way of following chemical processes:

- Steam reforming (steam methane reforming SMR).
- Partial oxidation (POX).
- Autothermal reforming (ATR).

1.5.1.1 Steam Methane Reforming



Figure 1.8 Block diagram of steam methane reforming process (EAJV 2014)

Steam methane reforming (SMR) is the process by which natural gas or other methane stream, such as biogas or landfill gas, is allowed to react with steam in the presence of a catalyst to produce hydrogen and carbon dioxide. Figure 1.8 shows the block diagram of steam methane reforming process. When SMR technology is introduced, its efficiency was approximately 72% with natural gas (Lipman 2011). This efficiency is somewhat lower with sources of methane that include sulfur or other impurities that require a pre-treatment cleanup step to remove the impurities upstream of the SMR process. SMR produces a hydrogen rich gas that is typically on the order of 70% to 75% hydrogen on a dry mass basis, along with 2% to 6% of methane, 7% to 10% of carbon monoxide, and 6% to 14% of carbon dioxide (Hirschenhofer et al 2000). Cost of hydrogen from SMR depends on feedstock cost, scale of production, and other variables. It is in the range of about \$2 to \$5 per kg.

1.5.1.2 Gasification of Coal and Other Hydrocarbons





In the partial oxidation (POX) process, also known as gasification, hydrogen can be produced from a range of hydrocarbon fuels, including coal, heavy residual oils, and other low-value refinery products (EIA 2008). The Block diagram of partial oxidation of coal/hydrocarbon process is shown in Figure 1.9. In this process, the hydrocarbon fuel is made to react with oxygen in a less than stoichiometric ratio. This yields a mixture of carbon monoxide and hydrogen at 1200°C to 1350°C. According to National Academy of Sciences/Engineering of US Department of Energy, hydrogen can be produced from coal gasification at delivered costs of about \$2.00 to \$2.50 per kg at large scale. But, in future this cost may get reduced to \$1.50 per kg (NAS/NAE 2004). Hydrogen can also be produced through pyrolysis-based hydrocarbon gasification processes in the absence of oxygen, with similar estimated delivered costs at large scale (NAS/NAE 2004).

1.5.1.3 Autothermal reforming

Autothermal reforming (ATR) of hydrocarbons is a combination of classic steam reforming (endothermic) and partial oxidation (exothermic) (Zeman et al 2011, Nezhad et al 2009) processes. A schematic diagram of ATR is shown in Figure 1.10. In this process, natural gas is mixed with a small amount of hydrogen and desulfurised over a hydrogenation catalyst followed by zinc oxide. This absorbs the hydrogen sulfide formed by the hydrogenation reaction. The desulfurised feed is mixed with process steam to an over-all steam to carbon ratio of 0.6 and passed to the pre-reformer. In pre-reformer all higher hydrocarbons are converted adiabatically over an Ni catalyst. In addition, the methane reforming reaction and the shift reaction are equilibrated (Singh & Malhotra 2004). The resulting mixture of methane, hydrogen, carbon monoxide, carbon dioxide, and steam is heated to the highest possible temperature and mixed with external recycle gas in the amount required to ensure the correct hydrogen to carbon monoxide ratio in the final synthesis gas. And, this mixture is passed to the ATR reactor. Here, it is partially burned with oxygen in the mixer/burner and in the combustion chamber above the catalyst bed (Singh & Malhotra 2004). It is further reacted to equilibrium for the methane reforming reaction and the shift reaction in the catalyst bed. At the same time, the catalyst converts any soot antecedents formed in the combustion reaction to harmless matters so that the product gas is free of soot (Singh & Malhotra 2004). The product gas from the ATR is cooled by the production of saturated high pressure steam and further by air and/or water cooling, before condensate is separated, and the final synthesis gas is introduced into the Fischer–Tropsch synthesis section for further synthesis of the product gas (Singh & Malhotra 2004).



Figure 1.10 Schematic diagram of Autothermal Reforming process (Singh & Malhotra 2004)

1.5.2 Electrolysis of Water

1.5.2.1 Alkaline electrolysis

Hydrogen can be produced via electrolysis of water from any electrical source, including utility grid power, solar photovoltaic (PV), wind power,

hydropower, or nuclear power. Electrolysis is currently done at a wide range of scales, from a few kW to up to 2000 kW per electrolyzer. Electrolysis is the process by which water molecules are split directly into hydrogen and oxygen molecules using electricity and an electrolyzer device. The overall electrolysis reaction is represented by the chemical Equation (1.1).

$$e^{-} + H_2 O \longrightarrow \frac{1}{2} O_2 + H_2$$
(1.1)



Figure 1.11 Hydrogen production by Alkaline Electrolysis

(Teledyne Energy Systems 2014)

The two most common types of electrolyzers in usage are i) Alkaline which uses a potassium hydroxide electrolyte and ii) Proton exchange membrane (PEM) which uses a solid polymer membrane electrolyte. A schematic diagram of an alkaline electrolysis system is shown in Figure 1.11. The electrolysis reaction produces pure oxygen as a by-product along with pure hydrogen. The oxygen can then be used for productive purposes such as enriching the oxygen content of green houses for food production. The large scale electrolyzer is shown in Figure 1.12.



Figure 1.12 Megawatt Scale Hydrogen Production by Electrolysis (ELT 2014)

According to National Academy of Sciences/Engineering of US Department of Energy, the delivered cost of grid power electrolysis is \$6 to \$7 per kg of hydrogen produced. But, it may get reduced in future to about \$4 per/kg. Wind electrolysis-derived hydrogen would cost about \$7 to \$11 per kg, with future potential delivered costs of \$3 to \$4 per kg, including the full costs of production from the wind power system. When compared with other sources of hydrogen production, the solar hydrogen would be more expensive and is in the order of \$10 to \$30 per /kg, with estimated future delivered costs of around \$3 to \$4 per kg (NAS/NAE 2004, EIA 2008).



Figure 1.13 Schematic diagram of steam electrolysis process (Greencar 2014)

The water decomposition at the temperature of range of 800°C to 1000°C is more advantageous because at this high range of temperatures, the energy is supplied in combined form of electricity and heat (Pham et al 2002). This increases the efficiency of the process since, the significant part of the energy needed for the process is added as heat, which is much cheaper than electric energy. In addition, the high temperature accelerates the reaction kinetics and reduces the energy loss due to electrode polarization (Zoulias et al 2004). This increases the overall system efficiency. The schematic diagram of steam electrolysis process is shown in Figure 1.13. This type of electrolyser achieves 92% electrical efficiency compared to low temperature electrolysers efficiency of 85% (Duruz & Jacques 1987, Pham et al 2002). This type of electrolyzer uses oxygen ion conducting ceramics as the electrolyte. The steam to be dissociated into hydrogen and oxygen is in the range of 800°C to 1000°C. After the steam is

split into hydrogen gas and oxygen ions, the oxygen ions are transfered through the ceramic material to the anode, where they discharge and form oxygen gas (Zoulias et al 2004). Despite its high efficiency, the cost of production of hydrogen by this method is nearly four times the cost of the steam reformed hydrogen (Zoulias et al 2004).

1.5.3 Hydrogen as a byproduct from chlor-alkali production

The main product of the chlor-alkali electrolysis process is chlorine and the byproducts are hydrogen and sodium hydroxide. The schematic arrangement of this process is shown in Figure 1.14. In this process NaCl is used as electrolyte material. The cathode and the anode compartments of the electrolysis cell are usually separated by a cation selective membrane of about 50-200 µm thickness. The anode compartment is supplied with brine solution with a concentration of about 180 g/L to 200 g/L of NaCl, and with pH of 1 to 4.5. At the anode, chloride ions are transformed to gaseous chlorine. The cathode compartment is fed with water. At the cathode, water is transformed into gaseous hydrogen and hydroxyl ions. The sodium ions disperse and migrate through the cation selective membrane from the anode to the cathode compartment (Zoulias et al 2001). Sodium combined with hydroxyl ions leaves the membrane cell as sodium hydroxide with a concentration of 23-25 wt%. A potential difference of 2V to 4V between the anode and the cathode is maintained in such a way that the desired current density is obtained. Owing to the presence of a small pressure difference of 0.1 bar between the cathode and the anode, the membrane is pushed against the anode to decrease the mass transfer from the anode to the membrane (Zoulias et al 2001). The distance between the membrane and the cathode is about 1mm. This type of electrolysis units operate at atmospheric pressure and at a temperature of 80°C to 95°C (Stegen et al 1999).



Figure 1.14 Schematic diagram of a chlor-alkali electrolysis process (Chemwiki 2014)

1.5.4 Hydrogen from Biomass

Biomass conversion technologies can be divided into

- Thermo-chemical
- Bio-chemical processes.

1.5.4.1 Thermo-chemical processes

Thermo-chemical processes are less expensive because they can be operated at higher temperatures and therefore higher reaction rates can be obtained. They can be further divided into

- Gasification
- Pyrolysis

1.5.4.1.1 Gasification

Gasification is one of the oldest methods of using coal for light and power. In the late 1790s, Scottish engineer William Murdoch developed this process using coal as a feedstock (Princeton 2014). The produced quantity of syngas is sufficient to light his home. Gasification uses only a modest amount of oxygen. This with steam burned under intense pressure. This kicks off series of reactions which produces a gaseous mixture called syngas. It primarily consists of carbon monoxide and hydrogen. This can be burned directly or used in the manufacture of fertilizers, pure hydrogen, methane or liquid fuels. Figure 1.15 shows the schematic diagram of a bio-mass gasifying process.



Figure 1.15 Schematic diagram of a bio-mass gasifying process (SES 2014)

1.5.4.1.2 Pyrolysis

Heating biomass in the absence of oxygen to produce a hydrogen-rich stream of gas known as "syngas" is called pyrolysis process. This syngas contains the mixture of hydrogen and carbon monoxide. Depending upon the range of biomass types, the quality of syngas gets varied. Figure 1.16 shows the block diagram of biomass pyrolysis process.



Figure 1.16 Block diagram of Biomass Pyrolysis process

(Bioenergyconsult 2014)

1.5.4.2 Bio-chemical process

The enzyme-based biochemical "digester" type processes are at present mainly limited to wet sugar-based feedstocks. The process can be extended to cellulosic based feedstocks in the future with continued improvements in process techniques and systems. At medium production scale and liquid distribution by tanker truck, current delivered costs of hydrogen from biomass would be in the range of \$5 to 7\$ per kg. However when hydrogen is produced on a large scale basis along with pipeline delivery, delivered costs as low as \$1.50 to \$3.50 per kg is believed to be possible (NAS/NAE 2004). According to NAS/NAE (2004) report, it is possible to produce hydrogen with delivered cost of \$1 per kg when it is produced on a large scale by pyrolysis process in the longer term. A more near-term effort is focused on achieving a plant-gate cost of \$2.90 per kg with costs competitive with gasoline by 2015. This can be achieved by focusing on the key research area of "fluidizable" catalysts that avoid high rates of abrasion in the catalyst material (Bair et al 2002, Bair et al 2003).

1.5.5 High Temperature Fuel Cells



Figure 1.17 High Temperature Fuel Cells – MCFC (Fuelcell 2014)

High temperature fuel cell based on molten carbonate (MCFC) or solid oxide (SOFC) technology is shown in Figure 1.17. It operates at sufficiently high temperatures. This means that fuels can be reformed within the fuel cell itself, eliminating the need for external reforming and allowing the units to be used with a variety of hydrocarbon fuels (Fuelcell 2014). This is called internal reforming. Thus, MCFC and SOFC systems do not need a pure or relatively pure hydrogen stream as do proton exchange membrane (PEM) and phosphoric acid (PAFC) systems, but can run directly on natural gas or biogas or landfill gas. Furthermore, such systems can be designed to produce additional purified hydrogen as a by-product by feeding additional fuel and then purifying the hydrogen rich anode tail gas from the fuel cell into purified hydrogen which can be readily used in automobile vehicles (Batawi 1997, Atkinson et al 2004).

1.5.6 Other Methods of Hydrogen Production

Hydrogen can also be produced through other resources, including algae, by direct solar electrochemical processes, and from various nuclear-powerassisted pathways. A significant progress has been made in recent years in these technologies. Some of them appear to be promising opportunities for producing hydrogen from renewable sources with a smaller amount energy loss and potentially lower costs and lesser GHG emissions than current technologies (Kalinci et al 2009).

1.5.6.1 Hydrogen production by biological water-gas shift reaction

The hydrogen can be produced via biological fermentation of carbon monoxide (CO). The flow diagram of hydrogen production by biological watergas shift reaction is shown in Figure 1.18. To produce hydrogen, the COfermentation microorganisms are suspended in a nutrient medium initially lacking a carbon source. And, they are exposed to a light source to activate a metabolic pathway that includes a water-gas shift reaction. Then, they are incubated anaerobically in a slow-flowing CO depleted stream. The stream of CO-starved microorganisms are then combined with a stream of CO-saturated liquid to provide a CO-enriched mixed liquor solids suspension (MLSS), which is then rapidly ejected to create a fast flowing CO-rich stream. The metabolically activated microorganisms metabolize the dissolved CO to form hydrogen and carbon dioxide. The gas coming out of solution from the ejected CO-saturated liquid creates a gas-lift pump that facilitates circulation of the microorganisms and nutrients from the fast-flowing phase back to the slow-flowing phase. The hydrogen and carbon dioxide are removed from the fast-flowing phase prior to return of the MLSS to the slow-flowing stream (Amos 2004, Amos et al 2003, Jensen & Dickman 2010).



Figure 1.18 Flow diagram of hydrogen production by biological water-gas shift reaction (Jensen & Dickman 2010)

1.5.6.2 Hydrogen production by Thermo-chemical method



Figure 1.19 Schematic diagram of Thermo-chemical IS Process (JAEA 2009)

For large scale production of hydrogen, thermochemical water-splitting process is the best one. This process concept was proposed by Funk & Reinstrom (1966). This production method uses multiple chemical reactions in a closed-loop cycle. In it water is the only input and hydrogen and oxygen gases are the only outputs. The main advantage of this process is that its cyclic processes do not produce any waste or effluent streams. Nearly more than 200 thermo-chemical cycles for the production of hydrogen have been evaluated (Sim et al 1992), and pilot plants have already been constructed to make use of both solar and nuclear heat to produce hydrogen. Two and three step cycles are the most interesting because of their simplicity, increased efficiency, and low cost (Kubo et al 2004). In particular, cycles that make use of common and low-cost raw materials have been identified as most promising (Kameyama 1989). Some of the processes of

this method require heat at temperatures as low as 220°C and some require hightemperature of 800° to 1100°C. The Japanese Atomic Energy Research Institute has developed and fully characterized a cycle based on sulphuric acid and hydrogen iodide reactions (Kubo et al 2004). The schematic diagram of Thermochemical IS Process is shown in Figure 1.19.

The Paul Scherrer Institute of Switzerland uses two step thermochemical cycles which use reduction and oxidization of Zn/ZnO (Palumbo et al 2004). The cycle which received significant research attention is the UT3 cycle. This makes use of calcium, iron, and bromine. It is generally presented as a fourstep cycle (Kameyama et al 1989). The efficiency of this production method is calculated as the ratio between the produced hydrogen chemical potential energy to incident solar radiation energy (Lodhi 2004). The average efficiency of the thermo-chemical cycles that have been studied is 44.4% (Wilhelm & Fowler 2006). These efficiencies are much higher than any other method of generating hydrogen from solar or thermal energy.

1.5.6.3 Hydrogen production by photo-electrochemical water splitting process

Photo-electrochemical (PEC) production of hydrogen is a promising renewable energy technology for generation of hydrogen for uses in the future hydrogen economy (James et al 2009). In this process, solar photons are used to generate a voltage in an electrolysis cell sufficient to electrolyze water, producing hydrogen and oxygen gases. Figure 1.20 represents the block diagram of photoelectrochemical water splitting process. The main advantage of this process is that it involves relatively simple processes steps when compared to other hydrogen production processes. Another advantage of this process is, it can be operated on wide temperature ranges. There is no intrinsic upper temperature limit and a lower temperature of slightly below 0°C without a warm-up period, and well below 0°C with a warm-up period dependent on outside temperature (James et al 2009). The immediate challenge for PEC process is to develop materials with sufficient photovoltage to electrolyze water and to minimize internal resistance losses (James et al 2009).

Using theoretical computations, the researchers established that an alloy formed by a 2% substitution of Antimony (Sb) in Gallium nitride (GaN) has the right electrical properties for use as a catalyst in PEC (Wood et al 2011). The researchers concluded that the GaN-Sb alloy is the first simple, easy-to-produce material to be considered as a future contender for PEC water splitting.





1.6 HYDROGEN STORAGE

If, a feasible solution for onboard storage of hydrogen is not found, the vision of using a clean renewable energy system in the long term will not get materialized. The low density of hydrogen is a critical fact to be considered seriously. When compared with density of liquid hydrogen, the density of compressed hydrogen gas of 200 bar with 20°C is nearly five times less. This means that for compressed hydrogen gas, it needs more storage space than liquid hydrogen.

Hydrogen can be stored in the following ways:

- Compressed hydrogen gas in the cylinders
- Liquified hydrogen in a cryogenic vessel/tank
- Metal hydrides
- Slush hydrogen storage

1.6.1 Compressed hydrogen gas in the cylinders

In general, hydrogen gas is stored in gaseous form in cylinders under ambient temperature and pressure of about 200 bar. The materials used for making the cylinders vary from low carbon steels to very high strength non-metallic composites. However, ultra-light weight carbon wrapped aluminium cylinders are being used in space craft industries. These cylinders can store hydrogen upto 690 bar (Feucht et al 1988) and thus are not in a position for commercial entry to the automobile sector. In recent times, some new innovations in the storage of hydrogen were made. One of them is making hydrogen cylinders with composite winding. These cylinders are capable of storing hydrogen upto about 300 bar. This resulted in the reduction of specific weight of the cylinder to about 30 kg per kg of hydrogen stored (Das 1996b).

1.6.2 Liquified hydrogen in a cryogenic vessel/tank

Owing to highest energy density on a weight basis, liquid hydrogen has found widespread application. Because of this property, it is a principal fuel in the space applications. However, to achieve the liquefaction temperature of about 20K, significant energy penalty occurs in the process.

As the temperature level is about 20K, the storage system needs perfect insulation. It is now available as rigid, closed cell porous material. This can be considered as a better mode of storage than compressed gas. However, there is a hydrogen loss of about 2% per day due to evaporation (Das 1996b). Usually liquid hydrogen is kept inside super insulated tanks usually referred to as Dewars or Cryostals. Such Dewars have a very specific construction feature in that they have an inner pressure vessel. In some other, technically superior, designs with high quality Dewars, such vessels are wrapped up with multi-layer insulation consisting of alternating layers of infrared reflecting films. If the size of the Dewar is more, the evaporation loss is very less (Das 1996b).

1.6.3 Metal hydrides

Hydrogen storage through rechargeable metal hydrides offers great promise for vehicular applications. This is because of its compactness and safety. Metal hydrides exhibit a number of distinctive advantages over compressed gas storage or liquid hydrogen. In vehicular applications, volume consideration is an important fact to be considered. Metal hydrides handle this fact very well. Apart from the simple principle there are a number of engineering properties that have a great influence on the practical applications of hydrides in the storage, processing, and handling fields. Some of the important engineering properties of rechargeable metal hydrides are plateau pressure, temperature and slope, specific heat, thermal conductivity, hydrogen capacity, change in volume, rate of decrepitation hysterisis, ease of activation, kinetics of reaction production factors, and safety (Das 1996b). Briefly discussing the working of metal hydrides as at the metal surface, hydrogen molecules separate into hydrogen atoms which get absorbed into the metal crystals as interstitials. Such an absorption reaction produces heat which needs to be removed during the charging operation. Similarly, the desorption reaction consumes heat which must be supplied during discharging. In fact, using different metals and by forming different alloys, it is possible to have different hydriding characteristics (Das 1996b). Such a situation is extremely useful as it gives a wide option for selecting a specific hydride substance for a particular application. Table 1.2 lists the properties of various metal hydrides.

Initial and final composition	Available weight (% H ₂)	Equilibrium temperature at	Ratio of dissociation heat to low heat of	
		1 atm of H ₂ (°C)	combustion	
Li → LiH	12.7	800	0.75	
$Mg \longrightarrow MgH_2$	7.7	290	0.31	
$Ca \longrightarrow CaH_2$	4.8	920	0.72	
Na → NaH	4.2	528	0.42	
$MgNiH_{0.3} \longrightarrow Mg_2NiH_{4.2}$	3.5	250	0.27	
К → КН	2.5	715	0.47	
UH _{0.95} → UH _{2.0}	2.0	12	0.17	
$FeTiH_{0.1} \longrightarrow FeTiH_{1.0}$	0.9	0	0-10	

 Table 1.2 Properties of certain metal hydrides (Das 1996b)

It is concluded that the metallic hydride tank of a vehicle should perform the following two functions effectively:

- Performance characteristic to store the fuel
- Discharging required level of hydrogen to cater to the fluctuating need of an engine.

Thus the selection of the proper hydride is very important while considering it in the automobile operation (Das 1996b).

1.6.4 Slush hydrogen storage

McClaine et al (2000) of the U.S. Department of Energy evaluated the potential of using slurries of chemical hydrides and organic liquids to store hydrogen. Slurry is a mixture of a solid and a liquid to make a pumpable mixture. The main concern in preparing slurry of a solid is to distribute the solid in the liquid in such a way that the solid does not settle out. After a detailed analysis of chemical hydrides, they chose the lithium hydride for their evaluation. They prepared lithium hydride as a slurry with light mineral oil and a dispersant, and has been found to be stable for long periods of time at atmospheric temperature and pressure.



Figure 1.21a

Figure 1.21b



They demonstrated that the lithium hydride slurry could be mixed with water to produce hydrogen on demand. They found that reactions between the lithium hydride slurry and water took place rapidly and completely. The resulting lithium hydroxide could be recycled either by electrolytic methods or by a carbothermal process. Experiments with the carbo-thermal process indicated that the regeneration of lithium hydride could be accomplished at temperatres of 1500K or less enabling the use of economically acceptable furnace materials. Their cost analysis of the regeneration process indicated that the process was cost competitive with H₂ produced from natural gas/stored as a liquid/ compressed gas.

1.7 HYDROGEN AS A FUEL

Hydrogen is a clean fuel and a competent energy carrier (MNRE 2006). Hydrogen is found in water, organic compounds and hydrocarbons such as petrol, natural gas, methanol, and propane. Table 1.3 compares the properties of hydrogen with other fuels. The energy content of hydrogen is about 120.7 MJ/kg which is the highest of all fuels at present. On volume basis, its energy content is low compared to other fuels.

 Table 1.3
 Comparison of hydrogen to diesel and gasoline (Andrea et al 2003)

Properties	Diesel	Unleaded Gasoline	Hydrogen	
Auto-ignition Temperature (K)	530	533-733	858	
Minimum Ignition Energy (mJ)	<u>-</u>	0.24	0.02	
Flammability Limits (vol % in air)	0.7-5	1.4-7.6	4-75	
Stoichiometric Air-Fuel Ratio on Mass Basis	14.5	14.6	34.3	
Limits of Flammability (equivalance ratio)	2	0.7-3.8	0.1-7.1	
Density at 16°C and 1.01 bar (kg/m ³)	833-881	721-785	0.0838	
Net Heating Value (MJ/kg)	42.5	43.9	119.9	
Flame Velocity (cm/s)	30	37-43	265-325	
Diffusivity in air (cm ² /s)	-	0.08	0.63	
Octane Number (RON/MON)	30/-	92-98/80-90	130/-	
Cetane Number	40-55	13-17		

This creates challenges to its storage for local applications. When burnt, hydrogen produces water as a by-product and is, therefore, environmentally benign. Although no CO_2 , etc. are produced if hydrogen is combusted in air, it produces NO_X because of its high temperature combustion.

The advantage of hydrogen as a fuel is that it can be readily used in the existing internal combustion engines. For the generation of electricity through fuel cells, hydrogen is used as a fuel. Hydrogen applications, besides industrial application, cover power generation, transport applications, and heat. However, when compared to other alternatives, use of hydrogen in automobiles sector is emerging as a fast growing technology because of its on-board production.

1.8 HYDROGEN INDUCTION METHODS

1.8.1 Carburetion

Carburetion is the oldest and the simplest technique for inducting the fuel - air mix into the cylinder. For liquid fuels, this method uses simple equipment and principles to distribute the liquid fuel across the air stream so that it gets vaporised more easily in the cylinder. The basic principle of carburettor operation is illustrated in Figure 1.22. The air flows through a venturi nozzle where its velocity gets increased. This leads to a pressure drop in the throat of the venture. Its magnitude depends on the air flow rate and this draws the fuel into the air stream (Heywood 1988). Thus it controls the power output of the engine by varying the amount of fuel - air mix drawn into the cylinder.



Figure 1.22 Fuel Carburetion Method (Overend 1999)

The technique of carburetion was used to operate hydrogen engines by several researchers (Sierens & Rosseel 1998, Vandenborre & Sierens 1996, Rosseel & Sierens 1997, Mathur & Khajuria 1984, Ding et al 1986, Billings et al 1983, Varde & Frame 1984). The advantage of this technique is that it does not require a high pressure hydrogen supply and the principles and equipment it uses are simple and well-established. This technique also allows the fuel to mix uniformly with the air before being allowed into the cylinder, leading to a more efficient combustion. However, this technique reduces power by 15% (Overend 1999). According to Prabhukumar et al (1985) if the engine is turbo-charged, the power and the thermal efficiency can be significantly improved, although abnormal combustion would become more of a problem due to increased peak pressures and NO_X emissions would increase due to elevated combustion temperatures.

1.8.2 Inlet manifold and Inlet port injection

As the name implies, inlet manifold and inlet port injection methods use a constant amount of air induction through the inlet manifold per cycle and the fuel is injected into the air stream by a low pressure injector (Overend 1999). A schematic diagram of this method is illustrated in the Figure 1.23. The power output of the engine can be controlled by the amount of fuel injected into the air stream, thus allowing the lean burn combustion. To achieve this, following methods can be used:

- Varying the injection pressure of the hydrogen
- Changing the injection duration by controlling the signal pulse to the injector
- Combination of above methods

In inlet manifold or port injection method, the injection of the fuel can be scheduled to start some time after the inlet valve is opened. This increases the cooling effect of pre-inducted air. This eventually eliminates the hot spots and the pre-ignition (Varde & Frame 1984). This also reduces the peak combustion temperature and leads to reduction in NO_X emission (Varde & Frame 1985).



Figure 1.23 Inlet port injection (Overend 1999)



Figure 1.24 Direct cylinder injection (Overend 1999)

The problem of back fire can be eliminated altogether if there is no combustible mixture present in the inlet manifold at any time during the combustion cycle (Overend 1999). This can be achieved with direct injection of the hydrogen gas into the cylinder. Figure 1.24 illustrates the direct injection technique. Most researchers adopt this technique of fuel induction to avoid such unwanted combustion phenomena (Ikegami et al 1982, Billings 1983, Furuhama & Kobayashi 1982, Homan et al 1983, Furuhama 1989, Kim et al 1995, Furuhama & Fukama 1986, Jorach et al 1997, Mathur & Das 1991, Wong 1990, Hedrick & Winsor 1994, Yi et al 1996, Glasson & Green 1994). In direct injection technique, only air is inducted during intake stroke. The high pressure gaseous hydrogen is injected into the cylinder at some time during the compression stroke and is ignited soon afterwards. The high pressure injection of hydrogen creates high turbulence in the fuel - air stream. This assists the mixing of the fuel with the air and forms more homogenous mixture of fuel and air. In this technique also, the fuel - air ratio can be controlled either by injection duration (Ikegami et al 1982, Billings 1983, Green & Glasson 1992, Wong 1990, Glasson & Green 1994) or by

injection pressure. The former appears to be a preferred method. In this method, the maximum volume of air available is utilised. This increases the energy available per cycle (Overend 1999).

1.9 ABNORMAL COMBUSTION PROBLEMS OF HYDROGEN

1.9.1 Pre-ignition

Pre-ignition is a problem which happens at an unscheduled time ahead of the planned ignition point that has hindered the experiments of many researchers (Swain et al 1996, Yi et al 1996, Homan et al 1983, Mathur & Khajuria 1984, Lee et al 1995, Glasson & Green 1994, Ikegami et al 1982). This is due to wide flammability limits and minimum ignition energy of hydrogen. This leads to the conditions in which ignition of the fuel and air can happen easily. Such uncontrolled combustion is termed as pre-ignition. Hence, it is necessary to ensure that uniform mixing of fuel and air is achieved away from ignition sources prior to scheduled ignition. Some researchers have concluded that the hot exhaust gases remaining in the cylinder after the previous cycle act as the ignition source for pre-ignition (Ding et al 1986).

1.9.2 Backfire

Backfire is a fierce consequence of the pre-ignition phenomenon. This problem mostly persisted in pre-mixed fuel inducted engines where there is a possibility of the presence of an ignitable fuel and air mixture in the inlet manifold (Sierens & Rosseel 1998). The inlet manifold of an engine is not designed to withstand the high pressures of combustion, so if any flammable mixture gets ignited in the inlet manifold, it resulted in severe damage to the system.

1.9.3 Methods to Prevent Pre-ignition and Backfire

Pre-ignition of the hydrogen fuel - air mix can be avoided if the fuel air ratio and the compression ratio are limited. At the same time, these restrictions severely affect the performance of the engine (Rosseel & Sierens 1997). Limiting the fuel - air ratio to below certain richness reduces the maximum combustion temperature. This means the engine runs cooler and results in less number of presences of hot spots. According to Sierens & Rosseel (1998), if the engine is operated between the fuel - air ratio of 1 to 1.3, the pre-ignition problem can be completely avoided. If the compression ratio is kept below 8:1, smooth operation of the engine can be ensured (Glasson & Green 1994).

Another way to reduce the pre-ignition is by operating the engine with an increased compression ratio. This reduces the relative amount of hot residual exhaust gases in the cylinder. This reduces the contact between the hot gases and the fresh charge thereby reducing the possibility of pre-ignition (Ding et al 1986, Mathur & Das 1991).

Dilution of the charge is another method of reducing the hot spots and the pre-ignition.

Two main methods to dilute the fresh charge are

- Using exhaust gas recirculation (EGR)
- Injecting water

When EGR is used in the combustion process, it decreases the overall combustion temperatures. And, this successfully eliminates pre-ignition (Norbeck et al 1996). The disadvantage of EGR is that the recycled gases displace some of the total available volume of charge, so the power output is compromised.

In water injection technique, water is sprayed into the hydrogen stream before it is mixed with air. By using this technique a few researchers have operated carburetted hydrogen vehicles successfully (Billings et al 1983).

If the charge is cooled before being let into the cylinder, it eliminates the pre-ignition problem and also this increases the density of the charge and results in increased performance (Ding et al 1986).

1.10 FOUR STROKE DIESEL ENGINES

Diesel engines are the main workhorses for heavy-duty vehicles because of their fuel economy and durability. They have higher thermal efficiency, resulting from high compression ratio and lean fuel combustion. Diesel engines are the backbone of the world industries. With high torque, durability, and economical on fuel under transient conditions, they dominate sectors like road and train transport, agricultural, military, construction, mining, maritime propulsion, and stationary electricity production (Akarte 2004).

1.11 CURRENT PROBLEMS OF FOUR STROKE DIESEL ENGINES

There have been continuous search for the most efficient prime movers right from the invention of diesel engines, which will do less harm to the environment. The research and development mainly focuses on the fuel economy and the exhaust emissions of the four stroke diesel engines.

The high levels of smoke and NO_X emissions are the main drawback of diesel engines. These facts put the diesel engines under pressure to cope with the stringent emission norms. The high level of smoke emissions is due to diffusive combustion of diesel engine, whereas NO_X emissions are mainly due to high

combustion chamber temperature and dissociation. It is very difficult to control simultaneously both the smoke and NO_X emission in a diesel engine due to their trade off.

1.12 OUTLINE OF THE THESIS

In order to accomplish the objectives of this research, experiments were carried out on five different flow rates of **O**xygen Enriched Hydrogen (OEH) gas. Based on the experiments carried out, the thesis is divided into six chapters. The core of each chapter is given hereunder:

- Chapter 1 outlines the need of this study.
- Chapter 2 furnishes a detailed study of the related literature available.
- Chapter 3 presents the objectives and methodologies of this study.
- Chapter 4 describes the experimental apparatus used in this study and procedure of the engine test experiments.
- Chapter 5 deals with the results and discussion of this study.
- Chapter 6 presents the conclusion and the possible extension work.