
A review on production processes, performance and emissions analysis of hydrogen as a fuel in I.C. engines

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Abstract: The energy demand increases continuously with rapid increase in the world's population. Continuous depletion of limited non conventional energy resources forces the move towards alternate energy solution. Hydrogen is the environment-friendly and most promising source to meet future energy demand. Non-toxic, non-metallic and high energy content make the hydrogen as a future generation fuel. The main sources of hydrogen production are hydro, biomass, nuclear, wind, geothermal, and solar. Hydrogen can be produced from different methods like thermal, biological, electrical, and photonic. This review article provides detailed information about the production processes of hydrogen, and performance and emissions analysis of hydrogen when it is used as a fuel in internal combustion engines. Brake thermal efficiency of the engine increases with the increase of hydrogen energy share at high and moderate loads. However, at low loads, the efficiency decreases. Carbon-based emissions (HC, CO and CO₂) under dual-fuel mode decreases substantially at all loads due to carbon content in the fuel. This review will help researchers to get the significant details of hydrogen production processes and its optimum utilisation in internal combustion engines.

Keywords: hydrogen; internal combustion engines; hydrogen production processes; performance analysis; emissions analysis.

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1 Introduction

Nowadays, energy demand of world has been rapidly increasing, with increase in industrialisation, urbanisation, transportation, modernisation, and global population (Mahfuz et al., 2014). Due to the high growth rate of the world's total population and enhanced living standards of every person, global energy consumption is gradually increasing from few decades (Nayyar et al., 2017, 2019). Hence, the alternative renewable energy sources are more important due to the increase in environmental pollution and the increase of global warming (Singh et al., 2019, 2020; Kazim and Veziroglu, 2001).

Currently, non-renewable resources mainly, coal, wood, natural gas and petroleum products are used worldwide to meet about 85% of the world energy demand, which highly contributes to environmental issues (pollution, climate change and global warming), political crises, economic issues, and international disturbance between OPEC and consumer countries. In 1970 during the oil crisis, the research of new and alternative energy system increases and leads to increase in level of carbon dioxide which manifold the level of pollution and lead to climate change all around the world. The development and assessment of new energy technology from sustainable or renewable resources was still a challenge to the researchers (Ley et al., 2014).

Therefore, researchers are working to find efficient and economics methods to harness renewable energy resources. The renewable resources have storage problem, location-dependent as per their availability in nature, and transportation is still a major challenge. Many resources can be implemented to produce hydrogen as a future fuel, such as solar thermal energy, solar PV panels, and wind energy. Hydrogen is a sustainable energy carrier as a future fuel and one of the most promising clean fuels among all alternative that emits by-product as water without any carbon emissions to the environment. Hydrogen has tendency to provide socially advantage, financial stability, energy efficiency, and economic feasibility to various energy issues and also have potential to meet the increasing global energy demand and reduction of global warming (Dutta, 2014).

The hydrogen does not readily exist as a chemical substance on earth, but it is available in the form of compound state with other atoms such as water and hydrocarbons. Steam methane reforming (SMR) of hydrocarbon is one of the direct and simplest production methods of hydrogen for commercial purpose in industry. Other important technologies also exist to get pure form of hydrogen, e.g., electrolysis, pyrolysis, gasification, and thermolysis (Stern, 2018; Graetz and Vajo, 2018; Burhan et al., 2017). Currently, the produced hydrogen has been widely used other than fuel for I.C. engines; such as petrochemical, fuel cells, fertilisers, chemical industries, and petroleum refining processes (Rakib et al., 2010; Lim, 2015; Lee et al., 2017). Global hydrogen production is limited to 500 billion cubic metres per year (Acar and Dincer, 2014; Rand, 2011). Worldwide, hydrogen demand can be met with the use of both non-renewable and renewable energy resources, i.e., oil/naphtha reforming (Trane et al., 2012; Iranshahi et al., 2011; Rahimpour et al., 2013), steam reforming of methane (Boyano et al., 2011; Xu et al., 2009), water electrolysis (WE) (Barbir, 2005; Atlam and Kolhe, 2011; Siracusano et al., 2012), biomass (Mujeebu, 2016; Abuadala and Dincer, 2012), coal gasification, and biological sources (Levin et al., 2004; Elsharnouby et al., 2013; Sivagurunathan et al., 2016).

Hydrogen production by using renewable energy is advantageous because only water is obtained as by-product that leads to zero-emission of carbon and greenhouse gases. Hydrogen has high energy density on mass basis, with high heating value (HHV) of 142 MJ/kg and low heating value (LHV) of 120 MJ/kg, which makes it suitable as an alternative fuel for internal combustion engines (Ouyang et al., 2013). Many research studies have been done on the feasibility and merits of hydrogen as a base fuel or with diesel and gasoline in dual fuel mode for internal combustion engines. In gasoline engines, excellent results have been demonstrated with the hydrogen fuel to achieve satisfactory performance and normal combustion behaviour with extremely reduced harmful emissions (Karim, 2003; Das, 1991; White et al., 2006). On the other hand, its implementation as a single fuel in diesel engines is challenging for researchers because of its high auto-ignition temperature, and it can only be achieved with the implementation of a lower auto-ignition fuel (pilot fuel) such as diesel or biodiesel to use for wide engine operation range with high energy share (Lilik et al., 2010; Kose and Ciniviz, 2013).

Therefore, improving the operation methods and combustion behaviour of internal combustion engines with hydrogen is an effective way to go green for short to long-term benefits to reduce their harmful emission and to fulfil the required energy demand. The compression ignition engine's reliability could be brought back by hydrogen fuel due to significant reduction of harmful diesel emissions. Various research studies have been performed on the usage of hydrogen as an alternative fuel for internal combustion engines with the use of advanced technologies. Some research reports show that hydrogen was also used to produce a moving power in thermal machinery.

Most of the review articles cover either the production of hydrogen or its use as a fuel in I.C. engines. Due to lack of availability of article that covers the production of hydrogen and its efficient use in I.C. engines motivates authors to write this article. This review article focuses on different production techniques as per commercial approach from various available renewable resources of hydrogen. It also included the details of the performance and emission behaviour of the I.C. engines fuelled with hydrogen as a primary fuel with diesel and gasoline. Finally, this review paper defines the main benefits of hydrogen to use as a future fuel with modern technologies and its benefits comparable to other available fuels.

2 Hydrogen

Hydrogen is widely considered to be a prospective cost-effective and green fuel to fulfil world's energy need because it's demonstrated to be:

- 1 the earth's most abundant element
- 2 sustainable and lightest element with least molecular weight (2.016)
- 3 high energy content on mass basis
- 4 non-toxic
- 5 environmental friendly.

Hydrogen has an impressive energy storage ability that exceeds double of most standard fuels (Hwang and Varma, 2014; Colozza and Kohout, 2002; Teichmann et al., 2012) and calculations have shown highest energy contained of approximately 120 MJ/kg

(33.33 kWh). Heating value of hydrogen fuel and some other fuels such as liquefied natural gas (LNG), gasoline, diesel, etc., which are used in I.C. engines are presented in Table 1 (Abe et al., 2019).

Table 1 Comparison of energy contents of different fuels

<i>Fuels</i>	<i>Low heating value</i>	<i>High heating value</i>
Hydrogen (gaseous)	141.88	119.96
Hydrogen (liquid)	141.77	120.04
Methanol	22.88	20.09
Crude oil (petroleum)	45.53	42.68
Liquefied petroleum gas (LPG)	50.14	46.60
Ethanol	29.84	26.95
Natural gas	52.21	47.13
Liquefied natural gas (LNG)	55.19	48.62
Coal	23.96	22.73
Diesel	45.76	42.78
Diesel (low-sulphur)	45.56	42.60
Gasoline	46.52	43.44
Gasoline (low-sulphur)	45.42	42.35

Source: Abe et al. (2019)

Hydrogen is an odourless, colourless, and makes zero emission of harmful gases during combustion with oxygen. Two hydrogen molecules and one single oxygen molecule combine and this reaction of atoms lead to formation of water and during this process ample amount of energy is released. Combustion of the hydrogen takes place at elevated pressure and temperature (Dimitriou and Tsujimura, 2017). Various physical properties associated with hydrogen fuel are given in Table 2.

Table 2 Various physical properties of hydrogen fuel at 25°C temperature and 1 atm pressure

<i>Properties</i>	<i>Units</i>	<i>Hydrogen</i>
Low heating value (LHV)	MJ/kg	119.7
Heat of combustion	MJ/kg _{air}	3.37
Density	kg/m ³	0.0824
Auto ignition temperature in air	K	858
Fuel/air mass ratio (stoichiometric)	-	0.029
Flame velocity	m/s	1.85
Volume fraction (stoichiometric)	%	29.53
Flammability limits (volume % in air)	%	4–75
Quenching distance	mm	0.64
Minimum ignition energy	mJ	0.02
Flammability limits (ϕ)	-	0.1–7.1
Adiabatic flame temperature	K	2,480

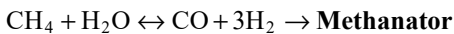
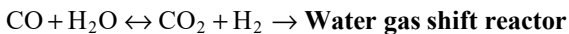
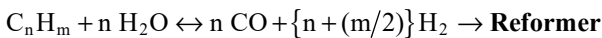
3 Production methods of hydrogen

Hydrogen is very light element found on earth and due to its least density; earth pushes it away from the earth's surface. So, presence of pure hydrogen is very less in amount and inconsiderable over earth (Dimitriou and Tsujimura, 2017). Hydrogen is found in abundant in its compound state of water and fossil fuels, which demand for extraction of it from these compound states by using advanced technologies. Hydrogen production is widely done from renewable sources through WE with the help of wind energy or solar energy and using pyrolysis or gasification of coal, biomass/biofuels. However, major contribution of worldwide hydrogen is from SMR, pyrolysis, partial oxidation (PO_x), auto-thermal oxidation, and gasification from fossil fuels (methane and other hydrocarbons) (Abdalla et al., 2018).

Domestic production of hydrogen makes an economic independence from petroleum products. Renewable resources contribute very less in total hydrogen production (biomass, wind and solar energy, geothermal) and approximately 95% of the total production is from fossil methods using methane and petroleum products (Serban et al., 2003; Dimitriou and Tsujimura, 2017). Some of the important and widely used hydrogen production techniques are discussed below.

3.1 Steam methane reforming

Methane have high H/C ratio among the available fossil fuels and contributes largely in hydrogen production. SMR is generally used with methane and includes various processes as impurities removal (sulphur) by sulphuriser, generation of synthesis gas (syn-gas) by catalytic reforming, gas purification, and water gas shift (WGS) reactions. In reforming reaction, various operating parameters are optimised such as steam to carbon ratio of approximately 3.5, temperature (700–850°C), and pressure (3–25 bar), this optimisation of parameters is done to prevent the formation of coke on the catalyst surface and to get the desired pure form of hydrogen (Ersöz, 2008). Metal catalysts used are non-precious due to the both heat and mass transfer constraints, but these catalysts have low effectiveness of Adris et al. (1996). A pressure swing adsorption unit is used to purify the processed hydrogen gas after the chemical reactions and pure hydrogen is generated with CO₂ as a by-product of the process (Chen et al., 2008). SMR method is considered as one of the most adaptive commercial method for hydrogen production compared to other available methods due to its low production cost and high hydrogen yield efficiency of approximately 74% (Acar and Dincer, 2013; Lighthart et al., 2011). The reactions involved in SMR method are given as follows:



3.2 *Partial oxidation (PO_x)*

For the partial oxidation (PO_x) method, hydrogen generation is similar to SMR but the chemical reactions are performed with temperature ranges of 1,150–1,315°C. PO_x method can be performed with or without using the catalyst; if it is done non-catalytically then the sulphur impurities can be neglected with hydrogen gas. Generally, high temperature range is used for PO_x method to complete the conversion and for the elimination of carbon formation or soot emissions. High temperature operations without catalyst provide the capability to feed heavy oil, coal, and methane products. However, feedstock in convertor ranges from methane to naphtha for catalytic process and operating temperature used is approximately 950°C (Abdalla et al., 2018).

3.3 *Coal gasification*

Coal is mainly one of the oldest fossil fuel and found in abundant all over the earth surface. As per the records of world coal association (WCO), only 1.1 trillion tones of coal reserves are estimated worldwide and will fulfil demand for next 150 years at current rates of its demand and production. Gasification of coal is an effective way for production of hydrogen. In gasification, solid fuel is converted to gaseous fuel by thermo-chemistry transformation process. Gasification is a familiar and long-time technology with an aim of emission reduction during burning of coal by enhancing the fuel density.

Fixed bed, fluidised bed or entrained flow are various coal gasification processes for hydrogen production but high temperature entrained flow is industrially used for maximum conversion of carbon to gas comparable to fixed or fluidised bed. In coal gasification method, the processes generate hydrogen gas along with synthetic gas (syngas) and CO. From the products, hydrogen is separated and WGS to reactors to process CO and syngas for more hydrogen extraction. Gasification process requires ample amount of heat, thus it is endothermic and energy-intensive method. Typical reaction (Abdalla et al., 2018) takes place in the gasification of coal is given below.



3.4 *Pyrolysis of biomass*

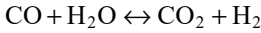
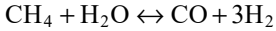
Biomass is animal or plant residue, forest and agricultural waste, and food crops material, can be used for energy production. Biomass mainly contains carbon and hydrogen compounds that can be used for hydrogen production by using advanced thermo-chemical technologies such as pyrolysis or gasification. Biomass conversion by pyrolysis, directly into liquid fuel is still limited because liquid products formed are high chemically and thermally unstable.

In this process, pressure (0.1–0.5 MPa) and temperature (650–800 K) are used in absence of air to get liquid oils. Pyrolysis of biomass can be achieved by both slow pyrolysis technique and speedy (flash) pyrolysis technique. Slow pyrolysis technique is used for the products contain charcoal whereas fast pyrolysis is used for rapid heating of biomass at elevated temperature in anaerobic conditions to form vapour, that vapour get condensed and became a dark brown mobile bio-liquid (Jalan and Srivastava, 1999).

Hydrogen can be generated by fast pyrolysis at an elevated temperature and by using volatile phase residue which include following reactions:



During fast pyrolysis, methane and other hydrocarbon vapours produced which can be further processed for more H₂ production with steam reforming technique followed by (Abdalla et al., 2018) reactions mentioned below.



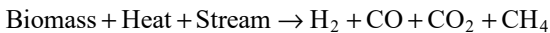
Hydrogen production from pyrolysis can be categorised as:

- 1 catalytic pyrolysis through analysis of the catalyst weight/biomass with fluidised bed reactor and continuous feeding (Garcia et al., 1998)
- 2 catalytic steam reforming of pyrolysis liquids (bio-oil) by the pyrolytic reaction and optimisation of the gas contents of N₂ and O₂ of the pyrolytic bio-oil (Renny et al., 2016)
- 3 in-line steam reforming of volatiles of biomass pyrolysis (Arregi et al., 2018; Santamaria et al., 2018).

3.5 Biomass gasification

Biomass gasification is widely implemented for direct conversion of biomass into gas and processed further to form hydrocarbons and methanol (Fischer-Tropsch synthetic route), which can be used for hydrogen generation. Gasification is used for coal rather than biomass because of the some issues such as biomass consists of 75–85% volatile matter while coal has 20–35% volatile matter and this large amount of volatiles get vaporised rapidly from biomass within a narrow range of temperature (250–400°C).

Biomass gasification has low thermal efficiency because of the high moisture content, thus it is used for moisture content of less than 35% to eliminate more complex structure formation in steam reforming process. Gasification is done with an aim to get only gaseous products but pyrolysis is done for bio-oils and charcoal formation. So, oxygen is must for the solid biomass gasification but pyrolysis does not need it. Gasification is performed at elevated temperature of more than 1,000 K so that biomass get converted into a gaseous product and particles through partial oxidation process to produce gas and charcoal which leads to H₂, CO, CO₂, and CH₄ products after charcoal reduction (Demirbas, 2013). The main chemical reaction is given below:



3.6 Water PV electrolysis

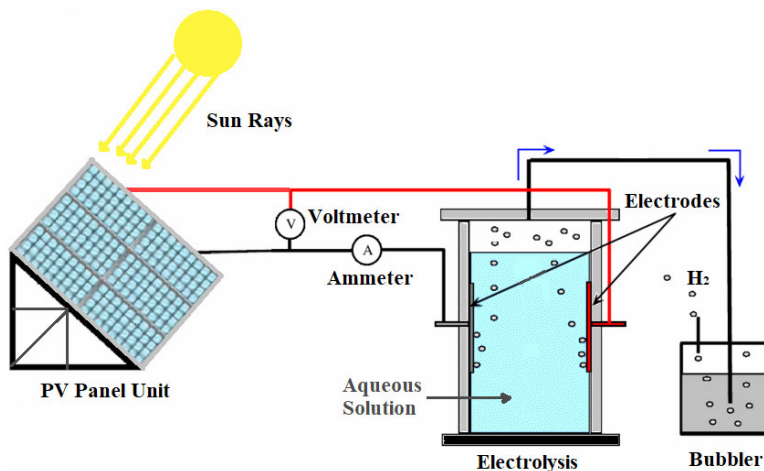
Energy from sun can also be utilised for hydrogen generation with the help of WE. In WE process, electric power generated from various sustainable resources (solar, wind, geothermal and biomass) are used. So, it is one of the most reliable methods for hydrogen production and only pure oxygen is generated as by-product from renewable water.

In late 1970, photovoltaic cells (PV cells) were first used and DC power generated by solar energy is utilised for the WE to produce H_2 from water (Khan et al., 2002; Hollmuller et al., 2000; Bilgen, 2001). After lots of research and development in this area, 20% photo-converter efficiency and 80% efficiency of the electrolyzers is achieved. The overall efficiency for hydrogen generation by conversion of solar energy method is approximated 16% (Rzayeva et al., 2001; Yilanci et al., 2009).

In electrolysis process of water, the electric current in the process dissociate the H_2O molecules into hydrogen and oxygen molecules. The process of hydrogen production using this method is shown in Figure 1. The main advantages of WE are production of hydrogen in pure form, high production rate, and high cell efficiency that make its more compatible for further use of this pure hydrogen in low temperature fuel cells technology to get electrical energy (Barbir, 2005). On the basis of operating parameters, electrolyte and its ionic agents (OH^- , H^+ , O_2^-), WE process (Kumar and Himabindu, 2019) can be classified in to the four types as:

- 1 alkaline WE
- 2 solid oxide electrolysis
- 3 microbial electrolysis cells
- 4 polymer electrolyte membrane (PEM) WE.

Figure 1 Hydrogen production through water PV electrolysis process (see online version for colours)



Even with the majority of research in this field, the technology has many barriers to overcome as high PV cells cost, large capital and maintenance costs and even high energy is consumed for large-scale production of hydrogen (Zahrani et al., 2013; Zeng and Zhang, 2010).

4 Hydrogen in I.C. engines

Across the world, India is the part of fastest economic developing countries and due to high consumption rate of diesel compared to gasoline, it is one of the largest diesel driven economy (Subramanian et al., 2005). Due to high availability of hydrogen on the earth and also can be extracted through different methods from wide variety of available renewable sources from nature, this high demand of diesel might be fulfilled effectively with hydrogen fuel (Chintala and Subramanian, 2017).

Worldwide, many of the government policies have widely proposed for implementation of hydrogen as a future fuel through a sustainable energy system. Ministry of New and Renewable Energy (MNRE) of India has formulated a National Hydrogen Energy Roadmap (NHER) in the year 2007, and envisaged the targeted for 1,000 MW electrical power generation from hydrogen-based system and use of hydrogen-based fuel vehicles of about one million in the country by the year 2020 (Chintala and Subramanian, 2017).

The use of hydrogen as a clean, efficient and renewable fuel is very promising for high-efficiency operations in I.C. engines. Homan et al. (1979) operated a hydrogen fuelled C.I. engine in 1978, and soon realised that because of the high resistance to auto-ignition behaviour, the operating range of hydrogen fuel was one of the constraints (Homan et al., 1979). Even for higher compression ratio (29:1), it was unable to resolve this limited operation range issue. Later, the authors revealed that ignition with the help of glow plug is a feasible method for smooth operation and reliable ignition in engines and investigated that results became efficient with the help of a multiple-strike spark plug and a glow plug by converting a diesel engine for hydrogen fuel only. The ignition delay with diesel oil was large but results obtained with hydrogen fuel found very short delay. Indicated mean effective pressures (IMEP) and efficiency were generally higher for hydrogen compared to diesel fuel. Due to the large amplitude pressure waves, some cyclic variations were observed in ignition delay period during combustion. It results in significantly higher NO_x concentrations at the low equivalence ratios of hydrogen and air (Homan, 1989).

Naber and Siebers (1998) have also investigated the auto-ignition behaviour of hydrogen fuel which shows strong dependency of hydrogen ignition delay over the Arrhenius temperature. The authors took a constant volume vessel for combustion and performed experiments using large amounts of dilution with top dead centre (TDC) of engine and for wide range of thermodynamic conditions. Moreover, lower level of O₂ concentration and the fuel temperature highly affects the ignition delay, but the H₂O and CO₂ concentrations have negligible dependence on ignition delay. Ikegami et al. (1982) has operated the hydrogen fuelled engine by assembling a single-cylinder, four-stroke, indirect injection and water-cooled, naturally aspirated engine and found limited operating range with hydrogen as a fuel (Ikegami et al., 1982).

5 Performance of I.C. engines fuelled with hydrogen

5.1 Power output and brake thermal efficiency (BTE)

Fuel energy density, volumetric efficiency and pre-ignition are primary factors to determine the peak power output of hydrogen fuelled I.C. engines. Several researches have been done with diesel and gasoline engines to determine peak power output for hydrogen as a fuel. Shin et al. (2011) has investigated effect on the performance characteristics with different amount of hydrogen (5%, 10%, 20%, 30%, 40%, and 50% by volume) with diesel. A significant increase in engine power and improvement in combustion have found due to hydrogen addition into diesel engines (Shin et al., 2011).

Ghazal (2013) found that the maximum power output get enhanced for 5% to 10% of hydrogen addition at different engine speeds and air-fuel (A/F) ratio of less than 15:1. At higher A/F ratio (>15), the maximum power output got affected only after 30–40% hydrogen substitution, which resulted considerable increase in the volumetric heating value and better combustion efficiency of the intake mixture during combustion. Ghazal (2013) found that by adding 40% of hydrogen with higher A/F ratio, power get increased by 70% compared to neat diesel fuel. The performance analysis of I.C. engine fuelled with hydrogen is given in Table 3.

Many studies reported the fact that high BTE can be attained by using high research octane number (RON) fuel in an internal combustion engine. Researchers found that dual-fuel engines based on hydrogen gives decreasing BTE trend for low loads and increasing BTE trend at moderate and high loads with increase in quantity of hydrogen (Chintala and Subramanian, 2014; Rao, 1983). Experimental analysis was performed to find the trend of BTE by using different induction techniques like inlet manifold and direct injection of hydrogen into the cylinder and found increased BTE with both the techniques for the increase in hydrogen addition with diesel (Hairuddin et al., 2014). However, compared to direct injection, efficiency obtained 19% higher with induction through inlet manifold because of homogeneous mixture of hydrogen with air. Complete heat release is obtained because mixture get completely burnt with the initiation of flame with this injection method (Masood et al., 2007a).

5.2 Brake mean effective pressure (BMEP)

BMEP defines the capacity of engine to generate power output after combustion of fuel at its full speed range and is considered as an effective tool for performance comparison of two engines. High BMEP is an indication of capacity of engine to perform desired operations even at high load (Hairuddin et al., 2014). BMEP is also used to get comparable study of performances of engines with same fuel in different engine or different fuel mode for same engine.

Mean effective pressure is found to increase about 15% with hydrogen compared to the neat diesel fuels with same operating conditions (Ghazal, 2013). The maximum increase of effective pressure of about 30% to 40% for hydrogen can be the resulted in ample amount of energy released per unit fuel mass for a A/F ratio more than 15 and for all engine's speeds. Korakianitis et al. (2011) used hydrogen and demonstrate large

abnormal combustion noise for high BMEP tests in C.I. engines. Thus, to eliminate the risk of blast and damage to engine parts, there is minor decrease in the maximum attained engine load is required during normal combustion (Korakianitis et al., 2011).

5.3 Volumetric efficiency

With the large volume replacement by the hydrogen during air intake at the time of suction stroke, the volumetric efficiency of hydrogen operated I.C. engines inherently decreases. A considerable effect on volumetric efficiency can be seen on the volume basis, because a fully vaporised gasoline stoichiometric mixture have only 2% gasoline by volume, whereas approximately 30% hydrogen by volume can be found in hydrogen and air (stoichiometric mixture) (Furuhama et al., 1978).

Geo et al. (2008) investigated for hydrogen energy share of 13.4% and found volumetric efficiency reduced from 91% to 85% with hydrogen dual-fuel mode compared to diesel in C.I. engine. It is due to intake air displacement which can be inducted in place of hydrogen (Geo et al., 2008). The similar trend of the decrease in volumetric efficiency is observed as hydrogen energy share increases (Varde and Frame, 1983). It is found that that increase in hydrogen amount and engine load, considerable reduction in the volumetric efficiency is observed (Morais et al., 2013). As the engine intake manifold has high injection of gaseous hydrogen, gradual decrease in intake air flow rate is observed because of replaced air molecules with the hydrogen molecules. As per the experimental analysis of results, with 20% of hydrogen energy share, maximum decrease in the volumetric efficiency (up to 6%), is reported (Morais et al., 2013).

5.4 Exhaust gas temperature, in-cylinder pressure and temperature

Hydrogen has higher heating value than diesel (mass basis), so hydrogen release high amount of heat than diesel during the combustion, which leads to the fact that in-cylinder temperature would always remain higher with hydrogen fuel in C.I. engine. Hydrogen gas is primary energy carrier for hydrogen-diesel dual fuel engines; in-cylinder temperature (combustion temperature) is considerably high as compared to engine operated with neat diesel, which require better engine cooling technique during engine modification. Elevated in-cylinder temperature also increases the exhaust gas temperature. This high rate of heat energy release (because of HHV) during combustion in expansion stroke is the main cause of enhanced in-cylinder temperature and exhaust gas temperature (Geo et al., 2008). An increase in share of hydrogen energy up to 10.1% leads to increase of exhaust temperature to 427°C from 364°C.

Varde and Frame (1983) stated that the increase in hydrogen addition is the main reason of exhaust temperature increase because at a given equivalence ratio, there would be high flame temperature and rapid combustion of hydrogen. Chintala and Subramanian (2017) reported that at 75% engine load and 33.6% hydrogen energy share, energy of exhaust gas show increment of 25.7% from 24% with neat diesel fuel (Chintala and Subramanian, 2014).

Table 3 Performance and emissions analysis of I.C. engines fuelled with hydrogen

H_2 (%) in fuel	Performance				Emissions			References
	EGR	BTE	BSFC	PM	HC	NO_x		
98%	17%	Increases	Increases	Decreases	Decreases	Increases	Increases	Dimitriou et al. (2018)
25%	30%	Increases	Increases	-	Increases	Increases	Increases	Yu et al. (2019)
15%	No	Increases	Increases	-	Increases	Increases	Decreases	Yilmaz and Tastan (2018)
45.1%	No	Increases	Increases	Decreases	Increases	Decreases	Decreases	Akansu et al. (2017)
25%	No	-	-	-	Increases	Increases	Decreases	Wu et al. (2016)
14%–17%	No	Increases	Increases	-	Decreases	Decreases	Decreases	Varde and Frame (1983)
2.5%–15%	13%	-	-	Increases	Increases	Decreases	Decreases	Lilik et al. (2010)
10%–40%	No	Increases	Increases	Increases	Increases	Decreases	Decreases	Zhou et al. (2014)
83%	29%	Increases	-	No change	Increases	-	-	Suzuki and Tsujimura (2015)
2%–10%	2%–31%	Increases	-	-	Increases	Increases	Increases	Shin et al. (2011)
2%–42%	No	Increases	Increases	Increases	Increases	Decreases	Decreases	Deb et al. (2015)
80%	No	-	-	Increases	No change	Decreases	Decreases	Tomita et al. (2001)

During combustion in the engine with addition of hydrogen, the rate of combustion and flame temperature increases. The decrease of in-cylinder pressure can be seen at lower loads but pressure rises significantly at high or medium loads with the increase in energy share of hydrogen (Geo et al., 2008; Masood et al., 2007b; Wagemakers and Leermakers, 2012). Santoso et al. (2013) found that for lower load even with addition of hydrogen, the in-cylinder pressure decreases from 50% to 97%. At medium and high loads, cylinder pressure has increase considerably due to high flame speed which results in fast and normal combustion of the hydrogen-air mixture.

Santoso et al. (2013) mentioned from their findings that lower in-cylinder pressure and late initiation of combustion is occurred due to less amount of diesel used and it is noticed that, the less use of diesel as pilot fuel in cylinder under dual-fuel mode form less density of ignition centres because of unmixed diesel fuel-air and resulted in poor spray characteristics of diesel.

6 Emissions of I.C. engines fuelled with hydrogen

Engines in dual fuel mode with hydrogen have positive effect on emission characteristics as per various studies. Use of hydrogen with diesel/gasoline in dual fuel mode shows an ample reduction of emissions including CO, HC, CO₂ and smoke/PM but considerable increase in NO_x emissions. The effect of hydrogen fuel on engines emissions is listed in Table 3.

6.1 Effect on HC emission with hydrogen

HC emissions are most common emissions from I.C. engines due to incomplete and abnormal combustion. The main reason behind the HC emissions is low cylinder temperatures and lack of oxygen presence at some spots of the cylinder (Ganesh et al., 2008; Yap et al., 2006), thus it is called unburned hydrocarbon (UHC). UHC leads to deposition of diesel in crevices and boundary layers of cylinder (Hairuddin et al., 2014). UHC emissions are specified as the presence of total concentration of hydrocarbon in exhaust and measured in parts per million (ppm) of carbon atoms (Heywood, 1988).

From various research studies authors (Geo et al., 2008; Varde and Frame, 1983) confirmed that at all loads, there was considerable reduction of HC emissions with hydrogen due to the increase of in-cylinder pressure and temperature. Reduction in HC emission level at 100% load was observed up to 0.44 g/kWh (10.1% HES) with dual-fuel mode and 0.55 g/kWh HC level was recorded with base diesel (0% HES).

Saravanan and Nagarajan (2008) also observed the same trend for variation of hydrocarbon with load and find that due to carbonless hydrogen fuel; UHC concentration is considerably reduced comparable to base diesel operations. At full load operation, HC mass level observed up to lowest value of 56 ppm with 30% hydrogen addition against 127 ppm with diesel (Saravanan and Nagarajan, 2008). Miyamoto et al. (2011) has also observed this similar trend of HC emissions reduction due to better and rapid combustion of diesel.

6.2 *Effect on carbon dioxide and carbon monoxide emission with hydrogen*

Carbon monoxide (CO) and carbon dioxide (CO₂) emissions are usually measured as the ratio of CO₂ in exhaust to the total fuel carbon (CO, CO₂ and UHC) which is present in the exhaust of the combustion. The amount of CO and CO₂ exhaust is generally reliant on the combustion efficiency of engine.

For hydrogen operated dual-fuel engines, CO emission decreases because the equivalence ratio decreases with increase in amount of hydrogen substitution. In most of the studies, a CO emission trend show substantially decreases at all operating conditions of loads with increasing hydrogen addition. At 100% load and 10.1% HES with diesel, CO emission decreased to 2.31 g/kWh from 3.14 g/kWh (0% HES).

6.3 *Effect on NO_x emission with hydrogen*

Nitrogen oxide (NO_x) is mainly referred to nitric oxide (NO) and nitrogen dioxide (NO₂) which are generally produced due to combustion of fuel at high temperature. However, amount of NO₂ is lesser (5–10%) so, NO_x is comprised mostly of NO (90–95%). Hydrogen has high tendency to form NO_x emissions because of elevated combustion temperatures and high pressure. It is due to high energy content. Castro et al. (2019) has found the decrease in the NO_x emissions with increase of hydrogen content at 30 % load. Further increase of engine load (from 60% to 100%) leads to increase of the NO_x emissions due to ample increase of the combustion chamber temperature during the combustion (Castro et al., 2019).

Emission reduction technologies such as exhaust gas recirculation (EGR) and selective catalyst recovery (SCR) can be implemented to eliminate the barrier of high NO_x emissions with hydrogen. EGR uses some part of emitted gases which dilutes with the fresh air at inlet port and drops the in-cylinder temperature and also rate of pressure rise during combustion and results in dramatic fall of NO_x emission in exhaust. Nag et al. (2019) found a drop in NO_x levels by 3.45 g/kWhr with only 10% EGR even at 100% load (30% HES). EGR decreases in-cylinder temperature and rate of pressure rise which helps to lower the NO_x levels and further hydrogen addition shows negligible increase in NO_x (Nag et al., 2019).

7 **Conclusions and future scope**

Hydrogen is a clean and safe energy source that can be extracted from different energy resources (fossil, renewable and nuclear) by using different production methods. Limitation of production, storage, transportation and utilisation can be managed to become hydrogen as the most reliable energy sources. Hydrogen can be produced from different methods like SMR, partial oxidation, pyrolysis of biomass, biomass gasification, and water PV electrolysis. Among all these methods SMR is the best suitable method of hydrogen production on commercial scale. BTE of the engine increases with increase of hydrogen energy share at high and moderate loads. However, at low loads, the efficiency decreases. Carbon-based emissions (HC, CO and CO₂) under dual-fuel mode decreases substantially at all loads due to carbonless fuel. Some studies show considerable drop in NO_x formation at low loads. But, NO_x formation mainly increases particularly at high load conditions due to higher energy content fuel leads to increased in-cylinder

temperatures and pressure. NO_x problem could be resolved by low temperature combustion strategies and EGR in the engine which shows ample drop in NO_x level.

Hydrogen engines require more research studies and work to make it feasible for commercial purpose so that societies would have enough time in future to modify petroleum-based infrastructure towards hydrogen economy. Production, storage, transportation, and implementation of hydrogen still have some barriers to overcome and researchers need to focus over these problems.

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Abbreviation

HES	Hydrogen energy share
EGR	Exhaust gas recirculation
BTE	Brake thermal efficiency
CA	Crank angle
CV	Calorific value
IT	Injection timing
BTDC	Before top dead centre
CO ₂	Carbon dioxide
CO	Carbon monoxide
HC	Hydrocarbon
NO _x	Nitrogen oxides