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Hydrogen Production from Light Hydrocarbons

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Abstract

Recognizing and procurement of a sustainable energy system are among the supreme important problems that today's scientists should tackle. Interchanging the existing fossil fuels and transforming them into a sustainable fuel is one of the vital pieces in that system. Hydrogen as an energy carrier, obtained from light hydrocarbons, can take an essential role in the matters of sustainability, eco-friendly emissions, and energy saving. Our enthusiasm in stirring toward a hydrogen economy has its root in the vision of securing energy requirements at a satisfactory price, with larger competence and small environmental destruction associated with the utilization of traditional fuels. Hydrogen production pathways and relevant issues are discussed here. This chapter highlights the recent technological progress in the light hydrocarbons toward sustainable hydrogen production.

Keywords: light hydrocarbons, hydrocarbon reforming, H₂ production

1. Introduction

The atmospheric emission of greenhouse gases as result of the constant burning of fossil fuels put a grave risk to the worldwide environs and subsequent climate variation [1]. Greenhouse gases such as CH₄, CO₂, N₂O, and others organic pollutants result from the burning of carbon-based fuels [2]. Fossil fuel combustion affects negatively the climate change [3]. Furthermore, the mounting energy requirement has necessitated the price rise of conventional fuel which is diminishing. It is estimated that coal reserves will be depleted in around 200 years [4]; however, the world's growing population and industrialization are driving an ever-increasing demand for energy [5, 6]. With the pressure of climate change and the structural problems in the energy sector, discovering and developing renewable energies to replace current dominant energy sources is necessary to ensure a sustainable energy future [7]. Because hydrogen has

significant advantages as an energy transporter, a hydrogen-based economy has been emerging as a clean, efficient, zero-carbon alternative to current energy structures [8].

Hydrogen is not easily available in nature like fossil fuels. Though it might be obtained from any main energy source, it can be then employed as a straight fuel to the internal combustion engine in a fuel cell. The by-product of hydrogen is the water by-product [8–12]. The crucial trouble challenged by the modern world is the shortage of fossil. Therefore, it is indispensable to work out an alternative fuel that can substitute non-renewable fossil fuels. Hydrogen gas is one of the extremely versatile, efficient and sustainable clean energy carriers that may be used to substitute the fossil fuels due to its high energy yield when compared to conventional hydrocarbon fuels [13, 14]. The energy storage capacity of hydrogen is superb because a unit weight of it can generate nearly 33 kWh of energy [15]. Substituting hydrogen for fossil fuels in ultimate energy uses could bring this key environmental welfare [16] into accordance with the technical, green and cost challenges, and it is easy to overcome the difficulties in, for instance, production, storage and transport of hydrogen [17–19]. Hydrogen can be considered to be a secondary energy source since it can be converted to energy in the form of heat or electricity through either combustion or electrochemical reactions. The chief problem in using hydrogen fuel roots from its absence in nature and the requirement of cheap production systems [20, 21]. Extensive processes exist for H₂ production which depends on the kind of the raw materials considered. The processes could be separated into two main classes viz., traditional and technology that can be renewed. Class one process is the fossil fuels and comprises the techniques of pyrolysis and hydrocarbon reforming. In the latter process, hydrocarbon reforming process, involve the chemical methods of reforming: steam, dry, partial oxidation, autothermal steam and hydrocarbon decomposition.

The former class includes the techniques that bring hydrogen from biomass and water. The primary feeds of biomass are partitioned into two biological and thermochemical processes.

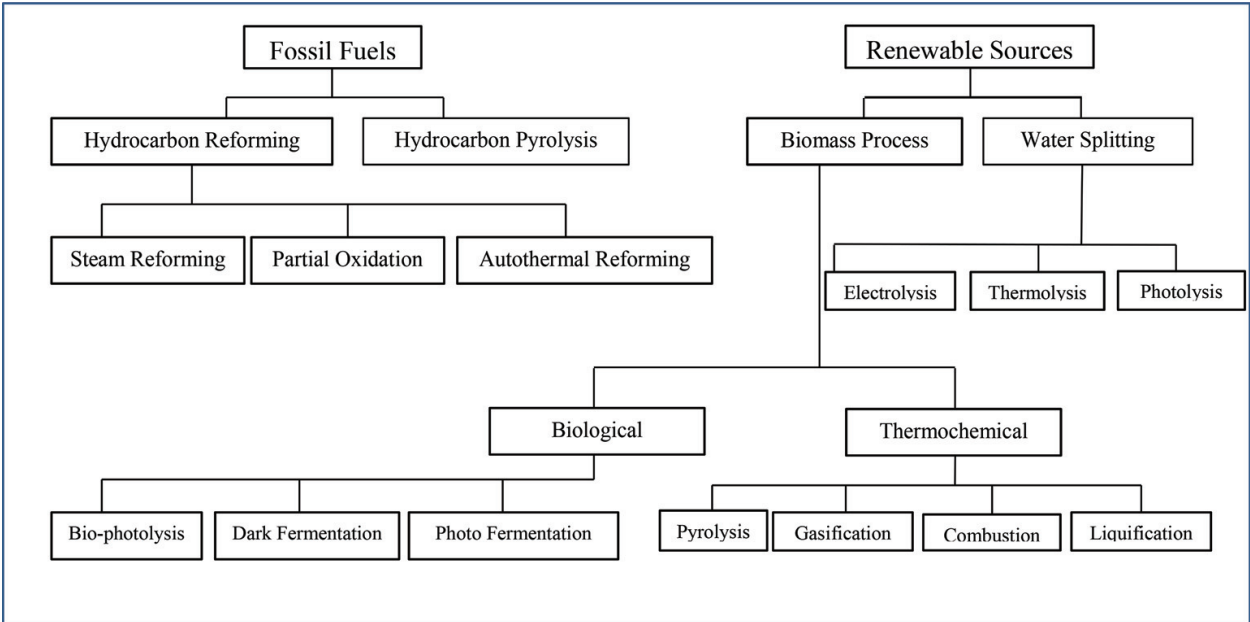


Figure 1. Hydrogen production methods.

The technology that concerns the thermochemical: primarily comprises combustion, gasification, pyrolysis, and liquefaction, while the biological processes are associated with photo-fermentation, bio-photolysis, dark fermentation, and sequential dark. The renewable knowhow involves the systems, which produces H_2 from electrolysis, photo-electrolysis and thermolysis. The material input to these technologies is water only. **Figure 1** displays the numerous pathways for hydrogen production.

Hydrogen can be obtained from different processes. Microorganisms for instance algae and bacteria through biological processes generate hydrogen [8]. Splitting of water into oxygen and hydrogen employing solar or electrolysis is another process. Chemical reactions and heat are used to discharge hydrogen from organic materials like biomass and fossil fuels via thermochemical processes.

2. Hydrogen and the environment

Hydrogen is regarded as a renewable and sustainable solution for mitigating global fossil fuel utilization and destroying the global warming [22]. The purpose of producing hydrogen as “Green Hydrogen” is to cause zero or low environmental impact. For this purpose all CO_2 and other pollutants must be removed when hydrogen is extracted from fossil fuels. Not only the environmental concern, but also the increase in energy demand inclines the researchers to develop new and current techniques and seek new energy sources. However, to ensure the sustainability of modern societies, hydrogen is a promising future energy carrier since it is a very important and environment friendly substitute to fossil fuels [23]. Hydrogen is counted as a green fuel since it is carbon-free henceforth CO_2 emission free. However, it can be generated from an extensive collection of fossil fuel and viable energy origin, so the type of hydrogen production process determines the emissions that will occur. Besides being abundance in the universe, hydrogen is not consumed like hydrocarbons; because it changes state from water to hydrogen back and forth when used as a fuel. However, production of hydrogen is not always CO_2 free. There exist various production methods such as gasification, electrolysis, and biological routes while these production methods can be performed using different feedstocks like water, biomass, or coal [24]. Some of these routes use non-renewable sources, some use extreme chemicals, and others have unknown life cycles. For the purpose of finding a clean energy route from the beginning of the circle to the end, a systematic approach to analysis is essential. This analysis should assess the whole production in such terms: terminating the dependency on non-renewable resources, reducing wastes, increasing efficiency or implementation of renewable sources to the systems.

3. Properties of hydrogen

Hydrogen is an element that possesses one proton and one electron. It is greatly plentiful and owns chemical properties that are exclusive and significant. Hydrogen is among the most available element in the world, which is chemically tied to the earth in great quantities and

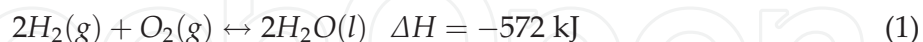
has to be free from an extensive assortment of feedstock. Other than water, the feed includes all hydrocarbon origin, namely natural gas, oil, biomass, and coal [25]. Currently, capital and maintenance costs, hazard and safety risk control, conversion performance, operation and design process flexibility are the key norms for the generating hydrogen. The selection of the feedstock and the minimization of the waste production play important role in setting criteria for maximizing hydrogen production.

3.1. Physical properties of hydrogen

Hydrogen is the simplest element chemically present. Hydrogen possesses only one proton, atomic number of unity, and average atomic weight of about 1 amu. H is the hydrogen symbol. Hydrogen is the most abundant chemical substance in the universe, particularly in planets and stars. Nevertheless, it is rare to find monoatomic hydrogen on Earth since it combines with other elements by covalent bonds. Hydrogen as such is not poisonous. It is nonmetal, tasteless, colorless, odorless, and highly flammable gas. The molecular formula is H_2 . On the Earth, hydrogen compounds exist as hydrocarbons and water. The most familiar isotope of hydrogen is protium, (1H). It has a single proton and a single electron with no neutron. Hydrogen is characterized by melting point of $-259.14^\circ C$, a boiling point of $-252.87^\circ C$, and density of 0.08988 g/L. Hydrogen is lighter than air. It has two separate oxidation states, (+1, -1), that facilitate it to react as both a reducing agent and an oxidizing agent. There are two separate spin isomers of hydrogen diatomic molecules, viz. orthohydrogen and parahydrogen. In the room temperature, the orthohydrogen constitutes 3/4 of hydrogen gas while the parahydrogen forms 1/4. Hydrogen is obtainable in different states, like compressed gas, liquid, slush, and solid and metallic forms [26, 27].

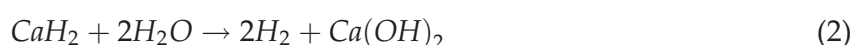
3.2. Chemical properties of hydrogen

Hydrogen is extremely combustible gas and burns in the air starting from low concentration of 4–75%. The enthalpy for the combustion reaction for hydrogen is -286 kJ/mol., and is defined by the equation:



Moreover, a mixture of chlorine and hydrogen from 5 to 95% can cause an explosion. The explosion of these mixtures can be easily triggered by sunlight, heat and spark [28, 29]. The temperature at which the hydrogen autoignition happens is at $500^\circ C$. Invisible ultraviolet light to bare eyes are radiated by flames of pure hydrogen-oxygen. Therefore, a flame detector is essential to monitor the leak of burning. Because hydrogen floats in air, its flames cause less harm than hydrocarbon fires, and rises rapidly. H_2 reacts with oxidizing elements, like chlorine and fluorine to form the corresponding hydrogen halides. Since hydrogen is an effective reducing agent, compounds of hydrogen halides are easily formed from the reaction of hydrogen and chlorine and fluorine. H_2 commonly forms compounds with a lot of elements in spite of its stability. In the case of reaction, hydrogen can react with more electronegative elements like oxygen or halogens and therefore can have a partial positive charge. On the other hand, it

can react with more electropositive elements like alkali metals and assume a partial negative charge. In addition, there is an intermolecular bonding known as hydrogen bonding that exists between hydrogen and elements like oxygen, fluorine, or nitrogen. This type of bonding is vital for the stability of many biological units. Hydrogen compounds with metals and metalloids are known as hydrides. H^+ ion is formed when hydrogen is oxidized its electron is removed. Frequently, the H^+ in aqueous solutions is termed as the hydronium ion, which is crucial in the chemistry of acid-base. There are three hydrogen isotopes in the universe: tritium, deuterium, and protium denoted as 3H , 2H , and 1H respectively. Compounds of hydrides are characterized by the participation of one or more hydrogen anions that possess reducing, nucleophilic, or basic properties. The bonding of hydrogen to a more electropositive element or group generates hydrides. While hydrides compounds usually react as reducing agent or Lewis bases by giving electrons, other metal hydrides react as hydrogen-atom donors and acids and. For example, the common drying reaction of calcium hydride:



Categories of hydrides are as follows:

- a) Saline or ionic, these hydrides are formed by the bond between a very electropositive metal, mostly an alkaline earth or an alkali metal and hydrogen atom. Reducing reagents and heterogeneous bases are good examples of the uses of ionic hydrides in organic synthesis.
- b) Covalent hydrides, often seen in the complex metal hydride, transition metal hydrides, are hydrogen centers that form hydrides, or those that are nucleophilic.
- c) Interstitial hydrides usually occur in metals or alloys. They are often characterized by metallic bonding. Interstitial binary hydrides are formed when hydrogen gets in contact with transition metals.

3.3. Barriers fuel hydrogen

A major hurdle in the hydrogen economy lies in its transport and storage. Though H_2 is characterized by very low volumetric energy density, but it possesses high energy density based on mass. At ambient conditions molecular hydrogen is present as a gas, which is difficult. Liquefied or pressurized hydrogen gas is required to get sufficient fuel energy. When the gas pressure increased definitely the volumetric energy density will improve, however this entails a larger amount of energy be used to pressurize the gas. Otherwise, slush or liquid hydrogen can be employed [30–32]. An extensive amount of energy must be used to liquefy the hydrogen, which is cryogenic and hence boils at 20 K. Hydrogen is not suitable to be stored in tanks since hydrogen diffuses through any liner material arranged to preserve it, which eventually leads to the weaying of the container. Hydrogen is often kept in compound form like chemical hydride. The compounds can be shifted from place to place fairly easily and then decomposed into hydrogen gas. The requirements of compound to form at high pressure and temperatures and for the hydrogen to be desorbed lead the current barriers to practical storage. The surface of solid storage material adsorbs hydrogen and then be desorbed when needed. This technology is yet to be improved. Hydrogen has one of the widest explosive/

ignition mixes ranges with air. The leak of hydrogen from its mixture with air will most probable cause an explosion, since the mixture of air and hydrogen form a broad explosive/ignition when it gets contact with flame or spark. The utilization of hydrogen as a fuel is confined by this issue, particularly in non-open areas like underground parking or tunnels. The burning flames of pure hydrogen in the UV range are unseen; therefore flame detector is essential to sense the hydrogen leakage. Moreover, hydrogen can be detected by smelling since it is odorless. While the hydrogen economy is expected to make a smaller carbon footprint, there are lots complexities regarding the ecological matters of hydrogen manufacturing. Fossil fuel reforming represents the main source of hydrogen; nonetheless this technique eventually leads to larger carbon dioxide emissions when compared to fossil fuel used in an internal combustion engine. Other problems comprise hydrogen production through electrolysis entails a larger energy input than straight using renewable energy and the likelihood of other lateral outputs [33].

4. Hydrogen technology

Climate variation and fossil fuel exhaustion are the chief reasons leading to hydrogen technology. Various technologies are available for the production of hydrogen: These include electrical, thermal, hybrid and biological methods. Thermal conversion processes are the most utilized processes, with steam reforming becoming the best [34, 35]. Several reforming technologies are performed in industry. Hydrogen is also obtained from splitting water by electrolysis. Nevertheless, because of the strong bonds in water molecules, a 39.3 kWh of electrical energy is theoretically required to split 1 kg of water. Moreover, for hydrocarbon feedstock solar energy accomplishes most of the thermal conversion processes. Currently, in the refinery hydrogen is used as a raw material, rather than as an energy carrier. Often, hydrogen is transported via pipelines when it generated on-site. On the other hand, the procurement of an efficient, safe, and compact storage technology is vital for the transition from the fossil fuel-based energy carriers toward hydrogen. In recent days fuel cell applications are operated with liquefied hydrogen, kept in cryogenic tanks. Enormous research investigations are currently carried out in the arena of hydrogen solid-state storage. Nevertheless, the appropriate materials regarding the hydrogen storage capacity, cost, and thermodynamics are not yet enough. Lifetime, high storage density, prolonged cycle ability, satisfactory sorption kinetics and thermodynamics are the essential parameters for a hands-on storage material. No doubt hydrogen is a future energy carrier needed to have the proper the infrastructural technologies and logistics. Fossil fuel has the potential to balance between hydrogen as energy carrier of the future and the famous fossil fuel energy carriers. Hydrogen production processes are categorized as conventional and alternative energy resources like solar and wind, natural gas, coal, nuclear, biomass. There are several techniques for hydrogen generation from diverse raw materials and energy input selections. Having environmentally friendly properties, hydrogen became an eminent choice for an alternative fuel. The combustion techniques of fossil fuel destroy the environment and these days, less than 15% of total energy consumption of the world is not based on these techniques [36]. Consequently, hydrogen utilization as an alternative fuel is ideal since it is not an unsafe, poisonous or uncertain mode of production.

5. Hydrogen production from fossil fuels

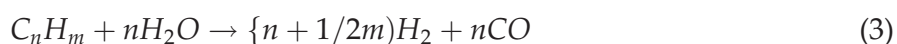
Hydrogen is generated from fossil fuels using numerous technologies, the principal of which are pyrolysis and hydrocarbon reforming. These techniques are the most advanced and normally employed, recovering virtually the whole hydrogen needs. About 48% of hydrogen is obtained from natural gas, 18% from coal, and 30% from naphtha and heavy oils [37–39]. Currently, the fuels from the fossil possess the principal role in the world hydrogen resource. Membrane reactors are used in the chemical and biochemical industries, to produce H_2 from traditional fuels. A membrane frame permits mass transfer by the influence of driving forces of pressure, concentration, electric potential, temperature, and other driving forces. Membranes are classified into biological and synthetic based on their nature. A high selectivity and permeability, excellent chemical and stability are the required characteristics of the efficient H_2 -production membrane. Consequently, for a composite membrane, indispensable parts include a permeable support permitting the gases crossing, blended with a barrier restrictive to the inter-diffusion in the metallic support.

5.1. Methods for hydrocarbon reforming

The process by which the hydrocarbon fuel is changed to produce hydrogen via reforming systems is termed hydrocarbon reforming. During the hydrocarbon reforming other components are employed along with the hydrocarbon. These include carbon dioxide and the system is termed as CO_2 reforming or dry reforming. Moreover steam may include as reactants in the reforming system of the hydrocarbon. This system is branded as steam reforming. Both dry and steam reforming reactions are endothermic, Therefore, it necessary to furnish energy. Reforming the hydrocarbon with oxygen is known as partial oxidation, and the reaction is exothermic. When the steam and partial oxidation reactions are combined the system is called autothermal reforming [40].

5.1.1. Method of steam reforming

In the steam reforming process, the catalytic conversion of hydrocarbon into hydrogen and carbon monoxide is carried out in the presence of steam in the feed. The reforming procedure comprises gas purification, methanation, water-gas shift and synthesis gas production. Most feedstock contains natural gas, methane, and a mixture of light hydrocarbons, which include propane, butane, ethane, pentane, and both light and heavy naphtha. When the feed is contaminated with organic sulfur compounds, a desulphurization stage should precede the reforming step to circumvent the deactivation of the reforming catalyst which CO_2 is seized and put in the ocean or geological reservoirs [41]. The primary chemical reaction that occurs during the steam reforming is:



Depending on the values n and m dictate the hydrocarbon type. For instance, methane reforming n and m are equal to 1 and 4 respectively. The methane steam reforming is the best and well- advanced method employed for extensive hydrogen output. The conversion performance amounts to 74–85%. When natural gas and steam are reacted over a nickel-based catalyst

to generate synthesis, the reaction temperature is usually set to 850–900°C. About 30–35% of the entire amount of natural gas as a process fuel provides the needed energy of 63.3 kJ/mol of H₂. To inhibit coke deposition on the catalyst and achieve a purified H₂ output, the process operation is adjusted to 3.5 MPa pressure, steam-to-carbon ratios of 3.5, and high temperatures [42]. After the reformer, the mixture of gases goes through a heat recovery, and water gas shift reactor where an additional H₂ is produced from the reaction between the steam and carbon monoxide then, the mixture of gases goes through either a pressure swing adsorption or through a CO₂-removal and methanation producing virtually pure H₂ [43]. Membrane reactors offer a remarkable solution. Since the topmost process of producing huge amounts of H₂, SMR has been broadly evidenced by incorporating a delicate membrane which is operated right inside the reaction environs or downstream to reaction units (**Figures 2 and 3**).

Palladium-based membrane reactors of the second method provide considerable advantages by uniting the gas separation and chemical reaction in a unit. Generated H₂ adsorbed and dissociated atomically on one side of the membrane in the reformer, diffuses, and lastly desorbs on the other side [44]. Similar reactant conversion is permitted by the Pb-based membrane reactors. Contrary to normal SMR which operate at high temperature 850–900°C, the membrane reactors operate at a lower temperature of 450–550°C and produce methane conversions up to 90–95% [45].

5.1.2. *Partial oxidation technique*

Partial oxidation (POX) technique chiefly comprises the reaction transformation of hydrocarbons, oxygen, and steam, to synthesis gas which consists of hydrogen, carbon monoxide, and carbon dioxide. Feedstocks starting from methane to naphtha are often used in the catalytic process at about 950°C, while the process operation takes place at 1150–1315°C for non-catalytic systems [44]. Pure O₂ is used to incompletely oxidize the hydrocarbon feedstock, after the elimination of sulfur content in the feed removal. The generated synthesis is additionally

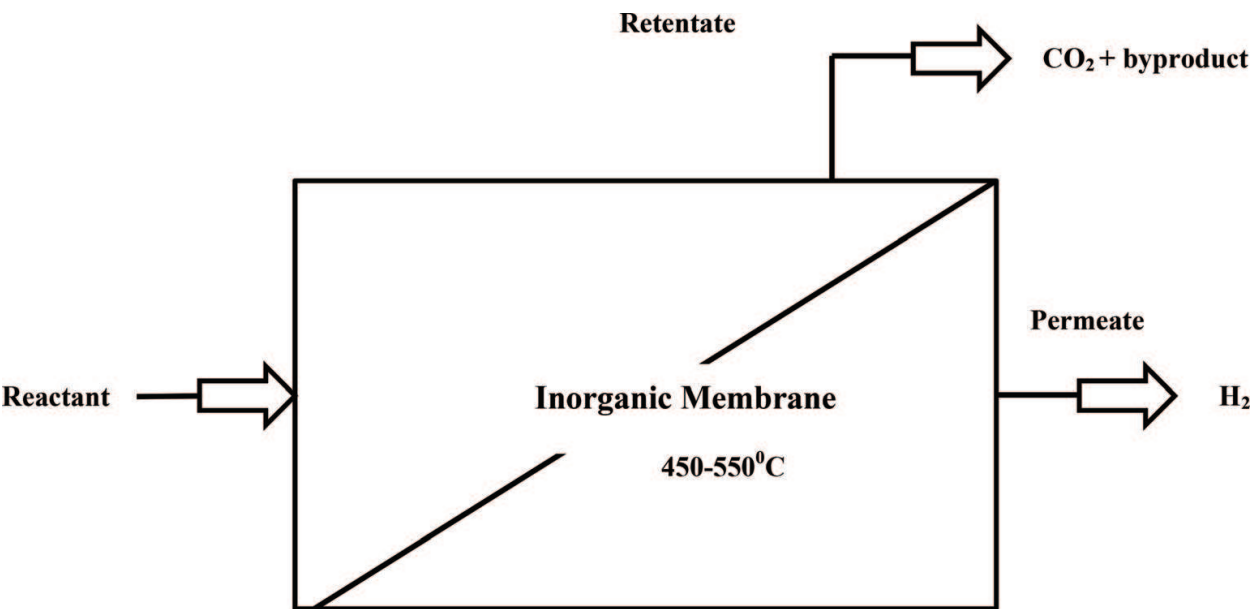


Figure 2. Flow illustration of steam methane reforming unified-membrane process.

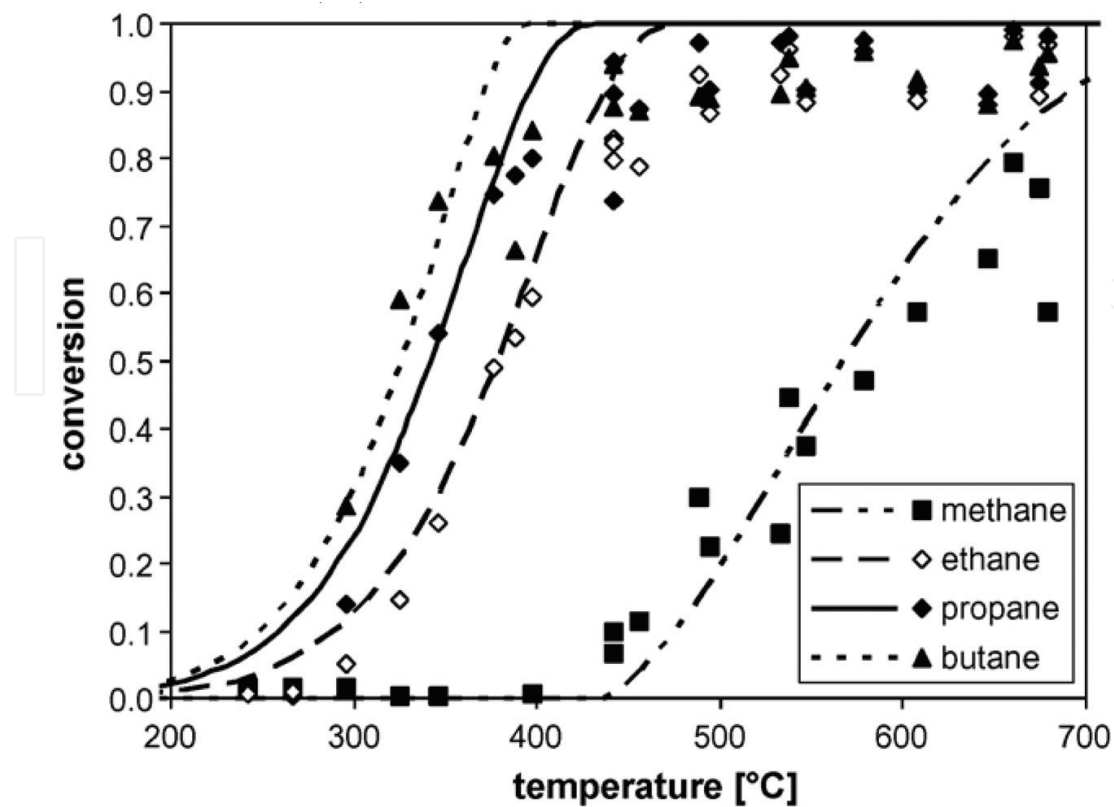


Figure 3. Methane (•), ethane (◊), propane (◆), and butane (▲) conversion as function of temperature for S/C 2.5 in SR of natural gas (catalyst with 900 cps); symbols: Experiment; lines: Model predictions [58].

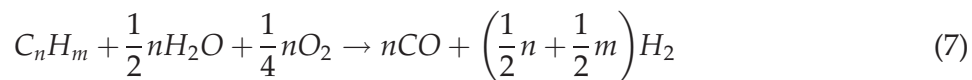
purified and separated in a similar way as the output gas of the steam reforming method. The formidable price of the oxygen manufacturing and the extra expenses of desulphurization perform the process significantly expensive. In the process dealing with catalyst, the heat is delivered through the monitored combustion. Eq. (4), presents the catalytic reforming, while Eqs. (5) and (6) represent the chemical reactions of water gas shift and methanation.



Heavier feedstock like coal and heavy oil residues are suitable resources for the production of hydrogen when partial oxidation technique is applied.

5.1.3. Autothermal reforming technique

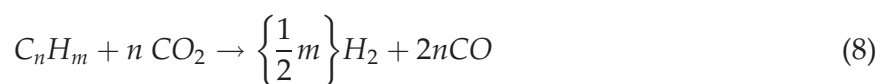
In the process of autothermal reforming technique (ATR), the endothermic steam reforming receives heat from the combined exothermic partial oxidation to promote the production of hydrogen. Fundamentally, steam, air, and oxygen are fed to the reformer, starting the oxidation reactions as well as the reforming to happen simultaneously, as presented in Eq. (8).



When methane is autothermally reformed at 700°C inlet temperature and the proper ratios of steam to carbon and oxygen to carbon, a thermal efficiency of 60–75% and maximum hydrogen yield of about 2.8 are achieved [42]. The investment cost is about 50% lower than coal gasification. A small improvement is reported when the ATR reactor is combined with a Pd membrane. The high operating temperature of 900°C needed by the system ruins the efficiency improvement brought by the membrane [43].

5.1.4. Dry reforming

The dry reforming is a chemical process that consists of converting hydrocarbon and carbon dioxide, considered as one of the world's most abundant greenhouse gases to synthesis gas with a proper H₂/CO molar ratio [46]. As a result, this process has the potentials to alleviate the environmental challenges related to greenhouse gases emissions and to transform biogas and natural gas to synthesis gas. Furthermore, the produced H₂/CO ratio synthesis gas is suitable for the production of hydrocarbons via Fischer-Tropsch synthesis, in addition to the synthesis of oxygenated chemicals [47]. The dry reforming reaction is:



Being an extremely endothermic reaction, dry reforming requires high operating temperatures, usually in the range of 900–1273 K, to achieve the desired conversion levels. The forward reaction is favored at low pressures as dictated by stoichiometry. Additionally, it has been observed that an nCO₂/C_nH_m molar ratio higher than the stoichiometric requirement of unity can also provide high synthesis gas yields. The positive effects of high reaction temperatures, low pressures, and high nCO₂/C_nH_m molar.

5.2. Pyrolysis of hydrocarbon

The pyrolysis of hydrocarbon is a famous method where hydrogen solely comes from the hydrocarbon subjected to thermal decomposition via the following universal reaction:



Light liquid hydrocarbons having boiling points 200°C are decomposed thermo-catalytically to generate elemental carbon and hydrogen, however, dealing with residual fractions having boiling temperatures above 350°C, the production of hydrogen requires hydrogasification and cracking of methane. The direct reduction of carbon content in the natural gas known as often de-carbonization, which constitutes mainly methane, is performed at 980°C temperature and atmospheric pressure in the environment, where there is no water and air. Furthermore, pyrolysis does not involve CO₂ removal steps and water gas shift. Carbon control and

sequestration, which is energy intensive stage is replaced by carbon control that could be employed in the chemical industries and metallurgy. Therefore, the processes of partial oxidation or steam conversion are higher than investments for big plants causing 25–30% hydrogen production cost [45]. The price of hydrogen would be less if markets are found for the extensive amounts of carbon resulting from the natural gas decomposition. From the environmental perspective it would be more beneficial to dissociate catalytically natural gas to carbon and hydrogen, instead of H₂ production by steam reforming of methane attached with CO₂ sequestration [48]. For a specified temperature, the reduction of carbon content is increased by the constant elimination of hydrogen by membrane separation. For H₂ separation, Pd-Ag alloys, which operate at lower temperatures and mitigate the carbon deposition, are normally used. The chief disadvantages of the present method are attributed to the very low hydrogen separation, which results from the membrane stability influenced by high temperatures required for the equilibrium of the reduction of the carbon content and the low H₂ partial pressures in the reaction mixture [43].

6. Light hydrocarbons (LHs)

Hydrocarbons, as their name denotes, are compounds of hydrogen and carbon. They represent one of the vital classes of organic chemistry. They exist in gaseous states such as propane and methane, a liquid state like benzene and hexane, and solid state as paraffin wax, polystyrene, naphthalene, and polyethylene.

Hydrocarbons are classified into:

- a. Saturated hydrocarbons which are formed completely of single bonds between carbon-carbon and are saturated with hydrogen. The compound formula with a linear structure, alkanes are C_nH_{2n+2} . The universal formula of saturated hydrocarbons is $C_nH_{2n+2(1-r)}$, where r represents the number of rings. One ring hydrocarbons are termed cycloalkanes. Linear and branched species of saturated hydrocarbons are the sources of petroleum.
- b. Unsaturated hydrocarbons have one or more double or triple bonds between carbon atoms. Those with double bond are called alkenes. Those with one double bond and non-cyclic structure have the formula C_nH_{2n} . Those having triple bonds are named alkyne. Those with one triple bond have the formula C_nH_{2n-2} .
- c. Aromatic hydrocarbons are hydrocarbons that have at least one aromatic ring. The hydrocarbon is characterized by strong covalent (sigma) bonds and delocalized pi electrons between carbon atoms forming a circle. Some simple hydrocarbons and their variations are given in **Table 1**.

Hydrocarbons are a primary energy source for current civilizations. The predominant use of hydrocarbons is as a combustible fuel source. In their solid form, hydrocarbons take the form of asphalt (bitumen) [49]. Methane and ethane are gaseous at ambient temperatures and cannot be readily liquefied by pressure alone. Propane is however easily liquefied and exists in 'propane bottles' mostly as a liquid. Butane is so easily liquefied that it provides a safe,

Alkadiene	Cycloalkane	Alkyne (triple bond)	Alkene (double bond)	Alkane (single bond)
—	—	—	—	Methane
—	—	Ethyne	Ethene	Ethane
Propadiene	Cyclopropane	Propyne	Propene	Propane
Butadiene	Cyclobutane	Butyne	Butene	Butane
Pentadiene	Cyclopentane	Pentyne	Pentene	Pentane
Hexadiene	Cyclohexane	Hexyne	Hexene	Hexane
Heptadiene	Cycloheptane	Heptyne	Heptene	Heptane
Octadiene	Cyclooctane	Octyne	Octene	Octane
Nonadiene	Cyclononane	Nonyne	Nonene	Nonane
Decadiene	Cyclodecane	Decyne	Decene	Decane
Undecadiene	Cycloundecane	Undecyne	Undecene	Undecane

Table 1. Simple hydrocarbons and their variations.

volatile fuel for small pocket lighters. Pentane (C_5H_{12}) is a clear liquid at room temperature, commonly used in chemistry and industry as a powerful nearly odorless solvent of waxes and high molecular weight organic compounds, including greases. Hexane (C_6H_{14}) is also a widely used non-polar, non-aromatic solvent, as well as a significant fraction of common gasoline. The C^6 through C^{10} alkanes, alkenes and isomeric cycloalkanes are the chief components of gasoline, naphtha, jet fuel and specialized industrial solvent mixtures. Hydrocarbons with low molecular weight such as methane, ethane, propane and ethane are termed as light hydrocarbons (LHs). Light hydrocarbons are the largest petroleum fraction which in between C_1 and C_9 . They are catagenic products, formed between 75 and 140°C. The higher hydrocarbons are too stable to generate the LHs at these temperatures. Additionally, LHs are different from cracking products [50]. Many are structurally like bio-precursors. Basically, all isomers are found within the alkanes, cycloalkanes and aromatics with no visible preference for natural structures. It is improbable that the LHs are formed without support. The LHs constitute well over 50% of the carbon in petroleum. They seem to be a random mixture of classes (isoalkanes, cyclopentanes, cyclohexanes, and aromatics). For instance, the gasoline fraction of different crudes may be branded by identifying the relative amounts of the following five classes of hydrocarbons: normal paraffins, isoparaffins, alkylcyclopentanes, alkylcyclohexanes, and aromatics. Of analogous significance to hydrogen, is the production of its mixture with carbon monoxide ($H_2 + CO$), normally named synthesis gas or syngas, which is a valuable raw material for numerous industrial uses. The significant natural sources of light hydrocarbons comprise leakage from oil and gas reservoirs and anaerobic production of methane. There are some reports of low molecular weight hydrocarbons in open ocean water. The coastal waters act as a source for atmospheric methane. The vital man-derived sources of methane in the coast are ports with their accompanying shipping and industrial activity, offshore petroleum drilling and production operations, and open ocean shipping activity. In 2010 almost, 50% of global

anthropogenic methane emissions came from sources like agriculture, coal mines, landfill, oil and natural gas systems and waste water. Mobile sources in specific are famous to give meaningfully to urban hydrocarbon and nitrogen oxide levels. For instance the vehicle exhaust accounts for most of the non-methane hydrocarbon concentrations in metropolitan cities [51–53].

6.1. Production of hydrogen from liquefied petroleum gas

Steam reforming of liquefied petroleum gas (LPG) is a practical choice for producing hydrogen in isolated regions where there is no pipeline natural gas supply. The most common LPG gases include propane, butane (n-butane) and isobutane (i-butane), as well as mixtures of these gases. Fuel processing converts LPG into hydrogen and carbon dioxide. Lopez-Ortiz et al. elaborated the utilization of cobalt tungstate in a chemical looping partial oxidation of methane process to generate syngas [54]. They carried out simulations and thermodynamic analysis. Results acquired indicated no carbon formation and syngas yield (89.6%) were calculated. Wang et al. investigated the autothermal reforming of LPG in a fixed-bed reactor by changing essential parameters like steam-to-carbon ratio (S/C), the oxygen-to-carbon ratio (O/C), reforming temperature, and catalyst [55]. It was established that temperature, S/C, and O/C were the most key parameters for fuel conversion and lowering carbon deposition. Similarly, steam reforming is applied to convert LPG to hydrogen using Rh, Ru, Pt, and other noble metal catalysts. For instance, Laosiripojana et al., used Ni- and Rh-based catalysts supported on GdCeO₂ (CGO) and Al₂O₃ in steam reforming of LPG at 750–900°C [56]. They obtained that Rh/CeO₂ catalyst gave the highest H₂ yield. Steam reforming of LPG employing nickel-based perovskites (La-Ni-O) partly replaced with cobalt was examined [57]. The suitable selection of water/LPG feed ratio together with the proper Co/Ni ratio in the synthesis of perovskite precursors was vital to retain the catalyst active during LPG steam reform and hence the hydrogen production.

6.2. Production of hydrogen from alkanes

A broad experimental study of steam reforming (SR) of alkane components: methane, ethane, propane, butane, and natural gas for the catalytic conversion over a Rh-based catalyst was carried out and compared to numerically predicted conversion and selectivity [58]. The result established a mechanism for predicting product distribution in steam reforming of natural gas mixtures with varying compositions. Likewise, the developed simulation, permit the numerical calculation of chemical species profiles and surface coverage within catalytic monoliths. Steam reforming of ethane, propane, and butane display virtually same conversion and selectivity as a function of temperature and steam to carbon ratio (S/C).

Rhodium-based catalyst with different Rh content (1, 2.5 and 5 wt. %) and high surface area alumina support were tested for steam reforming of propane [59]. All catalysts exhibited complete conversion at 750°C with hydrogen selectivity over 98% and high stability for more than 140 hours' time on stream. In the work of Ferrandon et al., Mono-metallic nickel and rhodium catalysts and bimetallic Ni-Rh catalysts supported on La-Al₂O₃, CeZrO₂, and CeMgO_x were arranged and assessed for catalyzing the steam and autothermal reforming of n-butane [60]. The bimetallic Ni-Rh supported on La-Al₂O₃ catalysts with low weight loading of rhodium showed higher H₂ yields than Ni or Rh alone. The Ni-Rh/CeZrO₂ catalyst

exhibited higher performance and no coke formation, in comparison to similar metals on other supports. Hydrogen was produced from butane steam reforming using Ni/Ag loaded MgAl_2O_4 catalyst to substitute the conventional fast catalytic deactivation and lower H_2 production from the hydrocarbon steam-reforming reaction [61]. The Ag-loaded catalyst showed considerably higher reforming reactivity than Ni/ MgAl_2O_4 catalyst. The silver-containing catalyst diminished the carbon formation and boosted the hydrogen product and selectivity. The production of H_2 was enhanced up to 68% at 700°C for 1 h and this high efficiency sustained for up to 53 h.

Mesoporous nanocrystalline Ni/ Al_2O_3 catalysts were used to examine the Partial oxidation (POX) of methane, ethane, and propane [62]. Different feed conditions were considered during the study. 5 wt. % Ni/ Al_2O_3 catalysts displayed the maximum catalytic activity in the temperature range of 500–700°C. The catalyst was substantially stable for 48 h time on stream in methane partial oxidation. Moreover, increased carbon deposition on the catalysts was observed when ethane and propane in stoichiometric feed ratio were considered. Alternatively, the performance of CO_2 -reforming of methane over mesoporous Co-Ni/SBA-15- x ($x = \text{Mg, La, and Sc}$) was tested in continuous fixed bed at 700–800°C reaction temperature [63]. When the catalyst support was modified by adding Mg and Sc, the CH_4 conversion was improved markedly by 28 and 26%, respectively at 700°C higher than the corresponding bare SBA-15 supported catalysts. TEM and TGA/GTA characterizations of spent catalyst established that the coke resistance was considerably upgraded as a result of the support alteration, leading to the formation of amorphous carbon. Consequently, Co-Ni/SC-SBA-15 catalyst remarkably promoted the stability and catalytic activity to produce synthesis gas.

6.3. Production of hydrogen from ethane

With the increased production of shale gas through a new drilling technology of hydraulic fracturing significant attention has been paid to the utilization of ethane which accounts for about 7% of shale gas [64]. Jeong et al. proposed a pathway for using ethane to generate hydrogen [65]. The investigators performed the analysis of membrane reactor using techno-economic analysis and process simulation using Aspen HYSYS[®] for ethane steam reforming. The process simulation indicated high H_2 selectivity. In ethane steam reforming, synthesis gas is produced as:



Alternatively, Veranitisagul et al. studied ceria and gadolinia doped ceria catalysts to produce syngas from ethane at the temperature range of 800–900°C via the steam reforming reaction [66]. The catalytic activity was enhanced with the addition of 0.15 Gd. It could generate a substantial amount of hydrogen and the carbon formation that deactivates at high temperature was prevented. Hypothetically, the carbon formation could take place through the reforming of ethane, as result of these reactions:





6.4. Production of hydrogen from methane

Methane (CH₄) is a light hydrocarbon and the most important component of natural gas. Methane is also a strong and plentiful greenhouse gas (GHG), which makes it a significant contributor to climate change. Methane like other LHs can be converted to hydrogen using different methods as mentioned. The natural gas comprising C₁, C₂, C₃, and C₄₊ have been widely used to produce hydrogen. As presented in **Table 2**, methane is a primary component in natural gas followed by ethane and propane [67].

Catalytic carbon dioxide reforming of methane (CO₂ reforming of CH₄), also called dry reforming of methane to distinguish this process from steam reforming, has attracted rigorous research interest during the last decades. The interest is ascribed to the fact that CO₂ reforming of CH₄ mitigates carbon emissions. The reaction is endothermic:



The equilibrium conversion and the equilibrium product composition are influenced by the reaction temperature, pressure, initial reactant ratio, and the content of the inert gas. Nevertheless, catalysts must be employed to allow the reaction to take place in reasonable kinetics. Ni catalyst is found suitable for this reaction. Aluminum oxide (Al₂O₃), particularly γ-Al₂O₃, is one of the best generally used catalyst support materials for CO₂ reforming of CH₄. Liao and Horng studied methane dry reforming to generate synthesis gas [68]. Their work concentrated

Elements	Volumetric composition (%)	
	Wet	Dry
Methane	84.6	96.0
Ethane	6.4	2.00
Propane	5.3	0.60
Isobutane	1.2	0.18
n-butane	1.4	0.12
Isopentane	0.4	0.14
n-Pentane	0.2	0.06
Hexanes	0.4	0.10
Heptanes	0.1	0.80

Table 2. Universal composition of dry and wet natural gas.

on the heat recovery of the designed reformers. An oven was employed for the simulation of the heat recovery. The results specified that the oven temperature is proportional to the reforming reaction temperature and hence promote the energy of the reformer. When the energy of reformer was increased the synthesis gas production enhanced and efficiency of reforming and CO₂ conversion was obviously raised. The production of hydrogen and carbon from the catalytic decomposition of methane via iron catalyst was explored [69]. The

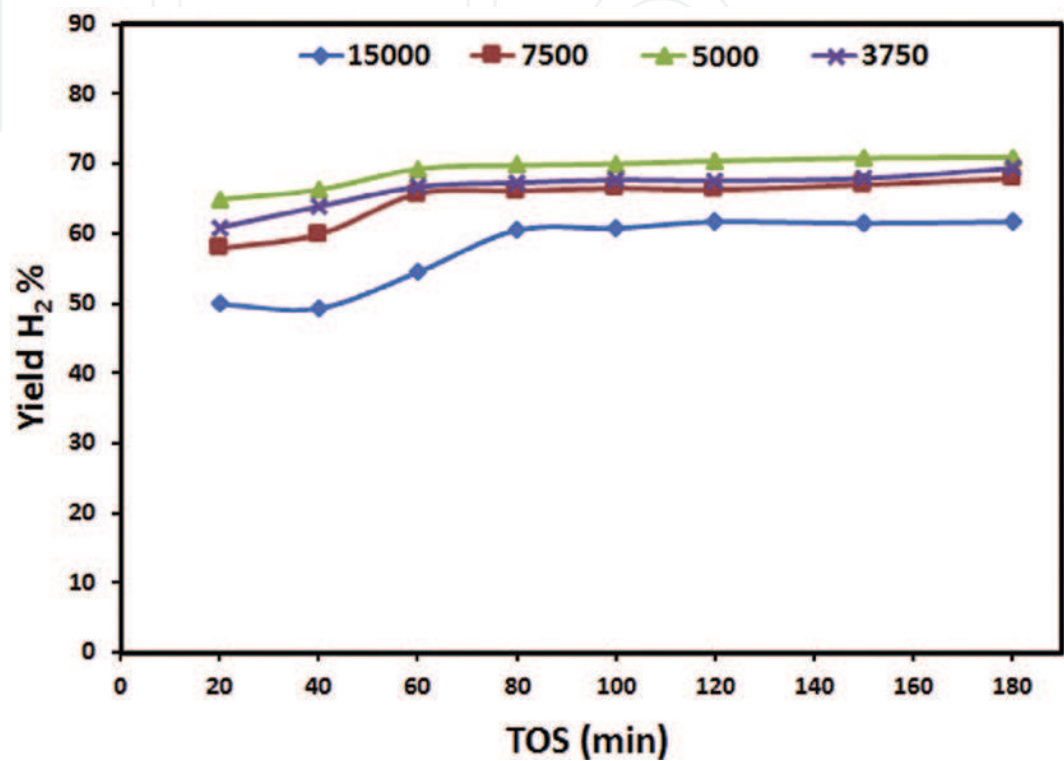


Figure 4. Stability performances in terms of H₂ yield (%) over 15Co-30Fe/Al catalysts as a function of TOS at 700°C at different GHSVs.

Hydrogen production techniques	Temperature (°C)	Hydrogen yield (%)	References
Dry reforming	750	43.0	[71]
	850	78.0	
Steam Reforming	500	98.7	[72]
Steam Reforming	750	85.0	[73]
Partial Oxidation	850	88.9	[74]
Partial Oxidation	750	36.8	[75]
Autothermal	700	83.0	[76]
Autothermal	850	78.0	[77]
Decomposition	700	75	[78]
	800	90	

Table 3. Summary of hydrogen yield from methane for various hydrogen production techniques.

investigation covered the utilization of alumina supported catalysts over various iron loadings. Multiwall nanotubes were formed and as the % loading of Fe was increased, the hydrogen yield increased. When 60% Fe/Al₂O₃ catalyst was employed, the highest H₂ yield of 77.2% was acquired. Similarly, mono-, bi- and tri-metallic catalysts obtained from iron-nickel-cobalt supported over alumina was examined for the decomposition of methane to hydrogen and value-added carbon. The catalytic activity of 30 wt. % Fe and 15 wt.% Co displayed the highest performance overall investigated catalysts. **Figure 4** illustrates the hydrogen yield versus time on stream (TOS). It is apparent that the gas hourly space velocity (GHSV) has some effect on the hydrogen yield [70]. **Table 3** reviews the technologies along with their reaction temperatures and percentage of hydrogen yield. It is important to note that hydrogen yield depends on the type of catalyst, pretreatment and operating conditions [71–78].

7. Future perspective

Currently, about 1/5 of global energy is utilized as electricity, whereas 80% is utilized as fuel. Hydrogen energy is a clean and alternative energy that has been suggested as the energy carrier of the future. Solar-driven microalga hydrogen production is both a favorable and inspiring biotechnology, which play a significant role in the global drive to decrease GHG emissions. One of the major barriers with regard to the hydrogen economy is its production cost and inefficient storage methods, which need to be resolved. Current research efforts are focused on strain improvement by systems metabolic engineering and finding suitable conditions to increase the levels of hydrogen production. In the near future, it may be possible to perform knockouts and insertions based on the data available by modeling previous studies. The advent of synthetic biology necessitates such models since it aims at standardizing biology, which should give predicted responses. With all these advancements, the commercial feasibility of H₂ production may rely on efficient production strategies with elevated yield, well-organized transport and storage systems ensuring the secured supply of hydrogen. Moreover, the prospect of light hydrocarbon hydrogen production is determined by the research advances such as enhancement of productivity through catalytic engineering and the advance of chemical reactors, the economic attentions like the price of fossil fuels, social appreciation, and use of hydrogen energy systems in our society. Today, hydrogen is being used to power a fleet of busses in some countries. More industries will accept hydrogen energy when a renewable economically viable process of hydrogen production is achieved. Last but not least, the integrated effort of both scientists and engineers is needed to fully implement hydrogen energy as the energy for the future. Mass hydrogen production is the foundation for the transition to a “hydrogen economy”, which has the potential to enable the development of distributed power generation networks [79].

8. Conclusions

The global crisis of fossil fuels has greatly stimulated worldwide interest to develop sustainable sources of energy carriers. Light hydrocarbons can be used as a potential source of hydrogen energy due to their inherent capacity to decompose the hydrocarbon into H₂ using

the thermochemical energy. Photo-biological hydrogen production is considered as a more efficient and less energy-intensive process. Hydrogen powered fuels can be used in different types of fuel cells as a clean energy to generate electricity with high efficiency. At present, hydrogen energy from microalgae is economically less feasible due to its high production cost. Nevertheless, efficient bio-hydrogen production from microalgae may be accelerated by recent technological advancements in metabolic and genetic engineering approaches.

Biography

Dr. Ibrahim is renowned for his pioneering work on fossil fuel conversion energy technologies; he has authored and co-authored more than a seventy refereed journal and conference papers. His main research interests include catalysis, hydrogen energy technologies.

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