

Conference Paper

Hydrogen Production Technologies: Current State and Future Developments

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Hydrogen (H_2) is currently used mainly in the chemical industry for the production of ammonia and methanol. Nevertheless, in the near future, hydrogen is expected to become a significant fuel that will largely contribute to the quality of atmospheric air. Hydrogen as a chemical element (H) is the most widespread one on the earth and as molecular dihydrogen (H_2) can be obtained from a number of sources both renewable and nonrenewable by various processes. Hydrogen global production has so far been dominated by fossil fuels, with the most significant contemporary technologies being the steam reforming of hydrocarbons (e.g., natural gas). Pure hydrogen is also produced by electrolysis of water, an energy demanding process. This work reviews the current technologies used for hydrogen (H_2) production from both fossil and renewable biomass resources, including reforming (steam, partial oxidation, autothermal, plasma, and aqueous phase) and pyrolysis. In addition, other methods for generating hydrogen (e.g., electrolysis of water) and purification methods, such as desulfurization and water-gas shift reactions are discussed.

1. Introduction

Hydrogen is the simplest and most abundant element on earth. Hydrogen combines readily with other chemical elements, and it is always found as part of another substance, such as water, hydrocarbon, or alcohol. Hydrogen is also found in natural biomass, which includes plants and animals. For this reason, it is considered as an *energy carrier* and not as an energy source.

Hydrogen can be produced using diverse, domestic resources, including nuclear, natural gas and coal, biomass, and other renewable sources. The latter include solar, wind, hydroelectric, or geothermal energy. This diversity of domestic energy sources makes hydrogen a promising energy carrier and important for energy security. It is desirable that hydrogen be produced using a variety of resources and process technologies or pathways. The production of hydrogen can be achieved via various process technologies, including thermal (natural gas reforming, renewable liquid and biooil

processing, biomass, and coal gasification), electrolytic (water splitting using a variety of energy resources), and photolytic (splitting of water using sunlight through biological and electrochemical materials).

The annual production of hydrogen is estimated to be about 55 million tons with its consumption increasing by approximately 6% per year. Hydrogen can be produced in many ways from a broad spectrum of initial raw materials. Nowadays, hydrogen is mainly produced by the steam reforming of natural gas, a process which leads to massive emissions of greenhouse gases [1, 2]. Close to 50% of the global demand for hydrogen is currently generated via steam reforming of natural gas, about 30% from oil/naphtha reforming from refinery/chemical industrial off-gases, 18% from coal gasification, 3.9% from water electrolysis, and 0.1% from other sources [3]. Electrolytic and plasma processes demonstrate a high efficiency for hydrogen production, but unfortunately they are considered as energy intensive processes [4].

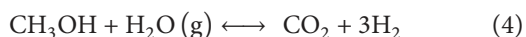
The fundamental question lies in the development of alternative technologies for hydrogen production to those based on fossil fuels, especially for its utilization as a fuel in the transportation sector. This problem can be faced by the utilization of alternative renewable resources and related methods of production, such as the gasification or pyrolysis of biomass, electrolytic, photolytic, and thermal cracking of water. However, it is not possible to consider only the ecological perspective, since for example, photolytic cracking of water is environmentally friendly but its efficiency for industrial use is very low. It is thus clear that the processes to be taken into account must consider not only environmental concerns but also the most favorable economics.

2. Hydrogen from Fossil Fuels

Fossil fuel processing technologies convert hydrogen-containing materials derived from fossil fuels, such as gasoline, hydrocarbons, methanol, or ethanol, into a hydrogen-rich gas stream. Fuel processing of methane (natural gas) is the most common commercial hydrogen production technology today. Most fossil fuels contain a certain amount of sulfur, the removal of which is a significant task in the planning of hydrogen-based economy. As a result, the desulfurization process will also be discussed. In addition, the very promising plasma reforming technology recently developed will also be presented.

Hydrogen gas can be produced from hydrocarbon fuels through three basic technologies: (i) steam reforming (SR), (ii) partial oxidation (POX), and (iii) autothermal reforming (ATR). These technologies produce a great deal of carbon monoxide (CO). Thus, in a subsequent step, one or more chemical reactors are used to largely convert CO into carbon dioxide (CO₂) via the water-gas shift (WGS) and preferential oxidation (PrOx) or methanation reactions, which are described later.

2.1. Steam Reforming. Steam reforming is currently one of the most widespread and at the same time least expensive processes for hydrogen production [5]. Its advantage arises from the high efficiency of its operation and the low operational and production costs. The most frequently used raw materials are natural gas and lighter hydrocarbons, methanol, and other oxygenated hydrocarbons [6]. The network of reforming reactions for hydrocarbons and methanol used as feedstock is the following [7]:



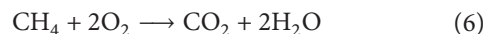
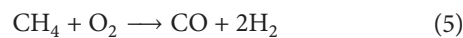
The whole process comprises two stages. In the first stage, the hydrocarbon raw material is mixed with steam and fed in a tubular catalytic reactor [8]. During this process, syngas (H₂/CO gas mixture) is produced with lower content in CO₂ ((1) and (2)). The required reaction temperature is achieved

by the addition of oxygen or air for combusting part of the raw material (heating gas) inside the reactor. In the second stage, the cooled product gas is fed into the CO catalytic converter, where carbon monoxide is converted to a large extent by means of steam into carbon dioxide and hydrogen (3). The steam reforming catalytic process requires a raw material free of sulfur-containing compounds in order to avoid deactivation of the catalyst used.

The SR process requires modest temperatures, for example, 180°C for methanol and oxygenated hydrocarbons and more than 500°C for most conventional hydrocarbons [9, 10]. The catalysts used can be divided into two types: nonprecious metal (typically nickel) and precious metals from Group VIII elements (typically platinum or rhodium). Due to severe mass and heat transfer limitations, conventional steam reformers are limited by the effectiveness factor of pelletized catalysts, which is typically less than 5% [11]. Therefore, kinetics is rarely the limiting factor with conventional steam reformer reactors [12], and, therefore, less expensive nickel catalysts are used industrially.

An important factor characterizing the SR process is the H:C atom ratio in the feedstock material. The higher this ratio is the lower carbon dioxide emission is formed. A membrane reactor can replace both reactors in a conventional SR process for achieving the overall reaction (2) [13]. The heat efficiency of hydrogen production by the SR of methane process on an industrial scale is around 70–85% [14]. A number of other raw materials are also possible to achieve this efficiency in the near future, such as solid communal waste, wastes from food industry, oils, purposefully cultivated or waste agricultural biomass, and fuels of fossil origin such as coal. The disadvantage is the high production of CO₂, ca. 7.05 kg CO₂/kg H₂.

2.2. Partial Oxidation. Partial oxidation (POX) and catalytic partial oxidation (CPOX) of hydrocarbons have been proposed in hydrogen production for automobile fuel cells and some other commercial applications [15, 16]. The gasified raw material can be methane and biogas but primarily heavy oil fractions (e.g., vacuum remnants, heating oil), whose further treatment and utilization are difficult [17]. POX is a noncatalytic process, in which the raw material is gasified in the presence of oxygen ((5) and (6)) and possibly steam ((7), ATR) at temperatures in the 1300–1500°C range and pressures in the 3–8 MPa range. In comparison with the steam reforming (H₂:CO = 3:1), more CO is produced (H₂:CO = 1:1 or 2:1). The process is therefore complemented by the conversion of CO with steam into H₂ and CO₂. This reaction contributes to the maintenance of equilibrium between the individual reaction products [18]:



The gaseous mixture formed through partial oxidation contains CO, CO₂, H₂O, H₂, CH₄, hydrogen sulfide (H₂S), and carbon oxysulfide (COS). A part of the gas is burned

to provide enough heat for the endothermic processes. The soot created by the decomposition of acetylene as an intermediate product is an undesired product. Its amount depends on the proportion of H:C in the initial raw fuel material. There has been, therefore, like with the SR, an endeavor to shift to raw materials containing a higher H:C ratio, for example, to natural gas. While the operation of the reactor is less expensive in comparison with the steam reforming, the subsequent conversion makes this technology more expensive. Since the process does not require the use of a catalyst, it is not necessary to remove sulfurous elements from natural gas, which lowers the efficiency of the catalyst. The sulfurous compounds contained in the gasified raw material are converted into hydrogen sulfide (ca. 95%) and carbon oxysulfide (ca. 5%) [19].

Catalysts can be added to the partial oxidation system (CPOX) in order to lower the operating temperature, ca. 700–1000°C. However, temperature control is proving hard because of coke and hot spot formation due to the exothermic nature of the reactions [10, 15, 16, 20]. For natural gas conversion, the catalysts are typically based on Ni or Rh. However, nickel has a strong tendency to coke, and the cost of Rh has increased significantly. Krummenacher et al. [16] had succeeded in using catalytic partial oxidation for decane, hexadecane, and diesel fuel. The high operating temperatures (>800°C) [16] and safety concerns may make their use for practical and compact portable devices difficult due to thermal management [21]. Typically, the thermal efficiency of POX reactors with methane as fuel lies in the range of 60–75% [22].

2.3. Autothermal Reforming. As previously mentioned, in the autothermal reforming (ATR), steam is added in the catalytic partial oxidation process. ATR is a combination of both steam reforming (endothermic) and partial oxidation (exothermic) reactions [23]. ATR has the advantages of not requiring external heat and being simpler and less expensive than SR of methane.

The range of operation of a fuel processor for hydrogen production is depicted in Figure 1. The selection of operation conditions of the reformer depends on the specific target. A main target is the high hydrogen yield with low carbon monoxide content. Maximum hydrogen efficiency and low carbon monoxide content are possible for steam reforming. However, steam reforming is an endothermic process and therefore energy demanding. This energy has to be transferred into the system from the outside.

Another significant advantage of ATR over SR process is that it can be shut down and started very rapidly, while producing a larger amount of hydrogen than POX alone [23]. There are some expectations that this process will become attractive for the “Gas to Liquid” fuel industry due to favorable gas composition for the Fischer-Tropsch synthesis, ATR’s relative compactness, lower capital cost, and the potential for economies of scale [24]. For methane reforming, the thermal efficiency is comparable to that of POX (ca. 60–75%) and slightly less than that of steam reforming. Gasoline and other higher hydrocarbons may be converted into hydrogen on

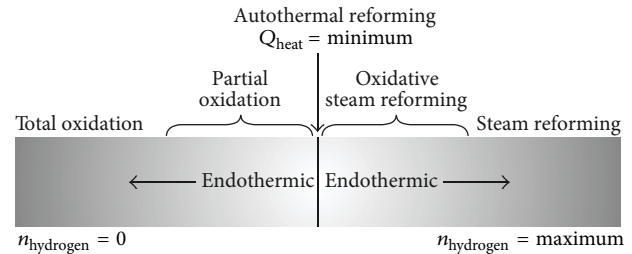


FIGURE 1: Operating conditions for POX, ATR, and SR.

board for use in automobiles by the autothermal process, using suitable catalysts [25].

2.4. Water-Gas Shift, Preferential Oxidation, and Methanation.

The reforming process produces a product gas mixture with significant concentrations of carbon monoxide, often 5 vol% or more (ca. 10 vol%) [10]. To increase the amount of hydrogen, the product gas is passed through a water-gas shift (WGS) reactor to decrease the carbon monoxide content, while at the same time increasing the hydrogen content (3). Typically, a high temperature is desired in order to favor fast kinetics. However, this results in high equilibrium carbon monoxide selectivity and decreased hydrogen product yield. Therefore, the reduction in the CO content of syngas is achieved in a two-step process that involves a high- and a low-temperature water-gas shift reaction, known as “HTS” and “LTS” processes, respectively (Figure 2). In the first step, carried out in the 310–450°C range with the use of $\text{Fe}_3\text{O}_4/\text{Cr}_2\text{O}_3$ catalyst, the CO concentration is reduced from 10 to 3 vol%. In the second step, carried out in the 180–250°C range, the CO content is further reduced to the low level of 500 ppm using $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts [26].

To further reduce the carbon monoxide content in the product gas, a preferential oxidation (PrOx) reactor or a carbon monoxide selective methanation reactor is used [10, 27]. Sometimes, the term selective oxidation is used in place of preferential oxidation. Selective oxidation refers to carbon monoxide reduction within a fuel cell, typically a proton exchange membrane (PEM) fuel cell, whereas preferential oxidation occurs in a reactor external to the fuel cell [27]. The PrOx and methanation reactors have their own advantages and challenges. The preferential oxidation reactor increases the system’s complexity because precise concentrations of air must be added to the system [10, 27]. However, these reactors are compact, and if excessive air is introduced, some hydrogen is burned.

Methanation reactors are simpler in that no air is required. However, for every CO reacted, three H_2 molecules are consumed. Also, CO_2 reacts with hydrogen, and careful control of reactor’s conditions needs to be maintained in order to minimize unnecessary consumption of hydrogen. Currently, preferential oxidation is the primary technique in development [27]. The catalysts are typically noble metals such as platinum, ruthenium, or rhodium supported on Al_2O_3 [10, 27]. At the same time, H_2 is purified by alternative

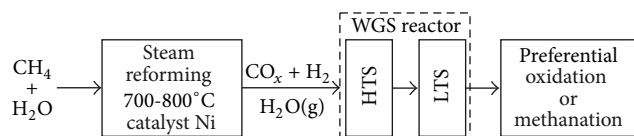


FIGURE 2: A diagram of methane steam reforming with subsequent carbon monoxide conversion into carbon dioxide and hydrogen.

approaches, namely pressure-swing adsorption, cryogenic distillation, and membrane technologies, which can ensure the necessary purity of hydrogen (ca. 98-99%). The most advantageous gas-purification method is the pressure-swing adsorption for its high efficiency (>99.99%) and flexibility.

2.5. Desulfurization. As discussed before, current hydrogen production arises primarily from the processing of natural gas, although with the substantial advances in fuel cells, there is an increased attention to other fuels, such as methanol, propane, gasoline, and logistic fuels, such as jet-A, diesel, and JP8 [28]. With the exception of methanol, all of these fuels contain some amount of sulfur, with the specific sulfur-containing compounds dependent on the fuel type and source. For this reason, desulfurization is considered as a very important step in fuel processing technologies.

The desulfurization processes can be classified based on the nature of the key physicochemical process used for sulfur removal (Figure 3). The most developed and commercialized technologies are those that catalytically convert organosulfur compounds with sulfur elimination. Such catalytic conversion technologies include conventional hydrodesulfurization (HDS), hydrotreating with advanced catalysts and/or reactor designs, and a combination of hydrotreating with some additional chemical processes to maintain fuel specifications [29, 30]. The main feature of the technologies of the second type is the application of physicochemical processes different in nature from catalytic HDS to separate and/or transform organosulfur compounds from refinery streams. Such technologies include, as a key step, distillation, alkylation, oxidation, extraction, adsorption, or combination of these [31].

2.6. Plasma Reforming. In the case of plasma reforming, the network of reforming reactions is the same as that in conventional reforming. However, energy and free radicals used for the reforming reaction are provided by plasma typically generated with electricity or heat [32–35]. When water or steam is injected with the fuel, H^{\bullet} , OH^{\bullet} , and O^{\bullet} radicals in addition to electrons are formed, thus creating conditions for both reductive and oxidative reactions to occur. Plasma reforming technologies have been developed to facilitate POX, ATR, and steam reforming, with the majority of the reactors being POX and ATR [35]. There are essentially two main categories of plasma reforming, namely, thermal and nonthermal [35].

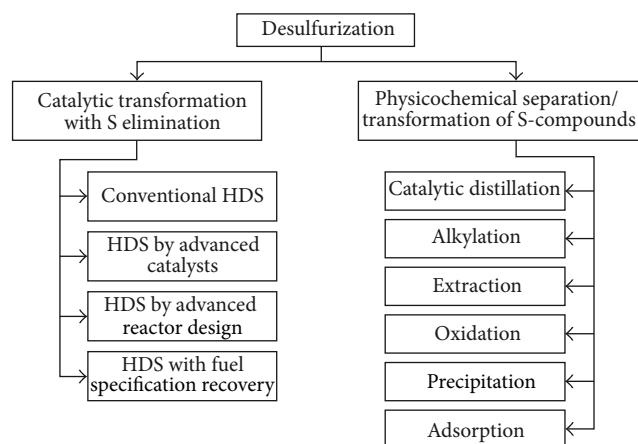


FIGURE 3: Desulfurization technologies classified by the nature of the key process to remove sulfur.

Plasma devices referred to as plasmatrons can generate very high temperatures (ca. >2000°C) with a high degree of control using electricity [32–35]. The heat generated is independent of reaction chemistry, and optimal operating conditions can be maintained over a wide range of feed rates and gas compositions. Compactness of the plasma reformer is ensured by high energy density associated with the plasma itself, and by the reduced reaction times, resulting in short residence times. Hydrogen-rich gas streams can be efficiently produced in plasma reformers from a variety of hydrocarbon fuels (e.g., gasoline, diesel, oil, biomass, natural gas, and jet fuel) with conversion efficiencies close to 100% [32, 36]. The plasma reforming technology has potential advantages over conventional technologies of hydrogen manufacturing [32–35]. The plasma conditions (e.g., high temperatures, high degree of dissociation, and substantial degree of ionization) can be used to accelerate thermodynamically favorable chemical reactions without a catalyst or provide the energy required for endothermic reforming processes to occur. Plasma reformers can provide a number of advantages, namely compactness and low weight (due to high power density), high conversion efficiencies, minimal cost (simple metallic or carbon electrodes and simple power supplies), fast response time (fraction of a second), operation with a broad range of fuels, including heavy hydrocarbons (crude) and “dirty” hydrocarbons (high sulfur diesel). This technology could be used to manufacture hydrogen for a variety of stationary applications, such as distributed and low-pollution electricity generation for fuel cells [32]. It could also be used for mobile applications (e.g., on-board generation of hydrogen for fuel cell powered vehicles) and for refueling applications (e.g., stationary sources of hydrogen for vehicles).

The only disadvantages of plasma reforming are the dependence on electricity and the difficulty of high-pressure operation (required for high-pressure processes such as ammonia production). High pressure, while achievable, increases electrode erosion due to decreased arc mobility and, therefore, it decreases electrode lifetime [33].

3. Hydrogen from Renewable Sources

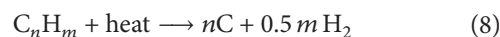
Hydrogen could be also produced by other methods than reforming of fossil fuels. A brief description of the biomass-based approaches (e.g., gasification, pyrolysis, and aqueous phase reforming) along with production of hydrogen from water (e.g., electrolysis, photoelectrolysis, and thermochemical water splitting) is described later.

3.1. Biomass Gasification. In the near term, biomass is anticipated to become the most likely renewable organic substitute to petroleum. Biomass is available from a wide range of sources, such as animal wastes, municipal solid wastes, crop residues, short rotation woody crops, agricultural wastes, sawdust, aquatic plants, short rotation herbaceous species (e.g., switch grass), waste paper, corn, and many others [37, 38].

Gasification technology commonly used with biomass and coal as fuel feedstock is very mature and commercially used in many processes. It is a variation of pyrolysis, and, therefore, is based upon partial oxidation of the feedstock material into a mixture of hydrogen, methane, higher hydrocarbons, carbon monoxide, carbon dioxide, and nitrogen, known as “producer gas” [37]. The gasification process typically suffers from low thermal efficiency since moisture contained in the biomass must also be vaporized. It can be performed with or without a catalyst and in a fixed-bed or fluidized-bed reactor, with the latter reactor having typically better performance [38]. Addition of steam and/or oxygen in the gasification process results in the production of “syngas” with a H_2/CO ratio of 2/1, the latter used as feedstock to a Fischer-Tropsch reactor to make higher hydrocarbons (synthetic gasoline and diesel) or to a WGS reactor for hydrogen production [38]. Superheated steam (ca. $900^\circ C$) has been used to reform dry biomass to achieve high hydrogen yields. However, gasification process provides significant amounts of “tars” (a complex mixture of higher aromatic hydrocarbons) in the product gas even operated in the $800\text{--}1000^\circ C$ range. A secondary reactor, which utilizes calcined dolomite and/or nickel catalyst, is used to catalytically clean and upgrade the product gas [38]. Ideally, oxygen should be used in these gasification plants; however, oxygen separation unit is cost prohibitive for small-scale plants. This limits the gasifiers to the use of air resulting in significant dilution of the product as well as the production of NO_x . Low-cost, efficient oxygen separators are needed for this technology. For hydrogen production, a WGS process can be employed to increase the hydrogen concentration followed by a separation process to produce pure hydrogen [39]. Typically, gasification reactors are built on a large scale and require massive amounts of material to be continuously fed. They can achieve efficiencies in the order of 35–50% based on the lower heating value [4]. One of the problems of this technology is that a tremendous amount of resources must be used to gather the large amounts of biomass to the central processing plant. Currently, the high logistics costs of gasification plants and the removal of “tars” to acceptable levels for pure hydrogen production limit the commercialization of biomass-based hydrogen production.

Future development of smaller efficient distributed gasification plants may be required for this technology for cost effective hydrogen production.

3.2. Pyrolysis and Copyrolysis. Another currently promising method of hydrogen production is pyrolysis or copyrolysis. Raw organic material is heated and gasified at a pressure of 0.1–0.5 MPa in the $500\text{--}900^\circ C$ range [40–43]. The process takes place in the absence of oxygen and air, and therefore the formation of dioxins can be almost ruled out. Since no water or air is present, no carbon oxides (e.g., CO or CO_2) are formed, eliminating the need for secondary reactors (WGS, PrOx, etc.). Consequently, this process offers significant emissions reduction. However, if air or water is present (the materials have not been dried), significant CO_x emissions will be produced. Among the advantages of this process are fuel flexibility, relative simplicity and compactness, clean carbon byproduct, and reduction in CO_x emissions [40–43]. The reaction can be generally described by the following equation: [41]



Based on the temperature range, pyrolysis processes are divided into low (up to $500^\circ C$), medium ($500\text{--}800^\circ C$), and high temperatures (over $800^\circ C$). Fast pyrolysis is one of the latest processes for the transformation of organic material into products with higher energy content. The products of fast pyrolysis appear in the entire phases formed (solid, liquid, and gaseous). One of the challenges with this approach is the potential for fouling by the carbon formed, but proponents claim that this can be minimized by appropriate design. Since it has the potential for lower CO and CO_2 emissions, and it can be operated in such a way as to recover a significant amount of solid carbon, which is easily sequestered [41, 44], pyrolysis may play a significant role in the future.

The application of the copyrolysis of a mixture of coal with organic wastes has recently received an interest in industrially advanced countries, as it should limit and lighten the burden of wastes in waste disposal (waste and pure plastics, rubber, cellulose, paper, textiles, and wood) [45, 46]. Pyrolysis and copyrolysis are well-developed processes and could be used in commercial scale.

3.3. Aqueous Phase Reforming. Aqueous phase reforming (APR) is a technology under development to process oxygenated hydrocarbons or carbohydrates of renewable biomass resources to produce hydrogen [47, 48], as depicted in Figure 4. The APR reactions take place at substantially lower temperatures ($220\text{--}270^\circ C$) than conventional alkane steam reforming (ca. $600^\circ C$). The low temperatures at which aqueous-phase reforming reactions occur minimize undesirable decomposition reactions typically encountered when carbohydrates are heated to elevated temperatures [49, 50]. Also, the water-gas shift reaction (WGS) is favorable at the same temperatures as in APR reactions, thus making it possible to generate H_2 and CO_2 in a single reactor with low amounts of CO. In contrast, typical steam reforming processes require multistage or multiple reactors to achieve

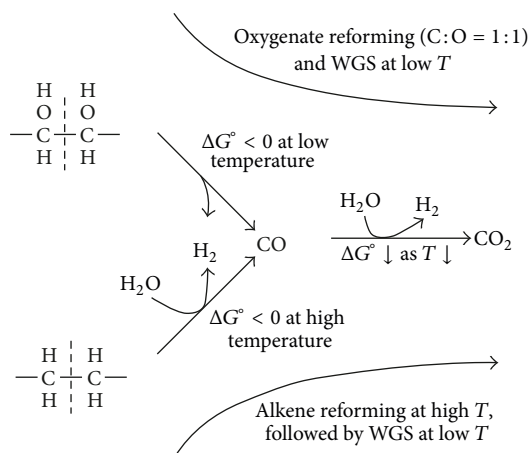
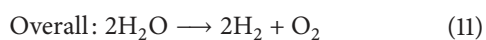
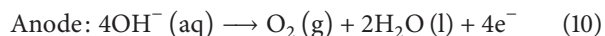
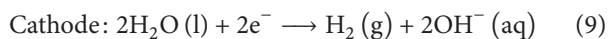


FIGURE 4: Reaction pathways for the production of H₂ by reactions of oxygenated hydrocarbons with water during APR.

low levels of CO in the product gas. Another advantage of the APR process is that it eliminates the need to vaporize water, which represents a major energy saving compared to conventional, vapor-phase steam reforming processes. Most of the research to date has been focused on supported Group VIII catalysts, with Pt-containing solids having the highest catalytic activity. Even though they have lower activity, nickel-based catalysts have been evaluated due to nickel's low cost [47]. The advocates of this technology claim that this technology is more amiable to efficiently and selectively converting biomass feedstock to hydrogen. Aqueous feed concentrations of 10–60 wt% were reported for glucose and glycols [51]. Catalyst selection is important to avoid methanation, which is thermodynamically favorable, along with Fischer-Tropsch products, such as propane, butane, and hexane [48, 52]. Recently, Rozmiarek [53] reported an aqueous phase reformer-based process that achieved an efficiency larger than 55% with a feed composed of 60 wt% glucose in water. However, the catalyst was not stable during long-term testing (200 days on stream) [53]. Finally, due to moderate space time yields, these reactors tend to be somewhat large. Improving catalyst activity and durability is an area where significant progress can be made.

3.4. Electrolysis. A promising method for the production of hydrogen in the future could be water electrolysis. Currently, approximately only 4% of hydrogen worldwide is produced by this process [2]. The electrolysis of water or its breaking into hydrogen and oxygen is a well-known method which began to be used commercially already in 1890.

Electrolysis is a process in which a direct current passing through two electrodes in a water solution results in the breaking of the chemical bonds present in water molecule into hydrogen and oxygen:



The electrolysis process takes place at room temperature. A commonly used electrolyte in water electrolysis is sulfuric acid, and the electrodes are of platinum (Pt), which does not react with sulfuric acid. The process is ecologically clean because no greenhouse gases are formed, and the oxygen produced has further industrial applications. However, in comparison with the foregoing methods described, electrolysis is a highly energy-demanding technology.

The energetic efficiency of the electrolysis of water (chemical energy acquired per electrical energy supplied) in practice reaches 50–70% [54]. It is essentially the conversion of electrical energy to chemical energy in the form of hydrogen, with oxygen as a useful byproduct. The most common electrolysis technology is alkaline-based but proton exchange membrane (PEM) and solid oxide electrolysis cells (SOEC) have been developed [55, 56]. SOEC electrolyzers are the most electrically efficient but the least developed. SOEC technology has challenges with corrosion, seals, thermal cycling, and chrome migration. PEM electrolyzers are more efficient than alkaline and do not have corrosion problems and seals issues as SOEC; however, they cost more than alkaline systems. Alkaline systems are the most developed and the lowest in capital cost. They have the lowest efficiency, so they have the highest electrical energy cost.

3.5. Photoelectrolysis. Photoelectrolysis is one of the renewable ways of hydrogen production, exhibiting promising efficiency and costs, although it is still in the phase of experimental development [57]. Currently, it is the least expensive and the most effective method of hydrogen production from renewable resources. The photoelectrode is a semiconducting device absorbing solar energy and simultaneously creating the necessary voltage for the direct decomposition of water molecule into oxygen and hydrogen. Photoelectrolysis utilizes a photoelectrochemical (PEC) light collection system for driving the electrolysis of water. If the semiconductor photoelectrode is submerged in an aqueous electrolyte exposed to solar radiation, it will generate enough electrical energy to support the generated reactions of hydrogen and oxygen. When generating hydrogen, electrons are released into the electrolyte, whereas the generation of oxygen requires free electrons. The reaction depends on the type of semiconductor material and on the solar intensity, which produces a current density of 10–30 mA/cm². At these current densities, the voltage necessary for electrolysis is approximately 1.35 V.

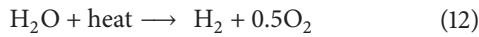
The photoelectrode is comprised of photovoltaic (semiconductor), catalytic and protective layers, which can be modeled as independent components [58]. Each layer influences the overall efficiency of the photoelectrochemical system. The photovoltaic layer is produced from light absorbing semiconductor materials. The light absorption of the semiconductor material is directly proportional to the performance of the photoelectrode. Semiconductors with wide bands provide the necessary potential for the splitting of water [54].

The catalytic layers of the photoelectrochemical cell also influence the performance of the electrolysis and require suitable catalysts for water splitting. The enclosed layer is

another important component of the photoelectrode which prevents the semiconductor from corroding inside the aqueous electrolyte. This layer must be highly transparent in order to be able to provide the maximum solar energy, so that it could reach the photovoltaic semiconducting layer.

3.6. Thermochemical Water Splitting. Thermochemical cycles have been developed already since the 1970s and 1980s when they had to contribute to the search for new sources of production of alternative fuels during the petroleum crisis. In thermochemical water splitting, also called thermolysis, heat alone is used to decompose water to hydrogen and oxygen [59]. It is believed that overall efficiencies close to 50% can be achieved using these processes [60].

The single-step thermal dissociation of water is described as follows:



One drawback of this process comes from the need of an effective technique to separate H_2 and O_2 to avoid ending up with an explosive mixture. Semipermeable membranes based on ZrO_2 and other high-temperature materials can be used for this purpose. Separation can also be achieved after the product gas mixture is quenched to lower temperatures. Palladium membranes can then be used for effective hydrogen separation.

It is well known that water will decompose at 2500°C , but materials stable at this temperature and also sustainable heat sources are not easily available. Therefore, chemical reagents have been proposed to lower the temperature, whereas more than 300 water-splitting cycles were referenced in the literature [61]. All of the processes have significantly reduced the operating temperature to lower than 2500°C , but typically require higher pressures. However, it is believed that scaling-up the processes may lead to improved thermal efficiency, overcoming one of the main challenges faced by this technology. In addition, a better understanding of the relationship between capital cost, thermodynamic losses, and process thermal efficiency may lead to reduced hydrogen production costs [60].

4. Economic Aspects on Hydrogen Production

At present, the most widely used and cheapest method for hydrogen production is the *steam reforming of methane (natural gas)*. This method includes about half of the world hydrogen production, and hydrogen price is about 7 USD/GJ. A comparable price for hydrogen is provided by partial oxidation of hydrocarbons. However, greenhouse gases generated by thermochemical processes must be captured and stored, and thus, an increase in the hydrogen price by 25–30% must be considered [62].

The further used thermochemical processes include gasification and pyrolysis of biomass. The price of hydrogen thus obtained is about three times greater than the price of hydrogen obtained by the SR process. Therefore, these processes are generally not considered as cost competitive of steam reforming. The price of hydrogen from gasification of

TABLE 1: Hydrogen production technologies summary.

Technology	Feedstock	Efficiency	Maturity
Steam reforming	Hydrocarbons	70–85%	Commercial
Partial oxidation	Hydrocarbons	60–75%	Commercial
Autothermal reforming	Hydrocarbons	60–75%	Near term
Plasma reforming	Hydrocarbons	9–85%*	Long term
Biomass gasification	Biomass	35–50%	Commercial
Aqueous phase reforming	Carbohydrates	35–55%	Med. term
Electrolysis	$\text{H}_2\text{O} + \text{electricity}$	50–70%	Commercial
Photolysis	$\text{H}_2\text{O} + \text{sunlight}$	0.5%*	Long term
Thermochemical water splitting	$\text{H}_2\text{O} + \text{heat}$	NA	Long term

*Hydrogen purification is not included.

biomass ranges from 10–14 USD/GJ and that from pyrolysis 8.9–15.5 USD/GJ. It depends on the equipment, availability, and cost of feedstock [1].

Electrolysis of water is one of the simplest technologies for producing hydrogen without byproducts. Electrolytic processes can be classified as highly effective. On the other hand, the input electricity cost is relatively high and plays a key role in the price of hydrogen obtained.

By the year 2030, the dominant methods for hydrogen production will be *steam reforming of natural gas* and *catalyzed biomass gasification*. In a relatively small extent both coal gasification and electrolysis will be used. The use of solar energy in a given context is questionable but also possible. Probably, the role of solar energy will increase by 2050 [1].

5. Conclusions

There is a tremendous amount of research being pursued towards the development of hydrogen (H_2) generation technologies. Currently, the most developed and used technology is the reforming of hydrocarbons. In order to decrease the dependence on fossil fuels, significant developments in other H_2 generation technologies from renewable resources such as biomass and water are considered. Table 1 summarizes the technologies along with their feedstock used and efficiencies obtained. It is important to note that H_2 can be produced from a wide variety of feedstock available almost everywhere. There are many processes under development with minimal environmental impact. Development of these technologies may decrease the world's dependence on fuels that come primarily from unstable regions. The “in-house” H_2 production may increase both national energy and economic security. The ability of H_2 to be produced from a wide variety of feedstock and using a wide variety of processes may make every region of the world able to produce much of its own energy. It is clear that as the technologies develop and mature, H_2 may prove to be the most ubiquitous fuel available.

Nomenclature

APR:	Aqueous phase reforming
ATR:	Autothermal reforming
CPOX:	Catalytic partial oxidation
HDS:	Hydrodesulfurization
PEC:	Photoelectrochemical
PEM:	Proton exchange membrane
POX:	Partial oxidation
PrOx:	Preferential oxidation
SOEC:	Solid oxide electrolysis cell
SR:	Steam reforming
WGS:	Water-gas shift.

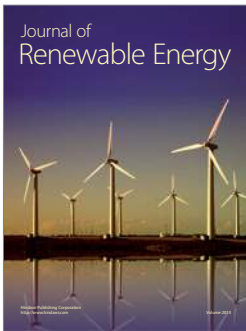
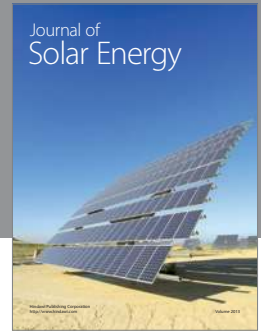
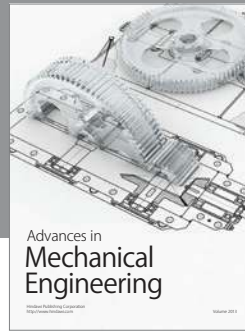
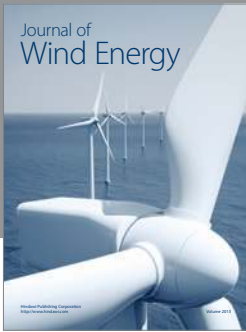
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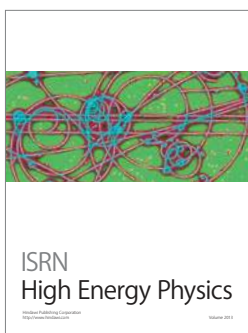
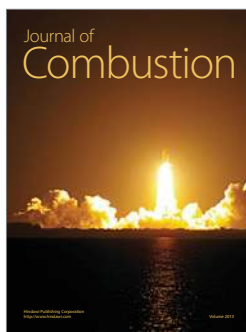
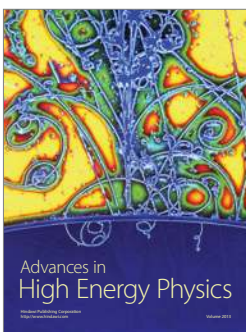
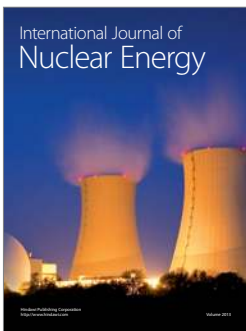
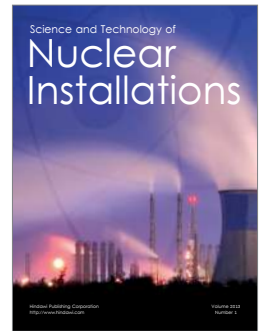
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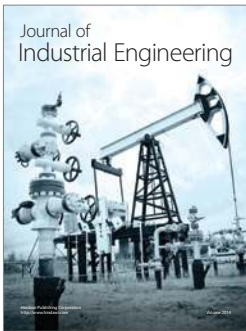
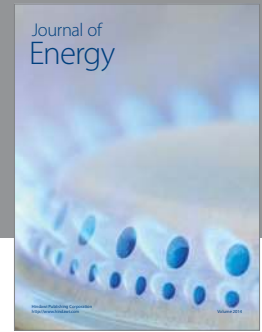
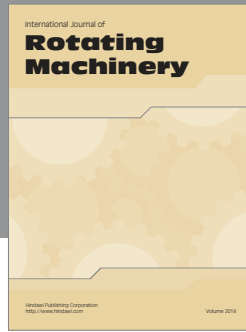
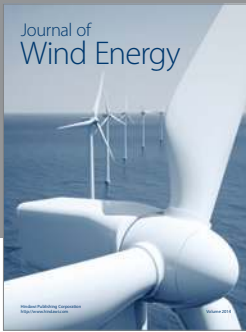
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