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Review

Green Energy based Thermochemical and Photochemical Hydrogen Production

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A significant amount of hydrogen is required to satisfy the hydroprocessing needs of petroleum refinery, natural gas cleaning, and biofuel upgrading. Meanwhile, hydrogen is a very promising candidate of energy due to its high energy output per mass unit as compared to other sources of energy. In this article, the production of hydrogen is overviewed from the traditional technology as the thermochemical processes of fossil fuels to the current development in photoelectrochemical processes or even hybrid technologies. The catalysts for methane reforming and visible-light absorption were summarized. Both processes employ oxides as the catalyst. Because catalytic oxides are mostly lack of visible-light absorption function, the visible-light absorption properties could be rendered by doping these oxides with metal, nitrogen, or even sulfur. Further complete substitution of the oxygen atoms leads to non-oxide catalyst. Moreover, multidimensional photochemical catalysts have acquired more attention over traditional powered catalysts. Finally, a vision is exhibited for the efficiency and the future trends on production of H_2.

Keywords: Hydrogen Production, Solar energy, Methane, Coal, Biomass, Steam Reforming, Dry Reforming, Autothermal Reforming, Tri-reforming, Gasification, Electrolysis, catalyst

1. INTRODUCTION

Hydrogen is a very promising candidate of energy due to its high energy output per mass unit as compared to other sources of energy. Moreover, a significant amount of hydrogen is required to satisfy the hydroprocessing needs of petroleum refinery, natural gas cleaning, and biofuel upgrading [1]. However, hydrogen does not naturally exist on earth in form of gas, but in form of a diverse range of resources, such as fossil resources, organics, and water. Extraction of hydrogen from those chemical compounds is still a popular yet challenging project nowadays. Currently, hydrogen is mostly reformed from natural gas, with the major component as methane producing over 90% of the whole hydrogen over the world. Nearly half of the methane is reformed to hydrogen by steam methane reforming

(SMR) [2], which is the most popular and an inexpensive procedure to produce hydrogen. Today, SMR accomplished 80-85% of the hydrogen production from natural gas globally and 95% of the hydrogen production in the United States [3]. With the fast depletion of fossil fuels, scientists now turn to renewable non-fossil fuel sources, such as biomass, or moreover, sustainable energy sources including wind, solar, hydro, nuclear, and geothermal energy [4].

Meanwhile, a significant number of technologies have been investigated to make hydrogen cheaper [5]. A wide portfolio of pathways for hydrogen production, including thermochemical processes, electrolysis, and biological processes in general is presented in Figure 1. Thermochemical process is a traditional technology to produce hydrogen, in which hydrogen is released from fossil fuels / biomass through heated chemical reactions. Typical thermochemical processes for H_2 production include coal/biomass gasification, natural gas reforming, biomass-based liquid reforming, and solar thermochemical hydrogen. Electrolysis is considered as a cleaner technology, which generates hydrogen via water splitting by using electricity. Electricity generated via clean sources (like solar and wind) is preferred. Newly developed solar technologies could deliver much lower impacts on the environment during H_2 production. These new technologies include photolytic or microorganism metabolism processes, enabling sustainable low-carbon H_2 production from renewable resources [6].

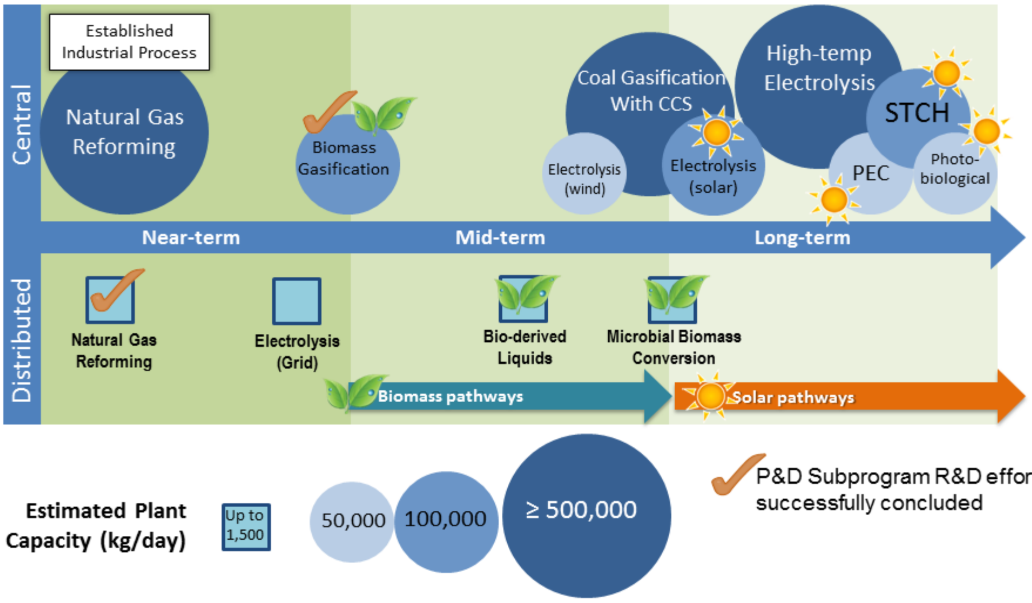

Figure 1. Hydrogen production pathways illustrated by U.S. Department of Energy, https://energy.gov/sites/prod/files/styles/borealis_default_hero_respondxl/public/h2_production_pathways.png. Public domain.

2. HYDROGEN RESOURCES

Currently, the major source of hydrogen is still fossil fuels. Fossil fuels are largely in the form of coal, oil, natural gas, accounting for 96% percent of the world's hydrogen production with the rest 4% H_2 prepared from water [7]. Nearly half of the fossil fuel is contributed from natural gas with the major composition in the form of methane. The depletion of fossil fuels and the emission of the greenhouse gases (GHGs) stimulate us to adjust our dependence on this kind of energy in order to satisfy the ever-growing needs in industries. This energy thirsty also leads an increasing interest in splitting water to acquire hydrogen. Recently, more efforts have been dedicated to preparing hydrogen from water through a carbon-free method.

2.1. Methane

Methane is the major component of the fossil natural gas and biogas [8]. A comparison of natural gas and biogas shows 20% more of methane in natural gas. Besides the primary component of methane, natural gas also includes some other hydrocarbons, CO_2, and sometimes trace percentage of N_2, H_2S, NH_3, siloxane, or inert gases as balance. In the balance, CO_2 and H_2S in biogas prevail over those in natural gas. Moreover, O_2 and NH3 only appear in biogas, while other hydrocarbons only appear in natural gas. The methane in the biogas could be as high as 60-70% by volume [9] with carbon dioxide (CO_2) in a range of 30-40%. In developing countries, biogas is an attractive energy alternative for regions relying heavily on traditional biomass for their energy needs. Biogas produced on a very small scale for household is used mainly for cooking and water heating [10]. Biogas produced on the large industrial scale can either be burnt in the biogas engine for cogeneration, or promoted to meet natural gas standards or directly for gas engine-based heavy duty trucks [11].

Methane is one of the GHGs, with other GHGs including CO_2 and nitrous oxides (NO_x), causing the “greenhouse effect” and global warming. Methane has an average lifetime of 28 years in the atmosphere. The potential risk on global warming for CH_4 is ~28 times higher than that of CO_2, which is ~3.5 years [12].

Methane (CH_4) can be converted to hydrogen and carbon monoxide via reforming technologies including steam reforming (SR), dry reforming of methane (DRM, i.e., from CO_2), autothermal reforming (AR), partial oxidation (PO), or tri-reforming (TR).

2.2. Coal and Biomass

Combustible sedimentary rock, sometimes named coal beds/seams, contains mostly of carbon, along with variable amounts of other elements including H, S, O, and N. Coal reacts with oxygen and steam through coal gasification procedure under high pressure and temperature to produce hydrogen. Coal gasification represents a mid-term frame for hydrogen production and concurrent capturing, exploitation, and storage of carbon [13].

Biomass gasification can produce hydrogen, CO, and CO_2 under a controlled ratio of oxygen/steam without combustion at temperatures over 700°C [14]. Other possible ways for hydrogen production from biomass may involve first conversion of biomass to ethanol or the bio-oil [15,16], which could be reformed to hydrogen. In addition, some microorganisms have the ability of digesting biomass and releasing hydrogen.

2.3. Water

As one of the most abundant resource on the earth, water could be electrolyzed to release hydrogen. For electrolysis, the optimum choice of electricity should deliver zero GHG emissions. To avoid the emission of GHGs by most of the grid electricity, the adoption of renewable/nuclear energy technology is a feasible option for the industrialization of the water splitting process for hydrogen production. Therefore, electricity from renewable source, such as solar and wind energy, has acquired increasing attention for sustainable development in hydrogen production [17].

3. HYDROGEN PRODUCTION PROCESSES

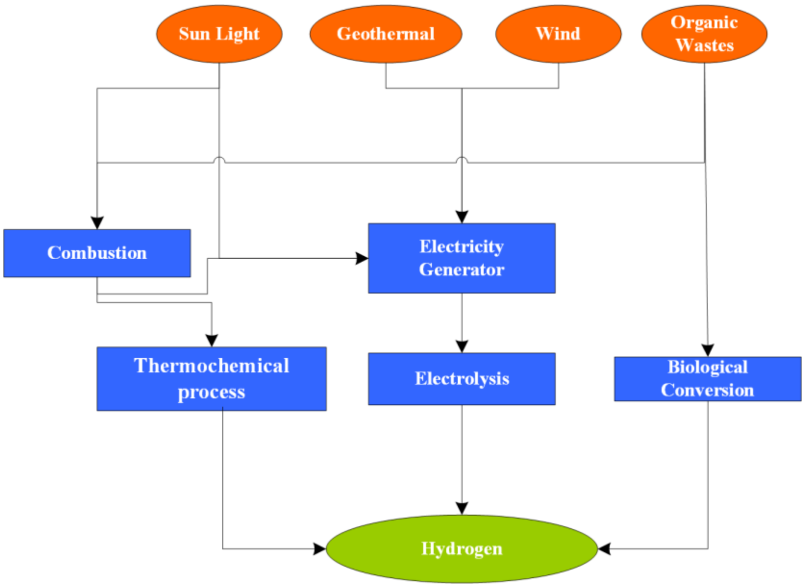

Figure 2. Techniques employing renewable energies for hydrogen production

Traditional thermochemical processes employ the fossil fuel as the energy source. A long-term technology pathway is energy-oriented and dedicating for low or zero GHG emissions. One solution is the technology of thermochemical water splitting that could utilize solar power or recycle the heat from nuclear power plants. Figure delivers a schematic presentation of renewable energy as sources for hydrogen production. For example, sunlight can induce the photoelectrochemical (PEC) water splitting reaction [18]. Alternatively, the photolytic biological processes can turn water or organic matters into hydrogen.

3.1. Thermochemical Processes

3.1.1. Steam Reforming

Steam reforming is an essential technology for hydrogen production. Majority of the hydrogen is produced in large scale plants by natural gas reforming with some on-site hydrogen produced in refineries in the United States. Steam reforming of hydrocarbon feedstock was introduced into industry over 80 years ago to produce H_2-enriched gases. Because of the higher H/C ratio and less carbon deposition than naphtha, methane became a more favorable feedstock about 50 years ago. A historical review on the steam reforming technology can be found in the literature [19].

Steam reforming can reform hydrocarbon [20], methane, or other biomass-derived fuels into hydrogen. One example of the hydrocarbon could be naphtha in a liquid stream, transforming into a gaseous mixture with H_2 and CO through reaction (1). Comparatively a mature technology, steam reforming of methane proceeds catalytically in a steam of 700-1000°C under a pressure of 0.3-2.5 MPa. In the major reaction (2), methane is transformed to H_2 and CO with relatively small amount of CO_2. Steam reforming is endothermic despite of the exothermic nature of the water-gas shift reaction (3). The heat generated by the exothermic reaction is too limited to provide enough energy for the SR process. So, significant amount of heat is required to support SR reactions. Reactions (4-7) [21] could generate hydrogen from biomass-derived fuels including low carbon alcohols (methanol and ethanol), biodiesel, and other forms of biomass-derived fuels.

Steam reforming reactions:
Reaction (1) $C_nH_{2n+2} + nH_2O \leftrightharpoons n\,CO + (2n + 1)\,H_2$
Reaction (2) $CH_4 + H_2O \leftrightharpoons CO + 3H_2$ ($\Delta H^\theta = +206$ kJ/mol CH_4)
Water-gas shift (WGS) reaction:
Reaction (3) $CO + H_2O \leftrightharpoons CO_2 + H_2$ ($\Delta H^\theta = -41$ kJ/mol)
Methanol reforming:
Reaction (4) $CH_3OH + H_2O \leftrightharpoons CO_2 + 3H_2$ ($\Delta H^\theta = 49.2$ kJ/mol)
Ethanol reforming [22]:
Reaction (5) $C_2H_5OH + 3H_2O \leftrightharpoons 2CO_2 + 6H_2$ ($\Delta H^\theta = 174$ kJ/mol)
Steam reforming of methyl-oleate as a model substance for biodiesel [23]:
Reaction (6) $C_{19}H_{36}O_2 + 17H_2O \leftrightharpoons 19\,CO + 35H_2$ ($\Delta H^\theta = 2645$ kJ/mol)
The overall steam-reforming reaction of bio-oil [24]:
Reaction (7) $C_nH_mO_k + (2n - k)\,H_2O \leftrightharpoons nCO_2 + (2n + m/2 - k)\,H_2$

The industrial steam reforming process typically utilizes a heated tubular furnace (reformer) and downstream cleaning units. In a simplified process for SRM, the feed is firstly hydrodesulfurized and subsequently mixed with superheated process steam in a heated furnace (reformer). The reformer contains a series of catalytic reforming tubes in a row. The catalyst bed (with catalysts normally containing nickel) is commercially operated with evident temperature gradient, under the representative temperatures of 450-650°C for inlet and 800-950°C for outlet. The steam reformers could reach capacities up to 300,000 Nm^3 of H_2 (or syngas)/h with average heat fluxes over 100,000 kcal/m^2/h (0.12 MW/m^2) [25].

In some processes, an adiabatic pre-reformer is added to solve the problem of carbon deposition, which is a critical issue shortening the lifetime of commercial catalysts. The advantages of a pre-reformer include: 1) Converting all higher hydrocarbons, and bringing the reactions into equilibrium [26]; 2) preheating the feed to downsize the tubular reformer; and 3) allowing flexible feedstock from methane to biomass derived liquid fuels [27].

Following the steam reformer, the process may use a shift reactor, in which an important portion of CO in the cracked gas is used for additional hydrogen generation via the exothermic WGS reaction (3), a process limited by the chemical equilibrium. The temperature of the shift reaction determines the CO content at the reactor outlet. The content can be brought down to 2.5% at high shift temperature of 300-450°C, 0.5% at medium shift temperature of 220-270 °C, and 0.2% at low shift temperature of 180-250 °C, respectively. The high temperature shift favors Fe/Cr catalysts for the good activity from Fe and reduced sintering from Cr), while the low/medium temperature shift favors Cu based catalysts either hybrid with Fe/Cr or Zn[28].

For steam reforming, nickel catalysts are usually selected. Although coke formation is common on the catalysts, the carbon deposited could be easily removed by adding excess steam or other oxidants (like CO_2 or air). Accordingly, the reformer is often operated with a higher steam/carbon relationship than theoretical necessity to hinder the carbon formation.

H_2 production from fossil fuels leads to significant CO_2 emission with ~20% from CH_4 combustion in conventional SMR. The solar SMR process could alleviate CO_2 and concomitant SO_x and NO_x by eliminating CH_4 combustion. An 85% reduction in CO_2 emission from hydrogen production could be obtained with nearly 100% conversion of CH_4 by integration of solar energy. The integrated process is more flexible with an equivalent efficiency of 6.5-8% higher than conventional SMR [2]. The advances in solar SMR meet the challenges in the stability of solar energy and facility design/cost. To convert clean and abundant solar energy into chemical energy, one of the most promising techniques is recognized as the water splitting into hydrogen. For example, Italian scientists employed molten salts to transfer heat collected from concentrated solar source to steam reformer, focusing on lower the SR temperature to 400-550 °C [29].

3.1.2. Drying Reforming

Fischer and Tropsch in 1928 [30] firstly studied the DRM (Reaction 8), which is a thermodynamically favored process and mostly performed at atmospheric pressure or lower. The DRM converts two greenhouse gases of CO_2 and CH_4 into synthesis gas (CO and H_2) at 700-900°C. This technology operates at a 20% lower cost with respect to other reforming processes [30] and is very promising for both industrial and environmental implications. A suitable substitute for reactant gases is biogas, containing a stoichiometric ratio of $CH_4 : CO_2$ = 1-1.5 for reforming reaction.

Table 1. Overall reactions in DRM system.

Reaction	Name	Chemical Reaction	ΔH^θ (kJ/mol)	ΔG^θ=0, T (K)	Reaction T (°C)
8	DRM	$CH_4+CO_2 \rightleftharpoons 2CO+2H_2$	247	61,770-67.32T	640^a
9	RWGS	$CO_2+H_2 \rightleftharpoons CO + H_2O$	41	-8,545+7.84T	820^b
10	Methane Cracking	$CH_4 \rightleftharpoons 2H_2+ C(s)$	75	21,960-26.45T	557^a
11	CO Reduction	$CO+ H_2 \rightleftharpoons C+H_2O$	-131		
12	Boudouard Reaction	$2CO \rightleftharpoons CO_2+C(s)$	-172	-39,810+40.87T	700^b

a: Lower limit
b: Upper limit

DRM process, being highly endothermic, requires high energy input. Side reactions are possible including reverse water-gas shift (RWGS) reaction, methane cracking, CO reduction, and Boudouard reaction (Table 1). Because of the significant higher chemical potential of coke deposition from the stoichiometric DRM reaction than that in the equivalent SR reaction, the carbon deposition occurring in side reactions often causes catalyst deactivation, which is an essential challenge hindering the industrial application of the DRM technology [19]. Thus, a high coking-resistant catalyst is decidedly needed to further commercialize the DRM process [31]. An ideal catalyst should demonstrate high activity towards preferred products and high stability over a long period. Generally, noble and nonnoble metal catalysts were widely used for this application. The most studied metal catalysts are the highly active and relatively cheap nickel (Ni)-based one, yet vulnerable to coke formation [32]. Choices of more robust catalysts are noble metals, including Pt, Ru, Rh, Pd, and Ir. The lower carbon solubility potential makes the noble metals less sensitive to carbon deposition than nickel [33]. The major barrier of the high cost from noble metals could be alleviated by doping the expensive ones into multi-metallic catalysts to advance the technology. A comprehensive review of noble metal catalysts for DRM can be found in the literature [34].

Table 2 summarizes recent studies of the DRM during 2007-2017 [28]. Studies on CO_2 reforming of methane were normally conducted between 700°C and 950°C at varying CH_4/CO_2 ratio (within a range of 0.5-4) and types of catalysts. From the thermodynamical point of view, the RWGS equilibrium enables higher CO_2 conversion than that of CH_4. It’s even desired to produce a H_2/CO ratio of 1 or lower, if syngas was employed to synthesize long chain hydrocarbons via the Fischer-Tropsch process [35]. Most studies fabricated new catalysts to enhance the dry reforming and minimize the carbon formation. Some catalysts comprise active metal(s) and supports such as C, SiO_2, Al_2O_3, MgO, ZrO_2, ZrO_2-SiO_2, CeZrO, and CeO_2 [36]. Generally, CH_4 is activated on metal, and CO_2 is activated on acidic or basic supports. If the supports were inert materials, such as C and SiO_2, both reactants are activated by the metal [34]. The catalysts include crystalline oxide catalysts such as Pyrochlores (formula $A_2B_2O_7$) [37] or perovskite (ABO_3) [38], molecular sieves [39], and hydrotalcite catalysts [40]. Moreover, the activity of catalysts towards DRM could be increased by promoters [41].

Carbon deposition, a major drawback of DRM, was observed in almost all studies. Although several studies announced that the carbon formation was either not detected [42] or negligible [43], those examines were only done in bench-scale reactors for limited time (400-500 h). Until the results can be further confirmed at the pilot scale and commercial scale, there are still many technique barriers to be overcome.

Recently, non-thermal plasma catalysis was introduced into the DRM process [44]. Plasma catalysis possesses non-equilibrium properties and requires low power input, and thus the reactions happened at a lower temperature below 300°C. By combining the advantages of the plasma field and catalysis science, this technology may have the prospect of minimizing the carbon deposition.

Table 2. Recent studies on dry reforming of methane

Input CH_4/CO_2	Catalytic Metals	Temp. (°C)	Output H_2/CO	CH_4 conversion (%)	CO_2 conversion (%)	Carbon formation (mg/g-catalyst)	Reference
0.5	Ce-Gd-O	800	1.07	50	88	N/A	[45]
0.8	Rh-Al	700	1	42	nr	N/A	[46]
1	NiCo/CeZrO_2	800	0.84	79	84	0.24-8.2% of catalyst	[43]
1	WC	900	0.96	95	95	None	[42]
1	Ni-$La_2O_2CO_3$	700	0.86	70	82	1.2-10.3%% of catalyst	[47]
1	Ni-Al	700	0.67	19	31	N/A	[48]
1	Ni-Pb-Al	700	0.88	60	78	N/A	[48]
1	Ni-Pb-1P-Al	700	0.77	55	71	N/A	[48]
1	Ni	700	1	54	66	41	[49]
1	Co	700	1	75	67-80	20-268	[49]
1	Ni-Co	700	1	56-71	83	290	[49]
1	Pt-Ru	700	<0.5	90	48	N/A	[50]
1	La-NiMgAlO	700	0.8	80	85	N/A	[51]
1	Ni	750	nr	32	36	3.6% of inlet C	[52]
1	Ni/Si	750	1	73	89	negligible	
1	Ce-Gd-O	800	0.96	68	72	N/A	[45]
1	Ru/ZrO_2-SiO_2	800	1.07	95.8	89.8	None	[53]
1	Ni/porous γ-Al_2O_3	850	0.82	99	nr	N/A	[54]
1	Pt-Al	900	nr	nr	nr	22% of inlet C	[55]
1	Ni-La-Al	950	nr	99	90	N/A	[56]
1	NiO–MgO	700	0.87	67	77	N/A	[57]
1.5	Ni-Al	750	0.9	49	81	N/A	[58]
1.5	Ni-Mg-Al	750	0.86	59	70	N/A	[58]
1.5	Ni-La-Mg-Al	750	0.95	61	70	N/A	[58]
1.5	Rh-Ni-Mg-Al	750	1	58	85	N/A	[58]
1.5	Rh-Ni-La-Mg-Al	750	1.06	50	94	N/A	[58]
1.5	Rh-Ni	800	1	65	100	N/A	[58]
1.5	Ni-Al	850	0.55	72	96	180	[59]
1.5	Ni-Ce-Al	850	0.65	73	97	170	[59]

2	Ce-Gd-O	800	0.84	66	46	N/A	[45]
2.1	Ni	750	nr	21	29	3.6% of inlet C	[52]

3.1.3. Partial Oxidation, Autothermal Reforming, and Tri-Reforming

Partial Oxidation

Hydrogen produced from other sources of fossil resources (hydrocarbons and coal) is mostly acquired via a partial oxidation procedure with a limited amount of oxygen provided. This limited oxygen could hardly oxidize the reactants completely to carbon dioxide and water. An example of partial oxidation of methane in reaction 13 is carried out with the oxygen less than the stoichiometric ratio. The incomplete oxidized product CO is further transformed into carbon dioxide and more hydrogen in water-gas shift reaction (3).

The partial oxidation of CH_4:

Reaction (13) $CH_4 + 0.5\ O_2 \leftrightharpoons 2H_2 + CO$ (ΔH^{θ} = -36 kJ/mol CH_4)

Being mildly exothermic, the partial oxidation reaction can be coupled with endothermic reactions, such as SR and DR, to increase the efficiency of both reactions [60]. Normally, a non-catalytic, large-scale partial oxidation process can yield syngas with an optimum ratio of $H_2/CO = 2$ for downstream synthesis such as production of methanol. Comparatively, a catalytic PO is appropriate for small-scale applications featuring fast catalytic conversion of hydrocarbons. Early work established that nickel-based catalysts are highly active towards partial oxidation reaction. Until now, many potential alternatives have been discovered, including supported Co or Fe, supported noble metal [61], or transition metal carbide catalysts [62].

Autothermal Reforming

Autothermal reforming (ATR) is a hybrid process of SR [reaction(2)] and PO [reaction(13)] [63]. Being endothermic, this reforming process is heated in situ by methane oxidization. However, during ATR of the biogas, a slow oxidation of Ni-based catalysts was discovered, attributing to deactivation of the metallic Ni[64].

Tri-reforming

The simultaneous reforming of methane with various combinations with O_2[reaction (13)]/H_2O [reaction (2)]/CO_2[reaction (8)] is called mixed reforming or tri-reforming (TR) [65]. By controlling the $O_2/H_2O/CO_2$ ratio in the feed stream, the product ratio of H_2/CO could be regulated in a range of 1~3. The process has been developed to integrate the advantages of all the above reforming reactions. Incorporating the partial oxidation of methane could minimize the energy requirements because of its exothermic mechanism. Moreover, the carbon deposition could be inhibited by using extra stream or O_2 in the system [35]. Currently, most studies concentrate on the exploitation of novel nickel-based catalysts for the TR process [66], and biogas is also proposed as a carbon neutral feedstock for this technology.

3.2. Gasification

Two types of gasification processes have been employed to produce hydrogen. One is coal gasification. The other is biomass gasification. Coal was historically gasified to produce coal gas and subsequently piped directly to consumers for daily application [67]. Currently, coal gas is burned mostly to generate electricity. Coal gasification yields the syngas consisting mostly of CO and H_2, CO_2, CH_4, and H_2O vapor. The unbalanced reaction for coal gasification is shown as:

Reaction (14) $CH_{0.8} + O_2 + H_2O \rightarrow CO + CO_2 + H_2$ + other species

During the coal gasification reaction, the coal is heated in the gasifier under a well-controlled oxygen and steam environment. Oxygen and water molecules partially oxidize the coal without resulting in combustion. The primary products are a desired gaseous mixture with by-products like tar and phenols.

Reserves of coal are abundant in countries such as Russia, the United States, and China. Coal gasification to produce H_2 is more energy efficient and environmentally favored over the direct burning of coal, because the coal gas delivers particular low burning emission of SO_x, NO_x, and other toxic gases.

The gasification of biomass is more difficult than that of coal. In general, drying biomass to 10-20% moisture content is considered the optimum for minimizing the size and cost of the biomass gasification plants [68]. Solid air-dried biomass of ~ 1 kg could be converted to nearly 2.5-3.0 Nm^3 gaseous combustible gas through a sequence of thermo-chemical reactions of biomass gasification. The obtained gas is of low-heating value in the range of 1000~1200 kcal/Nm^3. A simplified example reaction using glucose as a substitute for cellulose is presented as [69,70]:

Reaction (15) $C_6H_{12}O_6 + O_2 + H_2O \rightarrow CO + CO_2 + H_2$ + other species

Gasifier is the core of this technology. Most fixed-bed gasifiers provide low-energy product gases. The fixed-bed gasifiers are unfit for large scale applications, due to bridging problems such as inhomogeneous bed temperature, uneven gas flow, ash deformation, and slagging. Most fixed-bed gasifiers are air-blown, merely providing thermal energy of a few megawatts (MWt) [71].

Large-scale applications lead to development of more suitable bubbling fluid beds and circulating fluid beds. Both designs target a biomass size of approximately 2.0-2.5 inch to maintain a transport velocity. A smaller biomass size might benefit some technologies, however at the expense of increased capital and operating costs.

Biomass gasification is a multiple-step process. The first step of biomass pyrolysis decomposes biomass in the oxygen-lean condition below 600°C to produce a gas mixture of H_2, CO, CO_2, and other hydrocarbon (tars) compounds. In the second stage, tars are catalytically reformed to acquire a clean syngas. The syngas is purified to obtain the hydrogen product by conversion of CO into CO_2 in steam shift reaction and subsequent absorption of CO_2. Accordingly, pure H_2 product is acquired.

Two types of catalysts are used for biomass gasification [72]. The first type of catalysts, such as dolomites and alkali metals, is mixed with biomass before the gasification via wet impregnation or dry mixing. The primary purpose of using these catalysts is to reduce the tar. The second type of nickel catalysts is used in the tar reforming reactor.

As the most abundant renewable resources in the world, biomass effectively recycles CO_2, yielding low net greenhouse gas emissions. Nevertheless, being a less mature technology, biomass gasification shows limited market share in applications for heat, co-combustion in coal plants, and combined heat and power generation, mostly depending on the government regulations and support [73]. Challenges on biomass gasification include cost reduction related to facility and biomass supply. Corresponding technological barriers mainly include scaling up, tar reduction, and gas cleaning [74].

3.3. Photoelectrochemical process

The electrolysis activates the water molecules by auxiliary reagents (sensitizer and catalyst) through photon-activation with subsequent splitting of water molecules employing electric potential. A comprehensive review on the theoretical background and the technological advancement of hydrogen production from solar energy can be found in the literature [75]. Electrolysis of pure alkaline water satisfies 4% of the world's demands for hydrogen [7].

3.3.1. Hybrid solar-redox process

A two-step water-splitting process generates hydrogen via a hybrid solar-redox reaction of metal oxides, methane, and steam as follows.

Reaction (16) $M_xO_y + yCH_4 = xM + y(2H_2+CO)$

Reaction (17) $xM + y\,H_2O = M_xO_y + yH_2$

In reaction 16, syngas is produced through oxidation of methane by the metal oxides (usually iron oxide). The reduced metals are oxidized by steam to generate H_2 through reaction 17. The hybrid reactions produce H_2 of higher purity with lower CO_2 emission compared with the more complex SMR process, offering a promising substitute over traditional techniques.

Other metal oxides besides iron oxide are also effective for reforming of methane. For example, metallic tungsten could split water and generate hydrogen at relatively lower temperature of 1074K. WO_3 supported on ZrO_2 could deliver 70% conversion of methane and 86% selectivity of CO [76].

3.3.2. Electrolysis of Water

Catalyst plays a major role in hydrogen production through solar energy conversion. Majority of photocatalysts respond primarily to ultraviolet irradiation from sun light, merely a small portion of solar energy. One example is the traditional TiO_2 photocatalysts, with band gap energy ca. 3.2 eV, only active under the irradiation of UV light. UV light only accounts for 3-5% of the solar energy whereas visible light account for 46-53%, and infrared light account for the rest 43-50 % of the solar energy [77]. To make more effective utilization of solar energy, considerable efforts have been made to design visible-light-responsive photocatalysts. This category of catalysts is one of the most challenging topics in water-splitting because of the harsh thermodynamic and kinetic requirements. Thermodynamically, such photocatalysts should possess a narrow band gap energy (≤ 3.0 eV) and appropriate conduction and valence band positions for simultaneous H_2 and O_2 evolution (≥ 1.8eV). Kinetically, a high efficiency of charge separation is needed to allow the photo-generated charges to migrate to solid-liquid interface for the following redox reactions. Some recent achievements presented above are listed in Table3 for representative photocatalytic catalysts. The catalysts should be active for water splitting under irradiation up to 600 nm to achieve higher solar energy conversion efficiency at a reasonable quantum efficiency [77].

TiO_2 is a common photocatalyst, yet only active under UV irradiation. The major drawback of this most reported oxide is the weak visible light harvest ability. This ability could be enhanced by the addition of metallic atom dopants or cocatalysts to enable higher catalytic efficiency. Oxide doped with transition metals can absorb visible light through the excitation of impurity levels [78]. Cocatalysts play an essential role to promote charge separation during water splitting. Accurately-designed cocatalysts, and the elaboration of their roles in water splitting shall help promote progress in photocatalytic solar energy conversion. One good choice for cocatalysts is Pt nanoparticles that help reduce the potential of hydrogen evolution reaction and promote charge separation. Pt–loaded WO_3 was reported to lower the bandgap energy for absorption of the visible light [79].

Another way to promote the visible light response of oxides is the doping of N or S into oxides. For example, N doped TiO_2 can enable the bandgap narrowing by mixing with O2p states [80]. The N-doped oxide is called oxynitride. It was reported that drastic modification of semiconductor characteristics can be caused by doping of nitrogen into Ta_2O_5 [81]. The modification includes the visible light activation from 320 nm to 520 nm. Interestingly, a surface modification of N-Ta_2O_5 by Pt or Au greatly enhanced the H_2 evolution rate. Beside the nitrogen doping, the substitution of the oxygen atoms by sulfur leads to oxysulfide. Complete substitution of oxygen atoms in oxides lead to non-oxide photocatalysts. Those non-oxide photocatalysts, usually semiconductors, are engineered to enhance the light-harvesting ability and optimize the gas generation rate. The valence band edge is shifted negatively to overcome the problem of large overvoltage loss of oxygen evolution on oxide semiconductors. Non-oxide semiconductor materials for photocatalytic and PEC water splitting under visible light have been reviewed in the literature [77]. All these catalysts are semiconductors entailing specific band structure with suitable potentials for valence and conduction bands. All of the above catalysts are in the powdered form. In those powdered systems, H_2 and O_2 are produced as mixed gases, inevitably requiring the separation process toward practical usage of hydrogen as fuel. An integration of the photocataltytic water splitting and the hydrogen separation offers one solution to this issue. The solution could be either a 2D membrane or a 3D network composed of visible-light-responsive photocatalysts. In a 2D structure, the photocatalyst membrane functions as a photoanode for production of hydrogen, and a platinum cathode and electrolytes separated by a proton exchange membrane allow for the production of H_2 at cathode. This design delivers a H-type reactor/device in real practice [82]. More recently, zero dimension materials, such as the inexpensive carbon quantum dots (CQDs), have been established as a highly sustainable light-absorbing material and an excellent photosensitizers in combination with a molecular catalyst for solar light driven hydrogen production in aqueous solution [83]. The CQDs absorb the visible light and transfer photoexcited electrons to catalyst nickel bis(diphosphine) complex NiP. The photoinduced holes in CQDs are quenched by electron donor EDTA.

Scientists have developed novel hybrid materials with 3D structure for this application. One organic/inorganic material was reported [84] to be metal-organic frameworks (MOFs) in the form of metal-oxo clusters with 3D porous network structure, in which porous coordination polymers (PCPs) function as linkers. This hybridization of organic and inorganic materials opens up a new field in catalysts as well as adsorbents, separation materials, and ion conductive materials [85].

Table 3. A tabulated list of catalyst that functions under visible-light irradiation

Type	Category	catalyst	cocatalyst	Wavelength	Ref.
1D oxide particles	Metal doped oxide	$Bi_2Ga_4O_9$ Dopant: Cr^{3+}, Fe^{3+}, Mn^{3+}	NiO_x, Pt, RuO_x	420 nm 502 nm 731 nm	[86]
		$SiTiO_3$ Dopant: Rh, Sb	Cocatalyst: IrO2	500 nm	[87]
	N doped oxide	Nitrogen doped Ta_2O_5,	N Surface modified by Pt, Au		[81]
		Perovskite type $LaMg_xTa_{1-x}O_{1+3x}N_{2-3x}(x \geq 1/3)$		600 nm **QE 0.03% (440 nm)	[88]
	S doped oxide	Oxysulphide $Sm_2Ti_2S_2O_5$	S		[89]
	Nonoxide Chalcogenides cotaining Cu^I	$CuGaSe_2$, $CuZnSnS_4$, $Cu(Ga,In)(S,Se)_2$,			
2D nanosheet		TiO_2/CdS	N/A	≥420 nm 285μm/h Apparent AQY 6.9%	[84]
3D		MOF/PCP		370-420 nm	[85]
CQDs	NiP molecular catalyst	CQDs+Ni	EDTA	398μm/h > 455 nm	[83]

* Apparent quantum yield

** QE: quantum efficiency

Accordingly designated photocatalysts usually encounter a problem of instability under photocatalysis conditions [86]. Special measures need to be taken to protect the catalysts to survive the irradiation. For example, the surface modification plays an essential role in promoting the charge separation and the surface reaction kinetics. One such procedure could be a doubled coating of amorphous oxyhydroxides $MO_{2-m}(OH)_{2m}\cdot xH_2O$ (M =Si, Ti) over a complex perovskite-type oxynitride [88]. Besides the above discussed procedures that enhance the photocatalytic efficiency of catalyst under visible light irradiation, other processes are under investigation to improve the durability of the PEC and photocatalytic systems.

Water splitting reaction in reaction (18) is an endothermic one, with the Gibbs free energy change as 238 kJ mol^{-1} (2.47 eV). With lower applied potential of < 1.23 eV, PEC solar water splitting enables the solar energy storage in form of chemical energy. Electrolysis of water is a prospective option for production of H_2 gas from renewable sources. H_2 gas could reach relatively high purity within the range of 99.5-99.8%. The current challenge for this reaction is the low efficiency below 2% associated with high cost of equipment. Moreover, the on hand application of water splitting required solar batteries of high-energy demand [85].

Reaction (18) $H_2O \rightarrow H_2 + 1/2\ O_2$

The electrolysis of water proceeds in a reactor called electrolyzer composed of an anode and a cathode partitioned by an electrolyte. The variation of electrolytes is associated with different mechanisms. With a polymer electrolyte membrane (PEM), the electrolyzer is operated at 70-90 °C to decompose water molecules at the anode to form O_2 and protons shown in reaction (19). Protons diffuse through the electrolyte membrane to the cathode, whereas protons are neutralized by the electrons from the electrical flow to release H_2 according to reaction (20).

Reaction (19): Anode of the PEM electrolyzer $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
Reaction (20): Cathode of the PEM electrolyzer $4H^+ + 4e^- \rightarrow 2H_2$

With a liquid alkaline electrolyte of NaOH or KOH solution, hydroxide ions (OH^-) migrates from the cathode to the anode via the electrolyte. The electrolyzer is commercially operated at 100-150 °C to decompose water at the cathode to release H_2 as shown in reactions (21-22) [90]. One application of this technique is as a hydrogen generator to provide high purity hydrogen for gas chromatography (GC) equipped with a FID detector.

Reaction (21): Cathode of alkaline electrolyzer $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$
Reaction (22): Anode of alkaline electrolyzer $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

With a solid ceramic material (usually oxides) as the electrolyte, the electrolyzer is operated at 700-800 °C to form H_2 gas and anions of O^{2-} at cathode by combine water with electrons. The O^{2-} ions eventually form oxygen gas at the anode after penetrating through the membrane.

Both PEM and alkaline technologies can deliver hydrogen with high purity on site and on demand. Commercial electrolyzers are available from small-scale to large-scale production of H_2. Central production facilities that could be tied directly to electricity produced by using renewable resources such as solar energy and wind energy are available too. Hydrogen production via electrolysis powered by renewable energies can reduce environmental footprint and possibly lead to zero-carbon emission. Current challenges still rely on improving the efficiency of electrolyzers and reducing the production cost [91]. Photoelectrochemical and photobiological processes are subject to a low efficiency of typically less than 1% (solar to hydrogen).

3.4. Other Hydrogen Production Processes

Nuclear energy has been successful to generate electricity. The nuclear energy is also very promising in hydrogen production. Nevertheless, more investigation is indispensible for substitution of nuclear power for fossil fuels for non-electrical applications [92]. The photobiological processes such as algae cultivation can harvest hydrogen from biological systems [93,94]. The bio-processes require further developments to meet the long-term energy requirements.

The electrochemical hydrogen production via solar battery-based water splitting requires the use of solar batteries with high energy requirements. In a supercritical cycle, electricity is generated as the source of energy to produce hydrogen gas from water. Recently, a prototype powered by solar energy was designed, constructed, and tested based on Rankin cycle of CO_2 [92]. The CO_2 could be effectively heated by solar radiation to 250°C for a supercritical state. A concurrent hydrogen production and heat recovery is feasible with 1035.0 g H_2 in summer and 568.0 g H_2 in winter based on a 100 m^2 solar collector that is evacuated.

3.5 Efficiency discussion

The hybrid solar-redox process integrating the solar energy in SMR is potentially 16.3% more efficient in reduction of CO_2 emission with more than 100% conversion efficiency of methane to fuel [2]. The implement of H_2 production from renewable energy sources shall be based on a regional decision support system, such as the selection of locations based on the evaluation of the renewable energy sources.[95]

Shaner [96] performed a technoeconomic analysis of solar-hydrogen production from PEC and photovoltaic-electrolytic (PV-E) procedures. The comparison of two PEC systems and two PV-E systems established insufficient cost reductions on currently demonstrated technology in either single or combination application. Solar electricity are still more expensive than traditional electricity by an order of magnitude. The low conversion efficiency of solar-to-electricity limits the advancement in the production efficiency of H_2[7]. Consequently, hydrogen produced by the PEC system is currently not cost competitive with that produced by electricity generated from fossil fuels or nuclear power. Nevertheless, solar powered photoelectrochemical and photochemial technologies are preferred for hydrogen fueling station, because external power sources are unnecessary, leading to fewer processes and no extra hydrogen distribution systems.

5. CONCLUSION

In the near future, the primary method for hydrogen production shall remain to be the steam reforming of the natural gas. Other large-scale choices are commercially available coal gasification and alkaline electrolysis. Advanced processes require further efforts to economically produce hydrogen from sustainable resources.

In terms of the feedstock, technologies based on renewable resources are anticipated to reach the cost targets in the mid-term. In the longer term, solar-energy based technologies are expected to become viable for near-net zero carbon emission.

For future development in photocatalytic conversion by solar energy, concurrent development is needed in two aspects: stable and effective photocatalyst responsive to visible light; high efficiency system design for H_2 production and O_2 separation. For industrial application, a good option is the photocatalytic electrode.

The major challenge for H_2 production is the storage of the intermittent renewable energy sources (RES). Although there are some commercially mature techniques identified, new technologies are emerging for advancement solar H_2 production. All these efforts offer a promising future for the solar energy storage.

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