

Recent advances in production of hydrogen from biomass

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ABSTRACT

The aim of this paper is to highlight various processes for the conversion of biomass into hydrogen gas. Biomass energy has the potential to be “modernized” worldwide, i.e., produced and used efficiently and cost competitively, generally in the more convenient forms of gases, liquids, or electricity. Biomass will play an important role in the future global energy infrastructure for the generation of power and heat, but also for the production of chemicals and fuels. Biomass and biomass-derived fuels can be used to produce hydrogen sustainably. The methods available for the hydrogen production from biomass can be divided into two main categories: thermochemical and biological routes.

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1. Introduction

The dramatic increase in the price of petroleum, the finite nature of fossil fuels, increasing concerns regarding environmental impact, especially related to greenhouse gas emissions, and health and safety considerations are forcing the search for new energy sources and alternative ways to power the world's motor vehicles [1–3]. Hydrogen seems to be an ideal candidate, since hydrogen is a cleaner source of energy [4]. It holds the promise as a dream fuel of the future with many social, economic and environmental benefits to its credit [5].

About half of all the H_2 as currently produced is obtained from thermocatalytic and gasification processes using natural gas as a starting material, heavy oils and naphtha make up the next largest source, followed by coal, and only 4% is generated from water using electricity [6]. Approximately 49% of hydrogen produced is used for the manufacture of ammonia, 37% for petroleum refining, 8% for methanol production and about 6% for miscellaneous smaller-volume uses [7]. The future widespread use of hydrogen is likely to be in the transportation sector, where it will help reduce pollution. Vehicles can be powered with hydrogen fuel cells, which are three times more efficient than a gasoline-powered engine [8,9].

All primary energy sources can be used in the hydrogen-producing process [10]. The production of hydrogen from fossil fuels causes the co-production of carbon dioxide (CO_2), which is assumed to be the main responsible for the so-called “greenhouse effect” [11]. Hydrogen produced through a range of renewable primary energy sources such as wind, biomass, and solar energy

is ideal for gradually replacing fossil fuels [12]. Since the energy crises of the 1970s, many countries have become interested in biomass as a fuel source to expand the development of domestic and renewable energy sources and reduce the environmental impacts of energy production. Biomass energy potential is addressed to be the most promising among the renewable energy sources, due to its spread and its availability worldwide [13]. Biomass and biomass-derived fuels can be used to produce hydrogen sustainably. Using biomass instead of fossil fuels to produce hydrogen reduces the net amount of CO_2 released to the atmosphere, since the CO_2 released when the biomass is gasified was previously absorbed from the atmosphere and fixed by photosynthesis in the growing plants [14].

Hydrogen can be generated from biomass, but this technology urgently needs further development. The production of renewable hydrogen from biomass requires a co-product strategy to compete with conventional production of hydrogen from the steam reforming of natural gas. The process of biomass to activated carbon is an alternative route to hydrogen with a valuable co-product that is practiced commercially [15]. The production of hydrogen from biomass has several advantages and limitations compared to that of fossil fuels, as shown in Table 1 [2].

2. Overview of biomass

The most important biomass energy sources are wood and wood wastes, agricultural crops and their waste byproducts, municipal solid waste (MSW), animal wastes, waste from food processing, and aquatic plants and algae [16]. Biomass is the name given all the earth's living matter. Biomass as the solar energy stored in chemical form in plant and animal materials is among the most

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Table 1
Main advantages and limitations of biomass to hydrogen.

<i>Advantages</i>
Use of biomass reduces CO ₂ emissions
Crop residues conversion increases the value of agricultural output
Replacing fossil fuels with sustainable biomass fuel
Costs of getting rid of municipal solid wastes
<i>Limitations</i>
Seasonal availability and high costs of handling
Non-total solid conversion (char formation) and tars production
Process limitations: corrosion, pressure resistance and hydrogen aging

precious and versatile resources on earth. It is composed mainly of carbohydrate compounds, the building blocks of which are the elements carbon, hydrogen, oxygen and nitrogen. All biomass is produced by green plants converting CO₂ in the air, water and sunlight into plant material through photosynthesis [17]. Photosynthesis is a carbon fixation reaction by reduction of CO₂. The fixation or reduction of CO₂ is a light-independent process.

2.1. Importance of biomass

Biomass, mainly in the form of wood, is the oldest form of energy used by humans. Traditionally, biomass has been utilized by humans through direct combustion, and this process is still widely used in many parts of the world [18]. Traditional biomass provides about 7–11% of the world's energy supply [19]. The average majority of biomass energy is produced from wood and wood wastes (64%), followed by MSW (24%), agricultural waste (5%), and landfill gases (5%) [20–22]. Biomass energy has the potential to be “modernized” worldwide, i.e., produced and used efficiently and cost competitively, generally in the more convenient forms of gases, liquids, or electricity [23]. The importance of biomass energy will increase as national energy policy and strategy focuses more heavily on renewable sources and conservation. Biomass appears to be an attractive feedstock for three main reasons [24]:

- it is a renewable resource that could be sustainably developed in the future,
- it appears to have formidably positive environmental properties resulting in no net releases of CO₂ and very low sulfur content,
- it appears to have significant economic potential provided that fossil fuel prices increase in the future.

Biomass is burned by direct combustion to produce steam turns a turbine and the turbine drives a generator, producing electricity. Gasifiers are used to convert biomass into a combustible gas (biogas). The biogas is then used to drive a high efficiency, combined cycle gas turbine [25]. Heat is used to thermo-chemically convert biomass into pyrolysis oil. Pyrolysis oil, which is easier to store and transport than solid biomass material, is then burned like petroleum to generate electricity [20].

2.2. Components of biomass

The chemical structure and major organic components in biomass are extremely important in the development of processes for producing derived fuels and chemicals [26]. The components of biomass include cellulose, hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash, and other compounds. Two larger carbohydrate categories that have significant value are cellulose and hemicelluloses (holocellulose). The lignin fraction consists of non-sugar type molecules [27,28].

Cellulose is a high-molecular-weight (10⁶ or more) linear polymer of β-(1 → 4)-D-glucopyranose units in the ⁴C₁ conformation. Hemicellulose is a mixture of various polymerized monosaccharides such as glucose, mannose, galactose, xylose, arabinose, 4-O-methyl glucuronic acid and galacturonic acid residues. Hemicelluloses exhibit lower molecular weights than cellulose. The number of repeating saccharide monomers is only ~150, compared to the number in cellulose (5000–10000) [29]. Lignin is an aromatic polymer synthesised from phenylpropanoid precursors. The basic chemical phenylpropane units of lignin (primarily syringyl, guaiacyl and p-hydroxy phenol) are bonded together by a set of linkages to form a very complex matrix [30].

Hardwoods have a higher proportion of cellulose, hemicelluloses, and extractives than softwoods, but softwoods have a higher proportion of lignin. In general, hardwoods contain about 43% cellulose, 35% hemicelluloses, and 22% lignin while softwoods contain about 43% cellulose, 28% hemicelluloses, and 29% lignin (on an extractive free basis) [31,32].

3. Hydrogen production from biomass

The methods available for the hydrogen production from biomass can be divided into two main categories: thermochemical and biological routes. The major biomass-to-hydrogen pathways are shown in Fig. 1 [33].

Biomass can be thermally processed through pyrolysis [34,35] or gasification [36,37] to produce hydrogen. In the pyrolysis and gasification processes, water–gas shift is used to convert the reformed gas into hydrogen, and pressure swing adsorption is used to purify the product [38]. The major disadvantage of these processes is the decomposition of the biomass feed stock leading to char and tar formation [39].

Biological production of hydrogen (biohydrogen) as a byproduct of microorganism metabolism is an exciting new area of technology development that offers the potential production of usable hydrogen from a variety of renewable resources [40]. Biohydrogen provides a feasible means for the sustainable supply of hydrogen with low pollution and high efficiency, thereby being considered a promising way of producing hydrogen [41]. Biotechnology of hydrogen production might be a most important way for energy production in the near future because of its characteristics of low costs and regeneration [42].

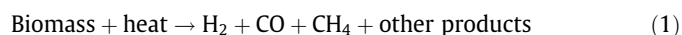
3.1. Thermochemical conversion of biomass to hydrogen

3.1.1. Hydrogen from biomass via pyrolysis

Pyrolysis of biomass is a promising route for the production of solid (char), liquid (tar and other organics), and gaseous products as possible alternate sources of energy. The most interesting temperature range for the production of the pyrolysis products is between 625 and 775 K [43,44].

Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional (slow) pyrolysis, fast pyrolysis and flash pyrolysis. Slow pyrolysis of biomass is associated with high charcoal content, but the fast pyrolysis is associated with tar, at low temperature (675–775 K) [45], and/or gas, at high temperature [46]. At present, the preferred technology is fast or flash pyrolysis at high temperatures with very short residence times [47]. Table 2 indicates the product distribution obtained from different processes of pyrolysis process [48].

Although most pyrolysis processes are designed for biofuel production, hydrogen can be produced directly through fast or flash pyrolysis if high temperature and sufficient volatile phase residence time are allowed as follows [49]:



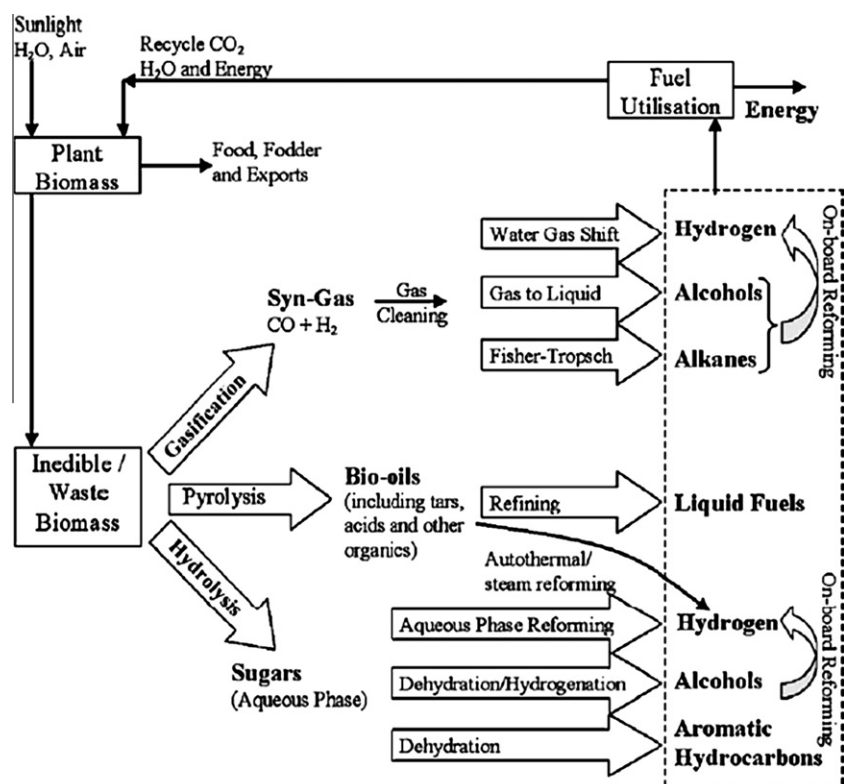


Fig. 1. Hydrogen and liquid fuels production from biomass sources. The waste CO_2 , H_2O , and energy produced from these fuels can be utilized to produce further biomass. Source: Ref. [33].

Table 2
Product distribution obtained from different processes of pyrolysis process.

Thermal degradation	Residence time (s)	Upper temperature (K)	Product yield (%)		
			Char	Liquid	Gas
Slow pyrolysis	200	600	32–38	28–32	25–29
	120	700	29–33	30–35	32–36
	90	750	26–32	27–34	33–37
	60	850	24–30	26–32	35–43
	30	950	22–28	23–29	40–48
Fast pyrolysis	5	700	22–27	53–59	12–16
	4	750	17–23	58–64	13–18
	3	800	14–19	65–72	14–20
	2	850	11–17	68–76	15–21
	1	950	9–13	64–71	17–24
Gasification	1500	1250	8–12	4–7	81–88

Methane and other hydrocarbon vapors can be converted into hydrogen and carbon monoxide (CO) by steam reforming:



A water–gas shift reaction can be applied in order to increase the hydrogen production:



Pyrolysis of biomass is complex functions of the experimental conditions, under which the pyrolysis process proceeds. The most important factors, which affect the yield and composition of the volatile fraction liberated, are: biomass species, chemical and structural composition of biomass, particle size, temperature, heating rate, residence time, atmosphere, pressure and reactor configuration [50]. Yield of products resulting from biomass pyrolysis can be maximized as follows:

- charcoal – a low temperature, low heating rate process,
- liquid products – a low temperature, high heating rate, short gas residence time process, and
- fuel gas – a high temperature, low heating rate, long gas residence time process.

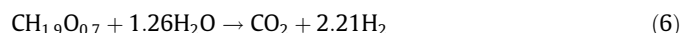
At 1023 K, the gaseous yield increases to around 45–50% compared to the yield of 30–35% at 773 K, based on the dry biomass feed [33]. Demirbas [51] investigated the yields of hydrogen-rich gases via pyrolysis at different temperature ranges. He reported that increasing the pyrolysis temperature resulted in an increase in the hydrogen yield as a percentage of the total gases evolved. The percent of hydrogen in gaseous products by pyrolysis from the samples of hazelnut shell, tea waste and spruce wood increased from 36.8% to 43.5%, 41.0% to 53.9% and 40.0% to 51.5% by volume, respectively, while the final pyrolysis temperature was increased from 700 to 950 K. One of the methods to increase the hydrogen yield is to apply catalytic pyrolysis. Three types of biomass feedstocks, olive husk, cotton cocoon shell and tea waste were pyrolyzed at about 775–1025 K in the presence of ZnCl_2 and catalyst-to-biomass ratios of 6.5–17 by weight [52]. The highest yield of hydrogen-rich gas (70.3%) was achieved from olive husk using about 13% ZnCl_2 at about 1025 K temperature. This study also investigated the effect of K_2CO_3 and Na_2CO_3 on yield of gaseous products from various biomass species with pyrolysis. The effect of K_2CO_3 and Na_2CO_3 as catalysts on pyrolysis depends on the biomass species. The catalytic effect of Na_2CO_3 was greater than that of K_2CO_3 for the cotton cocoon shell and tea factory waste, but the catalytic effect of K_2CO_3 was greater for the olive husk [52]. The study of Caglar and Demirbas [53] indicates that the catalytic effect of Na_2CO_3 is greater than CaCO_3 for rice straw pyrolysis. The yields of hydrogen-rich gas from pyrolysis of agricultural residues at different temperatures in the presence of Na_2CO_3

were investigated by Demirbas [54]. Results of this study are shown in Fig. 2. As indicated in Fig. 2, the highest yield of hydrogen-rich gas was obtained from the walnut shell sample. Among the different metal oxides, Al_2O_3 and Cr_2O_3 exhibit better catalytic effect than the others [49]. The use of noble metals (Rh, Ru and Pt) in large scale industrial steam reforming is not common because of their relative high cost [55].

Hydrogen can also be produced by catalytic steam reforming of bio-oil or its fractions [56,57]. Hydrogen production from bio-oil provides a new route for utilization of bio-oil. Hydrogen production from renewable bio-oil is an attractive idea for fuel, energy, and agricultural applications. In recent years hydrogen production via steam reforming of bio-oil has attracted more and more attention. But because of the complicated composition of bio-oil and carbon deposition on catalyst surface in reaction process, currently the studies mainly focus on the steam reforming of model compounds in bio-oil and reforming catalysts [58]. The bio-oil can be stored and shipped to a centralized facility where it is converted to hydrogen via catalytic steam reforming and shift conversion [59]. Catalytic steam reforming of bio-oil at 1025–1125 K over a Ni-based catalyst is a two-step process that includes the shift reaction [8]:



The overall stoichiometry gives a maximum yield of 0.172 g H_2 /g bio-oil (11.2% based on wood) [8].



In reality, this yield will always be lower because both the steam reforming and water–gas shift reactions are reversible, resulting in the presence of some CO and CH_4 in the product gas.

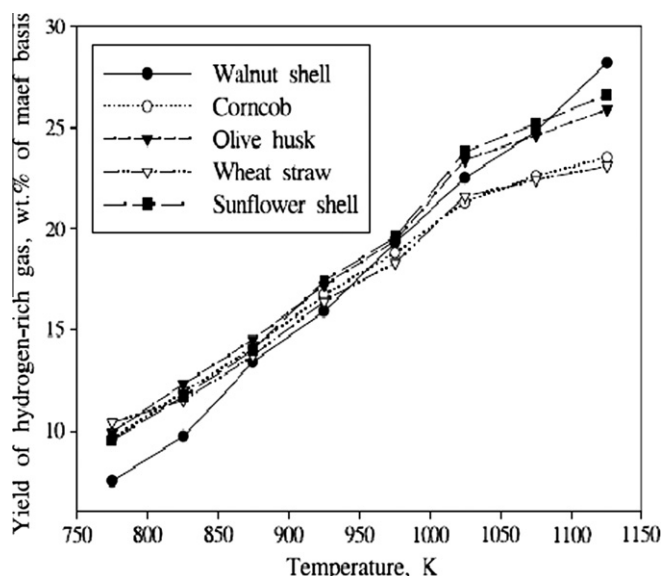


Fig. 2. Plots for yields of hydrogen-rich gas from pyrolysis of agricultural residues versus temperature in the presence 30% Na_2CO_3 . Source: Ref. [54].

Table 3

Typical gas composition data as obtained from commercial wood and charcoal downdraft gasifiers operated on low to medium moisture content fuels (wood 20%, charcoal 7%).

Component	H_2 (%)	CO_2 (%)	CH_4 (%)	CO (%)	N_2 (%)	Heating value (MJ/m^3)
Wood gas	12–20	9–15	2–3	17–22	50–54	5–5.9
Charcoal gas	4–10	1–3	0–2	28–32	55–65	4.5–5.6

In addition, thermal cracking that occurs parallel to reforming produces carbonaceous deposits [60].

3.1.2. Hydrogen from biomass via gasification

Gasification of biomass has been identified as a possible system for producing renewable hydrogen, which is beneficial to exploit biomass resources, to develop a highly efficient clean way for large-scale hydrogen production, and has less dependence on insecure fossil energy sources [61]. In general, the gasification temperature is higher than that of pyrolysis and the yield of hydrogen from the gasification is higher than that of the pyrolysis [35].

Biomass gasification can be considered as a form of pyrolysis, which takes place in higher temperatures and produces a mixture of gases with H_2 content ranging 6–6.5% [37]. The synthetic gas produced by the gasification of biomass is made up of H_2 , CO, CH_4 , N_2 , CO_2 , O_2 , and tar. When gasifying biomass, tar that is formed together with the synthetic gas is difficult to remove with a physical dust removal method [62]. The product distribution and gas composition depends on many factors including the gasification temperature and the reactor type [63]. The most important gasifier types are fixed bed (updraft or downdraft fixed beds), fluidized bed, and entrained flow gasifiers. All these gasifiers need to include significant gas conditioning along with the removal of tars and inorganic impurities and the subsequent conversion of CO to H_2 by water gas shift reaction as discussed in the pyrolysis section. Table 3 shows typical gas composition data as obtained from commercial wood and charcoal downdraft gasifiers operated on low to medium moisture content fuels [64].

Gasification technologies provide the opportunity to convert renewable biomass feedstocks into clean fuel gases or synthesis gases. The synthesis gas includes mainly hydrogen and carbon monoxide ($\text{H}_2 + \text{CO}$) which is also called as bio-syngas [65,66]. Bio-syngas is a gas rich in CO and H_2 obtained by gasification of biomass. Table 4 shows the composition of bio-syngas from biomass gasification [37]. Hydrogen production is the largest use of syngas. Biomass can be converted to bio-syngas by non-catalytic [67], catalytic [68], and steam gasification [69] processes.

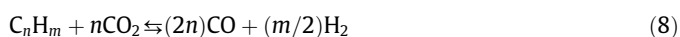
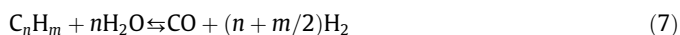
Steam gasification is a promising technology for thermochemical hydrogen production from biomass. Hydrogen is produced from the steam gasification of legume straw and pine sawdust [70], hazelnut shell [71], paper, yellow pine woodchips [72], mosses, algae [43], wood sawdust [73], wheat straw [74], and waste wood [75].

Rabah and Eldighidy [76] studied the production of hydrogen gas on a pilot scale by steam gasification of charred lignocellulosic waste material. In the study, the hydrogen gas was freed from moisture and CO_2 . They investigated the beneficial effect of some inorganic salts such as chlorides, carbonates and chromates on the reaction rate and production cost of the hydrogen gas. Steam reforming C_1 – C_5 hydrocarbons, nafta, gas oils, and simple aromatics are commercially practiced, well-known processes. Steam reforming of hydrocarbons; partial oxidation of heavy oil residues, selected steam reforming of aromatic compounds, and gasification of coals and solid wastes to yield a mixture of H_2 and CO, followed by water–gas shift conversion to produce H_2 and CO_2 , are well-established processes [77]. Steam reforming and so-called dry or CO_2 reforming occur according to the following reactions and are usually promoted by the use of catalysts.

Table 4

Composition of bio-syngas from biomass gasification.

Constituents	% by volume (dry and nitrogen free)
Carbon monoxide (CO)	28–36
Hydrogen (H ₂)	22–32
Carbon dioxide (CO ₂)	21–30
Methane (CH ₄)	8–11
Ethene (C ₂ H ₄)	2–4
Benzene–Toluene–Xylene (BTX)	0.84–0.96
Ethane (C ₂ H ₆)	0.16–0.22
Tar	0.15–0.24
Others (NH ₃ , H ₂ S, HCl, dust, ash etc.)	<0.021



Modeling of biomass steam gasification to synthesis gas is a challenge because of the variability (composition, structure, reactivity, physical properties, etc.) of the raw material and because of the severe conditions (temperature, residence time, heating rate, etc.) required [78].

The yield of H₂ from steam gasification increases with increasing water-to-sample (W/S) ratio [79]. The yields of H₂ from steam gasification increase with increasing of temperature. The yield of hydrogen-rich gaseous product in the gaseous products from the black liquor steam gasification run (W/S = 1.9) increased from 38.0% to 50.3% with increasing temperature from 975 to 1325 K [80]. The yields of H₂ from steam gasification of hazelnut shell at different temperatures were investigated by Demirbas [71]. Steam gasification runs were carried out over a temperature range from 925 to 1225 K. W/S ratios were 0.7 and 1.9 in steam gasification runs. The highest H₂ yield (59.5%) was obtained from the gasification run (W/S = 1.9) at 1225 K. Kriengsak et al. [72] investigated high-temperature steam gasification of paper, yellow pine woodchips, and Pittsburgh bituminous coal in a batch-type flow reactor at temperatures in the range of 973–1473 K at two different ratios of steam to feedstock molar ratios. Hydrogen yield of 54.7% for paper, 60.2% for woodchips, and 57.8% for coal was achieved on a dry basis, with a steam flow rate of 6.3 g/min at steam temperature of 1473 K.

The effect of catalyst on gasification products is very important. The use of the catalyst did not affect the gas yields, but the composition of the gases was strongly influenced. The content of H₂ and CO₂ increased, while that of CO decreased; a drastic reduction in the content of organic compounds could also be observed. Because the char yields remained almost constant compared to an equivalent no catalytic thermal run, the increase in the content of hydrogen was probably due to the influence of the catalyst on the water gas shift reaction [79]. Dolomite, Ni-based catalysts and alkaline metal oxides are widely used as gasification catalysts [49]. The yields of hydrogen from biomass with the use of dolomite in the fluidized-bed gasifier and the use of nickel-based catalysts in the fixed bed reactor downstream from the gasifier were investigated by Lv et al. [81]. They obtained a maximum hydrogen yield (130.28 g H₂/kg biomass) over the temperature range of 925–1125 K. Three types of catalysts were tested by Corte et al. [82]: alumina, aluminosilicate material, and nickel-supported catalysts. Minowa and Inoue [83] have carried out studies on the high-pressure steam gasification of cellulose and lignocellulose materials using a reduced metal catalyst. K₂CO₃ catalyst shows a destructive effect on the organic compounds, and H₂ and CO₂ form at the end of the catalytic steam reforming process [84]. The catalytic steam gasification of biomass in a lab-scale fixed bed reactor in order to evaluate the effects of particle size at different bed temperatures on the gasification performance was carried out by Luo et al.

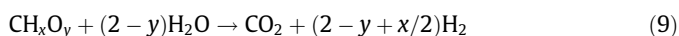
[85]. The study showed that with decreasing particle size, the dry gas yield, carbon conversion efficiency and H₂ yield increased, and the content of char and tar decreased.

3.1.3. Hydrogen from biomass via supercritical water (fluid–gas) extraction

The supercritical fluid extraction (SFE) is a separation technology that uses supercritical fluid solvent. Fluids cannot be liquefied above the critical temperature, regardless of the pressure applied but may reach the density close to the liquid state. Every fluid is characterized by a critical point, which is defined in terms of the critical temperature and critical pressure. Water is a supercritical fluid above 647.2 K and 22.1 MPa [86,87].

Supercritical water (SCW) possesses properties very different from those of liquid water. The dielectric constant of SCW is much lower, and the number of hydrogen bonds is much lower and their strength is weaker. As a result, high-temperature water behaves like many organic solvents so that organic compounds have complete miscibility with SCW. Moreover, gases are also miscible in SCW, thus a SCW reaction environment provides an opportunity to conduct chemistry in a single fluid phase that would otherwise occur in a multiphase system under conventional conditions [88].

The biomass gasification in SCW is a complex process, but the overall chemical conversion can be represented by the simplified net reaction:



where x and y are the elemental molar ratios of H/C and O/C in biomass, respectively. The reaction product is syngas whose quality depends on x and y . The reaction (Eq. (9)) is an endothermic. It is known from the reaction (Eq. (9)) that water is not only the solvent but also a reactant and the hydrogen in the water is released by the gasification reaction [89].

Compared with other biomass thermochemical gasifications, such as air gasification or steam gasification, the SCW gasification has high gasification efficiency at lower temperature and can deal directly with wet biomass without drying [90]. Hydrogen production by biomass gasification in SCW is a promising technology for utilizing high moisture content biomass [89]. Another advantage of SCW reforming is that the H₂ is produced at a high pressure which can be stored directly, thus avoiding the large energy expenditures associated with its compression [91]. The cost of hydrogen production from SCW gasification of wet biomass was several times higher than the current price of hydrogen from steam methane reforming. Biomass is gasified in supercritical water at a series of temperatures and pressures during different resident times to form a product gas composed of H₂, CO₂, CO, CH₄, and a small amount of C₂H₄ and C₂H₆ [37,92]. SCW is a promising reforming media for the direct production of hydrogen at 875–1075 K temperatures with a short reaction time (2–6 s). As the temperature is increased from 875 to 1075 K the H₂ yield increases from 53% to 73% by volume, respectively [91,92]. Only a small amount of hydrogen is formed at low temperatures, indicating that direct reformation reaction of ethanol as a model compound in SCW is favored at high temperatures (>975 K) [91]. With an increase in the temperature, the hydrogen and carbon dioxide yields increase, while the methane yield decreases [89].

Many researchers have investigated the aqueous conversion of whole biomass to hydrogen under low temperature but supercritical conditions. The earliest report of SCW gasification of wood is by Modell [93]. The author studied the effect of temperature and concentration on the gasification of glucose and maple sawdust in water, in the vicinity of its critical state (650 K and 22 MPa). Elliott and co-workers [94] from Pacific Northwest National Laboratory (PNNL) investigated a variety of commercial catalysts and support materials in hot liquid water at 20 MPa and 623 K to

convert organic compounds to gaseous products rich in methane. They reported that Ni-based catalyst showed an excellent activity on the gasification. Schmieder et al. [95] found that real biomass (wood as sawdust, straw) and wastes (sewage, sludge and lignin) were completely gasified by addition of KOH or K_2CO_3 at 873 K and 25 MPa, forming a H_2 -rich gas containing CO_2 as the main carbon compound. Kruse and co-workers [96] studied the gasification of pyrocatechol in SCW as part of a fundamental look at hydrogen production from high-moisture biomass and wastewater. In the study, batch and tubular reactors were used.

3.1.4. Comparison of thermochemical processes

In general, the gasification temperature is higher than that of pyrolysis and the yield of hydrogen from the gasification is higher than that of the pyrolysis. The yield of hydrogen from conventional pyrolysis of corncob increases from 33% to 40% with increasing of temperature from 775 to 1025 K. The yields of hydrogen from steam gasification increase from 29 to 45% for $(W/S) = 1$ and from 29% to 47% for $(W/S) = 2$ with increasing of temperature from 975 to 1225 K [74]. Hydrogen yields and energy contents, compared, with biomass energy contents obtained from processes with biomass, are shown in Table 5 [97].

Demirbas [74] investigated the yield of hydrogen from supercritical fluid extraction (SFE), pyrolysis and steam gasification of wheat straw and olive waste at different temperatures. The highest yields (% dry and ash free basis) were obtained from the pyrolysis (46%) and steam gasification (55%) of wheat straw while the lowest yields from olive waste. He also investigated the yield of hydrogen from SFE, pyrolysis and steam gasification of beech wood at different temperatures. Distilled water was used in the SFE (the critical temperature of pure water is 647.7 K). Results of this study are shown in Fig. 3. From Fig. 3, the yield of hydrogen from SFE was considerably high (49%) at lower temperatures. The pyrolysis was carried out at the moderate temperatures and steam gasification at the highest temperatures.

Table 5
Comparison of hydrogen yields were obtained by use of three different processes.

Processes	Hydrogen yield (wt.%)	Hydrogen energy contents/ biomass energy content
Pyrolysis + catalytic reforming	12.6	91
Gasification + shift reaction	11.5	83
Biomass + steam + except heat (theoretical maximum)	17.1	124

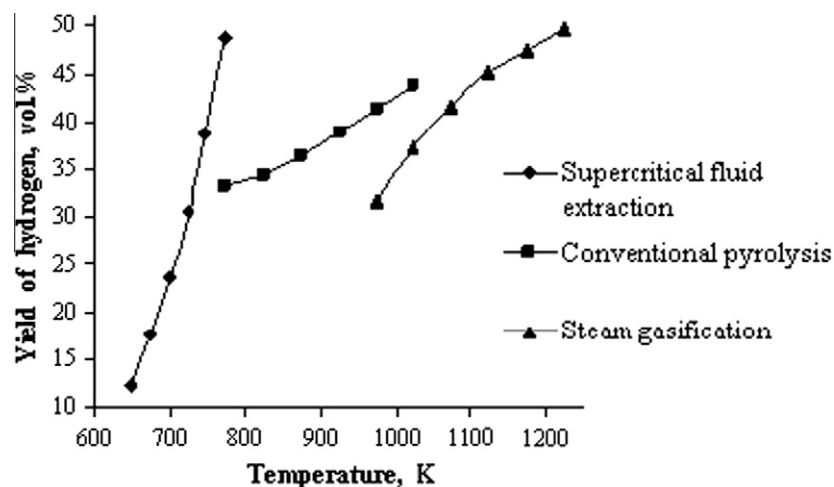


Fig. 3. Plots for yield of hydrogen from supercritical fluid extraction, pyrolysis and steam gasification [$(W/S) = 2$] of beech wood at different temperatures. Source: Ref. [74].

3.2. Biological process for hydrogen production

Hydrogen produced from water, renewable organic wastes or biomass, either biologically (biophotolysis and fermentation) or photobiologically (photodecomposition), is termed “biohydrogen”. Biological hydrogen production processes are found to be more environment friendly and less energy intensive as compared to thermochemical and electrochemical processes [98]. Researchers have started to investigate hydrogen production with anaerobic bacteria since 1980s [99–101]. The main advantages of different biological hydrogen production processes are given in Table 6 [102].

The processes of biological hydrogen production can be broadly classified into two distinct groups. One is light dependent and the other is light-independent process [5]. Specific ways in which microorganisms can produce H_2 are described below [103]:

- Biophotolysis of water using green algae and blue-green algae (cyanobacteria):
 - Direct biophotolysis.
 - Indirect biophotolysis.
- Photo-fermentation.
- Dark fermentation.
- Hybrid reactor system.

There are three types of microorganisms of biohydrogen generation: cyanobacteria, anaerobic bacteria, and fermentative bacteria. The cyanobacteria directly decompose water to biohydrogen and oxygen in the presence of light energy by photosynthesis. Photosynthetic bacteria use organic substrates like organic acids. Anaerobic bacteria use organic substances as the sole source of electrons and energy, converting them into biohydrogen. Biological hydrogen can be generated from plants by biophotolysis of water using microalgae (green algae and cyanobacteria), fermentation of organic compounds, and photodecomposition of organic compounds by photo-synthetic bacteria [99]. All processes of biological hydrogen production are fundamentally dependent upon the presence of a hydrogen-producing enzyme. Hydrogenases and nitrogenases are the known enzymes which catalyze biological hydrogen production [104]. Hydrogenases are the key enzymes for the biological hydrogen production, which can be classified as uptake hydrogenases and reversible hydrogenases. Uptake hydrogenases, such as Ni–Fe hydrogenases and Ni–Fe–Se hydrogenases, act as important catalysts for hydrogen consumption as follows [49]:



Reversible hydrogenases, as indicated by its name, have the ability to produce H_2 as well as consume H_2 depending on the reaction condition,



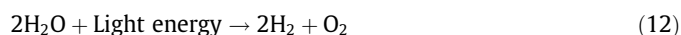
Despite increasingly conspicuous diversity in many respects, hydrogenase can be classified broadly into three distinct classes: Ni–Fe hydrogenase, Fe-hydrogenase and metal-free hydrogenase [105]. Classification of hydrogenases is given in Table 7.

3.2.1. Biophotolysis of water using microalgae

Biophotolysis is the action of light on biological systems that results in the dissociation of a substrate usually water into molecular hydrogen and oxygen. Photo-synthetic bacteria (e.g. *Rhodobactor*) can use broad organic substrates including lactic and acetic acids as the energy and carbon source under light irradiation. Photoautotrophic green algae and cyanobacteria use sunlight and carbon dioxide as the sole sources for energy and carbon [92]. Based on a preliminary engineering and economic analysis, biophotolysis processes must achieve close to an overall 10% solar energy conversion efficiency to be competitive with alternatives sources of renewable hydrogen [106].

3.2.1.1. Direct biophotolysis. Direct biophotolysis of hydrogen production is a biological process which utilizes light energy and pho-

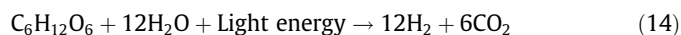
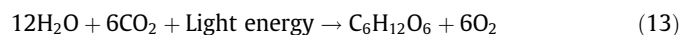
tosynthetic systems of microalgae to convert water into chemical energy.



The solar energy is absorbed by the pigments at photosystem I (PSI), or photosystem II (PSII) or both, which raises the energy level of electrons from water oxidation when they are transferred from PSI via PSII to ferredoxin [107]. The concept of “direct biophotolysis” envisions light-driven simultaneous O_2 evolution on the oxidizing side of PSII and H_2 production on the reducing side of PSI, with a maximum $\text{H}_2:\text{O}_2$ (mol:mol) ratio of 2:1 [108].

Since hydrogenase is sensitive to oxygen, it is necessary to maintain the oxygen content at a low level under 0.1% so that hydrogen production can be sustained. This condition can be obtained by the use of green algae *Chlamydomonas reinhardtii* that can deplete oxygen during oxidative respiration [49,103]. Reported hydrogen production rates using this method are approximately 0.07 mmol/h per liter [109,110].

3.2.1.2. Indirect biophotolysis. In indirect biophotolysis, the problem of sensitivity of the hydrogen evolving process to oxygen is usually circumvented by separating oxygen and hydrogen [110–112]. The concept of indirect biophotolysis involves the following four steps [49]: (1) biomass production by photosynthesis, (2) biomass concentration, (3) aerobic dark fermentation yielding 4 mol hydrogen/mol glucose in the algae cell, along with 2 mol of acetates, and (4) conversion of 2 mol of acetates into hydrogen. In a typical indirect biophotolysis, cyanobacteria can synthesize and evolve hydrogen through photosynthesis by following reactions:



Hydrogen production by cyanobacteria has been studied for over three decades and has revealed that efficient photoconversion of H_2O to H_2 is influenced by many factors [102]. Rates of H_2 production by non-nitrogen-fixing Cyanobacteria range from 0.02 $\mu\text{mol H}_2/\text{mg chl a/h}$ (*Synechococcus* PCC 6307) to 0.40 $\mu\text{mol H}_2/\text{mg chl a/h}$ (*Aphanocapsa montana*) [113].

3.2.2. Photo-fermentation

Purple non-sulfur bacteria evolve molecular hydrogen catalyzed by nitrogenase under nitrogen-deficient conditions using light energy and reduced compounds (organic acids) [114]. These bacteria themselves are not powerful enough to split water. However, under anaerobic conditions, these bacteria are able to use simple organic acids, like acetic acid, or even hydrogen disulfide as electron donor. These electrons are transported to the nitrogenase by ferredoxin using energy in the form of adenosine triphosphate (ATP). When nitrogen is not present, this nitrogenase enzyme can reduce proton into hydrogen gas again using extra energy in the form of ATP [110]. The reaction can be given as

Table 6

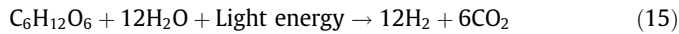
The main advantages of different biological hydrogen production processes. Source: Ref. [102].

Process	Advantages
Direct biophotolysis	It can produce H_2 directly from water and sunlight Solar conversion energy increased by 10-folds as compared to tress, crops
Indirect biophotolysis	It can produce H_2 from water Has the ability to fix N_2 from atmosphere
Photo-fermentation	A wide spectral light energy can be used by these bacteria It can use different waste materials like distillery effluents, waste, etc.
Dark fermentation	It can produce H_2 all day long without light A variety of carbon sources can be used as substrates It produces valuable metabolites such as butyric, lactic, and acetic acids as by products It is anaerobic process, so there is no O_2 limitation problem
Hybrid reactor system (combined dark and photo-fermentation)	Two stage fermentation can improve the overall yield of hydrogen

Table 7

Classification of hydrogenases. Source: Ref. [105].

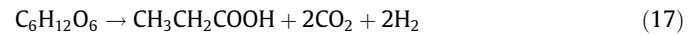
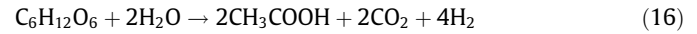
Classification	Occurrence/source	Structure	Features	
			Localization	Function
Ni–Fe	Anaerobic, photo-synthetic bacteria, cyanobacteria	Heterodimeric, multimeric	Membrane-bound, cytoplasmic, periplasmic	Uptake of hydrogen
Ni–Fe–Se	Sulphate-reducing bacteria, methanogenes	Oligomeric	Membrane-bound, cytoplasmic	Oxidation of hydrogen
Fe	Photo-synthetic bacteria, anaerobic fermentative bacteria, cyanobacteria, green algae, protozoan	Monomeric, heteromeric	Cytoplasmic, mambrane- bound, periplasmic chloroplast, hydrogenosomes	Production of hydrogen
Metal-free	Methanogens	Monomeric	Cytoplasmic	Formation of hydrogen



Among the various bioprocesses capable of hydrogen production, photo-fermentation is favored due to relatively higher substrate-to-hydrogen yields and, its ability to trap energy under a wide range of the light spectrum and versatility in sources of metabolic substrates with promise for waste stabilization [115]. In photo-fermentation processes, the yield of the order of 80% has been achieved [110]. However, these processes have three main drawbacks [49]: (1) use of nitrogenase enzyme with high-energy demand, (2) low solar energy conversion efficiency and (3) demand for elaborate anaerobic photobioreactors covering large areas.

3.2.3. Dark fermentation

Hydrogen can be produced by anaerobic bacteria, grown in the dark on carbohydrate-rich substrates. Dark fermentation of carbohydrate-rich substrates as biomass presents a promising route of biological hydrogen production, compared with photosynthetic routes [116]. Anaerobic hydrogen fermenting bacteria can produce hydrogen continuously without the need for photoenergy [117]. Dark hydrogen fermentation can be performed at different temperatures: mesophilic (298–313 K), thermophilic (313–338 K), extreme-thermophilic (338–353 K) or hyperthermophilic (>353 K) temperatures. While direct and indirect photolysis systems produce pure H_2 , dark-fermentation processes produce a mixed biogas containing primarily H_2 and CO_2 , but which may also contain lesser amounts of methane (CH_4), CO, and/or hydrogen sulfide (H_2S) [113]. Glucose yield different amount of hydrogen depending on the fermentation pathways and liquid end-products. A maximum of 4 mol hydrogen is theoretically produced from 1 mol of glucose with acetic acid as the end-product, while a maximum of 2 mol hydrogen is theoretically produced from 1 mol of glucose with butyrate as the end-product [117]:



Thus, the highest theoretical yields of H_2 are associated with acetate as the fermentation end-product. In practice, however, high H_2 yields are usually associated with a mixture of acetate and butyrate fermentation products, and low H_2 yields are with associated propionate and reduced end-products (alcohols, lactic acid). *Clostridium pasteurianum*, *Clostridium butyricum*, and *Clostridium beijerinckii* are high H_2 producers, while *Clostridium propionicum* is a poor H_2 producer [113,118,119].

The amount of hydrogen production by dark fermentation highly depends on the pH value, hydraulic retention time (HRT) and gas partial pressure. For the optimal hydrogen production, pH should be maintained between 5 and 6 [49]. Hydrogen production from the bacterial fermentation of sugars has been examined in a variety of reactor systems. Hexose concentration has a greater effect on H_2 yields than the HRT. Flocculation also was an important factor in the performance of the reactor [66,99]. The hydrogen yield from sucrose by dark-fermentation could be difficult to increase above 2.5-mol/mol hexose, owing to the formation of fatty acids during the fermentation process [120].

3.2.4. Two-stage process (integration of dark- and photo-fermentation)

A combination of dark and photo-fermentation in a two-stage hybrid system could be expected to reach as close to the theoretical maximum production of 12 mol of H_2 (mol glucose)^{−1} equivalent as possible, according to the following reactions [5]:

i. Stage I – dark fermentation (facultative anaerobes)

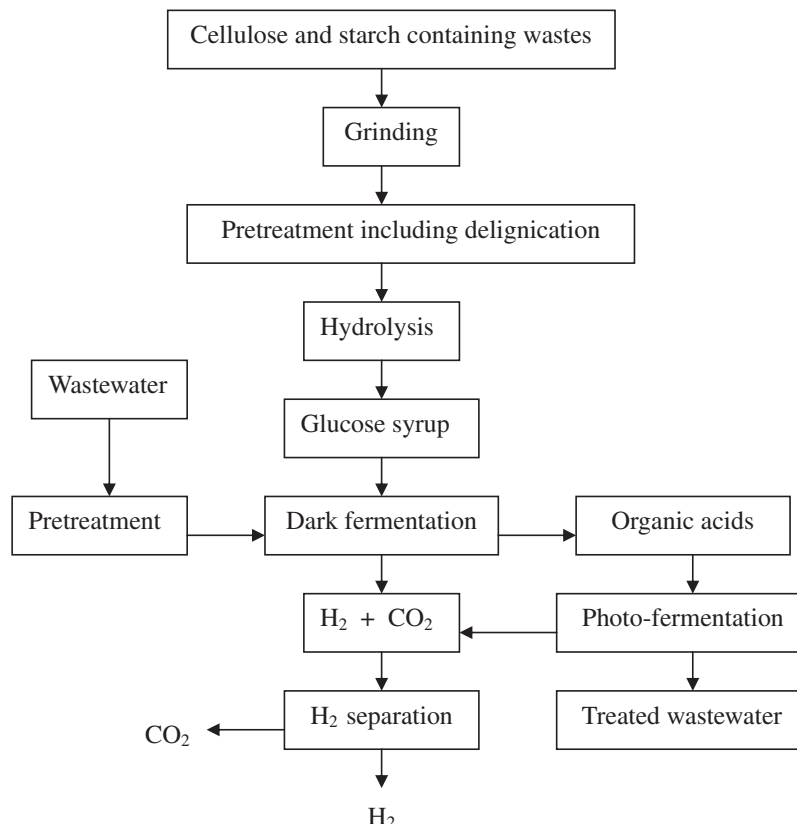
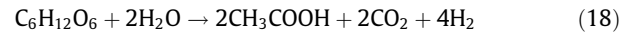


Fig. 4. A schematic diagram for biohydrogen production from cellulose/starch containing agricultural wastes and food industry wastewaters. Source: Ref. [123].

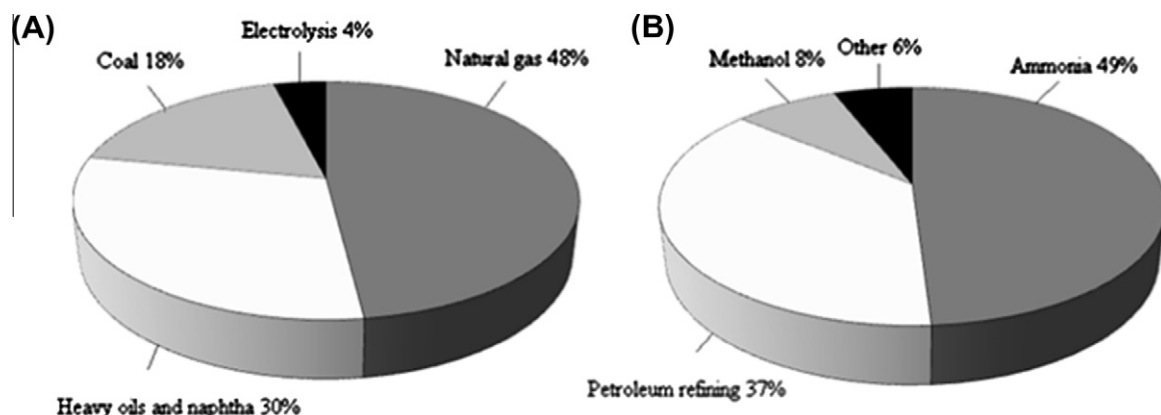
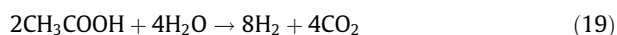


Fig. 5. (A) Global production of hydrogen by sources and (B) global use of hydrogen by sector.

ii. Stage II – photo-fermentation (photo-synthetic bacteria)



In the first step biomass is fermented to acetate, carbon dioxide, and hydrogen by thermophilic dark fermentation, while in the second step, acetate is converted to hydrogen and carbon dioxide [121,122].

Starch, cellulose or hemicellulose content of wastes, carbohydrate rich food industry effluents or waste biological sludge can be further processed to convert the carbohydrates to organic acids and then to hydrogen gas by using proper bioprocessing technologies. Fig. 4 shows schematic diagram for biohydrogen production from food industry wastewaters and agricultural wastes by two stage, anaerobic dark and photo-fermentations [123].

4. Present scenario and future prospects

Energy demand has grown strongly and will continue to increase, particularly in developing countries where energy is needed for economic growth and poverty alleviation [124]. According to the International Energy Agency (IEA) estimates [125], world energy demand will increase by half again between now and 2030, with more than two-thirds of this increase coming from developing and emerging countries. At the present time primary energy sources are dominated by fossil fuels, with nearly 80% of global energy demand supplied from crude oil, natural gas, and coal [126].

In 1985, total worldwide petroleum consumption was 2807 million tons, but in 2008, the figure reached 3928 million tons, with an average annual growth rate of almost 1.5% [127]. Today, the transportation sector worldwide is almost entirely dependent on petroleum-derived fuels. One-fifth of global CO₂ emissions are created by the transport sector, which accounts for some 60% of global oil consumption [127]. The dramatic increase in the price of petroleum, the finite nature of fossil fuels, increasing concerns regarding environmental impact, especially related to GHG emissions, and health and safety considerations are forcing the search for new energy sources and alternative ways to power the world's motor vehicles [3128,129]. Environmental, economical and political concerns are generating a growing interest in biofuels. Biofuels include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sectors of all countries in the world. Biofuels are environmentally friendly alternatives automotive fuel that can be used in an internal combustion engine [130–132].

Hydrogen can help reduce carbon emissions, if produced from renewable energy sources and nuclear energy. If hydrogen is pro-

duced from fossil fuels, the CO₂ generated must be captured and sequestered for there to be significant reductions in GHG emissions versus conventional transportation fuels used with advanced vehicle technologies [133].

Presently, 48% H₂ is produced from natural gas, 30% from heavy oils and naphtha, 18% from coal, and 4% from electrolysis (Fig. 5A) [134]. H₂ can be used either as the fuel for direct combustion in an internal combustion engine or as the fuel for a fuel cell [5]. However, the largest users of H₂ are the fertilizer and petroleum industries with, respectively, 49% and 37% (Fig. 5B) [7]. Present utilization of hydrogen is equivalent to 3% of the energy consumption and with a growth rate estimated at 5–10% per year [6].

Hydrogen is currently more expensive than conventional energy sources. In the longer-term renewables will become the most important source for the production of hydrogen. Hydrogen will play an important role in a future energy economy mainly as a storage and transportation medium for renewable energy sources. Renewable shares of 69% on the total energy demand will lead to hydrogen shares of 34% in 2050 (Table 8) [135].

Many experts think that hydrogen has a major role to play as an energy carrier in future energy supply [136–138]. There are many conventional methods for producing hydrogen, like thermochemical process, catalytic reforming of hydrocarbons and electrolysis of water, but these methods are not economical and are mostly non-renewable [4]. Production of hydrogen from renewable biomass has several advantages compared to that of fossil fuels [8]. Biological production of hydrogen as a byproduct of microorganism metabolism is an exciting new area of technology development that offers the potential production of usable hydrogen from a variety of renewable resources [113]. Biological production of hydrogen provides a feasible means for the sustainable supply of hydrogen with low pollution and high efficiency, thereby being considered a promising way of producing hydrogen, and it had got special attention in the last decade [139].

Biomass will play an important role in the future global energy infrastructure for the generation of power and heat, but also for the

Table 8

Share of individual primary energy sources in meeting final energy needs (%). Source: Ref. [135].

Source of energy	1998	2025	2050
Fossil fuels	88	62	29
Nuclear energy	10	2	2
Hydrogen from solar energy	–	7	31
Electricity from solar energy	–	11	16
Heat from solar energy	–	18	22
Energy from solar energy	2	25	35
Hydrogen	–	11	34

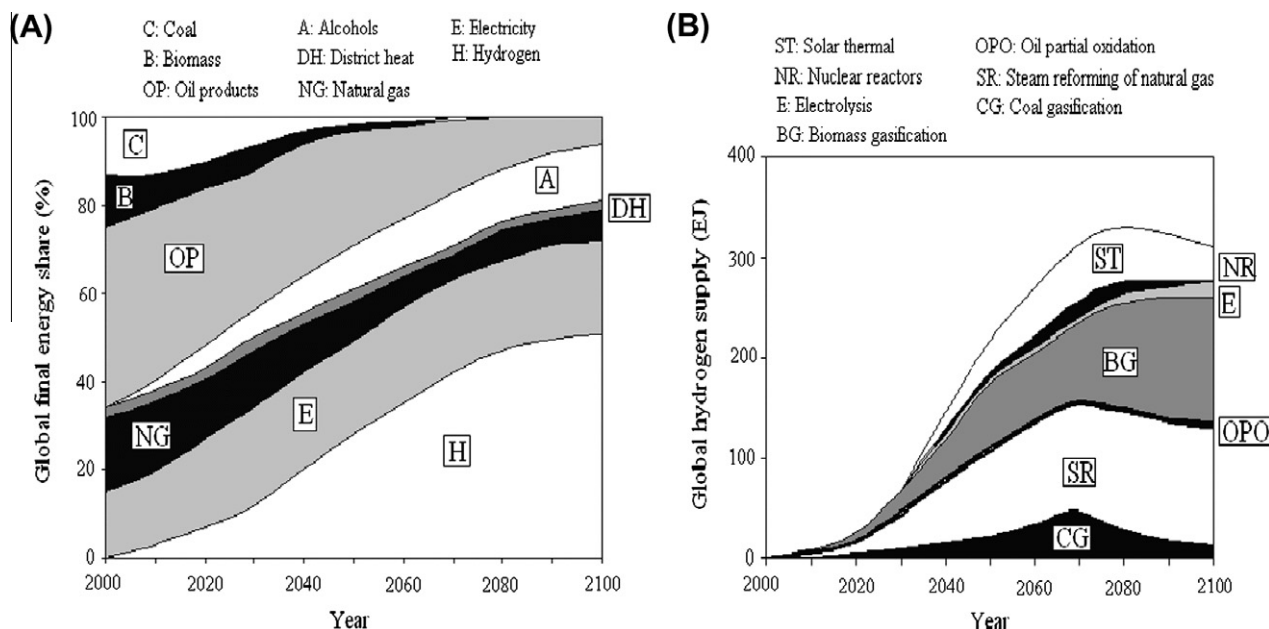


Fig. 6. (A) Evolution of global market shares of different final-energy carriers and (B) global hydrogen supply mix for the period 2000–2100 in the B1–H₂ scenario. Source: Ref. [142].

production of chemicals and fuels. The dominant biomass conversion technology will be gasification, as the gases from biomass gasification are intermediates in the high-efficient power production or the synthesis from chemicals and fuels [140]. Biomass gasification offers the earliest and most economical route for the production of renewable hydrogen [34]. IIASA's Environmentally Compatible Energy Strategies (ECS) project has developed a long-term hydrogen-based scenario (B1–H₂) of the global energy system to examine the future perspectives of fuel cells [141]. The scenario illustrates the key role of hydrogen in a long-term transition towards a clean and sustainable energy future. Fig. 6 is redrawn from the B1–H₂ scenario in order to show trends in global market shares of different final-energy carriers and in global hydrogen supply as a standard. Hydrogen, in particular, driven by the penetration of efficient end-use technologies, increases its share dramatically, accounting for approximately 49% of the global final consumption by the end of the 21st century, and becomes the main final-energy carrier (Fig. 6A). Biomass gasification will become a dominant technology in the future (Fig. 6B) [142].

5. Conclusion

Hydrogen produced from biorenewables is a sustainable energy carrier for promising alternative to fossil fuels. Biomass-based hydrogen includes energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sectors of all countries in the world. Due to its environmental merits, the share of hydrogen from biomass in the automotive fuel market will grow fast in the next decade. Hydrogen is currently more expensive than conventional energy sources. In the longer-term renewables will become the most important source for the production of hydrogen. Thermochemical (pyrolysis and gasification) and biological (biophotolysis, photo-fermentation and dark fermentation) processes can be practically applied to produce hydrogen. Biomass gasification offers the earliest and most economical route for the production of renewable hydrogen. Steam reforming of natural gas and gasification of biomass will become the dominant technologies by the end of the 21st century.

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