

Hydrogen from biomass

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Hydrogen is considered as a novel fuel for the twenty-first century, mainly due to its environmentally benign character. Production of hydrogen from renewable biomass has several advantages compared to that of fossil fuels. A number of processes are being practised for efficient and economic conversion and utilization of biomass to hydrogen. This article updates the developments of various hydrogen-production processes from biomass. Several developmental works are discussed, with a brief outline of different technologies employed therein. A comparative study of existing processes is given on the basis of their relative merits and demerits. In addition, some techno-economic considerations of hydrogen-production processes from biomass are also highlighted.

It is widely acknowledged that hydrogen is an attractive energy source to replace conventional fossil fuels, both from the environmental and economic standpoint. It is often cited as a potential source of unlimited clean power. When hydrogen is used as a fuel it generates no pollutants, but produces water which can be recycled to make more hydrogen (Figure 1). Apart from its use as a clean energy resource, hydrogen can be used for various other purposes in chemical process industries. It is used as a reactant in hydrogenation process to produce lower molecular weight compounds. It can also be used to saturate compounds, crack hydrocarbons or remove sulphur and nitrogen compounds. It is a good oxygen scavenger and can therefore be used to remove traces of oxygen to prevent oxidative corrosion. In the manufacturing of ammonia, methanol and synthesis gas, the use of hydrogen is well known. 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. As of today, all these areas of hydrogen utilization are equivalent to 3% of the energy consumption, but it is expected to grow significantly in the years to come.

The commercially usable hydrogen currently being produced is extracted mostly from natural gas. Nearly 90% of hydrogen is obtained by steam reformation of naphtha or natural gas. Gasification of coal and electrolysis of

water are the other industrial methods for hydrogen-production. However, these processes are highly energy-intensive and not always environment-friendly. Moreover, the fossil-fuel (mainly petroleum) reserves of the world are depleting at an alarming rate. So, production of hydrogen by exploiting alternative sources seems imperative in this perspective.

Biomass, as a product of photosynthesis, is the most versatile non-petroleum renewable resource that can be utilized for sustainable production of hydrogen (Table 1)¹. Therefore, a cost-effective energy-production process could be achieved in which agricultural wastes and various other biomasses are recycled to produce hydrogen economically. The objective of this article is to present an overview of different production technologies of hydrogen from biomass and to make a generalized techno-economic analysis of the processes. Attempts have also been made to give a brief comparative analysis of different processes on the basis of their relative advantages and disadvantages.

Biomass as renewable resource

As an energy source, biomass has several important advantages. Renewability is obviously a key feature. It also has unique versatility. The list of plant species, by-products and waste materials that can potentially be used as feedstock is almost endless (Table 2). Major resources in biomass include agricultural crops and their waste by-products, lignocellulosic products such as wood and wood waste, waste from food processing and aquatic plants and algae, and effluents produced in the human habitat. Moderately-dried wastes such as wood residue, wood scrap and urban garbage can be burned directly as fuel. Energy from water-containing biomass such as sewage sludge, agricultural and livestock effluents as well as animal excreta is recovered mainly by microbial fermentation. Moisture, ash content and gross calorific values of different solid biomass feedstock are given in Table 3.

Biomass as energy source is characterized in the form of both flow and stock. The amount of global forest is estimated at 700 billion tons and acts as storage of carbon dioxide. Available energy flow from forest is enormous and estimated to be 5 billion tons in petroleum equivalent. If these resources were used under appropriate control, they would become the major source of energy in the near future².

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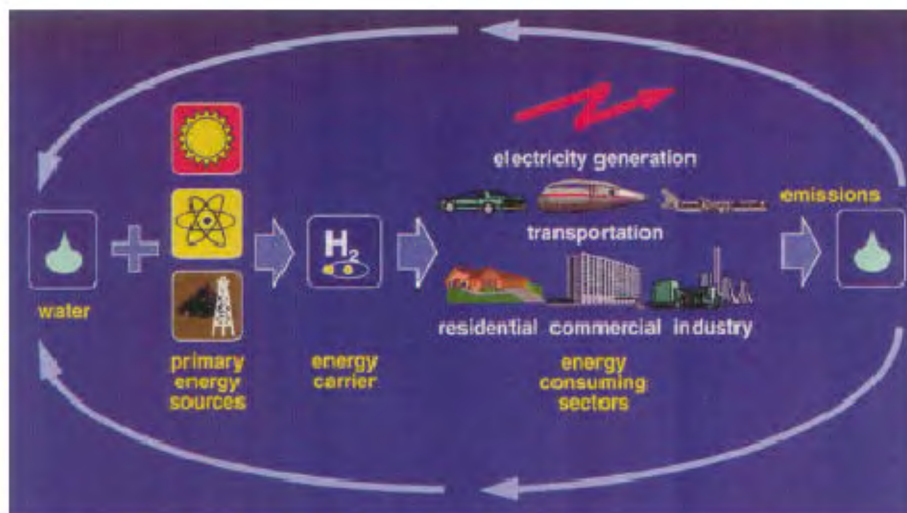


Figure 1. Hydrogen energy system [Source: International Association of Hydrogen Energy, USA].

Table 1. Earth-based world power sources and possible practical expectations¹

Source	Maximum output	Comment
Regenerative source		
Biomass	9×10^{12} W	For total world land coverage
Wind power	6×10^{12} W	For total world land coverage. Required heavy-duty storage system.
Geothermal source	Perhaps 10^9 W	Restricted to specific areas (mid-ocean ridges very long term)
High density source		
Nuclear power	10^5 W or more	No more than 1 K rise in environmental temperature. Problems of waste disposal and safety.
Fossil fuel	10^9 W maximum allowable	Pollution abatement is essential for small and large-scale application.

Production processes of hydrogen from biomass

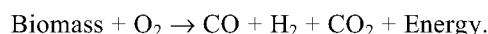
Different process routes of hydrogen-production from biomass can be broadly classified as follows:

1. Thermochemical gasification coupled with water gas shift.
2. Fast pyrolysis followed by reforming of carbohydrate fractions of bio-oil.
3. Direct solar gasification.
4. Miscellaneous novel gasification process.
5. Biomass-derived syn-gas conversion.
6. Supercritical conversion of biomass.
7. Microbial conversion of biomass.

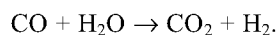
Thermochemical gasification coupled with water gas shift

Gasification coupled with water gas shift is the most widely practised process route for biomass to hydrogen (Figure 2). Thermal, steam and partial oxidation gasification technologies are under development around the world. Feed-stock include agricultural and forest product residues of hard wood, soft wood and herbaceous species. Thermal gasification is essentially high-rate pyrolysis carried out

in the temperature range of 600–1000°C in fluidized bed gasifiers. The reaction is as follows:



Other relevant gasifier types are bubbling fluid beds and the high-pressure high-temperature slurry-fed entrained flow gasifier. However, 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 H₂ by water gas shift reaction.



A study of almond-shell steam gasification in a fluidized bed reveals that over the range 500–800°C, smaller particle size yields more hydrogen than does higher temperatures³. Catalytic steam gasification of biomass has also been studied in a bench-scale plant containing fluidized-bed gasifier and a secondary fixed-bed catalytic reactor⁴. The catalytic converter using different steam-reforming nickel catalysts and dolomite can be tested over a temperature range of 660–830°C. Fresh catalyst at the highest temperature yields 60% by volume of hydrogen. Saha *et al.*^{5,6} have reported a laboratory-scale fluidized-bed auto thermal gasifier to gasify carbonaceous materials in the presence of steam. Pilot-scale experiments in the

steam gasification of charred cellulosic waste material have been discussed in Rabah and Eldighidy⁷. It has been observed that some inorganic salts such as chlorides, carbonates and chromates have a beneficial effect on the reaction. Steam gasification was also intensely studied by many researchers at the University of Saragossa during 1984–92 (ref. 8). Fifty-seven per cent (v/v) yield of hydrogen is reported using a secondary steam reformer⁹.

Generally, conventional gasification of biomass and wastes is employed with the goal of maximizing hydrogen-production. Researchers at the Energy and Environment Research Center, Grand Forks, USA have studied biomass and coal catalytic gasification for the production of hydrogen and methane^{10,11}. A brief experimental effort is described to demonstrate that the pilot-scale research on hydrogen-production by catalytic coal gasification can be extended to wood. The results show that the coal technology is fully transferable to wood, subject to minor substitution in feeding and solids-handling components. Two processes are compared using bench-scale methods to predict the approach best suited on specific coals or biomass. These are pyrolysis and subsequent cracking and steam char gasification. Catalysts can greatly enhance the efficiency of both processes. Gasification of

coal or wood catalysed by soluble metallic cations to maximize reaction rates and hydrogen yields is said to offer a potential for large-scale economical hydrogen-production with near commercial technology¹². Catalysis increases gasification rates about tenfold. Catalyst screening shows that potassium-rich minerals and wood ash provide the best gas production-rate enhancement.

A number of references are available on hydrogen-production by gasification of municipal solid waste^{13–17}. Most of these focus on pretreatment of municipal solid waste to prepare slurry of suitable viscosity and heating value for efficient hydrogen-production. Hydrothermal treatment at 300°C and mild, dry pyrolysis with subsequent slurrying are also highlighted. In the initial laboratory-scale municipal solid-waste treatment, the effects of viscosity, slurry solid content over a range of temperature and for newspapers and plastics are covered¹⁵. Development of the Texaco gasification process emphasizes on feed preparation and pretreatment¹⁸. To date, pumpable slurries from an MSW surrogate mixture of treated paper and plastics have shown heating values in the range of 13–15 MJ/kg. These process considerations can be extended to automobile shredder residues and other plastic or rubber wastes¹⁹. A study of the gasification of microalgae at 850–1000°C is described in Hirano *et al.*²⁰. Cox *et al.*²¹ portray a new approach to thermochemical gasification of biomass to hydrogen, which is based on catalytic steam gasification of biomass with concurrent separation of hydrogen in a membrane reactor that employs a perm selective membrane to separate the hydrogen as it is produced. The process is particularly well suited for wet biomass and may be conducted at temperatures as low as 300°C.

Fast pyrolysis followed by reforming of carbohydrate fraction of bio-oil

Pyrolysis produces a liquid product called bio-oil, which is the basis of several processes for the development of fuel chemicals and materials. The reaction is endothermic:

Table 2. Some biomass feedstock used for hydrogen-production

Biomass feedstock	Major conversion technology
Almond shell	Steam gasification
Pine sawdust	Steam reforming
Crumb rubber	Supercritical conversion
Rice straw/Danish wheat straw	Pyrolysis
Microalgae	Gasification
Tea waste	Pyrolysis
Peanut shell	Pyrolysis
Maple sawdust slurry	Supercritical conversion
Starch biomass slurry	Supercritical conversion
Composted municipal refuse	Supercritical conversion
Kraft lignin	Steam gasification
MSW	Supercritical conversion
Paper and pulp waste	Microbial conversion

Table 3. Moisture and ash content and gross calorific value of different biomass feedstock⁵⁹

Biomass	Moisture (%)	Ash (%)	CV (MJ/kg)
Bagasse	50	1–2	9.2
Bagasse pith	40	2	7.5–8.4
Spent bagasse	40	10	12.5
Sawdust	35	2	11.3
Rice husk	10–15	15–20	12.6–13.8
Rice straw	6	16	14.4
Deoiled rice bran	16	16	11.3
Coffee husk	11–14	2–5	15–17.5
Peanut shell	10	2–3	16.75
Coconut shell	10	1	18.8
Coir pith	8	15	16.75
Cotton stalk	7	3	18.4
Soya straw	7–8	5–6	15.5–15.9

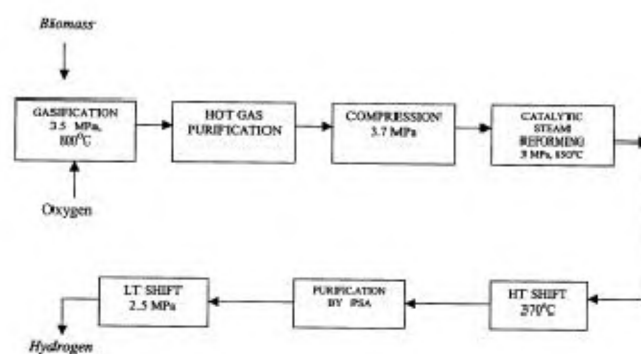
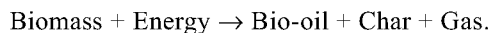
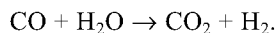
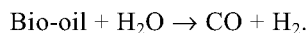


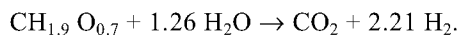
Figure 2. Overall flow diagram for hydrogen production from biomass. HT, High temperature; LT, Low temperature; PSA, Pressure swing adsorption.



Catalytic steam reforming of bio-oil at 750–850°C over a nickel-based catalyst is a two-step process that includes the shift reaction:



The overall stoichiometry gives a maximum yield of 0.172 g H₂/g bio-oil (11.2% based on wood)



The first step in pyrolysis is to use heat to dissociate complex molecules into simple units. Next, reactive vapours which are generated during the first step convert to hydrogen. The Waterloo fast-pyrolysis process technology carried out at 700°C is used for the steam gasification of pine sawdust using Ni–Al catalyst at a molar ratio 1 : 2. It has revealed that catalytic reactivation and high steam to biomass ratios diminish the rate of deactivation²². Methanol and ethanol can also be produced from biomass by a variety of technologies and used on board reforming for transportation. Caglar and Demirbas²³ have used pyrolysis of tea waste to produce hydrogen, while Abedi *et al.*²⁴ have studied hydrogen and carbon production from peanut shells.

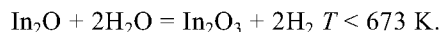
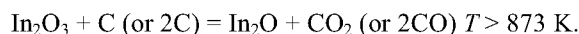
Direct solar gasification

In 1974, Antal *et al.*²⁵ examined the feasibility of using solar process heat for the gasification of organic solid wastes and the production of hydrogen. A detailed review with many references of the technology describes solar gasification of carbonaceous materials to produce a syn-gas quality intermediate for production of hydrogen and other fuels²⁶. Shahbazov and Usupov²⁷ have shown good yield of hydrogen from agricultural wastes using a parabolic mirror reflector. The use of a palladium diaphragm in this respect is reported to achieve solar-assisted hydrogen separations from the gases generated by pyrolysis of hazelnut shells at 500–700°C (ref. 28). Walcher *et al.*²⁹ have mentioned a plan to utilize agricultural wastes in a heliothermic gasifier.

Miscellaneous novel gasification processes

Several novel heat sources and chemistries have also been explored for hydrogen from organic biomass. Safrany³⁰ has proposed the use of a thermonuclear device to vapourize waste organic materials in an underground, large-scale plasma process. In the 1980s, two novel processes for hydrogen from carbonaceous materials were presented. Thakur³¹ tested the production of hydrogen by the electrolysis of a mixture of coal, lime and water. In

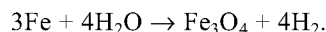
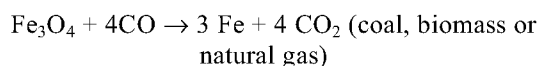
1981, an open-cycle two-step process was tested involving the reduction of In₂O₃ by carbon (chars) and its reoxidation by water to produce hydrogen³².



A set of biochemical reactions have been proposed to describe decomposition of water into hydrogen and oxygen using nuclear heat and a carbon cycle³³. Municipal waste is suggested as a possible source of carbon. Algae can be a by-product. Coughlin and Farooque³⁴ have showed that coals and other forms of solid carbonaceous fossil fuels could be oxidized to oxides of carbon at the anode of an electrochemical cell and hydrogen produced at the cathode. Gases produced are discussed as function of coal slurry concentration and electrode potential.

Biomass derived syn-gas conversion

Hydrogen production from gasified biomass by sponge-iron reactor is also reported^{35,36}. The sponge-iron process (or steam-iron process) offers a simple possibility to store the energy of synthesis gas. A number of recent studies have looked into the classical steam-iron process for upgrading synthesis gas (mainly CO and H₂) to pure H₂ for use in fuel cells and other energy devices. Friedrich *et al.*³⁷ worked on the purification of nitrogen containing reduction gas from a biomass gasifier using wood and wood waste. The process involves two steps: (1) Cleaning of gas from solid biomass or coal or methane, and (2) energy storage in sponge-iron. This study investigates woody biomass and commercially available sponge-iron. The reactions are:



Kniplles *et al.*³⁸ present laboratory and pilot-plant data showing the technical feasibility of hydrogen recovery from biomass gasification lean mixtures (e.g. producer gas).

Supercritical conversion of biomass

Many researchers have investigated the aqueous conversion of whole biomass to hydrogen under low temperature but supercritical conditions. The earliest report of supercritical gasification of wood is by Modell³⁹. He studied the effect of temperature and concentration on the gasification of glucose and maple sawdust in water, in the vicinity of its critical state (374°C, 22 MPa). No solid residue or char is produced. Hydrogen gas concentration up to 18% (v/v) is reported.

The first report of extensive work on supercritical conversion of biomass-related organics was given by Manarungson *et al.*⁴⁰, where glucose at 550°C and 5000 pound per inch² guage (Psig) has been converted largely into hydrogen and carbon dioxide. This was followed by a study of the uncatalysed solvolysis of whole biomass and hemicellulose in hot compressed liquid water⁴¹. The first study showed that complete gasification of glucose can occur at 600°C, 34.5 MPa and 30 s residence time. Inconel strongly catalyses the water gas shift reaction⁴². Following this work, a flow reactor has been used with newly discovered carbon-base catalysts to convert water hyacinth, algae, pithed bagasse, liquid extract, glycerol, cellobiose, whole biomass feedstock and sewage sludge to hydrogen. Wood sawdust, dry sewage sludge or other particulate biomass can be mixed with a corn-starch gel to form a viscous paste. This paste can be delivered to a supercritical flow reactor with a pump. Ongoing work indicates that the starch can be reduced to 3% (w/w) and the particulate biomass increased to 10% (w/w). At the critical pressure of water (22 MPa), the paste vapourizes without the formation of char. A packed bed of carbon catalyst, at 650°C, causes the tarry vapours to react with water to produce hydrogen, carbon dioxide, some methane and only a trace of carbon monoxide⁴³.

Microbial conversion of biomass

Highly concentrated organic waste water is one of the most abundantly available biomass which can be exploited for microbial conversion into hydrogen. A new and unique process has been developed when substrates such as carbohydrates are fermented by a consortium of bacteria; they produce hydrogen and carbon dioxide. Municipal solid wastes and digested sewage sludge have the potential to produce large amount of hydrogen by suppressing the production of methane by introducing low voltage electricity into the sewage sludge. Fascetti and Todini⁴⁴ have reported on the photosynthetic hydrogen evolution from municipal solid wastes. Batch-wise and continuous experiments show that the acidic aqueous

stream obtained from such refuse is a good substrate for the growth of *R. sphaeroides* RV. The substrate from the acidogenesis of fruit and vegetable market wastes gives higher hydrogen evolution rates (about threefold) compared to synthetic medium. Mixed culture of photosynthetic anaerobic bacteria provides a method of utilization of a variety of resources for hydrogen-production⁴⁵. Hydrogen production from whey by phototropic bacteria like *R. rubrum* and *R. capsulatus* has been discussed by Venkataraman and Vatsala⁴⁶. Roychowdhury *et al.*⁴⁷ have on reported hydrogen generation from fermentative bacteria. Kumar and Das⁴⁸ studied the suitability of starch-based residues for hydrogen-production. Lactate and lactate-containing waste water⁴⁹, cow dung slurry⁵⁰, vegetable starch, sugar-cane juice and whey⁵¹, bean-product waste water⁵², tofu waste water⁵³ are among other liquid biomass which are extensively used for hydrogen-production.

Comparative analysis

A comparison of different process routes for hydrogen-production on the basis of their relative merits and demerits is given in Table 4. In all types of gasification, biomass is thermochemically converted to a low or medium-energy content gas. Air-blown biomass gasification results in approximately 5 MJ/m³ and oxygen-blown 15 MJ/m³ of gas. However, all these processes require high reaction temperature. Char (fixed carbon) and ash are the pyrolysis by-products that are not vapourized. Some of the unburned char may be combusted to release the heat needed for the endothermic pyrolysis reactions. For solar gasification, different collector plates (reflectors) like parabolic mirror reflector or heliostat are required. In supercritical conversion, no solid residue or char is produced in most of the cases. A wide variety of biomass is nowadays being used to produce hydrogen using supercritical water. In microbial conversion of biomass, different waste materials can be employed as substrates. These wastes are also treated simultaneously with production of hydrogen.

Table 4. Merits and demerits of different processes of biomass conversion to hydrogen

Process	Merits	Demerits
Thermochemical gasification	Maximum conversion can be achieved	Significant gas conditioning is required Removal of tars is important
Fast pyrolysis	Produces bio-oil which is the basis of several processes for development of fuels, chemicals and materials	Chances of catalyst deactivation
Solar gasification	Good hydrogen yield	Requires effective collector plates
Supercritical conversion	Can process sewage sludge, which is difficult to gasify	Selection of supercritical medium
Microbial conversion	Waste water can also be treated simultaneously. Also generates some useful secondary metabolites	Selection of suitable microorganisms

Techno-economic aspects of hydrogen production from biomass

Many techno-economic assessments of hydrogen from renewable residues find place in the literature. However, these sources also contain discussions, insights and recommendations on biomass-to-hydrogen feasibility and research as well. The National Renewable Energy Laboratory (NREL), USA has explored the economic feasibility of producing hydrogen from biomass through various thermochemical routes. One study has been carried out to incorporate recent experimental advances in addition to plausible changes in direction from previous analysis performed by NREL. An assessment of hydrogen-production technologies concludes that biomass gasification is the most economical process for renewable hydrogen production⁵⁴, whereas other analyses have shown that biomass gasification/shift conversion is economically unfavourable compared to natural gas-steam reforming, except for very low-cost biomass and potential environmental incentives. Pyrolysis with valuable co-product approach yields hydrogen in the price range of US \$ 6–8/GJ, which is promising for near-term application.

The delivered costs of hydrogen as well as the plant gate hydrogen-selling price are determined using a cash-flow spreadsheet with crystal ball risk-assessment software⁵⁵. This software can predict the sensitivity of hydrogen-selling price with change in various analysis parameters. It can also determine which parameters are varied at once, resulting in a hydrogen-selling price that reflected the combined effect of the analysis assumptions.

Several studies were conducted for each of the biomass conversion technologies at varying plant sizes and internal rate of return (IRR) values. Three hydrogen-production rates were examined for the gasification technologies: 22,737, 75,790 and 113,685 kg/day. In the case of pyrolysis, since some of the bio-oil is used in the production of co-products, only the small and medium plant sizes are studied.

The results of this study have revealed that hydrogen could be produced economically from biomass. The pyrolysis-based technology, in particular, because of having co-products opportunity, has the most favourable economics. An added advantage of biomass as a renewable feedstock is that it is not intermittent, but can be used to produce hydrogen as and when required. With scientific and engineering advancements, biomass can be viewed as a key and economically viable component to a renewable-based hydrogen economy. Economic viability of different types of energy-generation processes^{56–58} is summarized in Table 5.

Purification of hydrogen

Hydrogen produced from biomass in all these processes mostly contains different gaseous impurities like O₂, CO,

Table 5. Unit cost of energy obtained by different processes^{56–58}

Type of energy	Conversion efficiency (%)	Unit cost of energy of fuel (US \$/MBTU)
Photobiological hydrogen	~ 10	~ 10
Fermentative hydrogen	~ 10	~ 40
H ₂ from coal, biomass	—	4
H ₂ from advanced electrolysis	—	10
H ₂ from photochemical	—	21
Fermentative ethanol	15–30	~ 31.5
Gasoline	—	—

CO₂, CH₄ and some amount of moisture. Sometimes, presence of these gases lowers the heating value of hydrogen, in addition to posing some problems in efficient burning of fuels. CO₂ acts as a fire extinguisher and it is sparingly soluble in water. Scrubbers can be used to separate CO₂. Fifty per cent (w/v) KOH solution is a good CO₂ absorbent. Monoethanolamine can also be used as a CO₂ absorber. The presence of O₂ in the gas may cause a fire hazard. Water solubility of O₂ is less compared to that of CO₂. Alkaline pyrogallol solution can be used as an absorbent of O₂. Another important problem is the presence of moisture in the gas mixture. It must be removed; otherwise the heating value of hydrogen will get reduced. This can be achieved by passing the mixture either through a dryer or a chilling unit (by condensing out vapour in the form of water). Nowadays, different membrane separation systems are being utilized efficiently for gas purification.

Conclusion

Hydrogen is currently more expensive than conventional energy sources. The production efficiency (the amount of gaseous energy recovery from the feedstock used to produce hydrogen) must be improved and an infrastructure for efficiently transporting and distributing hydrogen is to be developed. There are different technologies presently being practised to produce hydrogen economically from biomass. However, it is too early to predict which of these biomass-conversion technologies will be ultimately successful. Biohydrogen technology will play a major role in future because it can utilize the renewable sources of energy.

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Received 29 November 2002; revised accepted 16 April 2003