1st International Chemical and Environmental Engineering Conference
ICEEC2010
26-28 November 2010, Kuala Lumpur, Malaysia

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[†]Review of hydrogen production technologies: Pakistan’s Prospective

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† Presented at ICEEC 2010, Kl, Malaysia, (26-28-11-2010), 2nd day, Session B2 (2:00-5:00 Pm)

1 ABSTRACT

Currently, hydrogen (H_2) is primarily used in the chemical industry, but in the near future it will become a significant fuel. Hydrogen has great potential as an environmentally clean energy fuel and as a way to reduce reliance on imported energy sources. A combination of the need to cut carbon dioxide emissions, the prospect of increasingly expensive oil and the estimated growth in the world's vehicle fleet indicates that only hydrogen can plug the gap. There are many processes for hydrogen production. This paper reviews developments related to biohydrogen production from green algae. The current energy situation in Pakistan is presented followed by a road map to hydrogen economy in Pakistan. The hydrogen economy potentially offers the possibility to deliver a range of benefits for the country; however, significant challenges exist and these are unlikely to be overcome without serious efforts.

2 INTRODUCTION

At the start of the 21st century, we face significant energy challenges. The concept of sustainable development is evolved for a livable future where human needs are met while keeping the balance with nature. Driving the global energy system into a sustainable path is progressively becoming a major concern and policy objective. The world’s energy requirement is being fulfilled by fossil fuels which serve as a primary energy source. Fossil fuel has delivered energy and convenience, in our homes, for transport and industry. However, the overwhelming scientific evidence is that the unfettered use of fossil fuels is causing the world’s climate to change, with potential disastrous effect.

H_2 holds the promise as a dream fuel of the future with many social, economic and environmental benefits to its credit. It has the long-term potential to reduce the dependence on foreign oil and lower the carbon and criteria emissions from the transportation sector (see Table 1) [1].

H_2 has the highest energy content per unit weight of any known fuel (142 KJ /g or 61,000 Btu/lb) and can be transported for domestic/industrial consumption through conventional means. H_2 gas is safer to handle than domestic natural gas [2]. H_2 is now universally accepted as an environmentally safe, renewable energy resource and an ideal alternative to fossil fuels that doesn't contribute to the greenhouse effect.

The only carbon-free fuel, H_2 upon oxidation produces water alone. H_2 can be used either as the fuel for direct combustion in an internal combustion engine or as the fuel for a fuel cell.

Right now the largest users of H_2, however, are the fertilizer and petroleum industries with, respectively, 50% and 37%. It is also used in the petrochemical manufacturing, glass purification, semiconductor industry and for the hydrogenation of unsaturated fats in vegetable oil [3].

Although abundant on earth as an element, hydrogen combines readily with other elements and is almost always found as part of some other substances, such as water, biomass and hydrocarbons like petroleum and natural Gas. Currently 500 billion cubic meters H_2 are produced annually worldwide. Presently, H_2 is produced 40% from natural gas, 30% from heavy oils and Naphtha, 18% from coal, and 4% from electrolysis [4, 5]. Each method of H_2 production requires a source of energy, i.e., thermal or electrolytic.

The purpose of this paper is to provide a brief summary of significant current and developing H_2 production technologies focusing with Pakistan's prospective. The areas to be examined include: hydrogen production using green algae and, a vision for hydrogen economy in Pakistan.

3 IMPORTANT HYDROGEN PRODUCTION PROCESSES.

Worldwide, hydrogen is being considered as a fuel for the future. It is an environmentally benign replacement for gasoline, diesel, heating oil, natural gas, and other fuels in both the transportation and non-transportation sectors. However producing hydrogen using conventional methods defeats the purpose of using hydrogen as a clean alternative fuel. The production of hydrogen from non-fossil fuel sources, such as solar, hydropower, wind, nuclear, etc. has becomes central for better transition to hydrogen economy. The merits and demerits of the biomass processes are discussed in Table No 2 [6, 7].

4 BARRIERS FOR BIOHYDROGEN PRODUCTION

A large number of microbial species, including significantly different taxonomic and physiological types, can produce H_2. Biological processes use the enzyme hydrogenase or nitrogenase as hydrogen producing protein. This enzyme regulates the hydrogen-metabolism of uncountable prokaryotes and some eukaryotic organisms including green algae. The functioning of nitrogenase, as well as hydrogenase, is linked with the utilization of the products of photosynthetic reactions that generate reductants from water.

The processes of biological H_2 production can be broadly classified into two distinct groups. One is light dependent and the other is light independent process. Light mediated processes include direct or indirect biophotolysis and photofermentation whereas dark fermentation is the major light independent process. Table 3 provides comparison of important biological H_2 production processes [8-16].

Biological H_2 production advantages when compared to photo-electrochemical or thermochemical processes due to low energy requirement and investment cost. Scientific and technical barriers for biohydrogen production have been summarized in Table 4 [3].

The H_2 metabolism of green algae was discovered in the early 1940s by Hans Gaffron. He observed that green algae (under anaerobic conditions) can either use H_2 as an electron donor in the CO_2-fixation process or evolve H_2 in both dark and the light [16, 17]. Although the physiological significance of hydrogen metabolism in algae is still a matter of basic research, the process of photohydrogen production by green algae is of interest because it generates H_2 gas from the most plentiful resources, light and water [18-21].

The conversion of water to hydrogen by green algae may be represented by the following general reaction [2]:

4.5 $2H_2O + \text{lightenergy} \rightarrow 2H_2 + O_2$

The well-known H2-producing green algae, under anaerobic conditions, can either generate H2 or use H2 as an electron donor [22]. The generated hydrogen ions are converted into hydrogen gas in the medium with electrons (donated by reduced ferredoxin) by hydrogenase enzyme present in the cells. Light energy absorbed by photosystem-II (PSII) generates electrons which are transferred to ferredoxin using light energy absorbed by photosystem-I (PSI). A reversible hydrogenase accepts electrons directly from the reduced ferredoxin to generateH2 in presence of hydrogenase, as follows [2]:

Unfortunately, hydrogen production by this process is quite ineffective since the simultaneously produced oxygen inhibits the hydrogenase enzyme. Thus, in high light conditions, hydrogen evolution usually ceases after several minutes due to an accumulation of oxygen. Thus the strong inhibition effect of generated oxygen on hydrogenase is the major bottleneck for the process. Purging oxygen from a reactor system is expensive and impractical from a production point of view.

It has been reported that inhibition of the hydrogenase by oxygen can be partially overcome by cultivation of algae under sulfur deprivation for 2–3 days to provide anaerobic conditions under the light [7, 23].

Melis et al. [24] and Ghirardi et al. [25] devised a mechanism to partially inactivate PSII activity to a point where all the O_2 evolved by photosynthesis is immediately taken up by the respiratory activity of the culture. This mechanism is based on a two-step process. The steps, growth mode and hydrogen production mode, are initiated by cycling between sulfur-containing and sulfur-free culture medium. This results in a temporal separation of net O_2- and H2-evolution activities in the green alga *Chlamydomonas reinhardtii*. This discovery eliminates the need for a purge gas, but introduces the need for careful sulfate controls in the aqueous medium.

5 SYSTEM USING TWO CONTINUOUS-FLOW REACTORS

In 2002, NREL researchers developed a system using two continuous-flow reactors for producing hydrogen continuously for periods of up to several weeks [26]. The continuous hydrogen production process involves using two continuously-stirred tanks. Figure 1 shows the tank configuration. In Reactor 1, cells are cultured in media containing minimal levels of sulfur. PS-II is slowed and oxygen production remains lower than oxygen consumption for cellular respiration, but by bubbling the solutions with carbon dioxide and a small amount of oxygen, the cells are able to remain in Reactor 1 indefinitely, obtaining some energy from photosynthesis and some energy through respiration of acetate in solution.

Cells from Reactor 1 are transferred to Reactor 2, which is maintained under anaerobic conditions. Cells entering Reactor 2 already have suppressed PS-II systems, so they will not cause Reactor 2 to go aerobic. Any residual oxygen is quickly consumed by the algae in Reactor 2. Finding themselves under anaerobic conditions, the cells will start producing hydrogenase and subsequently, hydrogen. The transition step that consumes the oxygen in solution in the batch system is avoided by having Reactor 2 already anaerobic. At the same time, some cells are continuously removed from Reactor 2. The effect is that the cells are removed from Reactor 2 before they completely stop producing hydrogen. Successful operation has been shown with a dilution rate of 0.5/day, which is equivalent to an average residence time of 2 days for the cells. Because Reactor 2 is a continuously-stirred reactor (like Reactor 1), the average residence time is 2 days, but some individual cells removed from the reactor may have been there longer or shorter times. With an average residence time of 2 days, one would expect a hydrogen production rate lower than the initial production rate of the batch system, but higher than the production rate at the end of a batch production cycle.

6 IMMOBILIZATION

One of the largest challenges of optimizing molecular hydrogen production by *Chlamydomonas reinhardtii* cells is the transfer of the cells from sulfur deficient conditions to sulfur rich conditions (for regenerative purposes) and then back to sulfur deficient conditions (for further hydrogen production). Recent research in immobilization has provided a new technique to eliminate this challenge. Prior to the development of immobilizations, cells were suspended in aqueous media with either sulfur rich or deficient conditions present. This posed a problem for scientists because the cells had to be filtered out of the media to be transferred to the next media in the cycle of molecular hydrogen production. The filtration process was very time consuming and so was not feasible on an industrial scale. Another dilemma that plagued the free suspension in liquid media technique was the inability to make the media with cells very concentrated. This restricted the amount of light that could interact with the cells decreasing the overall yield of molecular hydrogen. To avoid difficulties with media transition or cellular concentration immobilization techniques were developed [27].

7 MAXIMUM POSSIBLE YIELD OF H_2 BY GREEN ALGAE

Application of the two-stage photosynthesis and H_2 production protocol to a green alga mass culture could provide a commercially viable method of renewable hydrogen generation. Table 5 [28-31] provides preliminary estimates of maximum possible yield of H_2 by green algae, based on the luminosity of the sun and the green algal photosynthesis characteristics. Calculations were based on the integrated luminosity of the sun during a cloudless spring day. In mid-latitudes at springtime, this would entail delivery of approximately 50 mol photons m^{-2} d^{-1} (Table 5). It is generally accepted that electron transport by the two photosystems and via the hydrogenase pathway for the production of 1 mol H_2 requires the absorption and utilization of a minimum of 5 mol photons in the photosynthetic apparatus (Table 5). On the basis of these "optimal" assumptions, it can be calculated that green algae could produce a maximum 10 mol (20 g) H_2 per m^2 culture area per day. If yields of such magnitude could be approached in mass culture, this would constitute a viable and profitable method of renewable H_2 production.

8 OPTICAL PROPERTIES OF LIGHT ABSORPTION BY GREEN ALGAE

Light absorption by the photosynthetic apparatus is essential for the generation of hydrogen gas. However the optical properties of light absorption by green algae impose a limitation in terms of solar conversion efficiency in the algae chloroplast. This is because wild-type green algae are equipped with a large size light-harvesting chlorophyll antenna to absorb as much sunlight as they can. Under direct and bright sunlight, they could waste up to 60% of the absorbed irradiance [32, 33]. This evolutionary trait may be good for survival of the organism in the wild, where light is often limiting, but it is not good for the photosynthetic productivity of a green algal mass culture. This optical property of the cells could further lower the productivity of a commercial H_2 production farm.

The analysis up to this point has shown that hydrogen production can be limited by the photons available or the capacity of algae to process the photons into hydrogen. Another observation is that the number of photons absorbed is much higher than the algae's ability to process the photons. By reducing the number of excess photons absorbed and let them reach deeper into the liquid, it may be possible to produce more hydrogen. By reducing the size of the algae's light collecting antennae, but not affecting the organism's ability to process the photons to produce hydrogen, one gets deeper light penetration for the same cell concentration, which means more photons are available at the lower depths for hydrogen production.

While regular green algae absorb most of the light falling on them, algae engineered to have less chlorophyll let some light left through. In University of California, Berkeley, Melis and his colleagues are designing algae that have less chlorophyll so that they absorb less sunlight. When grown in large, open bioreactors in dense cultures, the chlorophyll-deficient algae will let sunlight penetrate to the deeper algae layers and thereby utilize sunlight more efficiently [34].

The critical enzymatic component of this photosynthetic reaction is the reversible hydrogenase enzyme, which reduces protons with high potential energy electrons to form hydrogen. During normal photosynthesis, algae focus on using the sun's energy to convert carbon dioxide and water into glucose, releasing oxygen in the process. Only about 3 to 5 percent of photosynthesis leads to hydrogen. Because hydrogenase is sensitive to oxygen, this hydrogen production must be carried out in an anaerobic environment

Photosynthetic hydrogen production by green algae involves water splitting to produce hydrogen and oxygen. Unfortunately, hydrogen production by this process is quite ineffective since it simultaneously produces oxygen, which inhibits the hydrogenase enzyme. Thus, during light reaction, hydrogen evolution ceases due to an accumulation of oxygen. Therefore the prerequisite for photohydrogen production by green algae is that they have to adapt to an anaerobic condition.

By exposing the cells to specific conditions scientists are able to modify photosynthesis so that oxygen will not act as the final electron carrier of the electron transport chain; rather hydrogen will allow the cells to release molecular hydrogen as opposed to molecular oxygen.

Melis estimates that, if the entire capacity of the photosynthesis of the algae could be directed toward hydrogen production, 80 kilograms of hydrogen could be produced commercially per acre per day. The yield of hydrogen production currently achieved in the laboratory corresponds to only 15 to 20% of the measured capacity of the photosynthetic apparatus for electron transport

In a laboratory, Melis worked with low-density cultures and have thin bottles so that light penetrates from all sides. Because of this, the cells use all the light falling on them. But in a commercial bioreactor, where dense algae cultures would be spread out in open ponds under the sun, the top layers of algae absorb all the sunlight but can only use a fraction of it.

9 HYDROGEN ECONOMY

A typical energy chain for sustainable H_2 comprises the harvesting of sunlight into H_2 as energy carrier, the storage and distribution of this energy carrier to the end-device where it is converted to power. The U.S. Department of Energy has developed a multiyear plan with aggressive milestones and targets for the development of hydrogen infrastructure, fuel cells, and storage technologies. The targeted hydrogen cost is \$2–4 kg^{-1} (energy equivalent of 1 gallon of gasoline) delivered [35, 36].

A rollout of such a sustainable H_2 chain in developed countries could go either gradually via a H_2 economy based on fossil fuels or discontinuously in the case of inventions of disruptive technologies. For developing countries the situation may be different. Introduction of such H_2 chains for their fast-growing primary energy demands might enable them to skip the stage of conventional, fossil fuel-based technologies and markets and leapfrog directly to a sustainable H_2 economy [1]. The salient features of a hydrogen economy will be as follows [37]:

- A hydrogen-based energy system will increase the opportunity to use renewable energy in the transport sector. This will increase the diversity of energy sources and reduce overall greenhouse gas emissions.
- Hydrogen in the transport sector can reduce local pollution, which is a high priority in many large cities.
- The robustness and flexibility of the energy system will be increased by the introduction of hydrogen as a strong new energy carrier that can interconnect different parts of the energy system.
- The targets for reducing vehicle noise may be met by replacing conventional engines with hydrogen-powered fuel cells.

- Fuel cells for battery replacement and backup power systems are niche markets in which price and efficiency are relatively unimportant. Sales in this market will drive the technology forward towards the point at which fuel cells will become economic for the introduction into the energy sector.
- Hydrogen electrolysers/fuel cells connected directly to wind turbines are a convenient way to balance out local fluctuations in the availability of wind power.
- The development of fuel cells and a hydrogen economy will provide new market opportunities and new jobs.
- Present knowledge indicates that hydrogen as an energy carrier will involve little environmental risk.

10 PRESENT ENERGY SCENARIO OF PAKISTAN

Pakistan is basically an energy deficient country. Pakistan’s per capita energy consumption, 3894kWh as against the world average of 17620kWh, gives it a ranking of 100 amongst the nations of the world [38]. The demand for primary energy in Pakistan has increased considerably over the last few decades and the country is facing serious energy shortage problems.

The energy supply is not increasing by any means to cope with the rising energy demands. As a result the gap between the energy demand and supply is growing every year. The country is meeting about 86% of oil demand from imports by spending around US$6.65 billion per annum [39].

Pakistan’s future energy system looks rather uncertain. In recent years, the combination of rising oil consumption and flat oil production in Pakistan has led to rising oil imports from Middle East exporters. The balance recoverable reserves of crude oil in the country as on January 1^{st} 2008 have been estimated at 339 million barrels.

Natural gas accounts for the largest share of Pakistan’s energy use, amounting to nearly 50 percent of total energy consumption. As on January 1’ 2008, the balance recoverable natural gas reserves have been estimated at 31.266 trillion cubic feet. The average production of natural gas during July- March 2007-08 was 3,965.9 million cubic feet per day (MMCFD) [40]. As the demand of natural gas exceeds the supply, country is already facing shortage of natural gas and during the peak demand most of the gas fired generating units are shutdown while duel fuel units are fired by oil. Pakistan is presently facing shortage of around 300-350 MMCDF of natural gas which is likely to go up because of rising needs and slowing down of supplies at home[41].

According to The Energy Security Action Plan of the Planning Commission, Pakistan will be facing a shortfall in gas supplies rising from 1.4 Billion Cubic Feet (BCF) per day in 2012 to 2.7 BCF in 2015 and escalating to 10.3 BCF per day by the year 2025[42]. It is therefore a matter of economic security to develop alternative hydrogen resources to avoid mid century energy crises in the country.

Natural gas is used in general industry to prepare consumer items, produce cement, fertilizer and generate electricity. At present, the power sector is the largest user of gas accounting for 33.5 percent share followed by the industrial sector (23.8 percent), household (18.1 percent), fertilizer (15.6 percent), transport (5.4 percent) and cement (0.9 percent) [40].

Natural gas is used in the transport sector in the form of CNG. There are about 2,068 established CNG stations in the country and approximately 1.7 million vehicles are using CNG. Pakistan has become the largest CNG consuming country among Natural Gas Vehicle (NGV) countries. During 2007-08, the consumption of gas in transport sector increased by 27.8 percent. [40]. According to Petroleum Policy 1997; the use of CNG in vehicles was encouraged by Government to reduce pressure on petroleum imports, to curb pollution and to improve the environment [40].

Transport sector is one of the major consumers of commercial energy in Pakistan. It accounted for about 28% of the total final commercial energy consumed (33.95 MTOE) and 55.8% of the total petroleum products consumed (15 MTOE) in the country. About 1.15 million tonnes of gasoline was consumed by this sector during 2005–2006 [39]. The gasoline consumption in the transport sector is also a major source of environmental degradation especially in urban areas.

10.1 HYDROGEN PRODUCTION IN PAKISTAN.

In Pakistan hydrogen is largely produced in the fertilizer industry from natural gas, which is used for the production of anhydrous ammonia. All urea plants in the country are based on natural gas as feedstock. On an average, the fertilizer sector consumes 15.6 per cent of our natural gas. The government provides an indirect subsidy to fertilizer manufacturers by selling feedstock gas at rates ranging up to $1.0 against commercial rates of $4.0 per MMBTU. The return on paid-up capital in the fertilizer industry is about 80-100 per cent per annum. [41]. The current energy scenario in the country, already discussed above , identifies the transport sector and fertilizer sector as key sectors where the hydrogen gas can be immediately employed as substitute to fossil fuel.

U.K. Mirza et al, 2008 [43] has presented complete road map to hydrogen economy in Pakistan. They have concluded that the hydrogen economy potentially offers the possibility to deliver a range of benefits for the country including reducing dependence on oil imports, environmental sustainability and economic competitiveness. In medium term advent of hydrogen will bring about technological developments in many fields, including power generation, agriculture, the automotive industry, and other as yet unforeseen applications. It will increase employment, stimulate the economy, and will have a positive impact on the environment in which atmospheric pollution is all but alleviated and the so-called greenhouse effect is mitigated.

To ensure a sustainable energy future for Pakistan, it is necessary that the energy sector be accorded a high priority. In Pakistan efforts to reduce reliance on fossil fuels through increasing the share of renewable energy in the energy supply systems have met with little success so far. Mirza, et al., 2007 and Sahir, and Qureshi [44, 45] have discussed the barriers to development of renewable energy. Mirza, et al., 2007 [44] has broadly classified these barriers as policy and regulatory barriers, institutional barriers, fiscal and financial barriers, market-related barriers, technological barriers and information and social barriers. They have also suggested better coordination among various stakeholders and indigenization of renewable energy technologies to overcome these barriers.

Sahir, and Qureshi [45] has suggested an integrated energy planning approach, consistency in government policies and rational policy instruments to deal with the techno-economic and socio-political barriers are the pre-requisites for long-term sustainable development of the renewable energy technologies.

11 CONCLUSION

Concerns about global warming and environmental pollution due to the use of fossil fuels, combined with projections of potential fossil fuel shortfall toward the middle of the 21st century, make it imperative to develop alternative energy sources that would clean, renewable, and environmentally friendly. The vision for a hydrogen future is one based on clean sustainable renewable energy supply of global proportions that plays a key role in all sectors of the economy. However, extensive research and development efforts are required for developing biohydrogen production methods for commercialization.

The recently developed single-organism, two-stage photosynthesis and H_2 production protocol with green algae is of interest because significant amounts of H_2 gas were generated for the first time, essentially from sunlight and water. Further, this method does not entail the generation of any undesirable, harmful, or polluting byproducts and it may even offer the advantage of value-added products as a result of the mass cultivation of green algae. However, several biological and engineering challenges must be overcome before this promising technology becomes a practical reality. Foremost, the cellular metabolism and basic biochemistry that support this process must be well understood and much fundamental research on the mechanism of H_2 production by S- deprivation remains to be done.

For Pakistan the indigenous hydrogen production may increase both national energy and economic security. The ability of hydrogen to be produced from a wide variety of feedstocks and using a wide variety of processes makes it so Pakistan may be able to produce much of her own energy. Fertilizer sector is key area where the hydrogen gas can be immediately employed as substitute to natural gas.

The advent of hydrogen will bring about technological developments in many fields, including power generation, agriculture, the automotive industry, and other as yet unforeseen applications. It will increase employment, stimulate the economy of all nations on earth, and will have a positive impact on the environment in which atmospheric pollution is all but alleviated and the so-called greenhouse effect is mitigated.

Non-incorporation of renewable energy issues in the regulatory policy and lack of awareness among regulators restrict technology penetration. There is a lack of financial resources and proper lending facilities, particularly for small-scale projects in country. In addition, the absence of a central body for overall coordination of energy sector activities results in duplication of R&D activities. Unfortunately private sector especially transports and fertilizer sector has made no contributions to promote research activities to produce hydrogen from renewable resources.

12 References

[1] Vijayaraghavan, K., Soom, M.A.M., “Trends in biological hydrogen production—a review”, International Journal of Hydrogen Energy, In press. 2009.

[2]Das, D., T. Nejat Veziroglu, T.N., “Advances in biological hydrogen production processes”, International Journal of Hydrogen Energy, Volume 33, pp. 6046–6057, 2008.

[3] Kotay, S.M., Das, D., “Biohydrogen as a renewable energy resource—Prospects and potentials”, International Journal of Hydrogen Energy, Volume 33, pp. 258 – 263, 2008

[4] Suzuki, Y., “On hydrogen as fuel gas”, International Journal of Hydrogen Energy, Volume 7, pp. 227–30, 1982

[5] Nath, K., Das, D., “ Hydrogen from biomass”, Curr Sci, Volume 85, pp. 265–71 , 2003

[6] Das, D., Veziroglu, T.N, “Hydrogen production by biological processes: a survey of literature”, International Journal of Hydrogen Energy, Volume 26, pp. 13–28, 2001

[7] Nandi, R., Sengupta, S., “Microbial production of hydrogen: an overview”, Crit Rev Microbiol, Volume 24, pp. 24:61–84, 1998.

[8] Levin, D.B., Pitt, L., Love, M., “Biohydrogen production: prospects and limitations to practical application”, International Journal of Hydrogen Energy, Volume 29, pp. 173–85, 2004.

[9] Mahyudin, A.R., Furutani, Y., Nakashimada, Y., Kakizono, T., Nishio, N., “Enhanced hydrogen production in altered mixed acid fermentation of glucose by Enterobacter aerogenes”, J Ferment Bioeng., Volume 83, No. 4, pp. 358–363, 1997.

[10] Tanisho, S., Kuromoto, M., Kadokura, N., “Effect of CO2 removal on hydrogen production by fermentation”, International Journal of Hydrogen Energy, Volume 23, pp. :559 63, 1998.

[11] Kataoka, N., Miya, A., Kiriyama, K., “Studies on hydrogen production by continuous culture system of hydrogen producing anaerobic bacteria”, Water Sci Technol., Volume 36, pp. 41–7, 1997.

[12] Mizuno, O., Dinsdale, R., Hawkes, F.R., Hawkes, D.L., Noike, T, “Enhancement of hydrogen production from glucose by nitrogen gas sparging”, Bioresource Technol., Volume 73, pp. 59–65, 2000.

[13] Hussy, I., Hawkes, F.R., Dinsdale, R., Hawkes, D.L., “Continuous fermentative hydrogen production from a wheat starch co-product by mixed microflora”, Biotech Bioeng., Volume 84, No. 6, pp. 619–26, 2003.

[14] Lay, J.J, “Modelling and optimization of anaerobic digested sludge converting starch to hydrogen”, Biotech Bioeng, Volume 68, No 3. pp. 269–78, 2000.

[15] Lin, C.Y., Chang, R.C., “Hydrogen production during anaerobic acidogenic conversion of glucose”, J Chem Tech Biotech., Volume 74, No. 6, pp. 496–500, 1999.

[16] Kumar, N., Das, D., “Enhancement of hydrogen production by *Enterobacter cloacae* IIT- BT 08”, Process Biochem, Volume 35, pp. 589–593, 2000.

[16] Gaffron, H., “Reduction of carbon dioxide with molecular hydrogen in green algae”, . AmJ Bot, Volume 27, pp. 273–83, 1939.

[17] Gaffron, H., Rubin, J., “Fermentative and photochemical production of hydrogen in algae”, J. Gen. Physiol., Volume 26, pp. 219–240, 1942.

[18] Benemann, J., “Hydrogen biotechnology: progress and prospects” Nat Biotechnol., Volume 14, pp. 1101–3, 1996.

[19] Schulz, R., “Hydrogenases and hydrogen production in eukaryotic organisms and cyanobacteria”, J Mar Biotechnol, Volume 4, pp. 4:16–22, 1996

[20] Melis, A., Happe, T., “Hydrogen production. Green algae as a source of energy”, Plant Physiol, Volume 127, pp. 740–8, 2001

[21] Benemann, J.R., “Feasibility analysis of photobiological hydrogen production”, International Journal of Hydrogen Energy, Volume 22, pp. 979–87, 1997.

[22] Winkler, M., Hemsehemeier, A., Gotor, C., Melis, A., Happe, T., “[Fe]- hydrogenase in green algae: photo-fermentation and hydrogen evolution under sulfur deprivation”, International Journal of Hydrogen Energy, Volume 27, pp. 1431–9, 2002.

[23] Pinto, F.A.L., Troshina, O., Lindblad, P., “A brief look at three decades of research on cyanobacterial hydrogen evolution”, International Journal of Hydrogen Energy, Volume 27, pp. 1209–15, 2002.

[24] Melis, A., Zhang, L., Forestier, M., Ghirardi, M.L., Seibert, M., “Sustained photobiological hydrogen gas production upon reversible inactivation of oxygen evolution in the green alga Chlamydomonas reinhardtii”, Plant Physiol., Volume 122, pp. 127–135, 2000.

[25] Ghirardi, M.L., Zhang, L., Lee, J.W., Flynn, T., Seibert, M., Greenbaum, E., Melis, A., “Microalgae: a green source of renewable H2”, Trends Biotechnol., Volume 18, pp. 506–511, 2000.

[26] Wade A. A., "Updated Cost Analysis of Photobiological Hydrogen Production from Chlamydomonas reinhardtii Green Algae", Milestone Completion Report January 2004, NREL/MP-560-35593, 2004.

[27] Laurinavichene, T. V., et al. "Demonstration of sustained hydrogen photoproduction by immobilized, sulfur-deprived Chlamydomonas reinhardtii cells." International Journal of Hydrogen Energy, Volume 31, pp. 659-667, 2006.

[28] Melis,A., Happe, T.,"Hydrogen Production. Green Algae as a Source of Energy", Plant Physiol, Vol. 127, pp. 740-748, November 2001.

[29] Kirk, J.T.O., "Light and Photosynthesis in Aquatic Ecosystems", Ed 2. Cambridge University Press, Cambridge, England, 1994.

[30]Ley, A.C., Mauzerall, D.C., "Absolute absorption cross sections for photosystem II and the minimum quantum requirement for photosynthesis in Chlorella vulgaris", Biochim Biophys Acta, Volume 680, pp. 95-106, 1982.

[31] Greenbaum, E., "Energetic efficiency of hydrogen photoevolution by algal water splitting", Biophys. J., Volume 54, pp. 365-368, 1988.

[32] Neidhardt, J., Benemann, J.R., Zhang, L., Melis, A., "Photosystem-II repair and chloroplast recovery from irradiance stress: relationship between chronic photoinhibition, light-harvesting chlorophyll antenna size and photosynthetic productivity in *Dunaliella salina* (green algae)", Photosynth Res, Volume 56, pp. 175-184, 1998.

[33] Melis, A., Neidhardt, J., Benemann, J.R. , "*Dunaliella salina* (Chlorophyta) with small chlorophyll antenna sizes exhibit higher photosynthetic productivities and photon use efficiencies than normally pigmented cells", J Appl Phycol., Volume 10, pp. 515-525, 1999.

[34] MIT-Technology Review, Energy/Special Reports, Sep 27, 2007.

[35] U.S. Department of Energy, "Hydrogen, Fuel Cells and Infrastructure Technologies Program", Multi-Year Research, Development and Demonstration Plan, U.S. Department of Energy, 2007.

[36] U.S. Department of Energy, "Hydrogen, Fuel Cells and Infrastructure Technologies Program", Hydrogen Posture Plan, U.S. Department of Energy, 2006.

[37] Larsen, H., Feidenhans, R., Petersen, L.S., editors. "Hydrogen and its competitors". Risø Energy Report 3. Roskilde, Denmark: Risø National Laboratory, October 2004.

[38] IEA, "IEA Fact Sheet", International Energy Agency Statistics; 2006.

[39] Harijan, K., Memon,M., Uqaili,M.A., Mirza, U.K., "Potential contribution of ethanol fuel to the transport sector of Pakistan. Renew Sustain Energy Rev. In press 2007.

[40] Government of Pakistan, "Economic Survey of Pakistan 2007-2008. Ministry of Finance, Islamabad. 2008.

[41], Bhutto, A. W., Karim, S., "Natural gas resources expansion in Pakistan and energy security", Proceeding of Second International Conference: Environmentally Sustainable Development (26-28 August 2007), COMSATS Institute of Information Technology, Abbottabad, Pakistan, 2007.

[42] Government of Pakistan, "Medium Term Development Framework (MTDF) 2005-10", Planning Commission, Islamabad, 2005.

[43] Mirza, U.K., Ahmad, N., Harijan, K., Majeed, T., “A vision for hydrogen economy in Pakistan.” Renew Sustain Energy Rev. In press. 2008.

[44] Mirza, U.K., Ahmad, N., Harijan, K., Majeed, T., “Identifying and addressing barriers to renewable energy development in Pakistan”, Renew Sustain Energy Rev. In press 2007.

[45] Sahir, M.H., Qureshi, A.H., “Assessment of new and renewable energy resources potential and identification of barriers to their significant utilization in Pakistan”, Renewable and Sustainable Energy Reviews, Volume 12, pp. 290–298, 2008.

Table 1-Comparison of energy and emissions of combustible fuels [Adopted from 1]

Fuel type	Energy per unit mass (MJ/kg)	Energy per volume (MJ/l) (approx.)	Kg of carbon release per kg of fuel used
Hydrogen gas	120	2	0
Hydrogen liquid	120	8.5	0
Coal (anthracite)	15–19	—	0.5
Coal (sub-bituminous)	27–30	—	0.7
Natural gas	33–50	9	0.46
Petrol	40–43	31.5	0.86
Oil	42–45	38	0.84
Diesel	42.8	35	0.9
Bio-diesel	37	33	0.5
Ethanol	21	23	0.5
Charcoal	30	—	0.5
Agricultural residue	10–17	—	0.5
Wood	15	—	0.5

Table 2 – Advantages and disadvantages of different hydrogen production processes from biomass [Adopted from 3, 6]

Process	**Advantages**	**Disadvantages**
Thermochemical gasification	Maximum conversion can be achieved	Significant gas conditioning is required Removal of tar
Pyrolysis	Produces carbonaceous material along with bio-oil, chemicals and minerals	Chances of catalyst deactivation
Solar gasification	Good hydrogen yield	Required effective collector plates
Supercritical conversion	Can process sewage sludge, which is difficult to gasify	Selection of supercritical medium
Microbial conversion	Can be operated at ambient temperature and atmospheric pressure	Lower rate of hydrogen production and yield
Direct biophotolysis	Can produce H_2 directly from water and sunlight Solar conversion energy increased by ten folds as compared to trees, crops	Requires high intensity of light O_2 can be dangerous for the system Lower photochemical efficiency
Indirect biophotolysis	Cyanobacteria can produce H_2 from water Has the ability to fix N_2 from atmosphere	Uptake hydrogenase enzymes are to be removed to stop degradation of H_2 About 30% O_2 present in gas mixture
Photo-fermentation	A wide spectral light energy can be used by these bacteria Can use different organic wastes	O_2 has an inhibitory effect on nitrogenase Light conversion efficiency is very low, only 1–5%

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	O_2 is a strong inhibitor of hydrogenase Relatively lower achievable yields of H_2 As yields increase H_2 fermentation becomes thermodynamically unfavorable Product gas mixture contains CO_2 which has to be separated

Table 3– Comparison of important biological hydrogen production processes [Adopted from 3]

Process	Advantages	Representative organism	Maximum reported rate (mmol H2 /L h)	Ref.
Conventional				
Direct biophotolysis	Can produce H2 directly from water and sunlight Solar conversion energy increased by tenfold as compared to trees, crops	Chlamydomonas reinhardtii	0.07	[8,9]
Indirect biophotolysis	Can produce H2 from water Has the ability to fix N2 from atmosphere	Anabaena variabilis	0.36	[10,11]
Photo fermentation	A wide spectral light energy can be used by these bacteria Can use different waste materials like distillery effluents, waste, etc.	Rhodobacter spheroides	0.16	[12]
Dark fermentation	It can produce H2 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 O2 limitation problem	Enterobacter cloacae DM 11 *Clostridium* sp. strain No. 2	75.60 64.50	[13] [14]
Novel				
Two-stage fermentation (dark + photo)	Stoichiometric yield of 12 mol H2 per mol hexose represents the ultimate target for biohydrogen	Enterobacter cloacae DM 11 + Rhodobacter sphaeroidesOU 001 Mixed microbial flora + Rhodobacter sphaeroides OU 001	51.20 47.92	[15] [16]

Table 4– Scientific and technical barriers for biohydrogen production [Adopted from 3]

Type of barrier		**Barrier**	**Putative solution**
Basic science	Organism	Bacteria do not produce more than 4 mol H2/mol glucose naturally	Isolate more novel microbes and combinational screen for H2 production rates yields, and durability. Genetic manipulation of established bacteria.
	Enzyme (hydrogenase)	Hydrogenase over expression not stable O2 sensitivity H2 feed back inhibition	Greater understanding of the enzyme regulation and expression. Mutagenic studies. Low H2 partial pressure fermentation.
Fermentative	Feedstock	High cost of suitable feedstock (glucose) Low yield using renewable biomass	Renewable biomass as feedstock. Co-digestion/use of microbial consortia which can increase the yield
	Strain	Lack of industrial-suitable strain	Development of industrially viable strain(s)/consortia
	Process	Commercially feasible product yield Incomplete substrate utilization Sustainable process Sterilization	Hybrid system (photo + dark fermentation) Link fermentation to a second process that makes both economically possible Application and utilization of fermentation tools such as continuous culture Development of low-cost stream sterilization technology/process that can bypass sterilization
Engineering	Reactor	Lack of kinetics/appropriate reactor design for H2 production Light intensity in case of photo-bioreactor	Incorporation of process engineering concepts to develop a suitable reactor for the defined strain/process Flat panel or hollow tube reactor can be employed
	Thermodynamic	Thermodynamic barrier NAD(P)H → H2 (+4.62 kJ/mol)	Reverse electron transport to drive H2 production past barrier
	Hydrogen	H2 purification/separation Storage	Selection absorption of CO2 /H2S Basic studies on H2 storage

Table 5 –Yield of hydrogen photoproduction by green algae (Estimates are based on maximum possible daily integrated irradiance and algal photosynthesis characteristics.) [Adopted from 28]

Photoproduction Characteristics	Comments on Assumptions Made
Maximum photosynthetically active radiation, 50 mol photons m^{-2} d^{-1} (based on a Gaussian solar intensity profile in which the peak solar irradiance reaches 2,200 μmol photons m^{-2} s^{-1})	Daily irradiance can vary significantly depending on season and cloud cover. It can be greater than 50 mol photons m^{-2} d^{-1} in the summer and much less than that on cloudy days and in the winter. [29].
Theoretical minimum photon requirement for hydrogen production in green algae: 5 mol photons/mol H_2	Based on the requirement of 10 photons for the oxidation of two water molecules and the release of four electrons and four protons in photosynthesis [30, 31]
Theoretical maximum yield of H_2 production by green algae: 10 mol H_2 m^{-2} d^{-1} (20 g H_2 m^{-2} d^{-1}; ~80 kg H_2 acre^{-1} d^{-1})	Assuming that all incoming photosynthetically active radiation will be absorbed by the green algae in the culture and that it will be converted into stable charge separation.

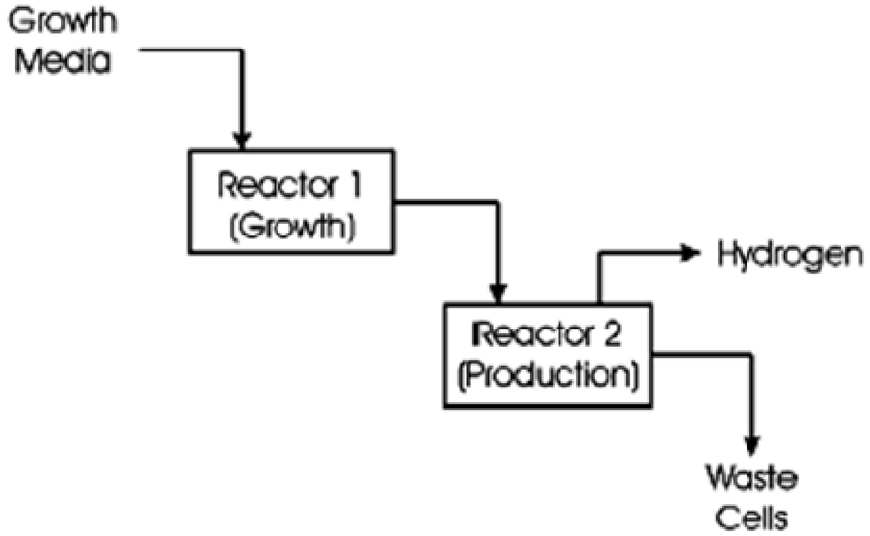

Figure 1– Continuous Hydrogen Production