# **Biohydrogen: Next Generation Fuel**

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### **Abstract**

 Concern over sustainability of fossil fuel use is raised due to depleting fuel resources and emitting greenhouse gases (GHGs) from it. Among many alternative energy sources, biofuels, natural gas, hydrogen, and synthesis gas (syngas) emerge as four strategically important sustainable energy sources. As hydrogen gas is renewable, it does not evolve GHGs, and releases large amount of energy in combustion of unit weight and hydrogen can also be easily converted into electricity by fuel cell. It could be a strong candidate for future alternate energy resource. Biological  $H_2$  production delivers clean  $H_2$  in sustainable manner with simple technology and more attractive potential than the current chemical production of  $H_2$ . Although present industrial hydrogen production system is based on chemical processing units, research trend on biohydrogen promises a deafening potential of industrial biohydrogen production in the near future.

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# **1.1 Introduction**

 The conventional fossil-based fuels contributed major share in the global primary energy consumption, while in the present scenario, the fossil fuel use is widely considered as unsustainable fuel due to depletion of fossil resources and accelerated accumulation of greenhouse gases (GHGs) in the environment that already has exceeded the "dangerously high" threshold of 450 ppm  $CO<sub>2</sub>e$  (Schenk et al. [2008](#page-8-0)). This contributes to different environmental challenges including global warming, climate change, biodiversity loss, receding of glaciers, sea level rise, etc.

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(Gullison et al.  $2007$ ). The researchers had pointed out the three basic assumptions in current policy debates on climate, energy, and GHGs emissions, viz., (a) strong requirement for cleaner energy production and conservation technologies on a global scale, (b) the need for future mandates on emission reduction to be aligned with the production of clean energy and energyconservation policies, and (c) the need to act with urgency (Subhadra and Edwards [2010](#page-9-0)).

 Traditional fuels like wood, charcoal, agricultural residues, and animal wastes are major contributors to household energy supply in many of the developing countries having agrarian economies (FAO  $2005$ ; Dhanya et al.  $2013$ ). The current disposal practices for agricultural residues have caused widespread environmental concern as they represent hindrance to sustainable development in rural areas as well as to national economies (Dhanya et al. [2013](#page-7-0); Sheehan [2009](#page-8-0)). Environmental contaminations due to faulty disposal of waste have also necessitated identification of environmentally sound and economically feasible technologies for waste management (Prasad et al. [2007a](#page-8-0), b).

 The concerns related to energy security, environmental safety, and sustainability have encouraged researchers toward alternative, renewable, sustainable, efficient, and cost-effective energy sources with lesser emissions (Singh and Olsen [2012](#page-8-0)). Renewable energy can play a decisive role at global and national levels in dealing with the concerns related to energy security, climate change, eco-friendliness, and sustainability (Singh et al.  $2010a$ , b,  $2011$ ). Hence, renewable energy sources as an alternative to conventional fossil fuels have been depicted as the main energy supplier in the future that could increase the energy-supply security and emission reduction and render a stabilized income for farmers (Singh and Olsen  $2012$ ). The production of sustainable renewable energy is a challenging task to replace the conventional fossil fuels to get cleaner environment, to reduce the dependency on foreign countries, and to cope up with the fuel price uncertainty (Singh and Olsen [2012](#page-8-0)).

 Among many alternative energy sources, biofuels, natural gas, hydrogen, and synthesis gas (syngas) emerge as four strategically important

sustainable energy sources in the foreseeable future (Nigam and Singh  $2011$ ). Currently, most of the biofuel production at commercial scale are made using the food crops as raw material, developing serious ecological and socioeconomical concern, e.g., land-use changes and food vs. fuel competition (Rathore et al. 2015). Most of the issues related to energy security, production, and consumption can be solved by utilization of biohydrogen as fuel, as biohydrogen is renewable and can be utilized as fuel for electricity, heat, and transportation purposes, with some modifications to existing technologies and have potential to improve sustainability and reduce GHG emissions significantly (Rathore and Singh 2013). This chapter is an attempt to bring out the sustainability and future prospectus of utilization of biohydrogen as an energy source.

## **1.1.1 Global Energy Demand, Supply, and CO<sub>2</sub> Emission**

 Energy is the backbone for civilization. Development of a nation is fueled by its energy availability because one of the major inputs for economic development of every country is energy. The energy sector assumes a crucial emphasis in view of the ever-increasing energy demands necessitating big investments to meet them. According to the recently published International Energy Agency (IEA) [2015](#page-7-0) Key World Energy Statistics (IEA [2015a](#page-7-0)), the primary energy supply of the world has grown by 122 % in 40 years, from approximately 6.10 billion tonne of oil equivalent (TOE) in 1973 to about 13.54 billion TOE in 2013. During this period, a shift of fuel source is noticed as the share of natural gas has enhanced from 16 % to 24.1 %, while coal share increased only 4.4 % and oil share is decreased by 15 %. The other/ alternate sources of energy were also explored and added about 5 % additional share during this period (Fig.  $1.1a$ ). It is expected in the future that the increase in the energy demand will depend upon economic growth of emerging market countries, e.g., India, China, and the Middle East (IEA, 2007, [2008](#page-7-0), 2015b). An estimation has



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been reported that there is an expected increase of 48 % over 25 years from about 11.43 billion TOE during 2005 to about 17 billion TOE in 2030 (Benchmarking of Biodiesel Fuel Standardization in East Asia Working Group [2010](#page-7-0)). IEA raised its forecast of global oil demand to 93.6 million barrels per day in 2015 (a gain of 1.1 million barrels a day on the year) due to increasing energy demand in India, China, and Europe and a spate of colder temperatures in the first quarter for heating purposes at homes and factories. The IEA named this hike a "notable acceleration" from 2014 growth levels of 0.7 million barrels per day (mb d<sup>-1</sup>) (Gallucci 2015).

 Energy production and consumption are affected by disruptions, from wars to extreme weather (BP 2015). The worldwide energy use in the central scenario of IEA is set to grow by onethird to 2040. The energy use growth is primarily

driven by China, India, Africa, Southeast Asia, and the Middle East. Non-OECD (Organisation for Economic Co-operation and Development) countries account for all the increase in global energy use because demographic and structural economic trends, allied with greater efficiency, reduce collective consumption in OECD countries from the peak reached in 2007 (IEA 2015b). As projected by IEA  $(2007)$ , the average annual rate of energy consumption is to grow by  $3\%$ from 2004 to 2020 in developing countries. Energy demand in industrialized nations with mature economies and relatively low population growth is expected to be at the lower rate of 0.9 % per year, admitted from a much higher starting point. About half of the increase in global energy demand by 2030 will be for power generation and one-fifth for transport needs, mostly in the form of petroleum fuels.

 IEA's Factsheet proclaimed that "rising crude oil-import needs of China and India, from the Middle East and other regions, increase their vulnerability to the implications of a possible shortfall in investment or a disruption to oil supply" (IEA 2014). Statistics of the factsheet demonstrated that natural gas share in total inter-regional fossil fuel trade rises by one quarter to more than  $20\%$  by 2040; the increasing availability of liquefied natural gas (LNG) eased the gas security concerns. The increase in coal trade is driven by strong Asian demand and likely to grow to 40 % by 2040. The rise in world oil supply trend from 14 to 104 mb  $d^{-1}$  in 2040 hinges critically on timely investments in the Middle East. The rise in the production of natural gas at global level is in a near-linear fashion to 5,400 bcm (billion cubic meter) in 2040, with a major role for unconventional gas which increases its contribution in output from 17 % to 31 %. The coal demand at global level rises to 6,350 Mtoe in 2040 at a much lower rate (0.5 % per year) than over the last 30 years. The coal demand growth is restricted by new air pollution and climate policies in the main markets of the United States, China, and Europe. The accelerated growth in coal use continues in India. Four countries, viz., India, China, Australia, and Indonesia, alone account for more than 70 % of global coal output by 2040 that underscore Asia 's importance in global coal trade and pricing.

 The carbon dioxide emissions by the consumption of fuels have increased by 107% during the period from 1973 (15,515 Mt of  $CO<sub>2</sub>$ ) to 2013 (32,190 Mt of  $CO<sub>2</sub>$ ). The emission share of natural gas increased with the similar magnitude of, while increase in the emission share of coal consumption  $(-10\%)$  more than doubled to the increase in the supply of coal  $(4.4\%)$  (Fig. 1.1b). The emission share of other fuels is very less  $(0.6\%)$  while it contributed about 18% of global energy supply . The share of energy supply by other sources is majorly contributed by biofuels and wastes (about 10 % of global energy supply during 2013). The remaining energy supply is contributed by nuclear energy, geothermal power, hydropower, wind energy, solar energy, etc. (IEA  $2015a$ .

 Presently most of the energy supply is based on fossil fuel with a minor portion coming from renewable resources. Renewables Global Status Report published in 2014 accounted that about  $19\%$  of global final energy consumption in 2012 rendered by renewable and continued to grow in 2013 (REN21's Renewables Global Status Report 2014). Among this 19%, about 10% is furnished by modern renewables and the remaining  $9\%$  is accounted for traditional biomass. The share of heat energy from modern renewable sources in the total final energy use is about 4.2 %, while hydropower contributed about 3.8 % and about  $2\%$  is coming from solar, wind, biomass, biofuels, and geothermal (REN21's Renewables Global Status Report 2014) .

### **1.2 Renewable Energy Sources**

 Global dependence on fossil fuels has led to the release of over  $1,100$  GtCO<sub>2</sub> into the atmosphere since the mid-nineteenth century. Currently, energy-related GHG emissions, mainly from fossil fuel combustion for heat supply, electricity generation, and transport, account for around 70 % of total emissions including carbon dioxide, methane, and some traces of nitrous oxide (Sims et al.  $2007$ ). With the situation of increasing energy demand and energy prices and implementation of policies for global warming reduction, the sources of renewable energy have popularized. Renewable energy is not only providing the energy but also a tool to solve several other problems associated with the fossil energy, viz., improving the energy security, resolving the health and environmental anxiety, decreasing greenhouse gas emissions, and reducing poverty by increasing the employment.

#### **1.2.1 Classification**

 The inexhaustible renewable energy sources include solar, wind, ocean, hydroelectric, biomass, and geothermal energy. These renewable energy sources offer many environmental benefits over to conventional energy sources. The different types of renewable energy sources have own specific advantages, which make them uniquely suited to limited applications. Almost all these renewable energy sources are not releasing gaseous or liquid pollutants during operation. In their technological development, the renewable ranges from technologies that are well established and mature to those that need further research and development (Hepbasli 2008). International Energy Agency classified renewable energy sources, viz., (i) first-generation source, the technologies have already reached up to maturity level, e.g., combustion, hydropower, and geothermal energy; (ii) second-generation source includes those technologies which are going through rapid development such as solar energy, wind power, and bioenergy; and (iii) third-generation sources, which are presently under developmental stages such as concentrating solar power, improved geothermal and ocean energy, and integrated bioenergy systems (IEA [2006](#page-7-0)).

### **1.2.2 Benefits of Biohydrogen Production**

 Biohydrogen economy has captured global consideration due to its social, economic, and environmental benefits (Sekoai and Daramola 2015). As biohydrogen can be produced by sunlight and minimal nutrients or organic waste effluents as a nutrient source, it has considerably less impact on environment and production cost . The production of biohydrogen does not have any competition with the food/fodder and it also not required fertile land, like first- and second-generation biofuels. By the virtue of the fact that hydrogen gas is renewable, does not liberate greenhouse gases, has unshackle large amount of energy per unit weight during combustion, and can easily be converted into electricity by fuel cell, it is considered as a strong participant for future energy [\(www.](http://www.oilgee.com/) [oilgee.com](http://www.oilgee.com/), 2012). Despite the existing technological constraint for industrial production of biohydrogen, its multidimensional advantages make it the most popular alternative over other renewable energy resources.

#### **1.2.2.1 Environmental Benefit**

Combustion and refining process of the finite fossil fuels cause severe environmental problems. The  $CO<sub>2</sub>$  generation by burning of hydrocarbon is a major cause of global warming and other greenhouse gases as well as left with the toxic compounds as in the case of coal. International Energy Agency predicted that 30 billion tons of  $CO<sub>2</sub>$  was emitted from hydrocarbon fuels in 2008, which is doubled since 1970 (Energy Information Administration [2011](#page-7-0)). Life Cycle Assessment studies suggested that biofuels such as biodiesel, bioethanol, and biomethane are considered as a better option for carbon saving (Rathore et al. 2013), although present biofuel feedstock develops a conflict over food and fuel. Despite the fact that meeting food demands remains the primary objective of agriculture, the promotion of energy crops for biofuel production has added an additional component to the conventional production portfolio of the agricultural sector and thus further intensifies the challenges of widespread land-use pattern and land grabbing (Venghaus and Selbmann [2014](#page-9-0)). Changing land-use pattern for production of biofuel crops resulted into distortion of ecological sustainability of the area. Hydrogen is characterized as a "clean fuel," as it produces only water vapor as the by-product after its use as an energy carrier, no emissions of toxic waste and adding no GHG to the atmosphere (Brentner et al. 2010). The hydrogen produced by physical and chemical processes does not liberate  $CO<sub>2</sub>$  during combustion though its production process required energy input which directly or indirectly comes from fossil fuel (Brentner et al.  $2010$ ; Lee  $2014$ ).

 Biological hydrogen production is a potentially carbon neutral process that is carried out at lower temperatures and pressures and is therefore less energy intensive than thermochemical and electrochemical processes (Levin and Chahine 2010). Production of biohydrogen does not cause burden on food product as it offers potential to generate renewable  $H_2$  from inexpensive "waste" feedstocks (Brentner et al. 2010; Ghimire et al. 2015), wastewater (Skonieczny and Yargeau 2009), sludge (Sittijunda et al. 2010), or microalgae (Rathore and Singh 2013).

#### **1.2.2.2 Economic Benefit**

 Developing hydrogen economy is broadly based on the need to provide a more sustainable energy system to overcome the climate change, diminishing fossil fuel resources, dwindling supplies, and lessen reliance on foreign oil (Brentner et al. [2010](#page-7-0)). Utilization of biohydrogen will not only be encouraged by its application in transportation sector but also by the superiority of the cost and competence to other energy production tech-nologies (Ma et al. [2013](#page-8-0)). The International Energy Agency (Maniatis 2003) stated that biohydrogen is now a weak technology but with potential to capture market. Lee and Chiu (2012) showed the effect of percentage increments in investment on the output of the biohydrogen sector in India, Japan, USA, and China and estimated the increment of US\$ 2.14, 3.61, 10.42, and 12.48 billion, respectively, in the biohydrogen sector output during years 2011–2050. Baseline results of Taiwan general equilibrium model by Lee and Hung  $(2012)$  indicated that wind, biofuel, biohydrogen, and hydrogen fuel cell technologies are sensitive to external support and will perform well without external support. In case government supported to clean energy, biohydrogen and hydrogen fuel cells will lead all clean energies.

### **1.2.2.3 Social Benefi t**

 Major impacts of biohydrogen on society include reduction in air pollution and global warming issues (Sørensen  $2012$ ). Due to operational costs and the high capital investment, nonthermal production of pure hydrogen, i.e., from biomass, will have significant income impacts (Claassen 2011). However, the biomass plant operation is a laborproficient process and has limited employment opportunities. Alternatively, employment opportunities and income multipliers are sensibly high, reflecting the intensive investment in goods and services. Report of European Union on 2 MW (Megawatt) nonthermal hydrogen production from biomass plants in 2030 anticipated varied result. This report suggested more than 100,000 jobs generated over a 15-year period by construction and operation of 2,300 biohydrogen plants [\(http://www.hyways.de/\)](http://www.hyways.de/).

# **1.3 Sustainability of Biohydrogen Production**

 Perhaps the most critical issues faced by today's society are identifying and building a sustainable energy system. Replacing our existing dependency on fossil fuel with a sustainable energy source is one of the major pieces in that system (Turner  $2004$ ). With  $2.75$  times greater energy yield (122 kJ/g) of hydrocarbon fuels, hydrogen is often cited as the green fuel (Das and Veziroglu 2008). Currently almost 96% of the total production of  $H_2$  comes from steam reforming of natural gas  $(48\%)$ , partial oxidation of refinery oil (about 30%), and coal gasification  $(18\%)$  (Holladay et al. 2009; Brentner et al. 2010; Corbo et al.  $2011$ ; Lee  $2014$ ). However, the hydrogen production process is energy intensive. It is also not environmentally friendly and unsustainable due to cost and high level of carbon emission.

 Biohydrogen holds the potential for a substantial contribution to the future renewable energy demands. Biological  $H_2$  production delivers clean  $H_2$  in sustainable manner with simple technology and more attractive potential than the current chemical production of  $H_2$  since it is suited for the conversion of a wide spectrum of substrate utilization such as organic wastes, industrial manufacturing process by-products, and biomass as feedstock costing almost zero (Venkata Mohan 2010; Maru 2014). However, present technology for biohydrogen production has its limitation. Development in process technology and pathways for industrial-scale biohydrogen production will make it more profitable, cost-effective sustainable energy option.

#### **1.4 Future Perspectives**

 Currently hydrogen use is largely for chemical industry mainly to produce ammonia and methanol. Nonetheless, in the near future, hydrogen is expected to a fuel that will significantly improve the air quality (Kalamaras and Efstathiou 2013), provide economic stability (Lee and Hung 2012), and demonstrate social equitability (Claassen 2011; Sørensen 2012). Intensive efforts are going on throughout the globe to make hydrogen as a carbon neutral fuel by producing it via biological process (biohydrogen) and making it as a strong candidate to replace fossil fuel. Several technologies, feedstocks , and pathways have been demonstrated by researchers to produce biohydrogen, and some laboratory and pilot-scale studies for biohydrogen production by fermentations have come up with the promising results for industrial biohydrogen production (Show et al.  $2011a$ , b).

 Biohydrogen can be produced in three broad ways: by biophotolysis (using microalgae), dark fermentation , and photo fermentation (Melis and Melnicki 2006; Manish and Banerjee 2008; Sinha and Pandey  $2011$ ; Show et al.  $2011a$ , b; Rathore and Singh 2013; Basak et al. 2014). Primarily the slow production rate and low hydrogen yield are two common challenges for the biological hydrogen-producing systems. Results from the last two decades suggested an encouraging scenario of biohydrogen production. There has been a significant improvement in the yield and volumetric production rate of hydrogen production and sanguine development in biological hydrogen production routes. However, for industrial approach that makes a sense in hydrogen economy, present production rate and hydrogen yield necessarily surpass the present achievements (Show et al.  $2011a$ , [b](#page-8-0),  $2012$ ).

 By an estimate 80 kg of hydrogen per acre per day could be produced by diverting the entire photosynthetic efficiency of the algae toward hydrogen production. In a realistic efficiency of 50 %, hydrogen production cost comes close to a \$2.80 a kilogram (Melis and Happe  $2001$ ). Though in the current scenario, below  $10\%$  of the algae photosynthetic capacity was utilized for biohydrogen production (Show et al. 2012). Researches on biotechnological approach to improve algal photosynthetic biohydrogen production are underway and demonstrating promising result (Lay  $2001$ ; Oncel et al.  $2015$ ).

 Choosing suitable process parameters such as illumination intensity, carbon to nitrogen ratio, age of inoculums, and bioreactor configuration can significantly improve the overall yield for biological hydrogen production by photo fermentation of purple non-sulfur bacteria (PNS) (Show

et al. 2012; Basak et al. 2014). Several researchers favor dark fermentation or heterotrophic fermentation under anaerobic conditions since it is low cost, high rate, and high hydrogen-yielding process which can utilize various organic substrates and carbohydrate-rich wastewater (Hallenbeck and Ghosh 2009; Ghimire et al.  $2015$ ; Marone et al.  $2015$ ). In the dark fermentation, hydrogen is produced as an intermediate metabolite at the first stage and used as an electron donor at the second stage by many methanogens. It might be viable to harvest hydrogen produced in the first stage, leaving the remaining acidification products for further methanogenic process (Show et al. 2012).

Bioreactor design to improve process efficiency is another major aspect for the industrial biohydrogen production. The yield and conversion rates of biohydrogen bacteria in dark fermentation are highly dependent on the reactor type, reactor operating parameters, and media conditions. A good reactor design for biohydrogen dark fermentation should be able to operate at very low hydraulic retention time (HRT) at the same time avoiding the associated biomass washout (Arimi et al.  $2015$ ).

### **1.5 Conclusion**

 Continues increase in energy demand from the individual to the national level keeping an extra burden on exhaustible fossil fuel. The use of fossil fuel not only causes threat to the environment but also influences development of the country. The use of renewable resources could be an alternative approach to resolve the problem of energy resource. Biohydrogen could be a next generation biofuel by eliminating constraints of firstand second-generation biofuels and able to provide a sustainable option to replace current energy carrier mix. Biohydrogen is a carbon neutral process, which can be obtained from a variety of feedstocks . Nevertheless, biohydrogen is a potential candidate for future energy source, which could largely contribute to the energy security, improve air quality, and provide economic stability and social equitability.

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