Available online at www.sciencedirect.com
ScienceDirect
International Journal of Hydrogen Energy 33 (2008) 279–286
International Journal of HYDROGEN ENERGY
www.elsevier.com/locate/ijhydene

Comparison of biohydrogen production processes

S. Manish, Rangan Banerjee*

Energy Systems Engineering, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

Received 20 June 2007; accepted 9 July 2007
Available online 10 September 2007

Abstract

For hydrogen to be a viable energy carrier, it is important to develop hydrogen generation routes that are renewable like biohydrogen. Hydrogen can be produced biologically by biophotolysis (direct and indirect), photo-fermentation and dark-fermentation or by combination of these processes (such as integration of dark- and photo-fermentation (two-stage process), or biocatalyzed electrolysis, etc.). However, production of hydrogen by these methods at commercial level is not reported in the literature and challenges regarding the process scale up remain. In this scenario net energy analysis (NEA) can provide a tool for establishing the viability of different methods before scaling up. The analysis can also be used to set targets for various process and design parameters for bio-hydrogen production.

In this paper, four biohydrogen production processes (dark-fermentation, photo-fermentation, two-stage process and biocatalyzed electrolysis) utilizing sugarcane juice as the carbon source, are compared with base case method steam methane reforming (SMR) on the basis of net energy ratio, energy efficiency and greenhouse gas (GHG) emissions. It was found that when by-products are not considered, the efficiencies of biological hydrogen processes are lower than that of SMR. However, these processes reduce GHG emissions and non-renewable energy use by 57–73% and 65–79%, respectively, as compared to the SMR process. Efficiencies of biohydrogen processes increase significantly when by-products are considered hence by-products removal and utilization is an important issue in biological hydrogen production.

Keywords: Net energy analysis; Biological hydrogen; Sugarcane; Net energy ratio; Greenhouse gas emission

1. Introduction

Hydrogen is being projected as a potential energy carrier of the future [1,2]. Conventionally hydrogen is produced from natural gas by steam reforming. Other industrial methods are coal gasification and water electrolysis [3]. However, these methods use non-renewable energy sources to produce hydrogen and are not sustainable. Therefore, it is necessary to explore hydrogen production from renewable energy sources such as biomass. In Fig. 1 the possible routes of hydrogen production from biomass are shown.

Processes for biological hydrogen production mostly operate at ambient temperatures and pressures, and are expected to be less energy intensive than thermochemical methods of hydrogen production. These processes can use a variety of feedstocks as carbon sources. Waste materials can also be used as a carbon source which facilitates waste recycling. Hydrogen can be produced biologically by biophotolysis (direct and indirect), photo-fermentation and dark-fermentation or by a combination of these processes (such as integration of dark- and photo-fermentation, or biocatalyzed electrolysis, etc.). At laboratory scale biological hydrogen has been produced continuously; however biohydrogen production at commercial scale is not reported in the literature and challenges regarding process scale up remain [4]. In this scenario net energy analysis (NEA) can provide a tool for establishing the viability of different methods before scaling up. The analysis can also be used to set targets for various process and design parameters for biohydrogen production.

Comparison of biological hydrogen production processes with existing methods of hydrogen production like steam methane reforming (SMR) will provide direction to the research in this area and will also indicate their relative position with respect to established hydrogen production technologies such as SMR. NEA of dark-fermentation has been performed earlier by the authors [5]. In that work three different feedstocks; sugarcane bagasse, sugarcane juice and potato processing wastewater

* Corresponding author. Tel.: +91 22 25767883; fax: +91 22 25764890.
E-mail address: rangan@iitb.ac.in (R. Banerjee).

0360-3199/$ - see front matter © 2007 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2007.07.026

Nomenclature

ATP	adenosine triphosphate	NEA	net energy analysis
CoA	coenzyme A	NER	net energy ratio
Fd	ferredoxine	PEM	proton exchange membrane
GHG	greenhouse gas	PSA	pressure swing adsorption
LCA	life cycle analysis	SMR	steam methane reforming

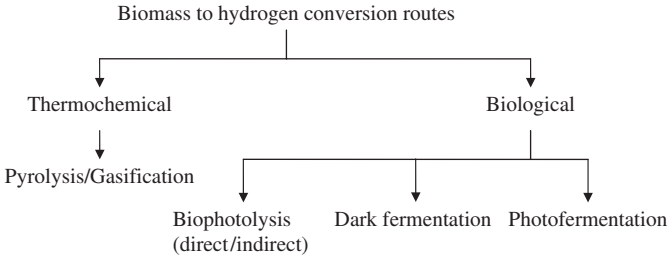

Fig. 1. Hydrogen production routes from biomass.

were compared on the basis of net energy ratio and greenhouse gas (GHG) emissions. It was found that sugarcane bagasse is not a viable option if by-products are not accounted, however sugarcane juice and potato processing wastewater are viable even without considering the by-products. In this paper we extend this work further to other biohydrogen production methods e.g. photo-fermentation, two-stage process and biocatalyzed electrolysis, etc., and compare them with SMR on the basis of net energy ratio (ratio of hydrogen output to the non-renewable energy input), energy efficiency and GHG emissions.

2. Biohydrogen production methods

The biological processes of hydrogen production are fundamentally dependent upon the presence of a hydrogen producing enzyme. These enzymes catalyze the chemical reaction $2H^+ + 2e^- \leftrightarrow H_2$. A survey of all presently known enzymes capable of hydrogen evolution shows that they contain complex metallo-clusters as active sites. At present three enzymes carrying out this reaction are known; nitrogenase, Fe-hydrogenase and NiFe-hydrogenase [6]. Fe-hydrogenase enzyme is used in the biophotolysis processes whereas photo-fermentation processes utilize nitrogenase. A brief description of these processes is provided below.

2.1. Biophotolysis

2.1.1. Direct biophotolysis

This method is similar to the processes found in plants and algal photosynthesis. In this process solar energy is directly converted to hydrogen via photosynthetic reactions (Eq. (1)). This is an attractive process since solar energy is used to convert a readily available substrate, water, to oxygen and hydrogen. However, only under special conditions hydrogen production is possible by this method since Fe-hydrogenase activity is extremely oxygen sensitive.

$$2H_2O + \text{'light energy'} \rightarrow 2H_2 + O_2. \quad (1)$$

A direct biophotolysis process must operate at a partial pressure of near one atmosphere of O_2, which is a thousand fold greater than the maximum likely to be tolerated. Thus, the O_2 sensitivity of the hydrogenase enzyme reaction remains the key problem [6]. In direct biophotolysis, hydrogen production rates of the order of 0.07 mmol/h per liter has been reported in the literature [7,8].

2.1.2. Indirect biophotolysis

In indirect biophotolysis, problems of sensitivity of the hydrogen evolving process are potentially circumvented by separating temporally and/or spatially oxygen evolution and hydrogen evolution. Thus indirect biophotolysis processes involve separation of the H_2 and O_2 evolution reactions into separate stages, coupled through CO_2 fixation/evolution. Cyanobacteria have the unique characteristics of using CO_2 in the air as a carbon source and solar energy as an energy source (Eq. (2)). The cells take up CO_2 first to produce cellular substances, which are subsequently used for hydrogen production (Eq. (3)). The overall mechanism of hydrogen production in cyanobacteria can be represented by the following reactions:

$$12H_2O + 6CO_2 + \text{'light energy'} \rightarrow C_6H_{12}O_6 + 6O_2, \quad (2)$$

$$C_6H_{12}O_6 + 12H_2O + \text{'light energy'} \rightarrow 12H_2 + 6CO_2. \quad (3)$$

Because of the higher rates of H_2 production by *Anabaena* species and strains, these have been subject to intense study [9]. In indirect biophotolysis mutant strains of *A. variabilis* have demonstrated hydrogen production rate of the order of 0.355 mmol/h per liter [10].

2.2. Photo-fermentation

Photosynthetic bacteria evolve molecular hydrogen catalyzed by nitrogenase under nitrogen-deficient conditions using light energy and reduced compounds (organic acids) [9]. These bacteria themselves are not powerful enough to split water. However, under anaerobic conditions, these bacteria are able to use simple organic acids, like acetic acid as electron donors. These electrons are transported to the nitrogenase by ferredoxin using energy in the form of ATP. When nitrogen is not present,