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Comparison of biohydrogen production processes

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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

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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

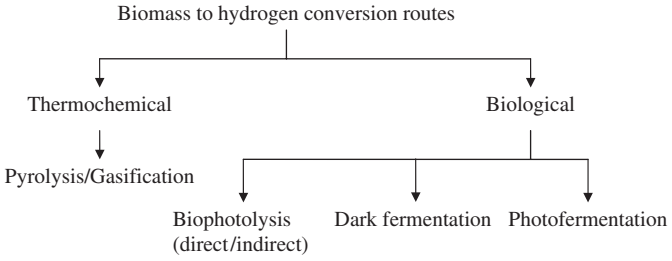

Fig. 1. Hydrogen production routes from biomass.

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,

this nitrogenase enzyme can reduce proton into hydrogen gas again using extra energy in the form of ATP [11]. The overall reaction of hydrogen production can be given as

$$C_6H_{12}O_6 + 6H_2O + \text{'light energy'} \rightarrow 12H_2 + 6CO_2, \quad \Delta G_o = +3.2\,\text{kJ}. \tag{4}$$

In literature hydrogen production rates of the order of 145–160 mmol/h per liter have been reported (reviewed by Levin et al. [9]).

2.3. Dark-fermentation

Hydrogen can be produced by anaerobic bacteria, grown in the dark on carbohydrate rich substrate. The majority of microbial hydrogen production is driven by the anaerobic metabolism of pyruvate, formed during the catabolism of various substrates. The breakdown of pyruvate is catalyzed by one of two enzyme systems [6]:

1. *Pyruvate*: *formate lyase* (PFL)

$$\text{Pyruvate} + \text{CoA} \rightarrow \text{acetyl-CoA} + \text{formate}. \tag{5}$$

2. *Pyruvate*: *ferredoxin oxido reductase* (PFOR)

$$\text{Pyruvate} + \text{CoA} + 2\text{Fd(ox)} \rightarrow \text{acetyl-CoA} + CO_2 + 2\text{Fd(red)}. \tag{6}$$

Carbohydrates are the preferred substrate for hydrogen-producing fermentations. Glucose yield different amount of hydrogen depending on the fermentation pathway and end-product(s). In strict anaerobic bacteria, a theoretical maximum of 4 moles of hydrogen per mole of glucose is obtained, however in facultative anaerobes like *Escherichia coli* maximum 2 moles of hydrogen per mole of glucose can be produced. In laboratory experiments, hydrogen production rate of the order of 77 mmol/h per liter has been achieved [12].

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

In fermentation, complete oxidation of 1 mole of glucose yields 12 moles of hydrogen. However, complete oxidation of glucose into hydrogen and carbon dioxide is not possible as the corresponding reaction is not feasible thermodynamically (Eq. (7)).

$$C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2, \quad \Delta G_o = +3.2\,\text{kJ}. \tag{7}$$

With external energy supply (photon-energy in photo-fermentation) theoretically 12 moles of hydrogen per mole of glucose can be produced. However this process cannot be operated in the absence of light. On the other hand, in the absence of external energy (in the case of dark-fermentation), oxidation of glucose by fermentative bacteria results in other by-products also and maximum 4 moles of hydrogen are produced per mole of glucose consumption (Eq. (8)) with acetate as the sole by-product.

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CO_2 + 2CH_3COOH, \quad \Delta G_o = -206\,\text{kJ}. \tag{8}$$

Acetate produced in the dark-fermentation stage can be oxidized by photosynthetic bacteria to produce hydrogen (Eq. (9)).

$$CH_3COOH + 2H_2O + \text{'light energy'} \rightarrow 4H_2 + 2CO_2, \quad \Delta G_o = +104\,\text{kJ}. \tag{9}$$

Hence continuous production of hydrogen at maximum yield can be achieved by integrating dark- and photo-fermentation methods. In Table 1, results of some of the laboratory studies on this two-stage process are summarized.

2.5. Biocatalyzed electrolysis

Another way of oxidizing the acetate (or the effluent of dark-fermentation process) to produce hydrogen is to provide external energy (in Eq. (9)) in the form of electrical energy instead of solar energy. Schematic diagram of this process is shown in Fig. 2.

In this approach (Fig. 2), the bioreactor containing acetate forms the anodic compartment of an electrolyzer cell and protons and electrons produced by bacteria (Eq. (10)) are collected at cathode (a platinum electrode catalyzing hydrogen evolution reaction). Anodic and cathodic reactions are as follows

$$\text{anode: } CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^-, \quad E^0 = -0.098\,\text{V}, \tag{10}$$

$$\text{cathode: } 8H^+ + 8e^- \rightarrow 4H_2, \quad E^0 = 0\,\text{V}. \tag{11}$$

From Eqs. (10) and (11), it can be concluded that an external supply of around 100 mV is required to produce hydrogen at cathode. However, because of over-potentials at the electrodes a voltage higher than 100 mV is required to produce hydrogen. Liu et al. [16] obtained the yield of 2.9 mol H_2 per mole of acetate (approximately 73% yield) at an external supply of 250 mV. Similarly, Rozendal et al. [17] obtained the yield of $53 \pm 3.5\%$ with acetate at an external supply of 500 mV.

3. Analysis of biohydrogen production processes

In the present work biophotolysis processes are not analyzed as these processes produce hydrogen at very low rate and are not suitable for practical application [9]. The processes analyzed in this paper are

(i) photo-fermentation;
(ii) dark-fermentation;
(iii) two-stage process (integration of dark- and photo-fermentation);
(iv) biocatalyzed electrolysis.

Sugarcane juice is chosen as the carbon source because of abundant supply of sugarcane in India. In the present work,

Table 1
Hydrogen production by integrated method

Sr. no.	Carbon source	Total yield (mol H_2/mol C_6)	Fermentation method	Microorganism	Reactor vol. (ml)	Yield (mol H_2/mol C_6)	Ref.
1	Sweet potato starch residue	7.2	Dark	*Clostridium butyricum* and *Enterobacter aerogenes* HO-39	200	2.7	[13]
			Photo	*Rhodobacter* sp. M-19	50	4.5	
2	Glucose	4.86–5.26	Dark	*Enterobacter cloacae* DM11	500	1.86	[14]
			Photo	*Rhodobacter sphaeroides* O.U.001	500	3–3.4	
3	Sucrose	3.32	Dark	Microflora from a biogas reactor	150	1.84	[15]
			Photo	*Rhodobacter sphaeroides* SH2C	35	1.48	

comparison of the selected biohydrogen processes is made on the basis of net energy ratio, energy efficiency and GHG emission. In order to find these three parameters, net energy analysis (NEA) is performed. In the first step of this analysis, material and energy balances are computed. Results of material and energy balances are provided as input to the life cycle analysis software SimaPro 6 [18]. This software calculates different inventories and corresponding energy use. The total energy consumption can further be classified into renewable and non-renewable energy consumption. This classification is necessary in view of establishing renewable or non-renewable nature of any energy conversion process. An energy conversion process can be termed as a renewable method only when the energy output of the process is greater than the non-renewable energy input. Net energy ratio is computed as

$$\text{net energy ratio} = \text{hydrogen output (MJ)}/\text{non-renewable energy input (MJ)}. \quad (12)$$

An NER value greater than 1 indicates the renewable nature of the process, similarly a process with NER value less than 1 can be termed as the non-renewable process. Using emissions factors, corresponding GHG emissions are obtained. Energy efficiency is calculated as

$$\text{energy efficiency} = \text{energy output}/\text{energy input}. \quad (13)$$

Here energy input includes energy content in the feedstock (sugarcane juice) also. Energy efficiency may not be a relevant comparison criterion when input energy is freely available (in the case of wastewater).

In this analysis two cases are considered. In first case, by-products of the processes are considered as waste material hence in this case only hydrogen is the output. In second case, by-products are also considered as the outputs hence in this case efficiency is likely to be more than the first case.

Later net energy ratio, energy efficiency and GHG emissions of above-mentioned biohydrogen processes are compared with those of SMR process. Inventory results for SMR process are taken from Spath and Mann [19]. The functional unit for comparison is 1 kg of hydrogen produced at ambient conditions (i.e. at 25 °C and 1 bar).

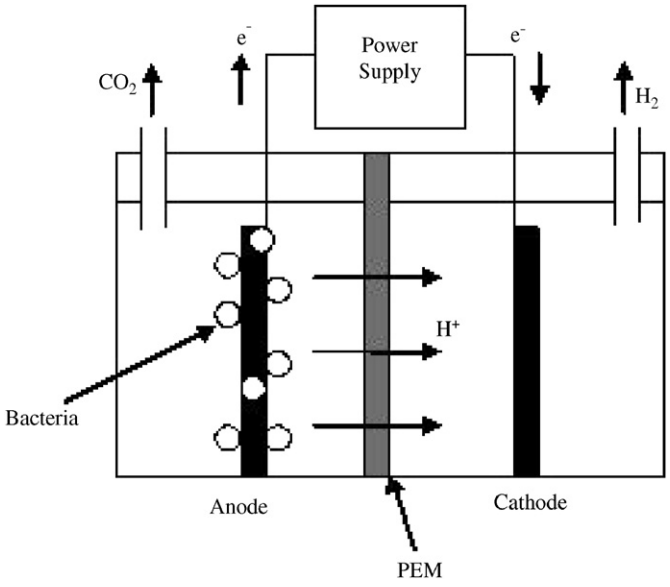

Fig. 2. Biocatalyzed electrolysis.

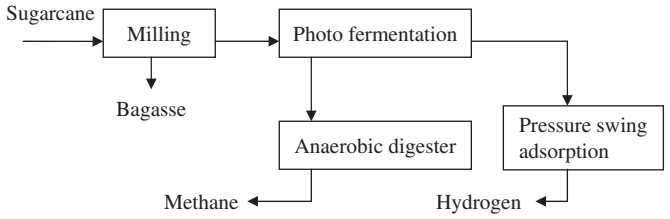

Fig. 3. Photo-fermentation process.

3.1. Energy and mass balance of biohydrogen production processes

3.1.1. Energy and mass balance of photo-fermentation process

The process flow diagram of this process is shown in Fig. 3. In photo-fermentation processes, the yield of the order of 80% has been achieved [11]. In the first step of this process, sugarcane is crushed to produce sugarcane juice (sucrose) which is fermented in photo-fermentation stage to produce hydrogen. The by-product of crushing stage is bagasse. Wastewater of fermentation stage is sent to an anaerobic digester to produce

Table 2
Input data used in the analysis

Input variable	Value	Unit	Ref.
Electricity use in sugarcane crushing	37.8	kJ/kg of sugarcane	[20]
Sucrose output	10.45	% of sugarcane	[21]
Dry bagasse output	17.34	% of sugarcane	[21]
Optimum sugar concentration in fermentation	2	%	–
Optimum C/N ratio	47	–	[22]
H_2 production in dark-fermentation	3.4	mol/mol C_6	[23]
CO_2 production in dark-fermentation	1.7	mol/mol C_6	–
H_2 production in photo-fermentation	9.6	mol/mol C_6	[11]
CO_2 production in photo-fermentation	4.8	mol/mol C_6	–
Methane/CO_2 molar ratio in biogas	60/40	–	–
Hydrogen recovery in PSA	90	%	–
Isothermal efficiency of compressor	65	%	–
Electricity requirement in biocatalyzed electrolysis	0.6	kW h/m^3 H_2	[16]
Platinum loading in biocatalyzed electrolysis	0.5	mg/cm^2	[16]

Table 3
Results of mass and energy balance

Particular	Unit (/kg H_2)	Dark-fermentation	Photo-fermentation	Two-stage process	Electrochemically assisted process
Input					
Sugarcane input	kg	281.45	99.68	93.09	90.56
Electricity input	kW h	5.8	3.89	3.82	6.42
Ammonia	kg	0.35	0.13	0.12	0.11
Platinum	mg	–	–	–	0.23
Output					
Bagasse (dry)	kg	46.06	16.31	15.23	14.82
Carbon dioxide	kg	24.59	13.44	13.04	12.39
Methane	kg	6.75	0.67	0.45	0.54

biogas. Hydrogen and carbon dioxide gas mixture from the fermenter is sent to pressure swing adsorber for hydrogen separation. Input data for the analysis are shown in Table 2. Results of the analysis are shown in Table 3.

3.1.2. Energy and mass balance of dark-fermentation process

The process flow diagram of this process is almost similar to that of photo-fermentation process (Fig. 3) with photo-fermentation stage replaced by dark-fermentation. In the first step of the process, sugarcane is crushed to produce sugarcane juice (sucrose), which is fermented directly in dark-fermentation process to produce hydrogen. Hydrogen and carbon dioxide gas mixture from dark-fermentation stage is sent to pressure swing adsorber for hydrogen separation. Wastewater of fermentation stage is sent to an anaerobic digester to produce biogas. Input data for the analysis are shown in Table 2. Results of the analysis are shown in Table 3.

3.1.3. Energy and mass balance of two-stage process

The process flow diagram is presented in Fig. 4. In this process effluent of dark-fermentation is sent to photo-fermentation stage (Fig. 4). Hydrogen and carbon dioxide gas mixture produced during both the fermentation stages is sent to pressure swing adsorber for hydrogen separation. Effluent of photo-fermentation is sent to anaerobic digester to produce biogas. To analyze this system, input data shown in Table 2 are used. Results of the analysis are shown in Table 3.

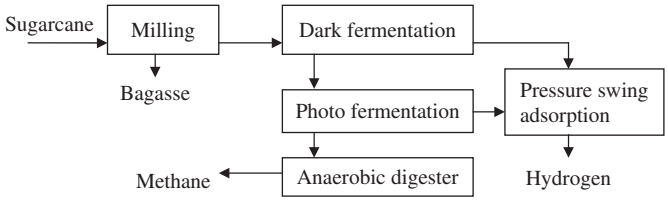

Fig. 4. Two-stage fermentation process.

3.1.4. Energy and mass balance of biocatalyzed electrolysis

The schematic diagram of this process is shown in Fig. 5. Effluent of dark-fermentation stage is sent to electrolyzer to produce hydrogen and carbon dioxide. During biocatalyzed electrolysis, hydrogen and carbon dioxide are produced in different chambers, which avoid the use of pressure swing adsorption step. Input data for the analysis are shown in Table 2. Results of the analysis are shown in Table 3.

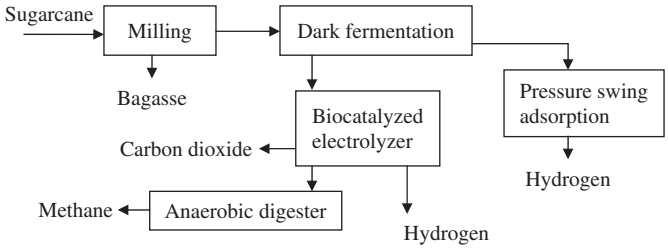

Fig. 5. Schematic diagram of biocatalyzed electrolysis.

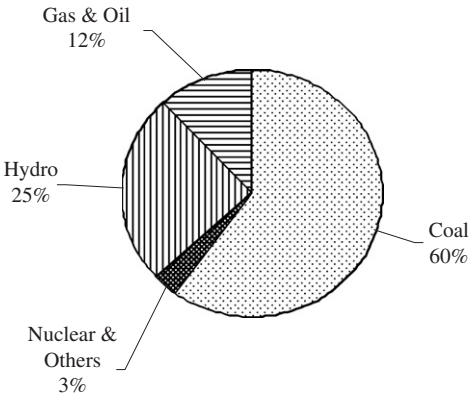

Fig. 6. Indian electricity mix.

3.2. Net energy analysis

In order to perform NEA, results of mass and energy balance are given as input to SimaPro 6 software. Some assumptions regarding electricity mix, heat source, by-products, etc., made in the analysis are described below:

1. Two cases are considered for by-products. In the first case, all by-products (methane, bagasse, etc.) are treated as waste material. In second case, it is assumed that these by-products are used for heat generation, which avoids the use of diesel oil for the same purpose.
2. It is assumed that heat is derived from diesel oil and bagasse with 90% and 70% combustion efficiency, respectively. The Indian electricity mix (see Fig. 6) is assumed for calculation.
3. Technologies based on biomass gasification generate carbon dioxide also. However, biomass absorbs carbon dioxide as they grow and percentage of carbon in the biomass to the process that is recycled through the system is termed as carbon closure. It is estimated to be approximately 95% when the biomass is grown renewably [24].
4. The calorific value of bagasse is taken as 14.28 MJ/kg (3400 kcal/kg) [25]. Emission factors for bagasse burning are taken from US environmental protection agency [26].

4. Results

Case 1. *Without by-products*: Results of the analysis are shown in Table 4. Biohydrogen processes are found to be renewable as the corresponding net energy ratio values are greater than 1. Biological processes also reduce GHG emissions and non-renewable energy use by 57–73% and 65–79%, respectively, as compared to the SMR process. When by-products are not considered, dark-fermentation has the highest GHG emissions and the least energy efficiency among the biohydrogen processes considered. It is because of lower yields of hydrogen per mole of glucose consumption, which results in higher sugarcane input requirement per kg of hydrogen production. Higher amount of sugarcane input implies increase in the electrical energy requirement during the milling process (Table 3). Increase in both sugarcane and electricity input reduces the efficiency of dark-fermentation process. Moreover, higher electricity consumption per kg of hydrogen production in dark-fermentation process means higher non-renewable energy consumption that leads to higher GHG emissions and lower net energy ratio.

Hydrogen yields in photo-fermentation and two-stage process are higher than the dark-fermentation process, which reduces requirement of sugarcane approximately by 65% as compared to dark-fermentation process. Reduction in sugarcane input also reduces the amount of electricity required during milling process by 30%. It results in higher energy efficiency, higher net energy ratio and lower GHG emissions (Table 4). Two-stage process has the least GHG emissions. This process also has the highest energy efficiency and net energy ratio among the biohydrogen processes considered.

Higher hydrogen yields in biocatalyzed electrolysis process also lead to lower sugarcane input that increases the energy efficiency of the process as compared to the dark-fermentation process. However, this process has the least value of net energy ratio among the biohydrogen processes mainly because of significant electricity consumption in the electrolyzer.

Case 2. *With by-products*: Energy efficiencies of biohydrogen processes are significantly lower than the SMR process when by-products are not considered (Table 4). However, when by-products are considered efficiencies of biohydrogen processes increase. In dark-fermentation, higher amount of sugarcane is required which results in higher amount of methane and bagasse as compared to other biohydrogen processes (Table 3). Higher amount of these by-products increases the efficiency of dark-fermentation from 9.6% to 89.1% (Table 4). The efficiencies of photo-fermentation and the two-stage process are comparable, but these are less than the efficiency of the dark-fermentation process. Efficiency of biocatalyzed electrolysis is the least among the biohydrogen production options considered due to higher electricity requirement demand in the electrolyzer (Fig. 2). All biohydrogen processes considered in the present analysis are net GHG emissions reducing and non-renewable energy-saving processes (Table 4) with dark-fermentation process having the highest potential mainly because of higher amount of by-products production. Because of higher fossil fuels savings achieved due to the use of by-products (methane and bagasse) instead of fossil fuels, corresponding GHG emissions and non-renewable energy use are reduced.

Table 4
Results of net energy analysis (per kg of hydrogen production)

Process	Case 1: Without by-products				Case 2: With by-products		
	GHG ($kg\,CO_2$)	Non-renewable energy use (MJ)	Energy efficiency (%)	Net energy ratio	GHG ($kg\,CO_2$)	Non-renewable energy use (MJ)	Energy efficiency (%)
Steam methane reforming	12.8	188	64	0.64	12.8	188	64
Dark-fermentation	5.5	61.7	9.6	1.9	−87	−1060	89.1
Photo-fermentation	3.5	40.1	25.6	3.0	−21.9	−247.5	82.3
Two-stage process	3.4	39.3	27.2	3.1	−19.5	−218.2	81.6
Biocatalyzed electrolysis	5.3	64.8	25.7	1.8	−17.5	−180	76.8

5. Conclusions

In this paper, four biohydrogen production processes e.g. dark-fermentation, photo-fermentation, two-stage process and biocatalyzed electrolysis were compared on the basis of net energy ratio, energy efficiency and GHG emissions and it was found that biohydrogen production processes are viable from net energy and GHG emissions reduction point of view. Efficiency of two-stage process is maximum (case 1) among the biohydrogen processes considered. For 1 kg of hydrogen generation, this process also reduces GHG emissions by 7.31–9.37 kg CO_2 (∼ 57–73%) and non-renewable energy use by 123.2–148.7 MJ (∼ 65–79%) as compared to SMR process. However when by-products are not considered, efficiencies of biohydrogen processes are significantly lower than the SMR process. Efficiencies of biohydrogen processes increase significantly when by-products are considered hence by-products removal and utilization is a critical issue in biological hydrogen production. When by-products are considered, biohydrogen production processes become net GHG reducing and non-renewable energy-saving.

Biocatalyzed electrolysis process has the least value of net energy ratio among the biohydrogen processes considered. Improvement in the cell design and optimization of design and process parameters in future may lead to lesser electricity consumption which will improve the net energy ratio of the process.

Thus, NEA can be used as a tool for analyzing and comparing different biohydrogen processes before their scaling-up. Biological hydrogen production processes utilizing sugarcane juice as feedstock are found to be renewable and have lesser GHG emissions than the SMR process.

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