An Overview of Hydrogen Fermentation, Methane and Bioelectricity as Key Contributions to Biorefineries of Organic Wastes

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ABSTRACT

Biohydrogen is an attractive and sustainable energy source as it can be produced from organic waste through fermentation processes involving dark fermentation (DF) and photofermentation (PF). Very often biohydrogen is included as a part of biorefinery approaches for reclaiming organic wastes that are abundant sources of renewable and low cost substrate, which in turn, can be efficiently fermented by microorganisms. The aim of this work is to critically review selected bioenergy alternatives from organic solid waste, with emphasis on biohydrogen as well as combinations of biohydrogen with other bioenergy-generating processes, and to evaluate their relative advantages and disadvantages in the context of biorefineries. Last, we will indicate the trends for future research and development. Biorefining is the sustainable processing of biomass into a spectrum of marketable products, which means: materials, chemicals, food and feed, and energy. Biorefineries are based on the Principle of Sustainability as well as a group of Principles that help to accomplish the first one. Among the second Group, we highlight the Principle of Cascading, that is, the use of the resource organic waste in subsequent processes for maximum yields and profits. DF of organic wastes could be the beach-head of complete biorefineries that generate biohydrogen as a first step and could significantly change the future of solid waste management. Series systems show a better efficiency than one-stage process regarding substrate conversion to hydrogen. The DF also produces fermented by-products (fatty acids and solvents), so there is an opportunity for further combining with other processes that yield more bioenergy. PF is one of them: photosynthetic heterotrophs such as non sulphur purple bacteria can thrive on the simple organic substances produced in DF and light, to give more hydrogen. PF can be combined with DF in series,

in sequence, or co-cultivation. Leacheates and extracts from PF digestates are then processed in microbial fuel cells for bioelectricity production and methanogenic digestion for methane generation, respectively, thus integrating a diverse block of bionergies. Digestates from either DF or methanogenesis could be used for bioproducts generation such as holocellulolytic enzymes, whereas the discarded solids mixed with fresh organic waste are subjected to saccharification processes to be ready for ethanol fermentation (another bioenergy), thus completing the cascading approach.

Biohydrogen, biomethane and bioelectricity could contribute to significant improvements on solid organic waste management in agricultural regions, as well as in urban areas. Indeed, biohydrogen production from solid organic wastes can be integrated with biorefinery approaches that will undoubtedly also lead to production of added value bioproducts such as enzymes, as well as other bioenergies.

1. Introduction

In the last 15 years, research interest on bioH_2 has resurrected, particularly from the dark fermentation (DF) of solid wastes [1,2] as a way to contribute to the crisis of fossil fuels occurring since the late 20th and early 21st centuries. From DF to the use of cyanobacteria and purple non-sulphur bacteria (PNSB), studies have focused on achieving better bioH_2 yields that can compete with H_2 costs from traditional non-renewable fuels [3]. In bioH_2 production by DF of organic wastes, several microbial groups that consume bioH_2 coexist with the H_2-producing microbes [4]. So, it is paramount to process feasibility to find techniques to inhibit the H_2-consuming microorganisms, such as the methanogenic archaea to cite one of the most important groups. It has been reported a variety of methanogenesis inhibitors, inter alia: acetylene, bromo-ethanesulphonate (BES), heat-shock pretreatment and low pH [5-9]. The pH strongly influences bacteria metabolism and viability, the overall bioH_2 production, the specific rate of bioH_2 generation, and type and concentration of organic acids and solvents, among others [10,11]. Another significant factor for hydrogen production is the total solids contents of feeds, because dry matter concentration of substrate or substrate concentrations is a crucial variable in solid substrate hydrogenogenic fermentation of organic wastes. Regarding the effect of substrate concentration, most of the research has been focused on submerged dark fermentation or slurry fermentation [12-17], whereas the information for dark SSF is still scarce [18].

Mass retention time is also an important parameter in biohydrogen production. It sets the amount of organic load to bioreactors. For instance, Robledo-Narváez [19] evaluated the effect of mass retention time (MRT) on hydrogen generation in mesophilic solid substrate fermentation of a feedstock mixture of sugarcane bagasse, pineapple bagasse, and waste activated sludge. Lab scale, semicontinuous reactors were run at four MRT of 7, 10, 13, and 22 d. and 35°C. The feedstock was conditioned to 35% total solids. The process performance was generally poor. Slight effect of MRT was observed on hydrogen productivity, the best results were achieved at MRT of 13d. Thus, even in this condition the organic acids production was low, which was consistent with the low productivity of hydrogen.

Escamilla-Alvarado et al. [18] studied the performance of a two-stage hydrogenogenic–methanogenic (H–M) semi-continuous process in terms of mass retention time (MRT) for hydrogenogenic stage (H-stage), feed source for methanogenic stage (M-stage) and thermal regime (35 and 55 ◦C) for both stages. The substrate was a model organic fraction of municipal solid wastes (OFMSW) at 35% total solids. Bioreactors in thermophilic regime performed better than mesophilic ones. Maximum methane productivity was 341 NmL CH4/(kgwmr d) that corresponded to the thermophilic bioreactor fed with fermented solids from H stage at 14 d MRT. The two-stage process showed higher gross energetic potential when compared to an only methanogenic process operated at equivalent MRT (control); this was due to a higher methane productivity in the M-stage of the series process.

Recently, there has been a growing interest on processes with coupled or in-series of two or more stages to obtain other products besides bioH_2, such as DF followed by another stage such as phototrophic biohydrogen or followed by microbial fuel cells (MFC) or other systems. This has the purpose of reclaiming increased amounts of bioenergy from organic wastes [18,20]. Moreover, especially because of the lucrative production of biogas, CH_4 and H_2, [21] a methanogenic stage has also been successfully coupled to bioH_2, which increased energetic potential [18,22]; methane generation also could be obtained from environmentally friendly bioremediation of effluents [23].

There is also interest in developing potential use for the chemical energy present in organic wastes. Indeed, organic solid wastes are a growing problem for modern societies: every year constantly rising amounts of municipal solid wastes are generated and disposed of in landfills [24]. In the country-side, similar problems are faced as constantly demand of feed and food of societies are corresponded by increased amounts of agricultural wastes, which also pose environmental concerns and management challenges [25,26]. So, agricultural wastes along with food industry wastes, which contain complex carbohydrates such as starch and/or cellulose, are suitable candidates for bioH_2 and other bioproducts generation [27,28]. In México alone, the annual generation of sugar-cane bagasse from the sugar industry is nearly 4 million metric tons. On the other hand, the annual production of pineapple in 2009 was 737 000 metric tons whose waste peelings represent 211 000 tons. These agro-industrial residues are rich in cellulose (44% for sugar cane bagasse and 31% for pineapple peel [29,30] that in principle can be fermented to generate biohydrogen.. Thus, the treatment of the degradable fraction of solid wastes, or biowaste, allows for the generation of carbon-neutral bioenergy, nutrients, and other resources or valuable bioproducts such as enzymes [22, 31-34].

The aim of this work is to critically review selected bioenergy alternatives from organic solid waste, with emphasis on biohydrogen as well as combinations of biohydrogen with other bioenergy-generating processes, and to discuss their relative advantages and disadvantages in the context of biorefineries; . Last, we will indicate the trends for future research and development.

2. Biorefineries

Exhaustion fossil fuel resources and environmental damages due to petroleum production and consumption highlight the importance of a shift to renewable sources for fuels and chemicals. The carbohydrate derived chemical furfural is widely seen as a promising biobased platform chemical, which can be further converted to a range of products including plastics, pharmaceuticals and agrochemicals [35-37].

Biorefinery is the sustainable processing of biomass into a spectrum of marketable products [18,32,33,38], which means: materials, chemicals, food and feed, and energy (Figure 1). Biorefininig is a worldwide growing technology. Biorefineries use biotechnological methods and processes that ultimately may make it possible to produce many things; biotechnology is using for novel uses like oilseed can be modified to produce fatty acids for detergents, substitute fuels and petrochemicals.

2.1. Main principles of biorefineries

Biorefineries are based on four principles: a main one, known as principle of sustainability and environmental friendliness, and other principles that contribute to the main, such as the principle of cascading, principle of non conflict food-bioenergy, and principle of neutral carbon fingerprint [39].

2.1.1. Principle of Sustainability and Environmental Friendliness

Sustainability and Environmental Friendliness are two concepts related in general to actual human development and progress; and biorefinery by its nature is bound to them. Sustainability defined by the Brundtland is: "…development that meets the needs of the present without compromising the ability of future generations to meet their own needs" [40]. Environmental friendliness proposes that processes and services to have the lower impact on environment as possible, and in order to accomplish this an assessment is required. The most common used methodologies that provide adequate assessments are life cycle analysis (LCA), environmental assessment, and cost benefit analysis (CBA), all of which have similar basis, but different objective.

The environmental assessment of a product or service can be defined as: "to define and quantify the service provided by the product, to identify and quantify the environmental exchanges caused by the way in which the service is provided, and to ascribe these exchanges and their potential impacts to the service" [41]. Mostly, environmental assessment covers the analysis of environmental impact from human activities, however its focus is to serve as decision support tool and acceptability in society rather than a decision tool.

Cost-benefit analysis (CBA) has been used to find the most optimal in respect to economic and environmental costs

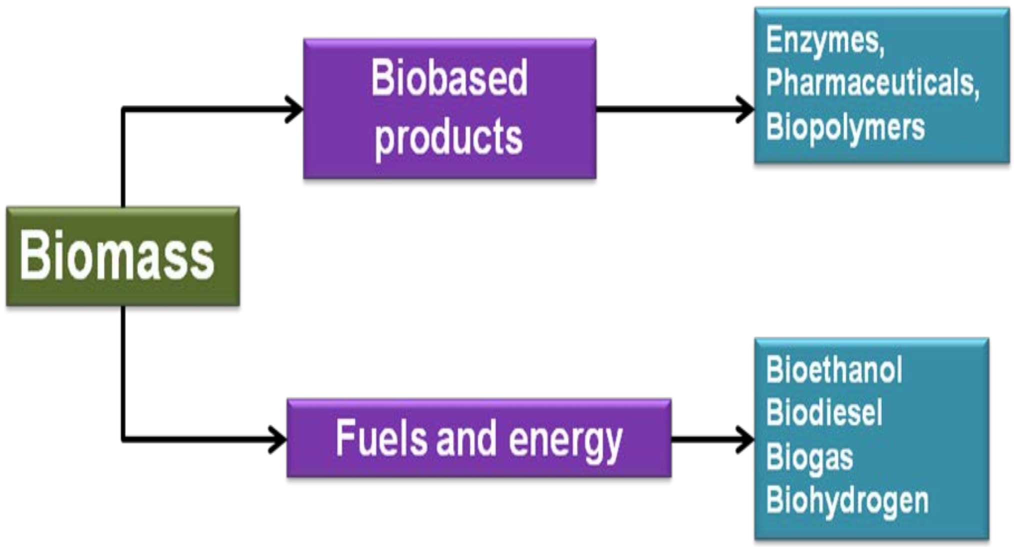

Figure 1. Diagram representing a generic biorefinery

and consequences. CBA has been applied on beverage containers, paper and organic waste, among others [42]. A main characteristic of CBA is optimising the benefits of society through an outweighing of economical and environmental consequences on preference based assumptions. However, CBA is often used on a national level disregarding environmental impacts occurring abroad and focusing on the costs for import of materials.

On the other hand, Life-cycle analyisis (LCA) has been regarded as one of the most complete tools for evaluating the environmental impacts and consumption of resources because of the holistic view, systematic approach and its standardization [42]. It was initially developed for evaluating the whole life cycle of products including extraction of resources, production, distribution, use and disposal. LCA was standardised [43] to evaluate product systems and services systematically and adequately on their environmental aspects from raw material extraction to final disposal, the “Cradle to grave” concept. In the development of an LCA of a product or service, like waste management, at least three main groups, also referred as areas of protection [44] have to be included: (i) human health, (ii) natural environment, and (iii) natural resources. According to some experts, a fourth area could be included, if there would be a human environment consisting of cultural, economic and intrinsic values. Traditionally, LCA does not include this area of protection, yet other tools more advanced than LCA can be used for evaluating this issue.

When comparing the most common transportation biofuels (bioethanol and biodiesel that can be produced in biorefineries) used to replace conventional diesel and gasoline, most LCAs have found a significant net reduction in green house gases (GHG) emissions and fossil energy consumption [45,46]. However some other LCA studies have also examined life cycle impacts on other environmental aspects, including local air pollution, acidification, eutrophication, ozone depletion, land use, etc. [47,48], and have concluded that most, but not all, biofuels substituting fossil fuels will lead to increased negative impacts [49]. This applies particularly to bioenergy crops where contamination of water and soil resources was a consequence of the intensive use of fertilizers (compounds based on N and P) and pesticides.

On this basis, biofuels and biorefinery technologies have focused on the use of waste biomass, as the organic fraction of municipal solid waste, agricultural and agroindustrial waste, which has proved through LCA to be energy profitable and environmentally friendly. In two models of biorefinery proposed by Cherubini and Ulgiati [50] the use of crop residues (corn stover and wheat straw) saved GHG emissions and reduced fossil energy demand. For instance, GHG emissions were reduced by about 50% and more than 80% of nonrenewable energy was saved. However these biorefinery systems needed a higher cumulative primary energy supply than the fossil reference system, but it was mainly based on renewable energy (i.e. the energy content of the feedstock itself). Yet, the energy output of these systems contains from 4 to 5 times the non-renewable energy invested.

Energetic and economic profit from bioethanol as only product has been very controversial. Most pretreatments of lignocellusic biomass and size reduction of particles are energy intensive processes, whereas enzymatic saccarification is expensive. Afterwards distillation and separation techniques employ more energy in form of heat and pressure [51]. In order to overcome these limitations, the production of biofuels other than ethanol (bioH_2, methane) and bioproducts (adhesives, dyes, pectins, solvents) has been suggested [18,50-52].

2.1.2. Principle of Cascading

The principle of cascading consists of using the organic wastes as raw material in sequential processes for maximum product yields and profits. We distinguish two cascading modes, direct and inverse cascading (Figure 2). In the direct or traditional cascading (Figure 2a), the organic wastes are first used for production of added-value bioproducts, and afterwards the remaining residues of these processes are subjected to bioenergy-generating processes. In the inverse cascading (Figure 2b), the organic wastes enter a bioenergy-bioproduct-bioenergy approach. The selection of cascading type depends on regional/national needs and priorities. For countries that are (or about to be) importers of fossil energy, such as USA, inverse cascading could be more attractive.

2.1.3. Principle of Non conflict food-bioenergy

The principle of non-conflict between food and energy can be considered a corollary of both sustainability and ethical issues. Yet, because of its importance, very often is highlighted and discussed in a separate way. Particularly in developing countries with typically up to 40-50% of the population below the poverty line, it is immensely a

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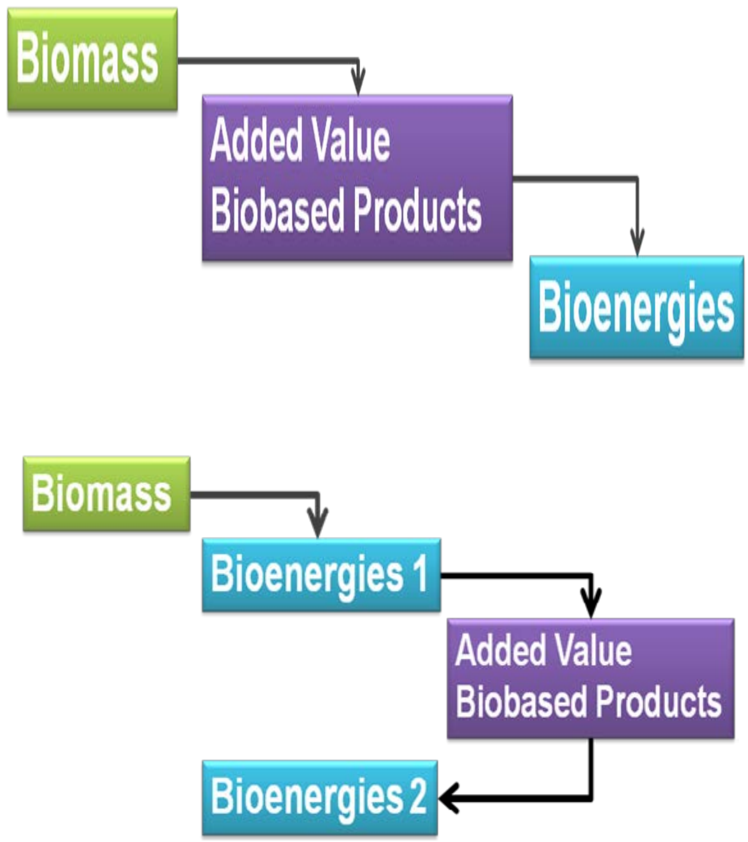

Figure 2. Diagram of Principle of Cascading in biorefineires: (a) direct cascading; (b) inverse cascading.

debatable to earmark food and feed crops for bioenergy generation. According to this idea, the European Union and independent researchers of developing countries advocate the use of organic wastes, such as agro-industrial waste and/or municipal organic waste to name a few, as the most convenient input to biorefineries. Hence the biomass energy potential is addressed to be the most promising among the renewable energy sources, due to the waste availability worldwide [53]. Biomass and biomass-derived fuels can be used to produce hydrogen sustainably and to reduce the net amount of CO_2 released to the atmosphere; but this technology urgently needs further development [54].

The production of renewable bioH_2 from biomass requires a co-product strategy to compete with conventional production of hydrogen from the steam reforming of natural gas. So far, the main advantages of bioH_2 technology are the ease and greenness of its required equipment/processes, and the widespread availability and apparent no cost of the substrate (biomass). However, research and development of this technology is still insufficient in order to reach the industrial scale needed to make the required paradigm shift before combustibles fossils are exhausted.

2.1.4. Principle of neutral carbon fingerprint

The continued use of fossil fuels to meet the majority of the world's energy demand has lead to increased concentrations of CO_2 in the atmosphere and the associated global warming [55]. So, the use of lignocellulosic biomass and other organic wastes is a viable option for generating renewable energy (Vancov et al., 2012) with a neutral carbon fingerprint [54]. It is known that bioprocessing these wastes to produce bioH_2 indeed reduces the net amount of CO_2 released to the atmosphere, because the CO_2 generated when the biomass is gasified was previously absorbed and fixed from the atmosphere by photosynthesis of plants [56,57]. In this way, the biorefinery is naturally integrated to the biogeochemical cycle of carbon and does not become a net generator of CO_2, in contrast with oil and coal exploration, exploitation and use.

2.2. Case studies of selected biorefinery approaches

Table 1 summarizes several biorefinery arrangements reported in the open literature. Escamilla-Alvarado et al. [58] proposed a biorefinery design coined H-M-Z-S that meets the four principles underlying the biorefinery and uses OFMSW as input material. In effect, their biorefinery approach is based on the principle of (inverse) cascading, since they use organic waste to generate hydrogen in a first stage and methane in a second stage, then get enzymes of commercial interest to be applied in a last stage of saccharification of digestates and OMFSW, where the sugars could be used to generate more energy in the form of bioethanol or lipids as precursors of biodiesel.

In another approach used waste biomass generated in an algae biorefinery was used to obtain fats and sugars [59], can be proposed that these value-added products and in turn used in the production of biodiesel complying with the principles of the biorefinery and exemplifies the principle of direct cascade. These are a few examples of efforts to develop biorefineries that respect the above mentioned four basic principles and especially the third principle which can develop sustainable processes using organic waste and therefore do not use arable land.

3. Biohydrogen from biomass

Biomass has been used since the beginnings of humankind as a fuel, then by burning wood for producing heat and light (a not so green process due to the generation of toxic gaseous products), and nowadays for producing a variety of new biofuels such as bioH_2, bioethanol, and diesel from organic sources (vegetables, algae, wastes). The

Table 1. Biorefinery approaches reported in the literature

Biomass type used/substrate	Bioenergy/Bioproducts manufactured	Scale up stage	Remarks	Ref.
Solid by-product (dry algae)	Algae biorefinery for production of lipids, sugars	Lab scale 110 mg glucose/g dry algae	R. toruloides Y4 Top:55°C Top:20h 75% conversion Increase the overall lipid yield by 5–15% depending on the carbohydrate content of the algae.	59
Lignocellulosic biomass (glucose, xylose, arabinose, cellobiose, among other sugars)	Lipid (fatty acid of 16-18C)	Lab scale	L. starkeyi AS 2.1560 Lipids produced by use for biofuel production Used mixtures cellobiose/xylose	92
Rice straw	Laccase (to oxidaze phenolic compounds)	Lab scale	Yarrowia lipolytica Laccase foster saccharification and demostrated its potencial for industrial uses, such as bioremediation, and in the textile, paper and pulp industries	93
Four types of biorefinery feedstocks (ethanol, butanol xylitol, lactic acid)	Wood adhesives*	Lab scale	* by using agricultural biomass to replace petrochemical materials	94
Syngas from black liquor gasification at pulp mills	Electricity, green automovile fuels	Demo	Waste industrial plant	95 96
Frying fat, food waste	Biodiesel, bioethanol, biogas	Full scale	Waste industrial plant	95 96
Glycerine from biodiesel plant	Biomethanol	Pilot to full	Waste industrial plant	95 96
Wood, black liquor	Specialty cellulose, bioethanol, CO2, methane, lignosulfonate for feed industry, soil conditions	Demo	Waste industrial plant	95 96
Grass, Lucerne and municipal waste	Insulation material from cellulose, agriPlast BW, protein, fertilizer	New		95 96
Starch and starch	Bioethanol, mauvais, fusel oil,	Existing	Starch industrial plant	95

derivatives	plant to send CO_2 to greenhouse, coproducts used internally			96
Starch	Bioethanol	Existing	Starch industrial plant	95 96
Lucerne, ryegrass, fescue grass, cocks-foot grass, rye fescue, forage grass, wheat straw	Cellulosic (to bioethanol production)	Existing		97
Agriculture residues Solid waste compost	Hydrolytic enzyme (xylanase, chitinase, proteases, α-amylases)		Streptomyces sp	98
Sugarbeet	Bioethanol, sugar, tomatoes, stones recovered from crop used for aggregate, topsoil from sugar on beet, betaine	Full scale	Waste industrial plant	99
OFMSW[a]	Biohydrogen, methane, enzymes, saccharified	Lab scale		33 58

Notes: [a] organic fraction of municipal solid waste.

advantages of using biomass for bioH_2 are the following: CO_2 and other pollutants emissions reduction, added value of crop residues conversion of agricultural waste and partial substitution of fossil fuels with sustainable biomass fuel, reduction of environmental and economical costs for diverging the disposition of municipal solid wastes. Limitations are for instance, seasonal availability of agro wastes, costs of collecting wastes in dispersed waste generation scenarios, and incomplete use of the organic matter present in biomass. To avoid these limitations, the regional-based biorefineries fed with flexible feedstocks of agro, municipal, and industrial organic wastes are a good option [31,39].

3.1. Maximizing biohydrogen from biomass

3.1.1. Dark fermentation and photo-fermentation

DF of organic wastes could be the beach-head of complete biorefineries that generate bioH_2 as a first step and could significantly change the future of solid waste management. The experience shows that in-series processes such as co-culture, or in series processes perform better than only one stage on substrate conversion to hydrogen [60,61]. Robledo-Narváez [19] evaluated the effect of mass retention time (MRT) on hydrogen generation in mesophilic solid substrate fermentation of a feedstock mixture of sugarcane bagasse, pineapple bagasse, and waste activated sludge. Lab scale, semi-continuous reactors were run at four MRT of 7, 10, 13 and 22 d (i.e., organic loading rates of 15, 25, 35 y 45 kg VS/(kg.d)) and 35°C. The feedstock was conditioned to 35% total solids. Bioreactors at the highest MRT showed the higher hydrogen production; at 22 and 13 d MRT the hydrogen production was nearly 50% higher than that at 10 and 7 d MRT. The pH was similar to all bioreactors. Concentration of ethanol in bioreactors was 451 mg COD/kg db at 13 d of MRT (the only solvent present).

Table 2 shows the average performance of mesophilic acidogenic digestor at different MRT. There was a slight effect of MRT on hydrogen production, with best results obtained at 13 d MRT. Process performance was generally poor. At MRT 13 d the concentration of VFA in the bioreactors was the lowest, which was consistent with the higher H2 productivity observed. Afterwards, and due to low production of hydrogen in semi-continuous systems, the production of hydrogen in a batch mode was evaluated [11]. The objective was to determine the effect of initial total solids content and initial pH on H_2 production in batch fermentation of the same agricultural wastes. The experiment was a response surface based on 2^2 factorial with central and axial points with initial TS (15 to 35%) and initial pH (6.5 to 7.5) as factors. Fermentation was carried out at 35°C, with intermittent venting of minireactors and periodic flushing with inert N_2 gas. Up to 5 cycles of H_2 production were observed; the best treatment in our work showed cumulative H_2 productions (ca. 3 mmol H_2/gds) with 18% and 6.65 initial TS and pH, respectively. There was a significant effect of TS on production of hydrogen, the latter decreased with initial TS increase from 18% onwards. Results of batch tests confirmed that the poor performance of semi-continuous hydrogen fermentation was due to the high TS contents of the feed to bioreactors, namely 35%TS. Cumulative H_2 productions achieved in this work were higher than those reported for organic fraction of municipal solid waste (OFMSW) [7,62] and mixtures of OFMSW and fruit peels waste from fruit juice industry [63], using the same process. Specific energetic potential due to H_2 in our work was attractive and fell in the high side of the range of reported results in the open literature. Batch dark fermentation of agro wastes as practiced in our work could be the beach-head of complete biorefineries that generate biohydrogen as a first step and could significantly change the future of agro-waste management. However such a process can be improved by coupling to a second stage.

A common approach is a series process of DF followed by PF. The DF produces fermented by-products (such as low molecular weight fatty acids and solvents) that can be used as substrates in photofermentation (PF) (Table 3). Purple non-sulfur bacteria (PNSB) can produce hydrogen when grown in presence of light and simple carbohydrates such as the organic compounds produced during DF. The PNSB are able to grow under 4 different metabolisms, is photo-heterotrophic metabolism under the sole which can produce hydrogen consuming organic compounds and light as source of carbon and energy source [64-66]. Such bacteria grow preferentially at low concentrations of N(III), which forces the bacteria to ‘dump’ the excess energy and reducing power through production of biohydrogen.

Table 2. Average performance of semi-continuous mesophilic acidogenic bioreactors for hydrogen fermentation of a mixture of agricultural wastes [19].

Parameter	MRT (d)			
	22	13	10	7
pH in digestates	6.20 ± 0.42	5.53 ± 0.17	5.48 ± 0.13	5.20 ± 0.28
TS [a] digestates (%)	33 ± 1	32 ± 0	34 ± 2	33 ± 1
Q_{bg} [b] (NmL_{bg}/d)	19 ± 11	27 ± 10	6 ± 4	2 ± 2
I_{bg} [c] ($NmL_{bg}/(kg.d)$)	46 ± 27	65 ± 21	13 ± 9	4 ± 3
$[H_2]$ in biogas (%)	6 ± 3	6 ± 3	6 ± 3	5 ± 3
Q_{H2} [d] (NmL_{H2}/d)	2 ± 2	6 ± 10	0.2 ± 0.5	0.2 ± 0.4
I_{H2} [e] ($NmL_{H2}/(kg.d)$)	4 ± 5	15 ± 26	0.4 ± 1	0.5 ± 1
VS [f] removal efficiency (%)	24 ± 4	19 ± 5	19 ± 4	21 ± 6
Y_{H2} [g] (NmL_{H2}/gVS_{rem})	0.25 ± 0.26	11 ± 20	0.01±0.03	0.01±0.03
VFA [h] (mg COD/kg dm)	13010 ± 1864	9358 ± 2020	9985 ± 1800	9766 ± 2801
Solvents (mg COD/kg dm)	227 ± 346	451 ± 1043	323 ± 614	175 ± 173

Notes: [a] total solids; [b] biogas flowrate; [c] biogas productivity; [d] hydrogen flowrate; [e] hydrogen productivity; [f] volatile solids; [g] hydrogen yield; [h] volatile fatty acids

BioH_2 production by photosynthetic bacteria is mainly mediated through nitrogenase enzyme complex, evolved to catalyze N_2 fixation:

$$2H^+ + 2e^- + 4ATP \rightarrow H_2 + 4ADP + 4P_i \qquad (1)$$

The activity of the enzyme is inhibited in the presence of oxygen, nitrogen (like ammonia or organic N), or at low C/N ratio [67]. It catalyzes bioH_2 production only in the absence of N_2 as shown in Eq. (1). Therefore, the process requires ammonium limited and anaerobic conditions (only mode resulting in hydrogen production). The metabolism shifts to utilization of organic substances for cell synthesis rather than hydrogen production in the presence of high nitrogen concentrations resulting in excess biomass growth and reduction of light diffusion. Ammonium salt concentrations as low as 20 µM have been found to rapidly inhibit existing nitrogenase activity in R. sphaeroides. However, the inhibition is reversible and nitrogenase activity could be recovered once ammonium is consumed or removed [68-71].

The PF can be combined with DF in series [72-74], in sequence [61,75-78], or co-cultivation [79]. It is estimated that DF combined with PF can increase the H_2 yield by 50% or more, depending on the substrate, lighting regime, and microbes. This value is definitively an attractive figure and conservatively low (Table 1). For instance, Sanchez-Hernández et al. [74] worked with batch photofermentation of leachate or extracts of spent solids from dark fermentation of agricultural wastes [19]. It was reported a hydrogen production that accounted for about 40% more energy compared to the hydrogen energy generated in the DF stage.

Another way of improving photoheterotrophic bioH_2 production is to utilize mutant bacterial strains. A few strains of PNSB bacteria, which are capable of producing hydrogen under illumination by the action of the nitrogenase enzyme, when devoid of uptake hydrogenase activity (Hup-) were shown to have higher bioH_2 productions [78,80]. There are reports that R. capsulatus, a PNS bacteria was improved for hydrogen production by eliminating polyhydroxyalkanote (PHA) synthesis and knocking out the uptake hydrogenase [60].
Another improvement strategy used in PNSB involved the genetic modification of the electron transfer chains in R. capsulatus. This study has proven that the modification increases nitrogenase expression and hydrogen production by 2-fold (Mathew &Wang, 2009). On the other hand, mutant microorganisms have been applied in the DF in order to reduce the amount of alcohols and so to increase the yield of bioH_2 in the PF stage [61].

3.1.2. Dark fermentation plus microbial electrolysis cells
Microbial electrolysis cells (MECs) have been proposed as an alternative technology for production of bioH_2 from waste and renewable materials (Fig. 3). In particular, simple organic substrates that are fermentation metabolites of DF can be used in an MEC to further increase H_2 production [81]. A MEC consists of an anode and a cathode, typically separated by a membrane (Fig. 3), with a potential of 0.3 V or higher applied across the two electrodes; the cell is loaded with a liquor with organic substrate(s) and biocatalysts [82,83]. Wang et al. [81] found, by integrating the fermentation and MFC–MEC systems, that the overall hydrogen yield of the process substantially improved to Y_I = 14.3 mmol H_2/g cellulose, or 41% more than dark fermentation alone, at an energy efficiency of 23%, in systems where the initial substrate complex the overall bioH_2 production for the integrated system could increase around 41% (Lu et al., 2012). In another work [83] a maximum of 72% energy efficiency was reported for conversion of acetate to hydrogen in a MEC and the energy content of the bioH_2 generated was estimated to be sufficient to meet 57% of the distillation energy demands in a lignocellulosic biorefinery.

Since poising the MEC with applied potential implies an energy expense, there is a need to assess the net energy gain of bioH_2 from MECs. On the one hand, there will be a positive amount of energy associated to the H_2 produced in the MEC; however, this energy should be compared to or discounted from the electric energy expended in poising the MEC. To the best of our knowledge, such a study is not yet available in the open literature.

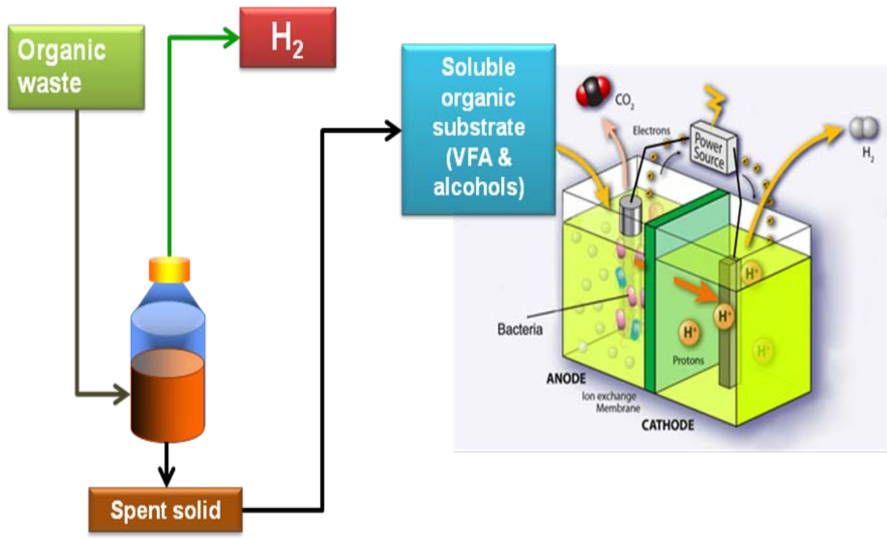

Figure 3. Dark fermentation and microbial electrolysis cells in series (adapted from http://www.rsc.org/chemistryworld/News/2011/February/11021103.asp)

3.2. Maximizing bioenergies from biomass

3.2.1. Dark fermentation coupled to methanogenesis

It is based on the simple and feasible idea that hydrolysis of the organic matter and its conversion to short-chain organic acids occurs in the acidogenic bioreactor where waste ferments and produces H_2, and so, microorganisms in the coupled methanogenic reactor would benefit from this and further degrade the substrate and organic metabolites to methane and CO_2. In fair justice, the two-phase anaerobic digestion of sludge in the 70 and 80 as published and practiced by sanitary engineers was based on this concept although the recovery of H2 as such was not an objective and was not reported.

Thus and in principle, by means of the two-stage process it is possible to attain a more thorough use of the substrate associated to the depletion of the organic load (as COD or VS), as well as increased yields of bioenergy and other valuable by-products [84]. Indeed methane yields have been improved when compared to one phase process [18,32].

Hydrogenogenic fermentation and methanogenic digestion, thus integrates a flexible and solid block of bioenergies from organic wastes. Methanogenic digestates could be used for bioproducts generation such as cellulolytic enzymes, and the discarded solids mixed with fresh organic wastes are subjected to saccharification processes to be ready for ethanol fermentation (another bioenergy), thus closing the inverse cascade biorefinery approach [18,33]. Escamilla-Alvarado et al. [58] reported that a series process DF-methanogenesis from the organic fraction of municipal solid waste, that they coined H–M (H: hydrogen production stage, M: methane production stage) in thermophilic and mesophilic processes were in average 76 and 42% higher in terms of energetic potential than methanogenic control bioreactors alone. They also found that thermophilic regime H-M increased the gross energetic potential over 65% in average compared to the mesophilic H-M. Indeed, this energetic increment was mainly due to an increase in methanogenic yield when compared to one-stage methanogenic process. Later on, in related other works [85,86] improvements on the hydrogen fermentation of the series process H-M of OFMSW were reported. Increments in hydrogen production definitively have positive effect on overall energetic potential, because of its higher combustion enthalpy compared to methane. However, some limitations still must be overcome, such as the lactic deviation, which was inferred to play a negative role on bioH_2 fermentation in DF of OFMSW. Wang and Zhao [87] also integrated a two-stage process with none-heat treatment of inoculum. The bench scale test demonstrated that the application of indigenous food waste microflora was applicable for the H_2 and CH_4 production in the integrated two-stage fermentation process and their reported an increase of approximately 45% of energy compared to one stage of methane production.

3.2.2. Dark fermentation coupled to microbial fuel cells

The energy efficiency and sustainability of DF process can be further improved if additional energy is harvested from these aqueous end products. Using DF to produce hydrogen and VFA and alcohols for their posterior conversion to electricity in MFC as a follow-up process can improve the overall net energy gain [88,89]. When organic waste streams are used as feedstock in DF, such two-step processing can stabilize the waste completely conserving the resources that would otherwise have been used in managing the waste, with simultaneous generation of clean energy [90], effluents from PF and digestates are then processed in MFC for bioelectricity production (Fig. 4). Ketheesan & Nirmalakhandan [90] used glucose like substrate in a system of two-stage (DF + MFC) and they found that an increase of 5-fold energy gain. In another research [91] it was found that combining DF + MFC the potential for electrical energy generation increased 4 times using sucrose like substrate, and up to 23 times more using sucrose plus manure. On the other hand, Vazquez-Larios et al. [89] indicated that depending on the architecture of the cell the power output could increase from 50% to 67%.

Table 3 below summarizes the typical energy gains achieved by combining biohydrogen dark fermentation with a second stage of processes discussed so far.

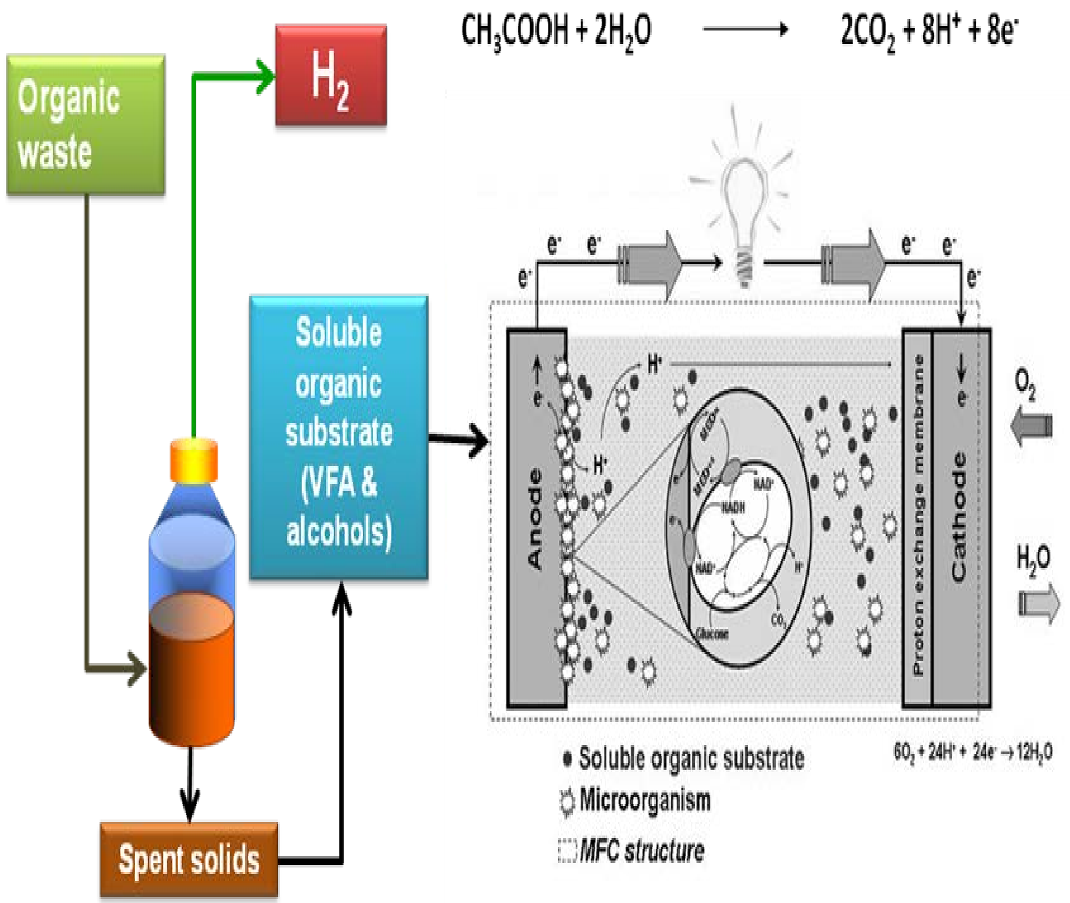

Figure 4. Dark fermentation and microbial fuel cells in series (modified from [88]).

Table 3. Increased bioenergy production by series processes where biohydrogen dark fermentation is the first stage.

Process	Second bioenergy	Energy increase (%)	Remarks	Ref.
DF [a] + PF [b]	Hydrogen production	40	Rotten fruit, batch, 2.9 L/L H_2 productions in DF, 0.8 L/L H2 production in PF	75
DF + PF	Hydrogen production	69	Glucose, batch, 3.2 L/L productions in DF, 2.2 L/L production in PF	76
DF + PF	Hydrogen production	59	Glucose, batch, 5.1 L/L production in DF, 3.0 L/L in production PF	77
DF + PF	Hydrogen production	19	Beet molasses, batch, 7.1 mmol/L in production in DF, 1.4 mmol/L in production in PF	78
DF + PF	Hydrogen production	65	Bagasse, batch, 54 mL/g production in DF, 35 L/g in production in PF	61
DF + M[c]	Methane	45-65	Organic solid waste artificial dog food (15 g / L) and waste paper (10 g / L) saccharified, 442mmol CH_4/L reactor/d 199 mmol $H_2/L_{reactor}$/d	100
DF + M	Methane	45-65	Powdered organic solid waste (restaurant) and waste (fiber) paper; 4.5 m^3/m^3/d H_2 6.1 CH_4 m^3/m3/d H_2 Yield: 2.4 mol / mol hexose Load: 56 L / Kg. COD	101
DF + M	Methane	45-65	Food wastes, 43 ml H_2/g VS, 500 ml CH_4/g VS	102
DF + M	Methane	45-65	Waste of food; 3.63 m^3H_2/m^3/d; 1.75 m^3CH_4/m^3/d	103
DF + M	Methane	45-65	Sucrose; 4.25 LH_2/(L.d); 1.39 LCH_4/(L.d)	104
DF + MFC [d]	Electricity	20-60	PEEG increases 4 times using sucrose as substrate, and up to 23 times more using sucrose plus manure.	91
DF + MFC	Electricity	20-60	Glucose as substrate; increases until 5 fold the energy gain	12

Notes: [a] H_2 by dark fermentation stage; [b] H_2 by photoheterotrophic fermentation; [c]methanization stage; [d]microbial fuel cell;[e] microbial electrolysis cell.

4. Conclusion and perspectives

In principle, bioH_2 and bioelectricity could contribute to significant improvements on solid organic waste management. Indeed, bioH_2 production from solid organic wastes can be integrated into biorefinery approaches for the production of added value bioproducts as well as other bioenergies (Fig. 5), which undoubtedly will be a significant step towards the sustainable development of modern societies. The increased energy production using two-stage on the basis of the dark fermentation, and it can be seen that these combination of steps favor biomass power generation and at the same time contributes to the management of organic waste.

Combinations of DF with either PF, MFC, or MEC represent alternatives capable of increasing the yields of bioH_2

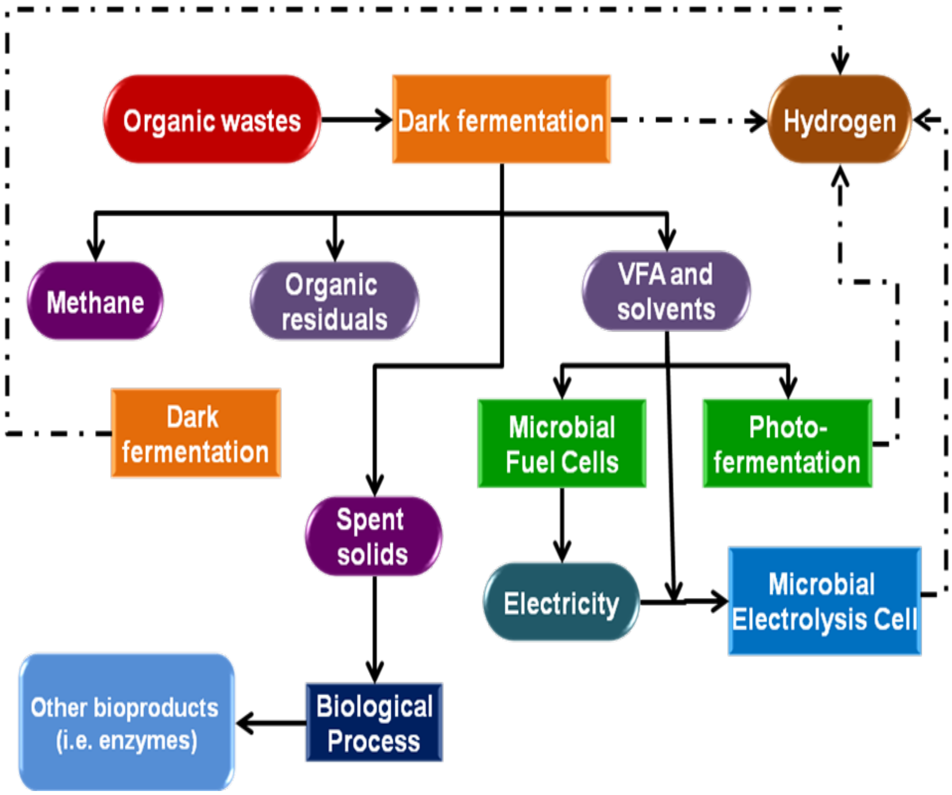

Figure 5. A biorefinery for the organic solid waste that combine hydrogen dark and photofermentation, methanogenic fermentation, bioelectrochemical processes for bioelectricity and hydrogen production, among other processes.

and/or bioenergy. Two stage systems seem to be good option for the management of solid organic wastes which allow treatment in a first step by DF of high concentrations of feedstock without sterilization but nutrient concentrations (i.e., inhibition of PF by N (III) and N_2) and dark color in the first stage effluents can be a problem for PF; in practice, effluent conditioning may be required (N removal, dilution, color removal, pH adjustment) before feeding to PF in order overcome inhibitory effects.

Interesting experiments with sequential and co-cultivation of DF and PF have shown good results. Metabolic engineering and genetic applications to H_2 processes can improve microbial metabolic capabilities and boost H_2 production, as well as preventing metabolic deviations that could impair bioenergy yields. There are promising results of such an approach for PF and DF.

Although there are selected examples of commercial biorefineries, they seem to evolve from the modification of existing conventional manufacturing plants. Most reported biorefinery approaches are at the concept (lab scale) and a few pilot scale level. The design of full scale biorefineries, that in turn depend on full scale bioreactors and ancillary equipment for DF, PF, and other bioenergies, is lagging behind. Scale-up and demonstration projects of DF combined with other H_2 and bioenergy processes should be fostered if we want an early integration of these processes to biorefinery setups for increasing the sustainability of modern societies.

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References

[1] K.L.Kovácsa, G.Maróti, G.Rákhelya, Int. J. Hydrogen Energy, 31, 1460 (2006).
[2] K.M. Muñoz-Páez, E. Ríos-Leal, I. Valdez-Vazquez, N. Rinderknecht-Seijas, H.M. Poggi-Varaldo, J. Environ. Manage., 95, S355 (2012).
[3] D. Das, T.N. Veziroglu, Energy, 33, 6046 (2008)
[4] I..Valdez-Vazquez, H.M. Poggi-Varaldo, Renew.Sustain. Energy Rev. 13, 1000 (2009).
[5] J.J. Lay, Y.J. Lee, T. Noike, Water Res., 33, 2579 (1999)..
[6] I. Valdez-Vazquez; H.M. Poggi-Varaldo, Int. J. Hydrogen Energy, 34, 3639 (2009).
[7] I. Valdez-Vazquez, E. Ríos-Leal, K.M. Muñoz-Páez, A. Carmona-Martínez, H.M. Poggi-Varaldo, Biotechnol. Bioeng., 95, 342 (2006).
[8] G.D. Sprott, K.F. Jarrell, K.M. Shaw, R. Knowles, J. Gen. Microbiol., 128, 2453 (1982).
[9] R. Sparling, D. Risbey, H.M. Poggi-Varaldo, Int. J. Hydrogen Energy, 22, 563 (1997).
[10] Y.F. Li, N.Q. Ren, Y. Chen, G.X. Zheng, Int. J. Hydrogen Energy, 32, 755 (2007).
[11] P. N. Robledo-Narváez, G. Calva-Calva, M.T. Ponce-Noyola, E. Ríos-Leal, J. Galíndez-Mayer, R. Olvera-Ramírez, C. Estrada-Vázquez, A. Ortega-Clemente, H.M. Poggi-Varaldo, 12th World Congress on Anaerobic Digestion. Noviembre 1-4, Guadalajara, Mexico (2010).
[12] G. Antonopoulou , H.M. Gavala, I.V. Skiadas, K. Angelopoulos, G. Lyberatos, Bioresource. Technol., 99, 110 (2008).
[13] A. Karlsson, L. Vallin, J. Ejlertsson, Int. J. Hydrogen Energy, 33, 953 (2008).
[14] Y. Akutsu, Y.Y. Li, H. Harada, H.Q. Yu, Int. J. Hydrogen Energy, 34, 2558 (2009).
[15] X. Wu, W. Yao, J. Zhu, Int. J. Hydrogen Energy. 35, 6592 (2010).
[16] C. Cavinato, D. Bolzonella, F. Fatone, A. Giulano, P. Pavan, Water Sci. Technol., 64, 715 (2011).
[17] C. Cavinato, D. Bolzonella, F. Fatone, F. Cecchi, P. Pavan, Bioresour. Technol., 102, 8605 (2011).
[18]C. Escamilla-Alvarado, E. Ríos-Leal, M.T. Ponce-Noyola, H.M. Poggi-Varaldo, Process Biochem., 47, 1572 (2012).
[19] P. N. Robledo-Narvaez Sc D Thesis Interim Report. CINVESTAV del IPN, Mexico D.F., Mexico, (2012).
[20] P.N.Robledo-Narváez, C. Escamilla-Alvarado, M.T. Ponce-Noyola, H.M. Poggi-Varaldo, Biohydrogen from wastes and combination of biological processes for energy yield improvement: a review. In: Proceedings 3rd Int. Meeting Environ. Biotechnol. Eng., Palma de Mallorca, Baleares Islands, Spain, 21-25 Sept. (2008).
[21] P. Lins, T. Schwarzenauer, C. Reitschuler, A.O. Wagner, P. Illmer, Waste Manage. Res., 30, 1031 (2012).
[22] C. Escamilla-Alvarado, M.T. Ponce-Noyola, H.M. Poggi-Varaldo, Energetic potential of two-stage hydrogenesis-methanogenesis fermentation of the organic fraction of municipal solid waste. In: 14th Int. Biotechnol. Symp. Rimini, Italy. Published in CD-ROM (2010).

[23] C. Garibay-Orijel, E. Ríos-Leal, J. García-Mena, H.M. Poggi-Varaldo, J. Chem. Technol. Biotechnol., 80, 1180 (2005).
[24] L. Márquez-Benavides, I. Watson-Craik, Water Sci. Technol. 48, 4, 245 (2003).
[25] C. Gallert, J. Winter, Naturwissenschaften 89, 483(2002).
[26] A.C.C. Chang, Y.H. Tu, M.H. Huang, C.H. Lay, C.Y. Lin, Int. J. Hydrogen Energy, 36,14280, (2011).
[27] I.K. Kapdan, F. Kargi, Enzyme Microb. Technol. 38, 569 (2006).
[28] M.J. Cuetos, X. Gomez, A. Escapa, A. Moran, J Power Sources, 169, 131 (2007).
[29] M. García-Pérez, A. Chaala, J. Yang, C. Roy, Fuel, 80, 1245 (2001).
[30] J. De La Cruz, G.H. Garcia, Pineapple post-harvest operations. FAO document from Internet site: www.fao.org/inpho/compendium (2004).
[31] P. Battistoni, F. Fatone, D. Passacantando, D. Bolzonella, Water Res., 41, 893 (2007).
[32] C. Escamilla-Alvarado, F. Esparza-Garcia, E. Rios-Leal, O. Perez-Avalos, M.T. Ponce-Noyola, H.M. Poggi-Varaldo, A contribution to biorefinery concept: integration of enzyme production as a third stage after bioenergy production from two-stage anaerobic treatment of organic solid wastes. In: 14th Int. Biotechnol. Symp. Published in CD-ROM (2010)..
[33] F. Fava, L. Diels, M. Reis, J. Duarte, O. Beserra-Carioca, O., H.M. Poggi-Varaldo, B. Sommer-Ferreira, (2012). Biowaste biorefiney in Europe: opportuties and R&D needs. Position Paper. European Federation of Biotechnology. Section of Environmental Biotechnology.
[34] V. Robles-González, J. Galíndez-Mayer, N. Rinderknecht-Seijas, H.M. Poggi-Varaldo, J. Biotechnol., 157, 524 (2012).
[35] F.W. Lichtenthaler, Carbohydrate-based Product Lines, in: Kamm, B., Gruber, P., Kamm, M. (Eds.), Biorefineries-Industrial Processes and Products. Status Quo and Future Directions, 1st edn. Wiley-VCH, Weinheim (2005)
[36] A.S. Mamman, J.M. Lee, Y.C. Kim, I.T. Hwang, N.T. Park, Y.K. Hwang, J.S. Chang, J.S. Hwang, Biofuels, Bioprod. Biorefin. 2, 438 (2008).
[37] K. Gairola, I. Smirnova, Bioresource Technology, 123, 592 (2012).
[38] E. Kirtay, Energy Conversion Manage. 52, 1778 (2011).
[39] H.M. Poggi-Varaldo, Invited Conference, Doctoral Programme of Science and Society, CINVESTAV del IPN, November, Mexico (2012).
[40]World Commission on Environment and Development. Our Common Future. United Nations, Oxford University Press, U.K. (1987)
[41]H. Wenzel, M. Hauschild, L.Alting, Environmental assessment of products, Vol.1: Methodology, tools and case studies in product development. Kluwer Academic Publishers, Hingham, MA, USA (1997).
[42]M.S. Hansen, U. M. Gilberg. Cost-benefit analysis and life cycle assessment in environmental decision-making - Potentials and limitations. Master thesis, E&R, Tech. Univ. Denmark, Denmark (2003).
[43] ISO, ISO 14040: Environmental management - Life cycle assessment - Principles and framework. International Organisation for Standardisation, Geneva, Switzerland (1997).
[44] H.A. Udo de Haes, O. Jolliet, G. , M. Hauschild, W. Krewitt, R. Mueller-Wenk, Int. J. Life Cycle Assessm., 4, 66 (1999)..
[45] S. Kim, B.E. Dale, Biomass Bioenergy, 29, 426 (2005)..
[46] H. von Blottnitz, M.A. Curran, J. Cleaner Prod., 15, 607 (2007).
[47] D. Pimentel, T.W. Patzek, Nat. Resour. Res., 14, 65, 511 (2005)..
[48]A.E. Farrell, R.J. Plevin., B.T. Turner, A.D. Jones, M. O'Hare, D.M. Kammen, Science, 311, 5760, 506 (2006).
[49] E.D. Larson, Energy Sustain Develop., 10, 109 (2006).
[50] F. Cherubini, S. Ulgiati, Appl. Energy, 87, 47 (2010).
[51] J.Y. Zhu, X.S. Zhuang, Progress Energy Comb Science, 38, 583 (2012).
[52] S. Fahd, G. Fiorentino, S. Mellino, S. Ulgiati, Energy, 37, 79 (2012)..
[53] A. Demirbas, Energy Education Sci. Technol., 22, 69 (2008).
[54] E. Lalaurette, S. Thammannagowda, A. Mohagheghi, P.C. Maness, B.E. Logan, Int. J. Hydrogen Energy, 34, 6201 (2009).
[55] M. Balat, Energy Sources Part A, 31, 1242 (2009).

[56] H. Larsen, R. Feidenhans'l, L.S. Petersen, Hydrogen and its competitors, Risø energy Report 3. Roskilde, Denmark: Risø National Laboratory; November (2004).
[57] H. Balat, E. Kırtay, Int. J. Hydrogen Energy, 35, 7416 (2010).
[58] C. Escamilla-Alvarado, J.A. Vazquez-Barragán, M.T. Ponce-Noyola, H.M. Poggi-Varaldo, A novel biorefinery approach for biofuels and holocelullolytic enzymes production from organic wastes. Battelle International Symposium on Bioremediation and Sustainable Environmental Technologies. Reno, NV, USA, 27-31 June (2011).
[59] A.P. Trzcinski, E. Hernandez, C. Webb, Bioresour. Technol, 116, 295 (2012).
[60] T.Y. Wu, J.X.W. Hay, L.B. Kong, J.C. Juan, J.M. Jahim, Renew. Sustain. Energy Rev., 16, 3117 (2012).
[61] X. Wu, Q. Li, M. Dieudonne, Y. Cong, J. Zhou, M. Long, Bioresour. Technol., 101, 9605 (2010).
[62]I. Valdez-Vazquez, E. Rios-Leal, A. Carmona-Martinez, K.M. Muñoz-Paez, H.M. Poggi-Varaldo, Environ. Sci. Technol., 40, 3409 (2006).
[63] K.M. Muñoz-Páez, E. Ríos-Leal, M.T. Ponce-Noyola, F. Esparza-García, J. García-Mena, H.M. Poggi-Varaldo, Hydrogen from fermentation of municipal organic wastes mixed with fruit-juice industry. In: Proc. IWA 5th Int. Symp. Anaer. Dig. Solid Wastes Energy Crops, Hammamet, Tunisia, 25-28 May (2008).
[64] H. Koku, I. Eroglu, U. Gündüz, M. Yücel, L. Türker, Int. J. Hydrogen Energy, 27, 1315 (2002).
[65] C.Y. Chen, C.H. Liu, Y.C. Lo, J.S. Chang, Bioresour. Technol., 102, 8484 (2011).
[66] G.S. Joshi, S. Romagnoli, N.C. VerBerkmoes, R.L. Hettich, D. Pelletier, F.R. Tabita, J Bacteriol., 191, 4243 (2009).
[67] Y. Ozturk, M. Yucel, F. Daldal, S. Mandac, U. Gunduz, L. Turker, Int. J. Hydrogen Energy, 31, 1545 (2006).
[68] A. Melis, M.R. Melnicki, Int. J. Hydrogen Energy, 31, 1563 (2006).
[69] N. Basak, D. Das, World J. Microbiol. Biotechnol., 23, 31 (2007).
[70] H. Zhu, H.H.P. Fang, T. Zhang, L.A. Beaudette, Int. J. Hydrogen Energy, 32, 4112 (2007).
[71] T. Keskin, M. Abo-Hashesh, P.C. Hallenbeck, Bioresour. Technol., 102, 8557 (2011).
[72]J.A. Acevedo-Benítez, H.M. Poggi-Varaldo, Hydrogen from recalcitrant leachates by photoheterotrophic fermentation. In: Sass, B. M. (Ed.), Remediation of Chlorinated and Recalcitrant Compoundsd-2008. Proc. 6th. Int. Conf. Remediation Chlorinated and Recalcitrant Compounds (Monterey, CA; May). Battelle, Columbus, OH, ISBN 1-57477-163-9 Book in CD-ROM. www.battelle.org/chlorcon-Paper G-012. (2008).
[73] G. Sanchez-Hernández, Biohidrógeno fotoheterótrofo a partir de residuales acidogénicos. M. Sc Thesis. CINVESTAV del IPN, Mexico D.F., Mexico (2012).
[74] G. Sánchez-Hernández, P. Robledo-Narváez, M.T. Ponce-Noyola, E. Ríos-Leal, N. Rindernecht-Seijas, H.M. Poggi-Varaldo, Environ. Eng. Manage. J., 11, S141 (2012).
[75] M.H. Abd-Alla, F.M. Morsy, A.W.E. El-Enany, Int. J. Hydrogen Energy, 36, 13518 (2011).
[76] K. Nath, D. Das, Int. J. Hydrogen Energy, 34, 7497 (2009).
[77] H. Su, J. Cheng, J. Zhou, W. Song, K. Cen, Int. J. Hydrogen Energy, 34, 8846 (2009).
[78] E. Özgür, A.E. Mars, B. Peksel, A. Louwerse, M. Yücel, U. Gündüz, P.A.M. Claassen, I. Eroglu, Int. J. Hydrogen Energy, 35, 511 (2010).
[79] M. Abo-Hashesh, D. Ghosh, A. Tourigny, A. Taous, P.C. Hallenbeck, Int. J. Hydrogen Energy, 36, 13889 (2011).
[80] E. Özgür, B. Uyar, Y. Öztürk, M. Yücel, U. Gündüz, I. Eroglu, Resources, Conservation and Recycling, 54, 310 (2010).
[81] A. Wang, D. Sun, G. Cao, H. Wang, N. Ren, W.M. Wu, B.E. Logan, Bioresour. Technol., 102, 4137 (2011).
[82] S. Manish, R. Banerjee, Int. J. Hydrogen Energy, 33, 279 (2008).
[83]A.P. Borole, J.R. Mielenz, Int. J. Hydrogen Energy, 36, 14787 (2011).
[84]L.T. Angenent, K. Karim, M.H. Al-Dahhan, B.A. Wrenn, R. Domíguez-Espinosa, Trends Biotechnol., 22, 477 (2004).
[85] C. Escamilla-Alvarado, M.T. Ponce-Noyola, E. Ríos-Leal, N. Rinderknecht-Seijas, H.M. Poggi-Varaldo, Biohydrogen production through solid substrate fermentation of organic municipal wastes: a multivariable evaluation. 9th International Symposium on New Materials and Nano-Materials for Electrochemical Systems. 12th. Int. Congress of the Mex. Hydrogen Soc.. July 9-13 Merida, Mexico (2012)
[86] C. Escamilla-Alvarado, M.T. Ponce-Noyola, E. Ríos-Leal, H.M. Poggi-Varaldo, Int. J. Hydrogen Energy,

Accepted for publication. (2013).
[87] X. Wang, Y.C. Zhao, Int. J. Hydrogen Energy, 34, 245 (2009).
[88] H.M. Poggi-Varaldo, A. Carmona-Martínez, A. Vázquez-Larios, O. Solorza-Feria, J. New Mater. Electrochem. Syst., 12, 49 (2009).
[89]A.L. Vázquez-Larios, O. Solorza-Feria, G. Vázquez-Huerta, F. Esparza-García, N. Rinderknecht-Seijas, H.M. Poggi-Varaldo, Int. J. Hydrogen Energy, 36, 6199 (2011).
[90] B. Ketheesan, N. Nirmalakhandan, N., Int. J. Hydrogen Energy, 36, 11693 (2011).
[91] K.R.J. Perera, Y. Arudchelvam, V. Gadhamshetty, N. Nirmalakhandan, Int. J. Hydrogen Energy, 37, 2267 (2012).
[92] Z. Gong, O. Wang, H. Shen, C. Hu, G. Jin, Z.K. Zhao, Bioresour. Technol., 117, 20 (2012).
[93] K.M. Lee, D. Kalyani, M.K. Tiwari, T.S. Kim, S.S. Dhiman, J.K. Lee, I.W. Kim, Bioresour. Technol., 123, 636 (2012).
[94] W. Zhang, Y. Ma, C. Wang, S. Li, M. Zhang, F. Chu, Ind. Crops Products, 43, 326 (2013).
[95] EC BREC, D.2.2.3 Report with the assessment resuls concerning environmental, BIOPOL Projet No. 34433-FP6-2005-SSP-5A, (2009). Available at: http:/www.biorefinery.nl/fileadmin/biopol/user/documents/PublicDeliverables/BIOPOL_D_2_2_3_-_Final_120609.pdf [March 12, 2010].
[96] M. Wellisch, G. Jungmeier, A. Karbowski, M.K. Patel, M. Rogulska, Biofpr., 4, 275 (2010).
[97] S.I. Njoku, B.K. Ahring, U. Uellendahl, Bioresour. Technol. 124, 105–110 (2012).
[98] S. Mokni-Tlili, I.B. Abdelmalek, N. Jedidi, H. Belghith, A. Gargouri, H. Abdennaceur, M.N. Marzouki, Waste Manage. Res., 28, 828 (2010).
[99] http://www.glycosbio.com/about.htm.
[100] Y. Ueno, M. Tatara, H. Fukui, T. Makiuchi, M. Goto, K. Sode, Bioresour. Technol., 98,1861 (2007).
[101] Y. Ueno, H. Fukui, M. Goto, Environ. Sci. Technol., 41, 1413 (2007).
[102] D. Liu, D. Liu, R.J. Zeng, I. Angelidaki, Water Res., 40, 2230 (2006).
[103] S.K. Han, H.S. Shin, J. Air Waste Manage. Assoc., 54, 242 (2004).
[104] G. Kyazze, R. Dinsdale, A.J. Guwy, F.R. Hawkes, G.C. Premier, D.L. Hawkes, Biotechnol. Bioeng., 97, 759 (2006).

Notation

BES	bromo-ethane sulphonate
CBA	cost benefit analysis
DF	dark fermentation
GHG	green house gases
H-M	series process hydrogen fermentation followed by methanogenic stage
H-M-Z-S	biorefinery scheme based on hydrogen fermentation, methane production, enzyme production, and saccharification of digestates and fresh organic waste for bioethanol or further bioproduct generation
I_{bg}	biogas productivity
I_{H2}	hydrogen productivity
LCA	life cycle assessment
MEC	microbial electrolysis cells
MFC	microbial fuel cells
OFMSW	organic fraction of municipal solid wastes
PEEG	potential for electrical energy generation
PF	photo-fermentation
PNSB	purple non-sulfur bacteria
Q_{bg}	biogas flowrate
Q_{H2}	hydrogen flowrate
VFA	volatile fatty acids
VS	volatile solids