BIOHYDROGEN PRODUCTION: LIMITS AND PROSPECTS[1]

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Abstract

In the last years we have been observing an increasing of the international scientific research in the field of innovative processes aiming at the production of hydrogen from different kinds of biomass.

The present study examines the scenario of the current situation as well as the prospects for production of hydrogen using biological conversion techniques. The above mentioned processes consist in the continuous production of hydrogen and biogas through fermentation of biomass, and the final purification of the same. The elective substrate consists of vegetable residues, wastes from food industries, livestock sewage, etc... The aim is to have an energy carrier generated from renewable materials, following some indicators of the sustainable development.

Riassunto

Negli ultimi anni si sta assistendo all'intensificarsi della ricerca scientifica internazionale nel settore delle tecniche innovative miranti alla produzione di idrogeno da varie tipologie di biomasse. Nel presente studio si esamina il quadro della situazione attuale e le prospettive di produzione attraverso le tecniche di conversione biologica. I suddetti processi prevedono la produzione in continuo di idrogeno e biogas per via fermentativa e la purificazione finale degli stessi: il substrato elettivo é costituito dai residui vegetali, dai reflui delle industrie

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alimentari, dai liquami zootecnici, ecc... Ciò potrà consentire di disporre di un vettore energetico generato da materie rinnovabili, conforme ad alcuni indicatori dello sviluppo sostenibile.

Keywords: biomass, bioenergy, biohydrogen, anaerobic digestion, dark fermentation, photo-fermentation.

Introduction

Interest in biologically generated hydrogen began in the early 1990's with the setting up of some international research programmes. In fact, by then it had already become evident that the use of fossil fuel in energy production, apart from emitting polluting substances into the atmosphere, could cause significant global climate change.

Most hydrogen obtained from biological resources in the biosphere comes from microbial fermentation processes through the decomposition of organic matter. In recent years the process of anaerobic digestion, whose main application was stabilization of biodegradable organic matter, aimed both at energy exploitation through co-digestion of various types of organic matter (sludge, organic fractions of MSW, agro-industrial and zootechnical liquid waste) and at the combined production of hydrogen and methane.

In this process hydrogen is, in fact, an intermediate product which is usually quickly transformed into methane by virtue of hydrogenotrophic methanogen bacteria which use for this purpose hydrogen and carbon dioxide.

Therefore, to sustain biological production of hydrogen, appropriate technology needs to be developed in order to create those specific conditions able to inhibit or limit the methanogenesis phase.

The choice of the biomass source also depends on availability of raw materials: use of inexpensive matter and the creation of efficient hydrogen production processes could, in the future, make this production process more competitive when compared to more conventional chemical and electrochemical ones, proving to be high energy consuming and costly.

Bioproduction of Hydrogen

Biological processes are characterised by a sequence of biochemical reactions at an environmental temperature and atmospheric pressure, due to various microorganisms able to capture and concentrate usable energy from water with high content of organic resources.

The process of microbial fermentation, based on the ability of acidogenic fermentative bacteria to transform carbon hydrates into hydrogen and volatile fatty acids, would appear to be of particular interest.

As mentioned, in nature the generation of hydrogen is an intermediate metabolic phase in methane production and presents a metabolic and energy yield greater than methanogenesis, although being rather unstable.

Therefore, the aim is to keep fermentation stable and controllable, inhibiting the methanogenesis phase (permanence of organic substance in the digestor needs to be limited and it is necessary to work in an acidic environment) which consumes the amount of hydrogen obtained during the previous phases (1).

The substrate

The use of biomass energy is rather interesting when applied on an industrial scale, especially where liquid waste products are available that, since often contain rather polluting organic compounds, would need to be appropriately treated in order to safeguard the environment. In this way, organic waste would be exploited, eliminating the social costs linked to its disposal.

Current studies and experiments foresee the possibility of creating a significant production of hydrogen from biodegradable organic substrates.

Criteria applied in the selection of the *substrates* take the following factors into account: availability, costs, carbohydrate content and level of biodegradability. Glucose, saccharose and to a lesser extent, starch and cellulose have been widely researched and are well-suited to being used as substrates in the dark fermentation process since, containing carbon, they are rapidly biodegradable and present in drainage water and agricultural waste products. However, they are not cost- effective compared to sludge or when mixed with other types of biodegradable waste and residues. On the other hand, waste rich in fatty substances and proteins, though less readily available, constitutes potential raw material from which to start converting organic waste into hydrogen. An ideal substrate, constituted by low cost raw materials, may be obtained from liquid waste from the agricultural and food industries or sewage disposal plants, mixed with liquids from animal livestock farms or vegetable waste containing fermentable organic substances and lacking in others which would inhibit microbial activity.

Recently, some experimental studies have shown that the use of organic fractions of MSW or drainage water with water solutions containing glucose, molasses, cellulose and starch leads to a hydrogen yield greater (approximately 5-10 mmol-H_2/g of substrate) than that obtainable from the biological conversion of sludge deriving from wastewater treatment (approx. 0,08 mmol-H_2/g of substrate). Therefore, two fundamental parameters need to be improved: a suitable renewable substrate biomass/drainage water and an ideal microbial combination able to efficiently convert the abovementioned biomass into hydrogen (3-5).
Data published in literature estimates that, on average, a theoretical yield of hydrogen equal to 10-20 $m^3/day \cdot m^3$ reactor and a substrate consumption of approximately 20 $kg/m^3 \cdot day$.

Biohydrogen production techniques

Conversion processes of biomass into hydrogen are divided into two categories: thermo-chemical and biological. The latter may either depend on light (direct or indirect ***biophotolysis*** and ***photofermentation***) or not (***dark fermentation***). The process of biophytolysis has not been examined in this study. This consists in the decomposition of water through light in the presence of microalgae or cyanobacteria, since hydrogen yield is very low and thus unsuitable for practical applications.
In *dark fermentation* the anaerobic heterotrophic organisms are able to produce hydrogen during oxidizing of the organic substrate. The process of biodegradation of said substrate foresees a *hydrolysis phase* in which complex molecules are transformed into simple compounds.

The main components of the waste in question, cellulose and hemicellulose, are not readily usable by the acidogenic bacteria, therefore, thermo-chemical hydrolysis pretreatment is necessary from which glucose and xylose, respectively, are obtained. At the same time, a *process of fermentation* of such substances with the formation of volatile fatty acids takes place. These are transformed into acetic acid, formic acid, carbon dioxide and molecular hydrogen during the *acetogenesis phase*. Lastly, in the *methanogenesis phase*, methane is formed starting from acetic acid and due to co-metabolisation of CO_2 and H_2 by hydrogenotrophic microorganisms (Figure 1) (5).

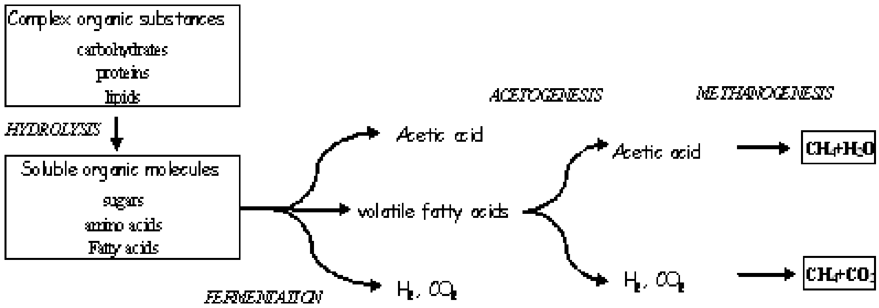

Fig. 1 - Diagram of the metabolic chain of anaerobic digestion

Dark fermentation is based on the following general reaction of complete glucose conversion, with a theoretical maximum yield of 12 moles of H2/moles of glucose : C6H12O6 + 6H2O → 12H2 + 6CO2.
Currently, the efficiency of conversion processes is lower than 30%, but were it possible to increase the value to 60-80%, a minimum of 7 moles H2/mol of fermented glucose could be obtained.

Realistically, due to thermodynamic limits, only 4 moles of H2/mol of glucose are obtained (in cases where production of acetic acid is the only byproduct) and 2 moles H_2/mol of glucose (in cases with production of butyric, lactic or propionic acid), based on the reactions illustrated below, since fermentative bacteria produce hydrogen in acidic conditions (pH 4,5-6,5) (3):

a) $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2$
b) $C_6H_{12}O_6 + 2H_2O \rightarrow CH_2CH_2CH_2COOH + 2H_2 + 2CO_2$

Among the innovative processes of hydrogen bioproduction, the combination of dark fermentation and photo-fermentation, within a *two-phase hybrid system* as in Figure 2, could represent a promising solution to improving production yield (6).

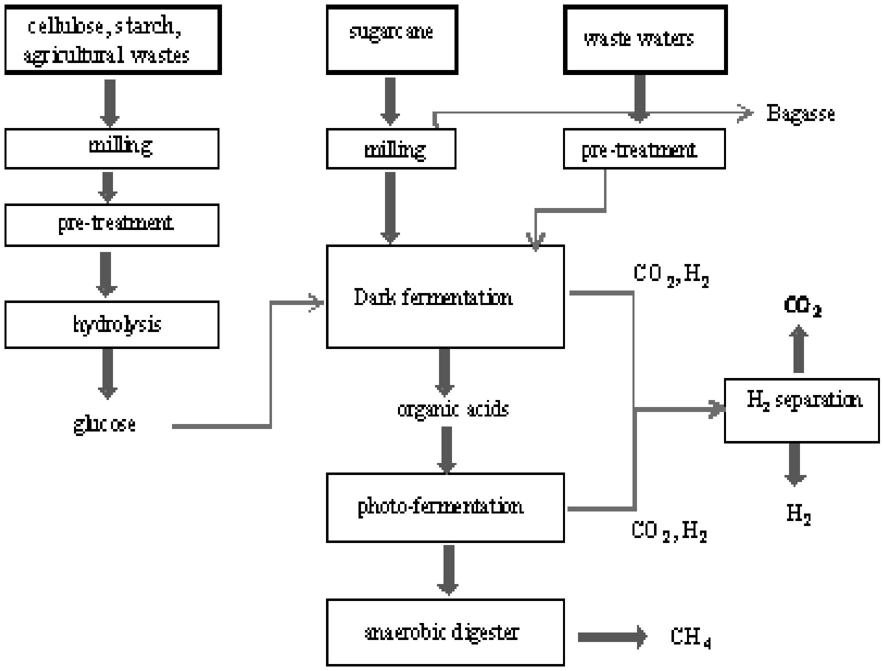

Fig. 2 – Diagram of the biological production of hydrogen in two phases.

The synergy of the process lies in the maximum use of the substrate since, otherwise, complete conversion would not be obtained due to the limits of thermodynamics. Both laboratory and pilot studies on a national and international level have shown the technical feasibility, and in some cases (also separately) the efficiency of both processes.

The most innovative aspect is the stability of this combination, sufficiently studied both as a process and as plant installation: in the first phase the biomass is fermented in acetic acid, carbon dioxide and hydrogen in thermophilic dark fermentation. Thereafter, in a separate photobioreactor, the acetic acid is converted into H_2 e CO_2 (second phase).

The experimental maximum yield obtained in the two-phase process was 7,1 moles of H_2/mol of glucose, compared to a maximum theoretical one of 12 moles of H_2/mol of glucose, with an energy requirement of approximately 3,82 kWh/kg H_2 (7).

The process may be summarised according to the following general reactions:

a) $C_6H_{12}O_6 + 2\ H_2O \rightarrow 4H_2\ +2CH_6COOH + 2CO_2$ (dark fermentation)
b) $2CH_3COOH + 4H_2O \rightarrow 8H_2 + 4CO_2$ (photo-fermentation)

Theoretically speaking, production of H_2 by fermentation has some advantages such as, rapid degradation by fermentative bacteria of solid products and other complex organic substances (present in waste and agricultural products), no need of light and the versatile nature of the substrate used.

The disadvantages lie in the low efficiency of conversion and unstable production of hydrogen. The process is sensitive to the operating conditions used, consequently improvement of process engineering and structure of the bioreactor, improvement of technical parameters (pH, water retention time and temperature) could enhance efficiency of hydrogen conversion. On the other hand, the instability of hydrogen production may be attributed to the metabolic change of the producing bacteria and this could be minimized by further study of microbial growth (2-4).

Another limiting factor of the process is the low efficiency of conversion of the substrate used: in fact, only 15% of energy deriving from the organic source is converted into hydrogen, however the aim is to increase this yield to approximately 85%.

In this context it has been experimentally shown that the removal or the use of byproducts generated during the course of the processes of biological production of hydrogen (for example, bagasse and methane) constitute a critical element when aiming to evaluate energy efficiency. In fact, if the abovementioned byproducts were reused as energy sources within the process, efficiency would increase significantly as opposed to removing them or treating them as a waste product.

In particular, it has been empirically highlighted that the use of byproducts within the processes of bioproduction has led to an increase in energy efficiency of approximately 80% in the case of fermentation and approximately 55% in the two-phase hybrid process. These values prove to be greater than those obtained in the chemical processes of hydrogen production using conventional sources, such as steam reforming of methane (SMR), which is around 64%. Generally speaking, the use of byproducts in bioprocesses also offers a saving in the use of fossil sources and a reduction of greenhouse gas emissions into the atmosphere (7).

With a view to containing production costs, perfecting the two-phase hybrid process could improve H_2 yield definitively, as well as costs of the process. In fact, it has emerged that, in order that the cost of hydrogen may prove competitive compared to traditional fuels, a fermentation yield of 10 moles of H_2/mol of glucose would be necessary in order to apply this type of process. The use of microbial cultures mixed with organic substrate waste products, such as wastewater or waste, would appear particularly interesting.

Currently H_2 yield from biological processes is too low to be used commercially and production costs are still rather high: the estimate, based on parameters of currently feasible processes, is approximately 4€/kg H_2. Raw material (whose costs weight upon the final fuel cost by 36-62%) and treatment costs must be added to this figure, thus rendering development of economic methods for the growth, collection, transport and management of energy substances and/or residual biomass products indispensible (4)(9)(10).

Conclusions

There is no single solution to solving the issue of global energy supply and its various aspects: therefore, diversification of resources would constitute a technological target towards which various knowledge and technical, economic and scientific knowhow should be geared. Within this context, biological production of hydrogen, together with the use of biomasses, may be a potential solution to meeting the current energy demands.

Over the last ten years, basic and applied research and development carried out in this field have aroused significant interest. As part of the international research in progress there is the project "Innovative methods in the production of hydrogen from biological resources (Idrobio)", financed by MIUR and carried out in collaboration with various partners from the Italian scientific field. This is a programme which, in effect, requires wide-ranging interdisciplinary skills such as molecular biology, genetic engineering, biochemistry and substance sciences etc.

Techniques in renewable hydrogen production from low cost biomass offer good potential to render it economically competitive in the future. Currently, however, conversion processes are still in the experimental phase on a small scale at research bodies which use laboratory fermentors. It is hoped that, over the medium to long term, further progress may be made by improving dark fermentation methods (above all, two-phase hybrid fermentation). A greater yield of hydrogen, representing the aim and the latest challenge in the field of research and development in this sector, may be realized using specific microbe types, modifying the process, a more efficient design of bioreactors and also specific genetic engineering techniques applied to bacterial metabolism.

However, until the system of biohydrogen production is used on an industrial scale, it is necessary to solve the technical and economic aspects linked to the real substrate. In fact, since such a highly innovative process, no extensive case studies exist in literature and, as such, a quantitative comparison of the various types of fermentable biomasses is not possible, due also to the fact that they are not well-known and the values of productivity for each single type of material have not been established as yet.

Furthermore, apart from the source of hydrogen used, there are still many logistic and market difficulties which have to be overcome until such times as "a hydrogen-based economy" becomes a reality. Currently, it proves to be more expensive than those fuels currently used and, therefore, should technological progress have an effect on costs, in the long term it may play an important role.

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