

Green Energy and Technology

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BioH₂ & BioCH₄ Through Anaerobic Digestion

From Research to Full-scale Applications

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*Non basta guardare, occorre guardare con occhi
che vogliono vedere, che credono in quello che vedono.*

*Watching is not enough, you need to look
with eyes that want to see, that believe in what they see.*

Galileo Galilei
Pisa, 1564—Arcetri, 1642

*To my son Diego and my daughter Alice
in the hope that the information contained
herein will contribute to
improve a little bit their world,
and to Mina, who gives my life meaning.*

Bernardo Ruggeri

*To my husband Miguel and to my family
in Salento (Italy) and Chile, for their
love and support.*

Tonia Tommasi

*To Amma, who teaches love to humanity;
to my dear partner Alessandro
and to my family, for being part
of my life.*

Sara Sanfilippo

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demonstrating that little personal choices can also make the difference in reducing the energy demand and environmental pollution.

Introduction

Nowadays, some of the most important problems in our society concern environment pollution and energy supply: the increasingly negative conditions of the environment, linked to the use of fossil fuel, and the real need to guarantee a greater safety of energy supply, have made the use of energy sources that respect the world in which we live of primary importance. Fossil fuels have ruled the world for more than a century and their intensive use has not only polluted the environment, but also exhausted our limited fuel reserves. The quest for a clean alternative energy should be independent from the availability of oil reserves, which could be used for other worthwhile purposes, such as in the chemical and pharmaceutical industries.

Biological hydrogen production is becoming important from the point of view of renewable fuel: it is becoming the most promising in the succession of fuels, with several technical and socio-economic benefits. This is why research on hydrogen has been increasing more and more in recent years. The use of hydrogen could satisfy three main requirements:

- it can be produced and utilized with a low impact on the environment (H_2O as a by-product);
- it can be obtained from renewable energy resources (water, organic refuse and solar energy);
- the surplus can be stored and used over time (e.g. when the demand for electricity is very high).

At present, hydrogen is produced mainly from natural gas through steam reforming (40 %), 30 % from heavy oils and naphtha, 18 % from coal, 4 % from electrolysis and about 1 % from biomass. Fossil fuel processing and water electrolysis require the input of energy, both directly and indirectly, but these methods of hydrogen production do not solve environmental issues, unlike the biological production of hydrogen, which can be carried out from renewable sources.

Anaerobic digestion (AD) of organic matter is a well-known process that is already utilized in the production of biogas. It represents a promising and environmental-friendly method that offers the possibility of obtaining H_2 using a wide variety of low-price renewable feedstock and leads to a suitable improvement

in organic waste refuse treatments. The use of biomass is therefore potentially interesting as a component of a sustainable energy market for many reasons:

- various organic wastes, such as agriculture residues and municipal and industrial wastewaters, which should have a negative value since they lead to disposal and treatment problems, can instead increase in value if used to produce a high-quality fuel;
- the contribution of greenhouse gases to the atmosphere is minimal, due to the lack of fossil fuel input in both the H_2 production step and the following utilization: H_2 is the only carbon-free fuel;
- there are no external costs due to environmental pollutants, as occur when conventional fuels are used.

External costs are heavy costs that societies have to pay, and they are very often hidden in the case of an apparently low-cost technology. They arise from environmental damage, due to the almost total dependence on petroleum, and they rebound on the environment and therefore on humans. The externalities are, for example welfare spending because of human diseases, air and soil contamination and agriculture underproduction. If in the total costs of conventional fuel we include external ones, bio H_2 production could become a cost-competitive process.

Although AD for biogas production is a widely diffused full-scale process in different countries around the world, including Europe and China, very little information is available on the geographical distribution of full-scale plants for biological hydrogen production. In fact it is an emerging technology that still needs careful study to understand the best and most economic conditions for setting up the plants.

Hydrogen is an important intermediate in the microbe-dominated degradation of organic material in anaerobic environments and it is utilized by methanogens to produce methane in conventional biogas plants. Two stages can be used, which involve separating the acidogenesis from the methanogenesis processes, leading to bio H_2 and bio CH_4 production, respectively, to enhance the energy and treatment benefits of AD.

The aim of the book is to find a good design via a scale-up procedure, and good anaerobic reactor operating conditions in order to produce H_2 from residual biomass and then use the volatile fatty acid, residues of the H_2 production, to produce methane obtaining higher energy recovery from the organic refuse. To reach these goals, it is necessary to consider many different aspects, connected to the biological and energetic features of the process, by analysing the reference literatures and by experimenting at a laboratory scale and at a pilot-plant scale; moreover less obvious aims are to promote environmental safety and to improve the value of organic refuse as a resource.

The book basically deals with an experimental approach, but the theoretical introduction is not neglected, especially concerning novel aspects connected to the sustainability of the process. Experimental tests to produce biological hydrogen from AD using organic wastes, mainly produced at several points in the food chain,

were conducted in flasks at a bench-scale bioreactors. They were conducted for optimizing the bioH_2 production on the basis of several parameters: temperature, pH, redox potential, substrate concentration and rheological behaviour. An energy study was conducted in order to discover the best design conditions and working temperatures of the bioreactor, using a net energy balance tool. The working temperature in fact plays a key role in the total energy balance of the process, and therefore in the global sustainability of the process.

The analysis of the energy process sustainability is carefully addressed from both a theoretical point of view and through practical applications; sustainable energy parameters, such as Energy Sustainability Index (ESI), Energy Return On Investment (EROI) and Energy Payback Time (EPT), are introduced and analysed to evaluate the sustainability of AD technology. They are moreover used as tools for selecting the most appropriate one among many technologies that are available to produce useful energy, i.e. the energy available to society. Theoretical models and applications are presented and fully described by analysing the two-step anaerobic fermentation of bioH_2 plus bioCH_4 .

The book provides a substantial body of useful information extracted from the literature and experimental tests oriented towards the main objective of highlighting the two-step anaerobic fermentation process. To accomplish this, several research studies are carefully reviewed in detail and to have a better understanding of the key steps of the biological, biotechnological and engineering nature of anaerobic H_2 production.

Chapter 1 is an overview of bioH_2 which is mainly dedicated to explaining the microbial processes that govern H_2 production, the microorganisms and their enzymes and electron shuttles involved in the electron chain towards H_2 generation. **Chapter 2** summarizes the pre-treatments reported in the literature to inhibit methanogens. Among these methods, particular attention is given to the acid treatment, which was selected as the method for obtaining hydrogen-forming bacteria in all the tests reported in the book. The experimental results of the investigation are reported in detail. **Chapter 3** is dedicated to a kinetic study of H_2 production from glucose by means of a mixed consortium of microorganisms, taking into account structural information on the enzymes involved in hydrogen production, such as ferredoxin and hydrogenase. Through the kinetics obtained, the dynamics of bioH_2 production is well explained, according to the pH and redox variations, as a direct consequence of bacterial activity. In **Chap. 4**, after looking at the working temperatures tested by other researchers, the effect of temperature on H_2 production and on liquid end-metabolites in the mesophilic range is analysed. **Chapter 5** looks at the energy balances at various temperatures, with the aim of optimizing the net energy production in a single stage of H_2 production. The diameter of the reactor was chosen as a key parameter in a scale-up procedure because it affects both the energy produced and the energy lost as heat. In **Chap. 6** attention is focused on waste organic residues for using them as electron donors for H_2 production. This chapter highlights suitable vegetable residues with the aim of understanding the easiest and most efficient pre-treatment for producing hydrogen. Several available pre-treatment approaches are reviewed and analysed with particular attention to their

combinations. **Chapter 7** is devoted to explore the potential of microbial fuel cell (MFC) technology in order to add value to the metabolic products of acetogenesis fermentation after H_2 production. Nevertheless, the aim of this book is to focus on anaerobic technology and its energy sustainability; the conversion of H_2 production residues, such as volatile fatty acids into additional H_2 or CH_4 or electricity needs to be investigated. Even though MFC is in a state of infancy, it deserves close attention because of the possibility of generating electrical energy or additional H_2 taking into account synergic effects among the $bioH_2$, $bioCH_4$ and electricity that are able to increase the recovery of energy present in the organic wastes. **Chapter 8** is dedicated to the methanogenic step, which is able to increase the value of the liquid end metabolites of the acetogenesis stage when $bioH_2$ shuts down. Experimental results are highlighted, considering that two-step AD is ready to move from laboratory scale to full plant application. In **Chap. 9** a theoretical energy sustainability approach is conducted in order to produce useful energy to provide an energy service to society. A detailed analysis of the sustainability of the whole process is presented using ESI, EROI and EPT approaches in a framework of life cycle assessment thinking.

The book ends with the **Conclusion** in which a general discussion is given about the two-step technology and its future trends and the role of AD in a sustainable future society.

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