



Perspectives for the use of biotechnology in green chemistry applied to biopolymers, fuels and organic synthesis: from concepts to a critical point of view



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ARTICLE INFO

Keywords:

Biotechnology
Green chemistry
Biofuels
Biopolymers
Organic synthesis

ABSTRACT

Since the eighteenth century, after the first industrial revolution, humans have been exploiting the planet's natural resources in an unsustainable manner. This has caused some irreversible impacts on the environment. Because of this, we are facing a change of philosophy within the scientific community about chemical and industrial processes. During the 1990s, the concepts of green chemistry began to solidify, while in parallel some major advances in biotechnology were achieved through developments of genomic sciences and genetic and metabolic engineering. This work will discuss some new insights into the use of biotechnology as an important tool in green chemistry, showing new applications to biopolymers, biofuels and as a new alternative to traditional organic synthesis, making chemical processes more sustainable and less damaging to the planet.

1. Background

Since the mid-eighteenth century with the first industrial revolution, mankind has been changing the way of extracting resources from the planet. Initially, we implemented a basically artisanal production system, in which humans themselves were the main production tools (de Vries, 1994). This was drastically altered by the introduction of machinery, driven by energy derived from fossil fuels such as coal (Fahrenkamp-Uppenbrink, 2015; Berg, 1978), mainly in the textile and metallurgical industries, which as a result expanded dramatically (Fores, 1981). At the end of the nineteenth century, the world experienced the second industrial revolution, in which rapid technological development led to most of the industrial advances that allowed the sale of consumer goods that still are important to the society today. This brought the establishment of the automotive and aviation industries, production of oil-derived materials, the pharmaceutical industry, and computing (the base for the ongoing information revolution) (Spilhaus, 1970).

However, the unsustainable exploitation of Earth's natural resources in the last 300 years has obviously caused impacts that threaten the well-being of future generations. The waste generated as a consequence of all the industrial advances of recent centuries is not adequately treated or sufficiently recycled, posing one of the greatest challenges to society (Giusti, 2009; El-Fadel et al., 1997; Houk, 1992; Robinson,

2009). After all, as proposed by the classic thought of A.L Lavoisier: "Nothing is lost, nothing is created, everything is transformed." Therefore, the industrial waste will continue to "exist" on this planet as long as a better destination is not given to it, because the natural processes of degradation are much slower than that of the producing new waste. Moreover, most of these advances depend on energy derived from fossil fuels, which besides contributing to global warming and other environmental problems are not renewable (at least not in the "short" run).

As known, pollution has caused much irreversible damage to the environment. The increase in the anthropogenic emission of greenhouse gases (GHG)¹ from burning fossil fuels and forest destruction is now a global concern that demands a unified effort from all nations, with the aim of slowing global climate change (Allison and Bassett, 2015). The rapid industrialization processes has also caused damage in other spheres, such as soils and water, impacting in multiple ways the life quality of all living beings (Kelly and Fussell, 2015; Grossman and Krueger, 1995).

In the twenty-first century, although belatedly, society in general and the scientific-industrial community now largely agree that the ways of interacting with the environment and exploiting resources need to be changed. In the midst of the third industrial revolution, characterized by an extremely refined and advanced chemical industry, we are also facing a new revolution that comes from the incredible advances of the

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¹ Green house gases abrangem CO₂, N₂O, CH₄ e gases fluorados.

genomic sciences (Abelson, 1998). The general hope is that this current revolution can address the impacts generated by the previous unsustainable revolutions.

2. Important concepts: green chemistry, biotechnology and white biotechnology

With the change in the mentality towards the planet's serious environmental problems and the general acceptance of the fact that something needed to be done to mitigate the damage, the concept of "green chemistry" was developed, which basically encourages a closer look at the impacts of industrial processes on nature.

The first principle of the United Nations Conference on Environment and Development, which met in Rio de Janeiro from 3 to 14 June 1992, states that:

"Human beings are at the center of concerns for sustainable development.

They are entitled to a healthy and productive life in harmony with nature."

The role of chemistry to achieve this goal is undeniable. According to data from the United States Environmental Protection Agency (US-EPA), around 278 million tons of toxic wastes were generated in 1991, of which the greatest portion came from the chemicals industry (Sanders, 2011). As a result, the biggest corporations, such as Dow Chemical and DuPont, have begun to devote efforts to comply with increasingly restrictive environmental regulations, thereby tapping into green chemistry practices. This term, which was proposed by the chemist Paul Anastas in the 1990s, basically aims to develop and implement chemical products and processes to reduce or eliminate both the use and generation of substances harmful to human health and the environment, by applying the twelve basic principles of green chemistry, already well known (Anastas, 1998).

In practice, these concepts of green chemistry have revolutionized the way of planning new projects and research in chemistry and have impacted its sub-areas in the most diverse applications (Horváth and Anastas, 2007; Fantke et al., 2015). Moreover, in parallel with this change of mentality, there have been significant advances in biotechnology, which - under some circumstances - can provide valuable or alternative tools for the implementation of some of the 12 concepts of green chemistry.

Therefore, biotechnology is a general term used over a very broad field of study. According to the Convention on Biological Diversity, biotechnology means (Zaid et al., 1999):

"Any technological application that uses biological systems, living organisms, or derivatives thereof, to make or modify products or processes for specific use."

It is an interdisciplinary area of science in which the main focus is studying the use of cells, microorganisms, in vitro or in vivo, for the production of new products through new processes. It is also an area of science that has been applied for centuries: a simple fermentative process for the production of alcoholic beverages can be considered a biotechnological process, since it uses microorganisms to transform sugar into alcohol. However, the main breakthrough in biotechnology was the provided by significant advances in the genomic sciences (Cañestro et al., 2007), and of genetic and metabolic engineering (Parekh, 2004).

The genomic sciences have had a great impact on the chemical industry, since it is now possible to genetically modify microorganisms to target certain metabolic behavior according to what one wishes to obtain. This is called metabolic engineering and these genetically modified microorganisms are known as "engineered" microorganisms (Parekh, 2004). Thus, instead of thinking about a longstanding chemical process that has reagents, catalysts, products and byproducts, the chemical process is designed to use some kind of starting material, such

as an industrial waste, and some microorganism or enzyme capable of transforming it into the desired final material or product. In practice, this process offers advantages to traditional methods, by improving the selectivity of chemical processes. In addition, genetic engineering offers new pathways to obtain desired products, sometimes with lower production costs and using safer and more sustainable materials.

During recent decades, biotechnology has been applied in several areas of medicine, for the development of new pharmaceutical drugs (Olsen et al., 2004; Drews and Ryser, 1997; Orive et al., 2003; Butcher et al., 2004), vaccines and antibodies (William, 2005; Luckow and Summers, 1988), and medical materials for transplants or prostheses (Yang et al., 2014; Gaharwar et al., 2014; Ding et al., 2014; Fu et al., 2013; Hench and Polak, 2002); in the area of food and agriculture, to produce eco-friendly food (Andrés et al., 2016; Alam et al., 2014; Kasmi et al., 2017); and for environmental protection, with the development of new biofuels derived from plants and other renewable sources (Peralta-Yahya et al., 2012; Georgianna and Mayfield, 2012), among other applications. In the early 2000s, more than 120 products obtained through biotechnology processes had been approved by the FDA (U.S. Food and Drug Administration) (<https://www.bio.org/media/press-release/biotechnology-fundamentals-solid>, 2016).

In this way, biotechnology is a science that can be applied as a tool to improve processes in virtually unlimited applications. It may be the key science by making traditional chemical processes into "green" processes, where the combination of biotechnology and green chemistry leads to so called "white biotechnology". It is an area that has emerged rapidly in recent decades and refers to the use of biotechnological approaches in the laboratory and industrial production of fine chemicals, biofuels and agricultural products, among many others (Gupta and Raghava, 2007). The main focus of white biotechnology is the development of "clean" processes that result in reduction of greenhouse gas emissions, water and energy consumption, and generation of industrial waste. It is a truly multidisciplinary frontier area, which closely links the main areas of chemistry and biology.

On the other hand, major challenges still exist when combining these two principles (biotechnology and green chemistry) still running around the upstream and downstream processes: from early cell cultivation, raw materials supply, to the final challenge to obtain the target material with the desired characteristics, after separation and purification procedures. All these steps must be critically evaluated, because they can be intensively demanding of energy, chemicals and water. Irrespective of whether a genetically engineered strain is used, both processes must be considered as they can make a biotechnological process unsustainable, and not green at all (Chmielowski et al., 2007; Junker et al., 2004).

This work will emphasize some examples of applications of biotechnology in green chemistry, also discussing some important points related to its true greenness.

3. Applications

3.1. Biotechnology applied to materials: biopolymers

The petrochemical industry is one of the major sources of air pollution and the increase in GHG emissions (<https://www3.epa.gov/climatechange/ghgemissions/>). The manufacture of petroleum-based polymers plays a significant role in generating this pollution (Fu et al., 2003). In addition, their high durability and strength, in the past seen as "good qualities", are now a serious environmental problem, since these polymers accumulate in the environment, and hundreds of years are required to completely decompose them, during which they often release toxic substances that can contaminate soil and groundwater (Webb et al., 2013; Alay et al., 2016). Biodegradable polymers are a sustainable alternative, since by definition they are degraded through enzymatic actions that tend to continuously decrease their molecular masses. The term "degradable" is used when hydrolysis or enzymatic

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